

Sixth FORUM on Geology of INDUSTRIAL MINERALS

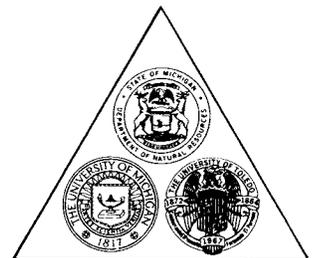
**I. CHEMICAL AND INDUSTRIAL ROCKS
AND MINERALS**

**II. BUILDING AND CONSTRUCTION STONES
AND MINERALS**



Miscellany 1

Geological Survey Division
Michigan Department of Natural Resources



PREVIOUS FORUMS

A symposium on Geology of Industrial Limestone and Dolomite (1965) published in *The Ohio Journal of Science*, 1966, vol. 66, pp. 97-224.
(Available from Central Office, The Ohio Journal of Science, 505 King Ave., Columbus, Ohio 43201)

A symposium on Geology of Cement Raw Materials (1966) published by Indiana Geological Survey, 1966, 197 pp.
(Available from Publication Section, Indiana Geological Survey, 611 N. Walnut Grove, Bloomington, Indiana 47401)

A symposium on Industrial Mineral Exploration and Development (1967) published by Kansas Geological Survey, Special Distribution 34, 1967, 183 pp.
(Available from State Geological Survey of Kansas, University of Kansas, Lawrence, Kansas 66044)

Proceedings: Fourth Forum on Geology of Industrial Minerals (1968) published by Texas Bureau of Economic Geology, December 1968, 174 pp.
(Available from Bureau of Economic Geology, The University of Texas, University Station, Box X, Austin, Texas 78712)

Proceedings: Fifth Forum on Geology of Industrial Minerals (1969) published by Pennsylvania Bureau of Topographic and Geologic Survey, Fourth Series Bull. M64, 1970, 278 pp.
(Available from Bureau of Publications, Tenth and Market Streets, Harrisburg, Pennsylvania 17125)



State of Michigan
Department of Natural Resources
Geological Survey Division

Miscellany 1

Papers presented at
Sixth Forum on Geology of Industrial Minerals

Themes:

- I. CHEMICAL AND INDUSTRIAL ROCKS AND MINERALS
- II. BUILDING AND CONSTRUCTION STONES AND MINERALS

Edited by
W. A. Kneller

Cosponsored by

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PREFACE

The papers in this volume are arranged in order of presentation at the meetings of the Sixth Forum on the Geology of Industrial Minerals. This volume, like earlier symposia and proceedings of the Forum, highlights some of the recent advances in the field. Hopefully, it measures the vitality and strength of our industry as well as of our Forum. The Sixth Forum was somewhat more general in scope than earlier ones. The themes were: "I. Chemical and Industrial Rocks and Minerals" and "II. Building and Construction Stones and Minerals". The reader of the proceedings of the Sixth Forum will undoubtedly note that the theme titles are more specific than the subject matter covered by some of the papers. The editor believes, however, that the papers compel the reader to look at these themes from an environmental as well as from a resource management viewpoint. Some of the papers, namely those by Lawrence F. Rooney, Robert E. Ives, W. E. Coates, William E. Hole, Jr., and P. P. Hudec, J. R. Dunn and S. T. Brown discuss this need. A speculative, but interesting, experimental contribution concerning limestone as a raw material for hydrocarbon fuels was presented by C. A. Salotti, E. W. Heinrich and A. A. Giardini. Other participants delivered papers which exemplified the themes of the Sixth Forum. Noteworthy examples of these contributions are those of R. D. Matthews, L. I. Briggs, C. E. Herdendorf and L. L. Braidech, and D. D. Carr, R. L. French and R. F. Blakely.

The keynote address by Dr. Lawrence F. Rooney set the stage for a stimulating meeting, the promise of which was borne out by the quality of the papers presented herein. Judging by comments and discussions both during and since the meeting, the papers presented in this forum helped to serve the purpose for which the Forums were designed and initiated by Dr. Robert L. Bates of Ohio State University. The authors are to be congratulated for both the quality and stimulation of ideas that their papers provide to readers of this volume.

The welcoming address by Gerald Eddy, State Geologist of Michigan, is included in the volume because he was unable, due to severe weather conditions, to attend the Forum. I. E. Odom, J. L. Hiatt and D. L. Kramer also were unable to participate in the program because of the air controllers strike as well as severe weather conditions. Their paper also is included in the Proceedings.

Considerable care was put into the details of the instructions of how the authors should prepare their manuscripts for publication. The deadline for the receipt of manuscripts was set at May 1, 1970, to allow minor editing of the special manuscript forms and to guarantee early publication. All authors must accept full responsibility for any minor errors found in their texts. It is virtually impossible for the editor to retype or return to the authors their manuscripts for minor corrections and meet the printer's deadline of the first of June.

In order to make the Forum a success, many people, including the members of the program committee, contributed greatly to the task. This committee consisted of Dr. William A. Kneller and Dr. Louis I. Briggs, co-chairmen, and Messrs. Harry O. Sorensen and Thomas Segall. The Michigan Geological Survey provided counseling, guidance and complete cooperation in undertaking a publishing venture which was new in format for them. I wish to extend my thanks to Mrs. Donna Palmer, secretary of the Geology Department, University of Toledo, for her capable handling of the correspondence and files which are the inevitable adjuncts of the organization of a program.

*Toledo, Ohio
May, 1970*

*William A. Kneller, Chairman
Department of Geology
The University of Toledo*

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WELCOMING REMARKS

by

Gerald E. Eddy
State Geologist of Michigan

It is a privilege for me to kick off this conference on the geology of industrial minerals. The location, occurrence, development and utilization of our mineral resources have been my major interests, as many of you know, since I left these "ivy covered halls" quite a few years ago. Even during the years I occupied the exalted position as Director of the Department of Natural Resources, I followed mineral developments as much as I was able. It is gratifying to share this interest with you and that's really why we are here - to listen and to share, in a forum, our knowledge and our concerns about the occurrence and availability of minerals.

I'm particularly proud to note the strength of the involvement of the Michigan Geological Survey in this conference. No less than three of my staff are giving papers and there are four or more of the staff in the audience -- which makes me wonder -- who is back in Lansing minding the store.

Although it is my place to welcome you to this conference, but not to keynote it, I still would like to share a thought or two with you.

All of us have been exposed, of late, to a great deal of rhetoric about environmental problems: water pollution, air pollution, noise pollution, soil pollution and people pollution - recently called "population". To the extent it has been awakening the general public to the existence of environmental problems, it is positive. To the extent it has tended to concentrate on industrial pollution, it may be misleading - and I'm referring directly to the extractive minerals industry. There is the problem and the danger that the public may come to believe that simply by imposing strict controls on industry that our troubles can be eliminated. However, environmental problems are far too complex for so simple a solution. Let me wax biblical for a moment. We are faced with these commandments: "Thou shalt not tear up the land; Thou shalt not contaminate the water; Thou shalt not pollute the air; Thou shalt provide the world population with the minerals vital to their survival."

As mineral resource people, as resource managers, or as potential mineral resource managers, you have a two-fold obligation: to find industrial minerals to meet future demands and also to protect those resources so they can be developed. You-we can no longer content yourselves-ourselves with just finding more

usable minerals, or evaluating them, or developing them. You-we must now also be concerned about protecting them for use and developing them in a manner to protect and preserve the environment.

By protecting them for use I mean participation in the planning to thwart restrictive covenants that may be placed on lands that would prohibit minerals use. And, I mean participation in planning to prohibit the creeping urbanization which is taking over lands for homes and roads that should be preserved or reserved for minerals extraction to provide the stone or the gravel to build the homes and offices and roads for our exploding population. It frightens me a little to think about where we minerals people are going to find the reserves to accommodate the 175% increase in iron or the 200% increase in copper and lead that we will need by the year 2000, -- or the projected six-fold increase in non-metals by 2020.

I would also like to remind you that we must develop our minerals in a manner acceptable to the natural controls of the environment and to the public who shares that environment with us. The mineral producer's image has been damaged considerably by some of the procedures of the past - procedures generally not as devastating as the strip coal mines have been pictured, but most not so good, even so. We must improve our methods of locating, evaluating and extracting in a manner offering simultaneous multiple uses of the land, examples of which are pumping of an oil well or brine well in the middle of a sugar beet field or underground mining which occupy minimum surface areas. Where surface mining necessarily must tear up the landscape we must attend to proper handling of wastes and reclamation. My friend Peter Flawn, State Geologist of Texas, has coined a phrase "sequential multiple use" which implies there is a time for growing of forests, a time for minerals extraction, and a time to put that land to recreation, building cities, or back to forests. Planned reclamation is the key and we will do it either voluntarily or by legislative order. I should note that federal legislation is pending on mine reclamation as it is in many statehouses. Two such bills are in the Michigan Legislative "hopper" this year.

Thank you for indulging me these several minutes, and again, let me welcome you to this conference on behalf of the University of Toledo, The University of Michigan, and the Michigan Geological Survey.

THE PARTY'S OVER: A RAMBLING DISCOURSE ON SUSPENDED CONTEMPT,
THE BITTERSWEET BOOM, AND OTHER HERESIES

by

Lawrence F. Rooney
Indiana Geological Survey

One of Edgar Allan Poe's stories that haunts my subconscious is the Masque of the Red Death. These days whenever I join a group like this, especially during the cocktail parties, I see myself and others as those mythical swingers seemingly isolated from the plague.

The world, but this country especially, has had a ball plundering, spending, and wasting its natural resources for 100 years. And, as in days of yore, it is fitting that we end this ball with a spectacular fireworks: trips to the moon, so that our grandchildren, huddled in their caves along the Ohio, will better understand how it all began.

As geologists many of you have read The Challenge of Man's Future, Affluence in Jeopardy, Mineral Resources of the Future, and other reports on the exhaustion of our wealth. You are aware of the growth in population and the staggering amount of minerals that have to be found to maintain our standard of living. You are also aware that in a finite world demands cannot be met forever; in fact, they can be met in this country only for a few decades by importing vast quantities from the underdeveloped nations and depriving them of their heritage.

But catastrophe is a few years from now, the die has been cast, and what is true of metals does not apply directly to most industrial minerals. High-grade limestone deposits located close to population centers are not infinite, but they will be here long after our civilization has perished. For the immediate future, the industrial minerals industry can look forward to tremendous demand and growth because of the increase in human population.

In fact, we are in and can look forward to a boom in minerals exploration. To be aware of this, all you have to do is glance through the job advertisements in such publications as Geotimes, the Northern Miner, or the Wall Street Journal. The minerals industry is looking for exploration geologists and geophysicists as never before, during my career at least. The number of advertisements for explorationists in metals and non-metals carried in Geotimes during 1969 was almost four times that during 1968. And we can only guess at the number of petroleum geologists who have been transferred by their companies into minerals exploration. The reason for

this upsurge is the realization that minerals are scarce, that they are essential, and that they are going to be exceedingly profitable. So the boom will be bittersweet, like the sale of coffins during an epidemic.

The boom will have its problems, too. Just when exploration is in full swing and new mines must be opened, public opposition is building against pollution. Many of us want to die at the age of 90 shot in the back by a jealous husband, but we are more likely to depart strangling on someone else's sewage (which I suppose is the ultimate in cannibalism) or even on our own waste (which I am certain is the ultimate of self-love). Some mines do contribute much to pollution, but my experience has been that the industrial minerals industry in general and limestone quarries in particular contribute little that is more than a nuisance. Yet a quarry, with its plume of dust, rumbling machinery, blasting, and galvanized metal sheds, seems more like a polluter than the sleek factory, its waste pipes buried in the ground. And it is easier to prevent a quarry that would employ 10 people than close down a factory employing 500.

The demand for geologists in economic geology and other applied fields directly related to the population explosion is one that our colleges are coming to realize, though slowly because many of their administrators live in an unreal world based on expanding affluence and increasing specialization. There are economists at Indiana University, for example, and I am sure they have their counterparts in the University of Michigan, who view the future as one of abundance, shorter work weeks, and an ever-rising standard of living. In geology, university faculties are still awash in a warm tide of federal grants, their soft bellies distended moonward, only barely cognizant of the wave of the future bearing down on them. Their graduates are in the same image: specialists wanting to breed specialists.

When one wins the local pie-baking or speech contest, he has achieved something but not much. When one gets a Ph.D. he has achieved something more but again not much, and in a sense much less because he has taken on a debt. Parents' chests swell with pride as junior swings down the aisle with his academic cape. Instead, the public might better form a gauntlet and toss rotten eggs.

For what have these young men and women done? They have lived off society for 7 or 8 years, eaten the wheat raised by some farmer in Kansas, driven around in automobiles built by automated people in Detroit out of minerals dug by miners in Minnesota. It's the farmers and miners who have sweated, the machinists with their scarred knuckles who have produced enough extra to let these kids live off them for years.

Punishment, of course, is absurd but college graduates should at least be treated with suspended contempt until they have accomplished something to merit their privilege. Our colleges have too many teachers who think that a Ph.D. is something significant in itself, an imprimatur that makes any research socially respectable.

In fact, all of us are conditioned to think in terms of more and more specialization, more and more instrumentation, and in careers that are ten times removed from the production of raw materials on which "the good life" is based. Our profession is only slightly removed from the basic reality, but think of the manufacturers of water skis or padded bras. How essential are they? Not that these are the first industries of that sort. Snuff boxes and powdered wigs were once the rage. And I am told that at the time of the Roman Empire, large vases were designed for a unique purpose. During their orgies, the Roman swingers would periodically disgorge so they could at least eat and drink all night. After the Empire collapsed, I doubt that there was much call for those receptacles. The craftsmen who survived were the simpler types.

There is a lesson there for us. We geologists might be well advised to take up a hobby such as hide tanning or agriculture. Perhaps that is what the rich have in mind when they buy their farms. Picture, if you will, Chet Huntley behind a mule in Maryland, the reins tucked under his arms as he tills the soil with a forked stick in order to feed himself and his family. But what about poor Brinkley, who will take care of him? The primitive society has no place for the artisan of either the vomit vase or T.V.

It is indeed difficult to see any basis for optimism. Business, like cancer, thinks growth is sublime. Thousands of civic leaders across this country are trying right now to lure new industry into their already-squalid towns and cities. Realtors delight in the pressure for houses and land. A trade journal for the oil and gas industry exults in the number of below-zero days. The average man wants a power boat as well as a car. Graduate students in biology, who should be our best-informed persons on population, want to be

parents of three or four children. It's always up to the other fellow to solve our problem. They will, some billions of other fellows.

There is one source of optimism available to us all: it is to establish a profound empathy and identification with some favorite creature. The dog has developed such empathy for the humans and will give his life for his master, something most animals will not do. Perhaps, with effort, we can rise to the unselfishness of the dog and view our own extinction in terms of a better life for the tiger, gazelle, or hippopotamus. If we are vegetarians, we might identify with a flower. And if we are truly pessimistic about the survival of life we might place our alter ego in a mineral and achieve certain immortality as quartz or calcite.

But these thoughts are fanciful, and I don't expect you to leave here as a tiger, pansy, or feldspar any more than I expect you to enroll in hide tanning. What then can the geologist do as a geologist to bend the future?

One small effort he might make is to bring pressure to bear on federal and state legislatures and agencies to spend more of our resources in acquiring basic data on the distribution and composition of rocks in the earth's crust. This information is fundamental and essential. Yet there is hardly a state in this union where the geologist can obtain readily for any given area a large-scale (and by large-scale I mean 1:24,000) geologic map and any information on the average chemical composition of the rocks within the area. He will probably find it easier to obtain a report on the distribution of a particular fossil or on the provenance of a sandstone.

But I think our major role during the decline of our civilization, is to fight a holding action, like the soldiers left at Thermopylae. No matter how much suspended contempt we show, we are not going to change society. No matter how sweet the boom, we are not going to find the minerals to provide a high standard of living for 30 billion people. But we can find the minerals, at least the industrial minerals, for the billions that are here now and some billions to come. Ours is a task that is at the same time noble and sordid, but above all stoic. To keep pace with the next 100 years' demand, we must loot the earth of minerals that would have lasted a controlled population living in peace more than a million years, and we must do this realizing that while we, the Thermopylae guard, hold our own, elsewhere by other people and by other forces the battle will be lost.

MICHIGAN'S MINERAL WELL ACT¹

by

Robert E. Ives
Department of Natural Resources
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Lansing, Michigan

Abstract

Recent legislation will have a definite bearing on many of the mineral operations in the state. Act No. 315 of the Public Acts of 1969 will become law on March 20, 1970. Its purpose is to provide control of the drilling, operating and abandoning of mineral wells to prevent surface and underground waste; to provide for a supervisor of mineral wells and prescribe his powers and duties; to provide for inspecting, repairing and plugging of mineral wells and for entering on private property for that purpose; to provide for the assessing of certain fees; to provide penalties.

Different classes of mineral wells have been incorporated into the act. These are as follows: 1) "Brine well" means a well drilled or converted for the purpose of producing natural or artificial brine; 2) "Test well" means a well, core hole, core test, observation well or other well drilled from the surface to determine the presence of a mineral, mineral resource, ore, or rock unit, or to obtain geological or geophysical information or other subsurface data, but shall not include holes drilled in the operation of a quarry, open pit or underground mine; 3) "Storage well" means a well drilled into a subsurface formation to develop an underground storage cavity for subsequent use in storage operations; 4) "Disposal well" means a well drilled or converted for subsurface facilities; and 5) "Exploratory purposes" means test well drilling for the specific purpose of discovering or outlining an ore body or mineable mineral resource.

Jurisdiction of the new law will be through the offices of the Michigan Geological Survey with the State Geologist being the Supervisor of Mineral Wells. He will be counceiled by a board made up of personnel from industries affected by the act.

¹The paper by Robert E. Ives was not submitted for publication.

SURFACE MINING REHABILITATION IN ONTARIO —
LEGISLATION AND IMPLEMENTATION

by

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Abstract

The concentration of surface mining operations in Southern Ontario in close proximity to major urban centers has created significant social, economic, and resource management problems. In a rare display of cooperation, the provincial government and mineral industry have prepared comprehensive legislation regulating the operation and rehabilitation of surface mining operations, particularly pits and quarries. The content of the legislation includes: definition of terms, site plan requirements, public notice and hearing procedure, performance deposits, technical details of rehabilitation procedure, mine operating conditions, and implementation of the act.

A case study of a typical site plan for progressive rehabilitation of a dolomite quarry is presented to illustrate the scope and significance of the pending legislation, as well as the values of comprehensive site planning with respect to mining operations and after-use of the site.

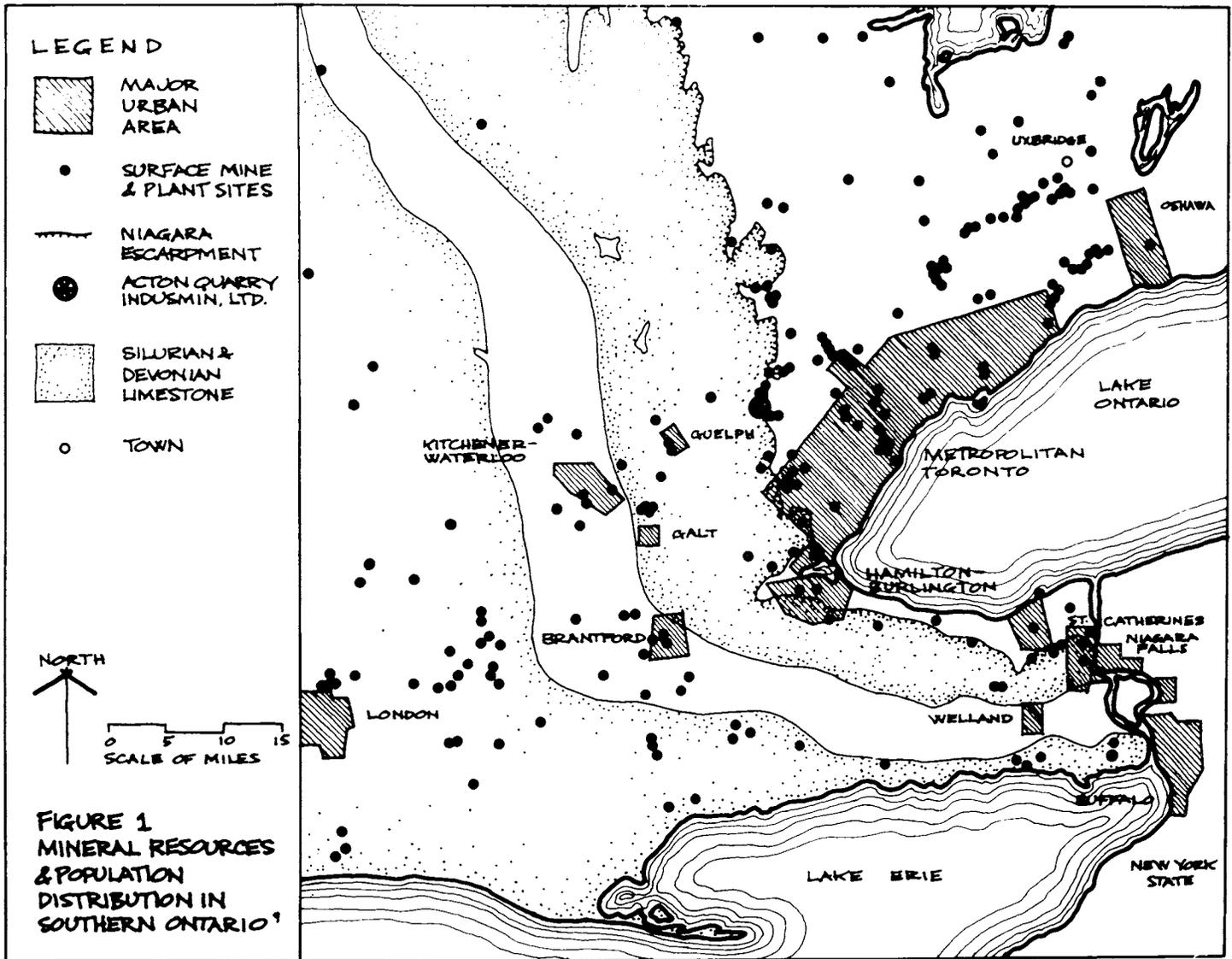
INTRODUCTION

The relationship between population concentration around the western end of Lake Ontario and the mineral resources of the area is obvious. It is quite likely that without an abundance of limestone, sand, gravel, clay, and shale in this area the major urban centers of central Ontario would never have developed to their present sizes. Population in this general area, Figure 1, is about 4,000,000. The number of mineral extraction and processing sites in the same area is 216. This parallel concentration of people and resource development has not evolved without significant social problems. A great deal of objection has been raised to the existence of surface mining, particularly sand and gravel, in the semi-rural, inland areas related to Metropolitan Toronto.

Typical complaints include the

normal "public nuisance" aspects of gravel pit operations, with heavy truck traffic, load spillage, plant noise, and dust, as well as reduction of adjoining property values and loss of landscape quality.

Popular understanding of resource development and management seems to be that of assuming that mineral products can always be mined "someplace else". This attitude is obviously in conflict with the physical realities of deposit locations, with the economic realities of market prices and hauling costs, and comprehensive physical planning on a regional scale. Sterilization of resource deposits through urban expansion becomes more significant each day. So far, the Province of Ontario has had no comprehensive method of dealing with these related problems.



LEGISLATION

In the fall of 1968 the surface mining industry, represented by The Aggregate Producers' Association of Ontario, and The Quarry Operators Section, Ontario Mining Association, petitioned the provincial government requesting that two significant changes in mining regulations be considered on a province wide basis.

1. That the Government consider the principle of designating, for pit and quarry use, lands at present owned specifically for that purpose as well as lands containing known deposits.
2. That Provincial legislation be introduced to regulate, in a reasonable manner, the

operation of pits and quarries and that consideration of the after-use of mining sites be included in this legislation.¹

Government response to this petition consisted of a multi-departmental investigation of the existing regulations, local bylaws and inclusion of mineral extraction zones in Official Plans of municipalities. This preliminary investigation revealed a maze of conflicting local laws and the desirability of establishing uniform regulations governing extractive industries throughout the Province. A Technical Committee was then established to investigate the problem in detail and submit recommendations for new government policy and legislation.

The Technical Committee recommended that three actions be taken as follows:

1. That a Provincial Mineral Resources Policy be instituted to identify all mineral resources in the Province and lead to the establishment of Mineral Resource Zoning as an interim land use.
2. That legislation be adopted to control the uniform establishment, operation, and rehabilitation of surface mining sites for purposes of improving the appearance of the operations, encouraging progressive rehabilitation, enforcing ultimate rehabilitation, and guaranteeing the availability of funds for rehabilitation.
3. That a "Rehabilitation and Operations Manual" be published to instruct the extractive industries in methods and techniques of rehabilitation as well as improvement of public relations.

The proposed legislation, which has not yet been introduced to the legislature, applies to two principal Provincial laws, the Municipal Act and the Mining Act.

Under the Municipal Act local jurisdictions are empowered to regulate surface mining and have responded with a bewildering variety of contradictory and inconsistent bylaws ranging in nature from enlightened acceptance to ironclad prohibition. Proposed amendments to the Municipal Act would give the Province power to control surface mining operations and cancel local authority over it except in cases where local Official Plans adequately recognize mineral deposits and provision for extraction. Response to the proposed legislation has included outspoken rejection on the part of many municipalities interested in jealously guarding their own power and concerned individuals ignorant of the possibilities of environmental improvement through enlightened operations control and site rehabilitation. Unfortunately there are very few examples of such control and

rehabilitation in Ontario and without a number of good examples, it will be difficult to change popular opinion.

Amendments to Mining Act

Proposed amendments to the Mining Act contain the following general provisions:²

1. Definition of terms and exemptions
2. Requirements for approval, by the Chief Engineer of Mines, of a site plan for each existing operation as well as new operations
3. Site plan requirements
4. Public notice of filing of site plan
5. Sixty day review period for government departments and public prior to approval of the site plan
6. Right of appeal of aggrieved parties
7. Periodic revision or updating of site plan
8. Performance deposits
9. Rehabilitation procedures
10. Conservation of top soil and overburden
11. Perimeter screening
12. Setbacks from property lines
13. Buildings and site maintenance
14. Times of operation
15. Dust control
16. Drainage of hazardous water accumulations
17. Fencing of site and access control
18. Truck entrances and traffic safety
19. Noise control
20. Blasting - limits of energy release
21. Roadside borrow pits
 - a. Exempt from regular site plan requirements
 - b. Temporary use only - 12 month maximum
 - c. Rehabilitation required by operator
 - d. Special administration and inspection procedure

Three of these general provisions, site plan requirements, performance deposits, and rehabilitation procedures are of outstanding significance and should be examined in detail to understand the scope and methods of enforcement of the proposed legislation.

Site Plan Requirements

Detailed site plan requirements include the following information:³

1. Site location, size, dimensions and true shape
2. Description of adjoining land use as well as location and use of all structures within 500 feet of mining property site boundaries
3. Description and location of all existing and proposed structures on the site
4. Complete topographic description of existing and proposed conditions
5. Drainage provisions and process water features
6. All roads and connections to public roads
7. Location of stockpiles of product, overburden and topsoil
8. Progressive and ultimate rehabilitation program
9. Proposed after-use of land upon completion of rehabilitation

Performance Deposits

Performance deposits would be required from each operator on a yearly basis, at a rate of \$0.01 per ton, of material shipped during the previous year, to a maximum of \$5,000 per year with deposits held in an interest bearing account by the Treasurer of Ontario until a total deposit, including interest, of \$100,000 had accumulated with respect to a single operation. Upon completion of rehabilitation and abandonment of the mining site, the accumulated deposit and interest would be refunded to the operator with provision for proportional, partial, repayment during progressive rehabilitation. In a case of non-rehabilitation the operator would forfeit the amount in his deposit account and the Province would have the necessary rehabilitation carried out and paid for from the forfeited deposit.⁴

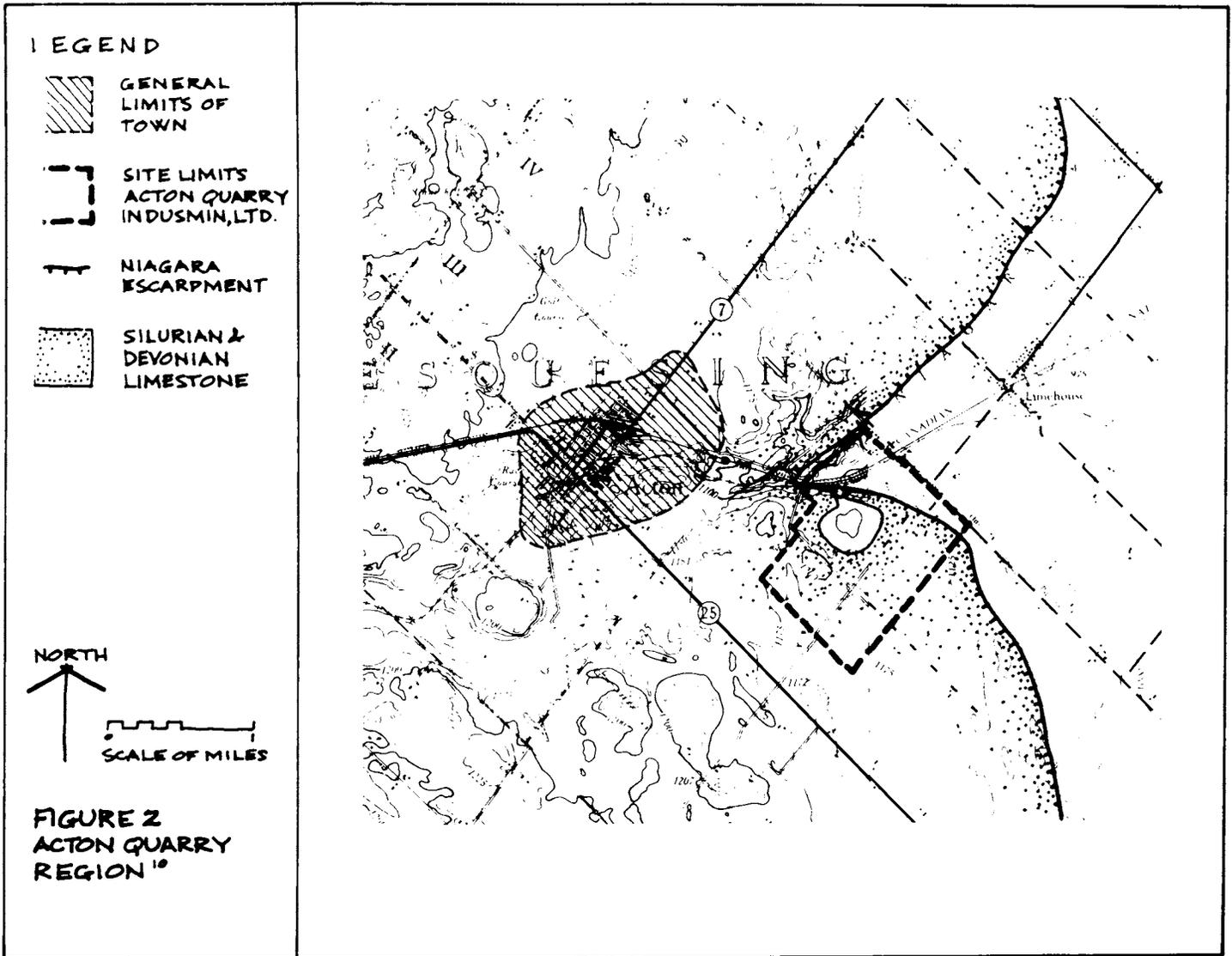
Rehabilitation Requirements

Rehabilitation requirements include the following:⁵

1. Final topography to be in accordance with the approved site plan.
2. Adequate amounts of topsoil and overburden be retained on the site, in erosion-free stock piles, to provide for rehabilitation earthwork.
3. Transition slopes be established on all perimeter working faces at the perimeter of the site.
4. Excavated areas be covered with topsoil and adequate vegetation cover be established to prevent surface erosion.
5. Surfaces intersecting water be at a maximum slope of 1½:1.
6. Sanitary landfill operations meet the requirements of various Provincial public health and water agencies, with respect to maintenance of ground water quality.
7. Tree screening be established to a minimum height and at a minimum density on all portions of the site within 50 feet of public road rights-of-way and within 300 feet of abutting residential property.

CASE STUDY

A preliminary site plan for the Acton Quarry, Aggregates Division Indusmin Limited, illustrates the development of a rehabilitation plan, some of the content of a comprehensive site plan, and the advantages of such planning in the improvement of quarry

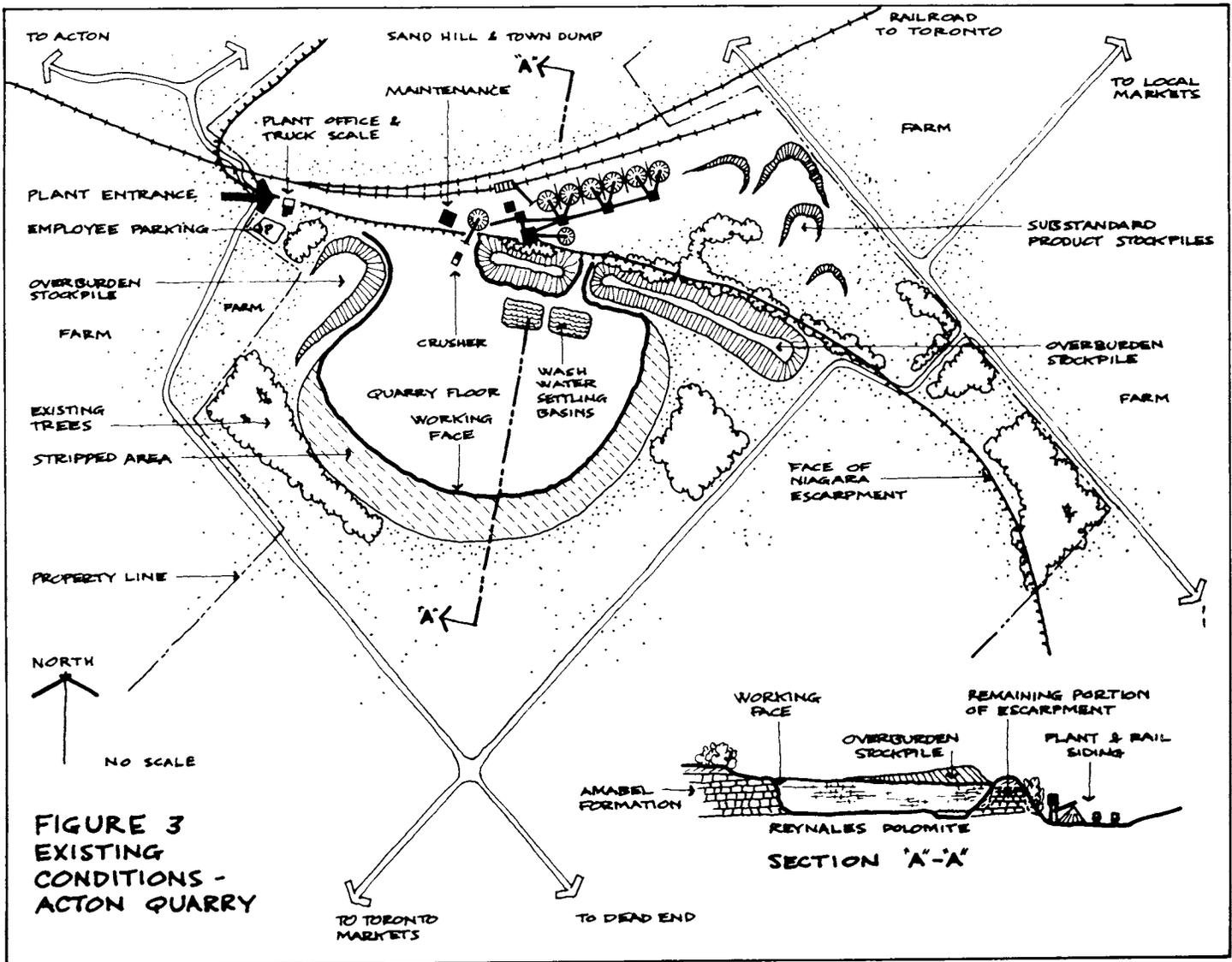


operation. The present quarry occupies a portion of an eight-hundred acre site along the Niagara Escarpment on the southeast edge of the town as shown in Figures 1 and 2. Acton has a population of about 6,000 and has grown toward the quarry with a group of new apartment buildings now within sight of the plant office. A farm overlooking the quarry from the northwest has been sold for residential development.

Production of dolomitic lime was the first activity on the site and remnants of the original kilns are still visible. The current operation was initiated in 1963 by Acton Limestone Quarries⁶ and later transferred to Indusmin Limited. Current estimates of reserves indicate another fifty years of operation on the existing basis.

Existing Conditions

Quarrying is taking place on a vertical face, 60-70 feet high, of the Amabel formation of Silurian dolomite. This material has been described as "light buff to light grey in colour, buff weathering, medium to coarsely crystalline, medium to thick and irregularly bedded, in part porous, highly fossiliferous, crinoidal."⁷ Overburden, immediately above the Amabel, is topsoil and glacial till ranging in depth from 0 to 50 feet. The Reynales dolomite formation underlies the Amabel and forms the quarry floor as it is not a saleable material at present.



**FIGURE 3
EXISTING
CONDITIONS -
ACTON QUARRY**

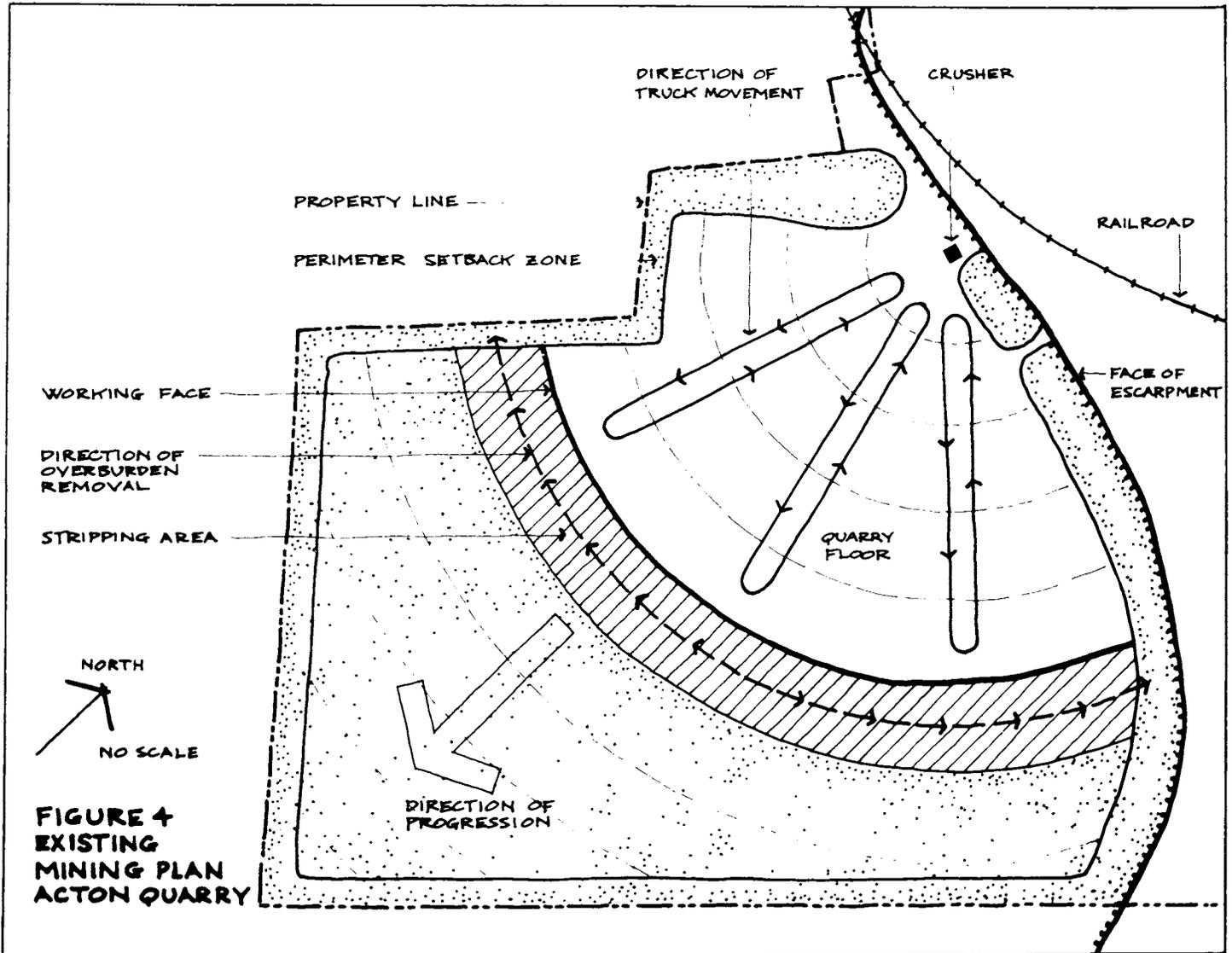
The plant product is crushed aggregate in the size range from $-2''$ to $+1''$ down to $-\frac{1}{4}''$ screenings and is suitable for most uses in concrete and highway construction. A high proportion of the total production is shipped to company owned sales yards in Metropolitan Toronto by rail with the balance trucked to local markets, primarily east of the quarry.

Mining consists of drilling, blasting, shovel loading of large Euclid trucks and hauling of ore to a 54" primary crusher. Ore processing consists of three stage crushing and screening with all operations, including washing, automatically controlled. The normal plant capacity is 1,000 tons per hour with design provision to double it in the future. Three screening towers and swing stacking conveyors feed six 50,000 ton stock piles. Product blending,

prior to shipment, is automatically controlled with electronic equipment to produce any desired mix. Supply from individual stock piles is through vibrating feeders on to a 42" wide, underground, reclaiming conveyor into a set of four, 400 ton blending bins at the railroad siding.⁸

Overburden is being stockpiled in a few non-operating areas and on top of remaining portions of the Niagara Escarpment. These remaining portions of the escarpment face are about 300 feet wide and have not been mined as the dolomite exposed to the atmosphere is not suitable for sale as aggregate. The pit floor is maintained as a clear and open haul route for trucks.

A schematic plan of existing conditions is shown in Figure 3.



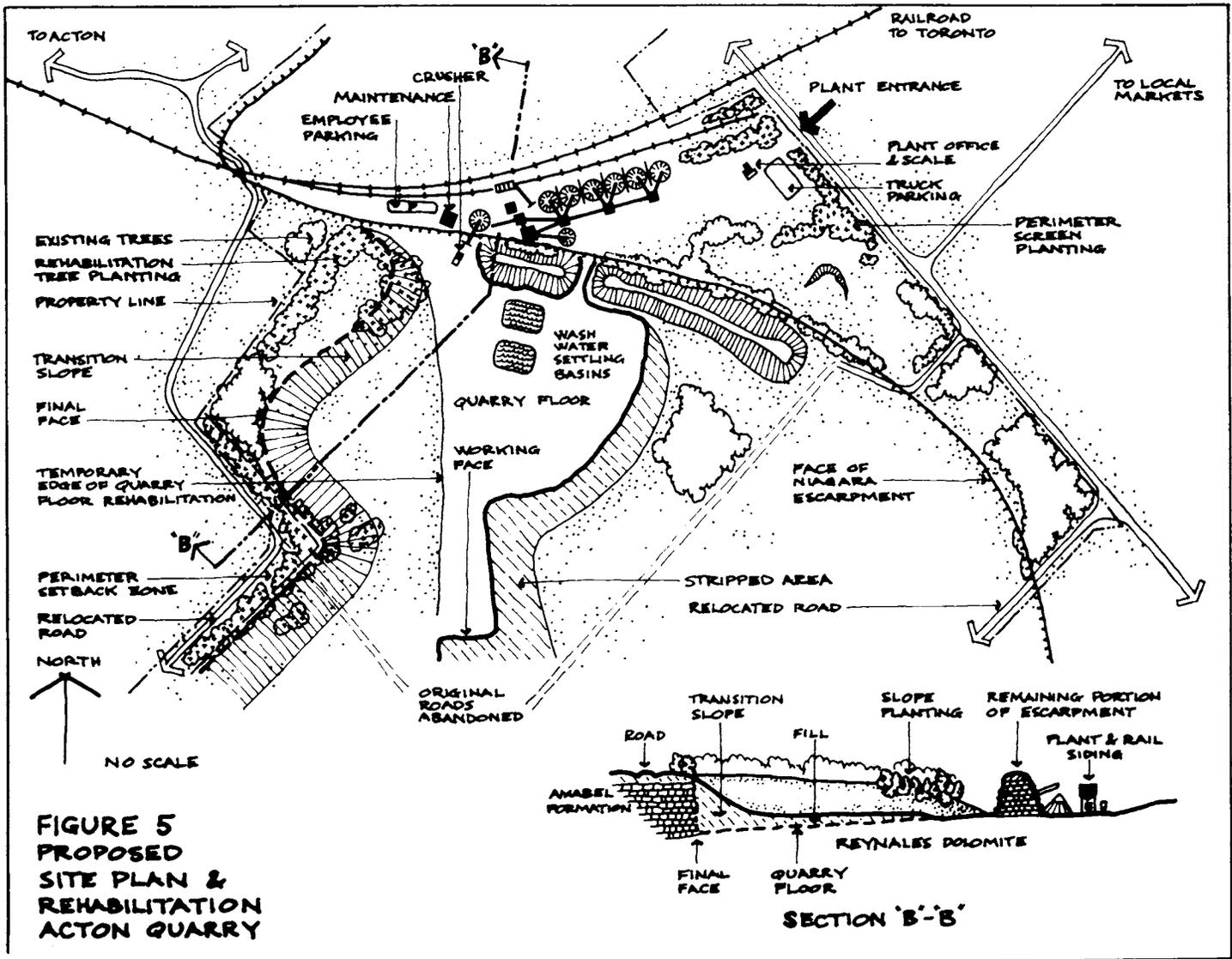
The current mining plan, Figure 4, is one of advancing concentric segments and was designed to maintain uniform production costs from all points of the face on the basis of uniform haul distance to the crusher.

The disadvantages of the existing plant and mining plans are as follows:

1. Little area is available for stockpiling of overburden.
2. Progressive rehabilitation of mined-out areas is not possible.
3. The entire quarry floor is exposed to public view as bare rock.
4. Dust control on the quarry floor is difficult.
5. Plant entrance is poorly located with respect to traffic safety - hill and curve.
6. Employee parking is not satisfactorily located with respect to work areas.

Proposed Conditions

The author was retained to prepare a comprehensive site plan and rehabilitation program as a means of forestalling public relations problems with the town of Acton and to resolve overburden disposal problems. The preliminary site plan is shown schematically in Figure 5 and includes the following significant revisions of plant organization and operation:

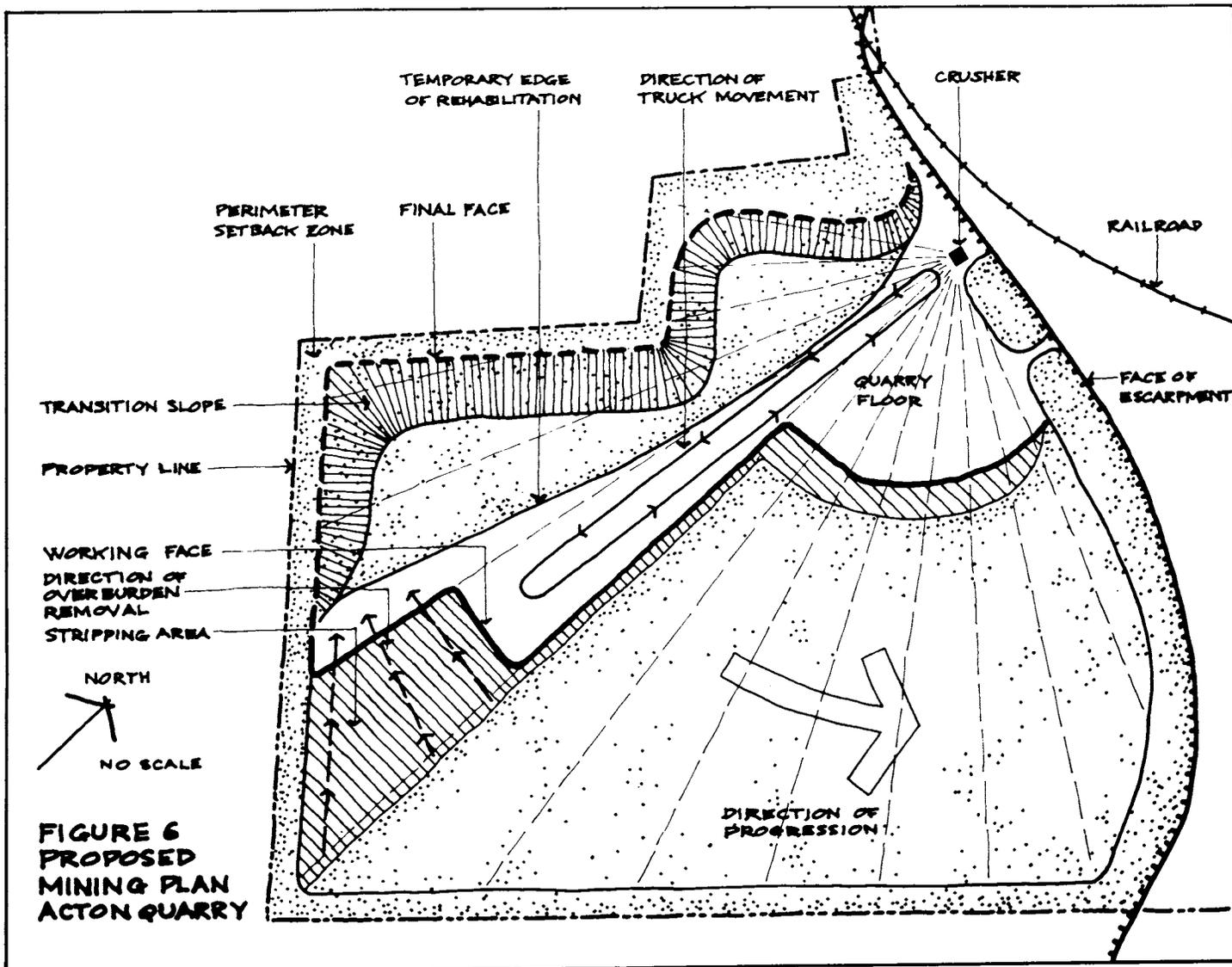


**FIGURE 5
PROPOSED
SITE PLAN &
REHABILITATION
ACTON QUARRY**

1. Relocation of plant office and truck scale
 - a) Improved traffic conditions at plant entrance - good sight distances
 - b) Adequate space for truck parking
 - c) Out of sight of edge of town
 - d) Adequate space for perimeter screening and planting
 - d) Office closer to center of site
2. Revised mining plan
 - a) Movement away from town
 - b) Overburden disposal adjacent to stripping area
3. Progressive rehabilitation plan

- a) Screening of areas adjacent to site
- b) Covering of exposed rock in mined-out areas
- c) Preservation of existing vegetation through discontinuation of overburden stockpiling outside quarry.

Details of the rehabilitation plan include covering of the pit floor with a minimum of four feet of soil, which provides a suitable base for a wide variety of future land uses including residential, industrial, commercial and agriculture, establishing of transition slopes between the quarry floor and undisturbed land with overburden fill, utilization of plant waste and washing residue in fill areas, stabilization of fill areas with vegetation, and establishment of a new surface drainage pattern.



**FIGURE 6
PROPOSED
MINING PLAN
ACTON QUARRY**

The advantages of this progressive rehabilitation scheme are that it will allow sale of portions of the site, prior to completion of all quarry operations, for capital recovery, reduce dust control requirements, integrate the rehabilitation procedures with normal quarry operation, and improve public relations.

The advantages of the revised mining plan, Figure 6, which progresses in radial segments, are that it provides unlimited overburden disposal with short haul distances, the opportunity for progressive rehabilitation of the pit floor and final working face, and requires a minimum area of exposed pit floor. A disadvantage of this scheme is that it requires relocation of both the drill and shovel at the completion of mining of each segment.

CONCLUSION

The basic design philosophy in approaching the client's problems was that of combining functional requirements, optimum resource utilization, and preservation of local landscape quality in recognition of contemporary social concerns. Matters of functional requirement and resource utilization have been covered in the revised site and mining plans. Social concern and public relations are covered in the rehabilitation program, in anticipation of future legislation, and in consideration of the visual qualities of the quarry site through reduction of contrast of on-site land forms and colour with those of the surrounding landscape.

The final comprehensive site plan will meet all of the detailed requirements of the proposed legislation with respect to ultimate development, site description, final topography, rehabilitation plans, etc..

By anticipating the requirements of this legislation Indusmin Ltd. is not only responding to social concern, over land use and environmental quality, but substantially increasing the return on their quarry by improving operating procedures and providing for optimum after-use of the site.

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DISCOVERY OF POTASH IN THE A-1 SALINA SALT IN MICHIGAN

by

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ABSTRACT

The bromine and potassium contents of salt taken by The Dow Chemical Company from a well core at Midland, Michigan, were determined on 120 samples. The samples represented A-1 Salina salt taken from the stratigraphic interval between 8,287 and 8,392 feet. Fifty additional samples covering a larger range of depths, from 8,150 to 8,600 feet, were analyzed for bromine only.

The bromine values ranged from less than 50 ppm to 1,600 ppm Br. The potassium values as K_2O ranged from less than 0.5% to more than 40%. The 92-foot interval between 8,295 and 8,387 feet has been estimated to contain an average of about 4% K_2O . The average K_2O for three 5 to 15-foot sections within this interval is appreciably higher.

The potash profile obtained correlates well with a gamma log run through the section some eleven miles southwest of the Midland well.

The bromine profile correlates well with one obtained from cuttings taken from a well located some forty-five miles to the north.

The sylvinite occurrence is somewhat unusual in that neither magnesium nor sulfate is present in appreciable amounts.

INTRODUCTION

It has long been speculated that potash salts might exist in the Michigan Basin. Following Valiashko's publication (1956) on the use of bromine in salt as a prospecting indicator for potash, a limited number of salt cuttings from several Michigan Salina wells were analyzed by Dow as early as 1957. The results were encouraging. Up to 280 ppm of bromine were found, but the work was discontinued. More recently Holser (1965) stated: "At the (Michigan) basin center the first, or A-1, salt starts out with the usual 40 ppm bromide, but rises near the top of this bed to

values high enough to suggest the presence of potash in this part of the basin." Our own studies of the geochemistry of brines found in the basin (Egleson, 1969) also suggested that potash should be present.

Dow had already cored the Salina salt at Midland in 1952, but only cursory attention had been given to the deep A-1 section. Late in 1966, however, it was decided to examine this section in more detail, and some 450 feet of core were withdrawn from storage.

PROCEDURE

A preliminary examination of the core along with spot sampling indicated that potash was indeed present, but that its occurrence was very erratic. It was found that areas of relatively constant potassium content could be delineated by using a scintillometer to supplement visual observation. Therefore, it was decided to take samples of a relatively constant composition at varying intervals, since such samples promised to provide more useful geochemical data than those taken at constant intervals. As a convenience, rather than splitting the core, one-quarter inch holes were drilled lengthwise through it and the powder so obtained was analyzed for potassium and bromine by X-ray fluorescence. Spot checks by wet chemical methods were in reasonable agreement. Samples for analysis of bromine only were taken by simply breaking off a few grams of salt with a hammer and chisel.

RESULTS

Figure 1 shows the location of the wells to be mentioned in the dis-

FIG. 1

AGGREGATE THICKNESS OF SALT IN SALINA FORMATION
(LANDES 1945) WITH WELL LOCATIONS SHOWN

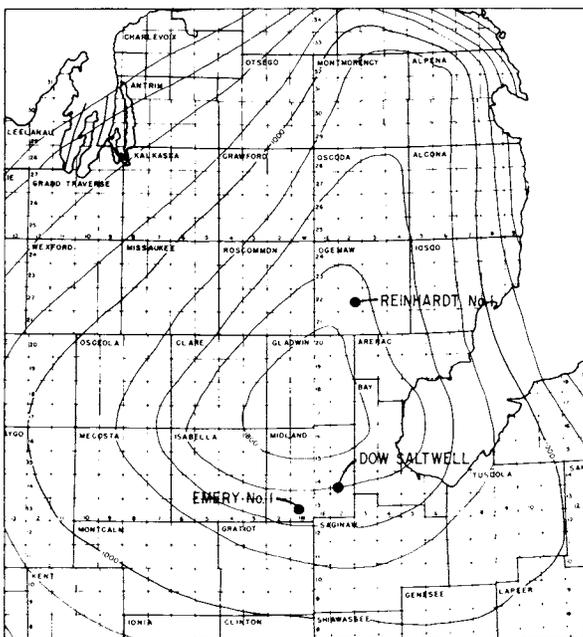
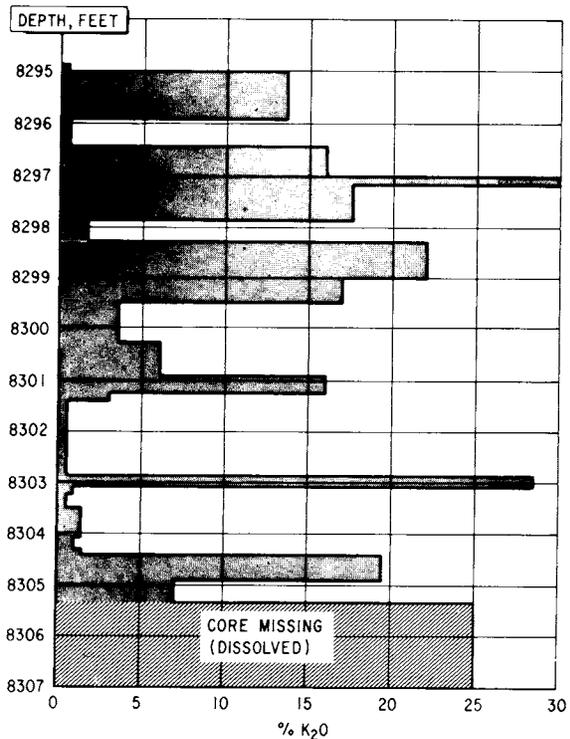


FIG. 2

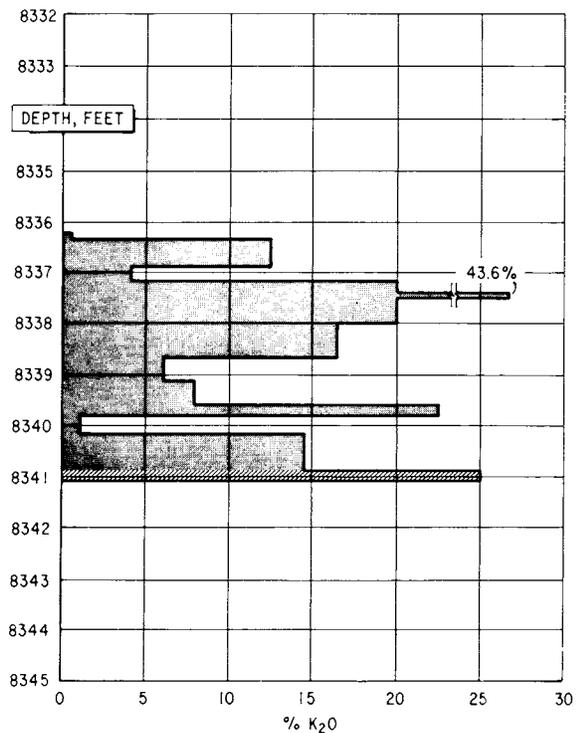
POTASH IN DOW SALTWELL CORE
(UPPER SECTION)



cussion. Figures 2, 3, and 4 give the concentration of potash found in three sections of the Dow well where it is most prevalent. In some of the sections the diameter of the core was reduced by dissolving action of the drilling fluid. In a few places,

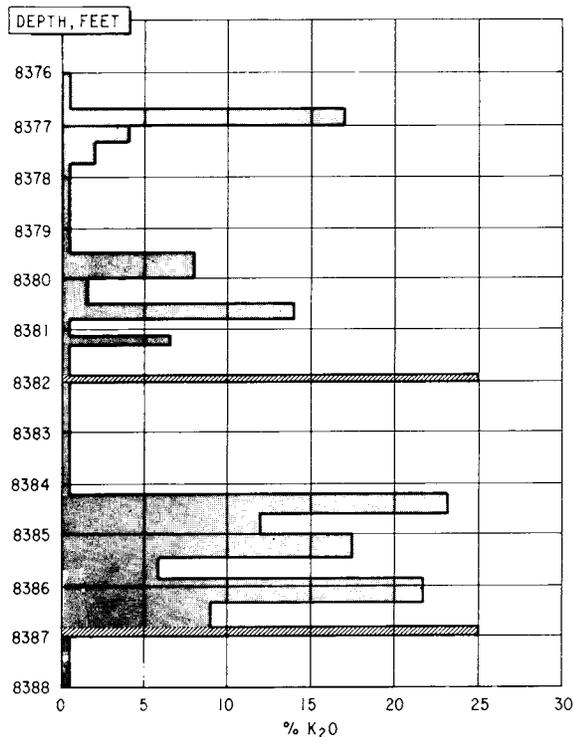
FIG. 3

POTASH IN DOW SALTWELL CORE
(MIDDLE SECTION)



inches, or even feet, of core were missing, but it is probably safe to assume that these missing sections would be relatively high in potash. The locations of the incomplete cores are indicated on the graphs. Assuming 25% K_2O as indicated in these charts, the 92-foot interval between 8,295 and 8,387 feet averages just over 4% K_2O .

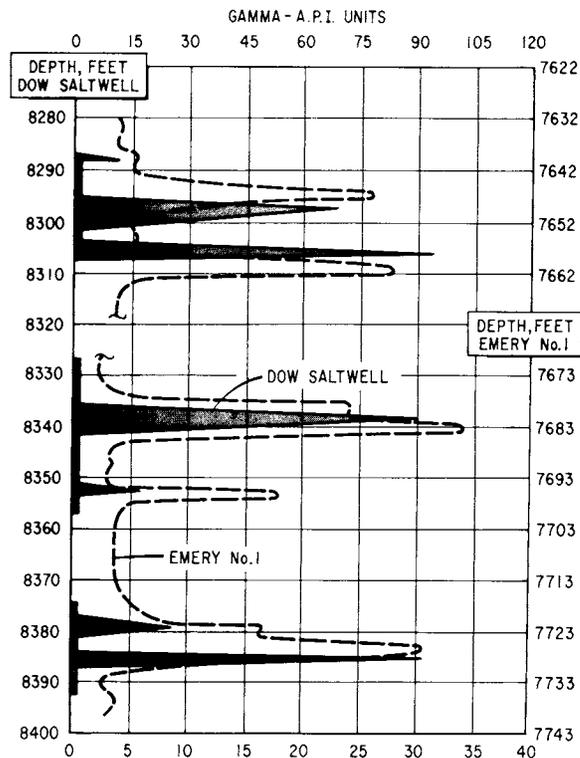
FIG. 4
POTASH IN DOW SALTWELL CORE
(LOWER SECTION)



CORRELATION WITH GAMMA LOG

No gamma log was run through the A-1 section when the Dow well was cored, but a log obtained for the Pure Oil Company, Emery No. 1, located some eleven miles southwest, provides some indication of the continuity of the potash content. Figure 5 shows the gamma log for Emery No. 1 superimposed as a broken line and at a convenient scale on the K_2O found in the Dow well. As an illustration of how this figure was prepared, note that the triangle peaking at 22% K_2O between 8,295 and 8,301 feet represents twice the average K_2O content shown for that interval in Figure 2.

FIG. 5
POTASH IN DOW SALTWELL CORE
AND GAMMA LOG OF PURE OIL,
EMERY No. 1

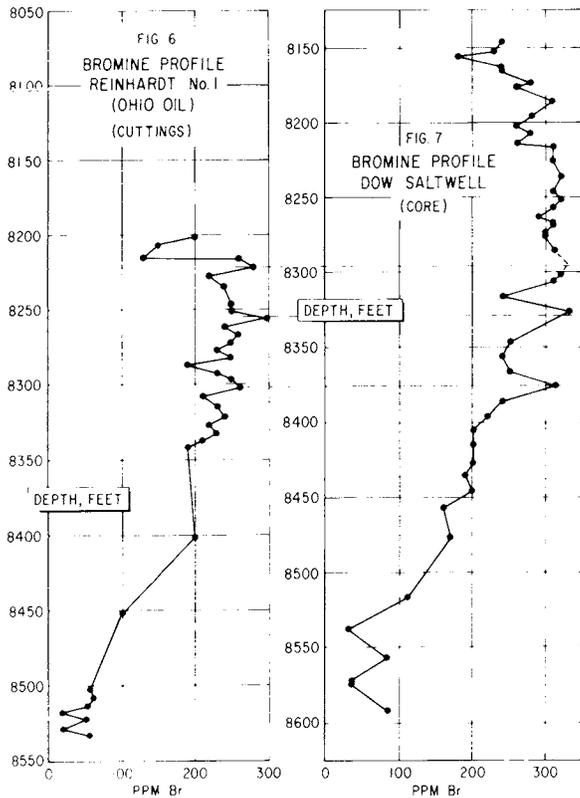


The potash is found at different depths in the two wells, occurring at a level some 650 feet lower in the Midland well than in Emery No. 1. Note also that the drillings showed nine feet less of halite between the upper and middle sections at the Emery well. In spite of these differences, the correlation is close enough to convince us that the gamma intensities observed at the Emery do indicate potash rather than shale or some other material.

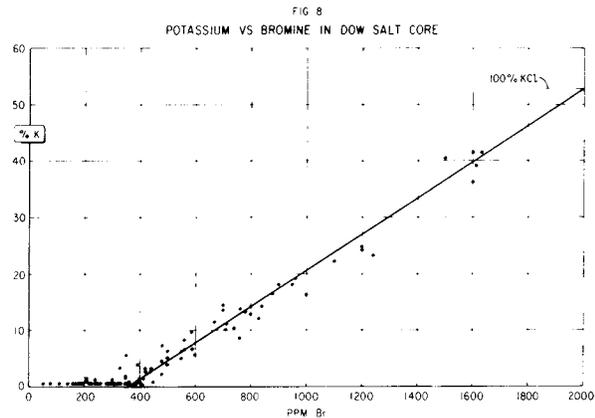
CORRELATION WITH BROMINE PROFILE

As a further indication of continuity of the deposits, salt cuttings obtained from the Ohio Oil Co. Reinhardt No. 1 well, in Ogemaw County, some 45 miles to the north, were analyzed for bromine. (No potassium was detectable.) Figure 6 shows the bromine profile for the Reinhardt well. Figure 7 shows for comparison the bromine profile determined on the Dow well core. The potash sections at the Reinhardt appear to be about 80 feet shallower. The maximum bromine contents of 280, 300, and 260 ppm are found at depths of 8,220-25, 8,255-60,

and 8,300-8,305 respectively, while the potash sections of the Dow well, shown in Figures 2, 3, and 4, occur at depths of 8,301, 8,339, and 8,383 feet. Here again the correlation is good enough to convince one of the probable continuity of the potash sections.



indicates that cooling played an important part in the crystallization of the potassium chloride. He reports that the first sylvite crystallized at 0°C contains about 2400 ppm Br, while that crystallized at 50°C contains about 3600 ppm Br.



The sylvinite sections are exceptionally clean. Several analyses were made for minor constituents with the results shown in Table I. Since the anhydrite is relatively low throughout the salt section and magnesium salts are non-existent, we are led to speculate that the brine was concentrated to a large extent before it reached the center of the basin -- perhaps even in another basin; and also that diagenesis may have occurred through dolomitization, leaving the bitterns, from which the sylvinite was precipitated, enriched in calcium and depleted of magnesium and sulfate.

OTHER ANALYSES AND RELATIONSHIPS

Figure 8 is a plot of all the potassium analyses compared with those for bromine. Two samples with a bromine content as low as 210 ppm contained 2 or 3% K, although K was generally absent when the bromine was less than 300 ppm. In only one sample with a bromine content greater than 400 ppm was it impossible to detect any K. Analyses of several samples showed that at low concentrations of potassium chloride in the sylvinite mixture (on the order of 2% KCl) the bromine content of the KCl is about 4300 ppm. At high concentrations of potassium chloride (on the order of 75% KCl) the bromine content of the KCl is about 2100 ppm. According to Braitsch (1965) this

TABLE I
MINOR CONSTITUENTS IN SALTWELL CORE SAMPLES

DEPTH	% K	% Na	% Cl	ppm SO ₄	ppm Mg	ppm Rb
8,237'	0.2	39.3	59.9	2900	470	<5
8,387'	1.9	40.0	59.5	5600	190	<5
8,297 ⁽¹⁾	23.7	20.9	53.5	1700	57	32
8,337'	39.2	10.7	50.4	900	71	54
8,385'	41.7	8.4	49.8	2600	21	57

(1) Also 7.8 ppm B and 0.13 ppm Li

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THE DISTRIBUTION OF SILURIAN POTASH IN THE MICHIGAN BASIN

by

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ABSTRACT

Bedded sylvinite, a mixture of sylvite (KCl) and halite (NaCl), has been core sampled by The Dow Chemical Company at Midland, Michigan. Geological and geochemical evidence supports the conclusion that potash underlies some 13,000 square miles of the Michigan Basin.

Stratigraphically, the potash is restricted to the basal salt member (A-1 Salt) of the Silurian age (Cayugan) Salina Group. The A-1 Potash occurs near the middle of the A-1 Salt except where the "recessive" salt, which covers the potash, was subjected to subaqueous re-resolution during the last half (the dilution phase) of the first evaporite megacycle. Lateral and vertical evaporite lithofacies successions are present around the deposit.

Because of radial influx, brine concentrations increased toward the center of the basin during the A-1 Salt megacycle. At any given time, the most soluble mineral was being deposited under a sinking column of centrally located brine. The concept of a transgressing-regressing body of brine acting on bottom, independent of shorelines, is used to explain evaporite lithofacies distribution. The existence of trapped brines during inter-cyclic carbonate deposition and the timing and influence of reflux currents during each evaporite megacycle are major factors explaining the potash-bearing Salina sequence. The A-1 Potash was deposited at the mid-point of the first evaporite megacycle before reflux currents developed in the newly restricted basin. Potash was never deposited during the younger megacycles (A-2, B, D, and the several F's) because these cycles were accompanied by early reflux currents. The presence of this newly-discovered evaporite lithofacies in the Michigan Basin is compatible with a deep basin origin for Salina salts through B Salt deposition.

INTRODUCTION

Over fifty years ago, Professor A. W. Grabau (1915) predicted in a letter to the State Geologist of Michigan that in the Silurian of Michigan "the lowest salt beds ought to carry the potash salts". He further stated, "this is true only for the lowest bed". Grabau's early prediction has been proven correct. The lowest bed does contain large deposits of potash. It has not been found, nor is it likely to be found in any younger bed, except in the trace amounts already described by Lucas

(1954) and by Dellwig (1955). More recently, Holtzer (1966) suggested that bedded potash should be present in Michigan.

The geochemical evidence which late in 1966 led to finding colorless sylvite (KCl) in a colorless halite (NaCl) section of a stored core has been described by Anderson and Egleson (1970). After they had confirmed the potash, I was asked to determine the extent and potential of the deposit. The geological study expanded to in-

clude more than 100 radioactive and other mid-basin logs.¹

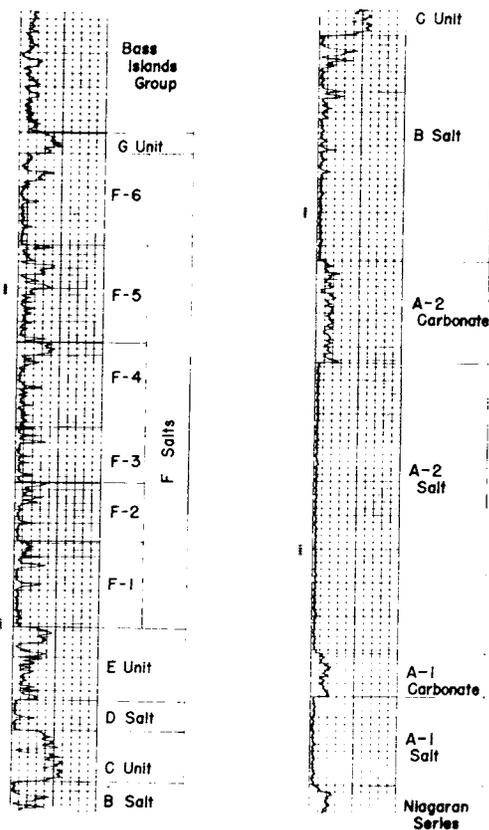


Fig. 1 Michigan Salina terminology. Typical Gamma Ray log beyond the limits of the potash (Good & Good, GG-1 Thom, Sec 10, T8N R9E, Lapeer Co.)

The Salina Group in the Michigan Basin was divided into lettered zones by Landes (1945) and has been further subdivided by Evans (1950) and Ells (1967). (Figure 1). This study was initially limited to one of these subdivisions, a single evaporite megacycle known to contain a new lithofacies. Later other subdivisions of the Salina were included. The study led to the conclusion that over 13,000 square miles of the Michigan Basin contain potash.

THE EXTENT OF PROVEN AND POTENTIAL POTASH

The A-1 Salt, which contains the A-1 Potash (a new term), underlies most of the Lower Peninsula. (Figure 2). It has a cored thickness of 449 feet at Midland and may exceed 500 feet in the central part of the basin.

¹The use of mechanical logs for the recognition of potash has been discussed by several authors (Alger, et al., 1965; Tixier, et al., 1967; Edwards, et al., 1967) and is not within the scope of this paper.

Four wells lie within the 400 foot thickness contour and seven additional wells show 300 or more feet of A-1 Salt. An anhydrite facies is present. Portions of the anhydrite zero line in the southeast are based on published maps by Briggs (1964). Both the salt and anhydrite margins are well marked by numerous control points, east, south, and west, but the northern edges are not as well defined. The rapid thinning of salt in the northwest and parts of the southwest appears to be evidence of truncation by re-resolution. Otherwise, the salt shows a gradual thinning and a well defined anhydrite facies beyond the salt, indicative of a normal depositional zero line. The A-1 Salt with its anhydrite facies probably was deposited beyond the present limits in the north, northwest, and to some lesser degree, in the southwest.

The probable extent of the potash in the A-1 Salt is shown related to the present limits of salt and anhydrite. (Figure 3). The zero potash line includes most of the area within the 300 foot salt isopach. Three points on this map are classed as proven; the Dow #8 Salt, Pure #1 Emery

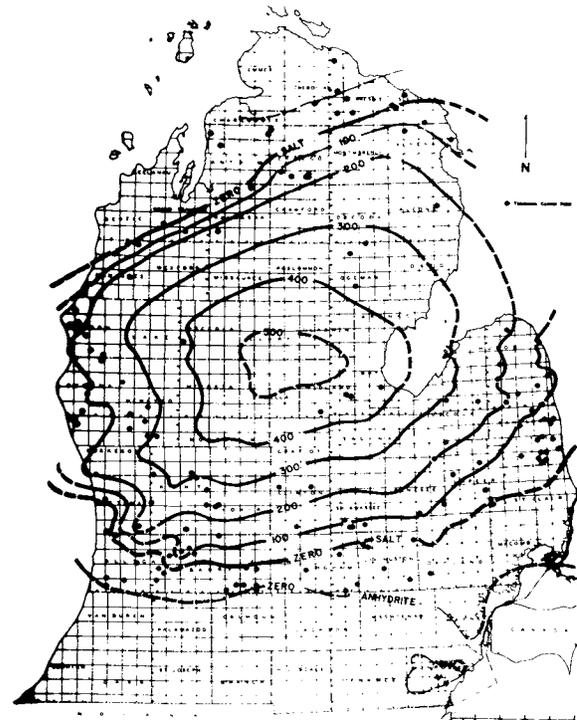


Fig. 2 A-1 Salt thickness. The numerous control points in the southern counties were not posted. Anhydrite zero line in southeast after Briggs (1964).

(Figure 4) both in Midland County, and the An-Son #1 Parmeter in Kent County (Anderson and Majeske, 1970). Seventeen wells were classed as indicated, fourteen on radioactive log evidence and three on chemical evidence, with three control points based on both methods. Seven basin wells have penetrated more than twenty feet of what is believed to be potash-bearing salt and at Midland the sylvite-bearing zone is 92 feet thick. The evidence suggests that potash will continue to thicken toward the depositional center of the A-1 Salt basin.

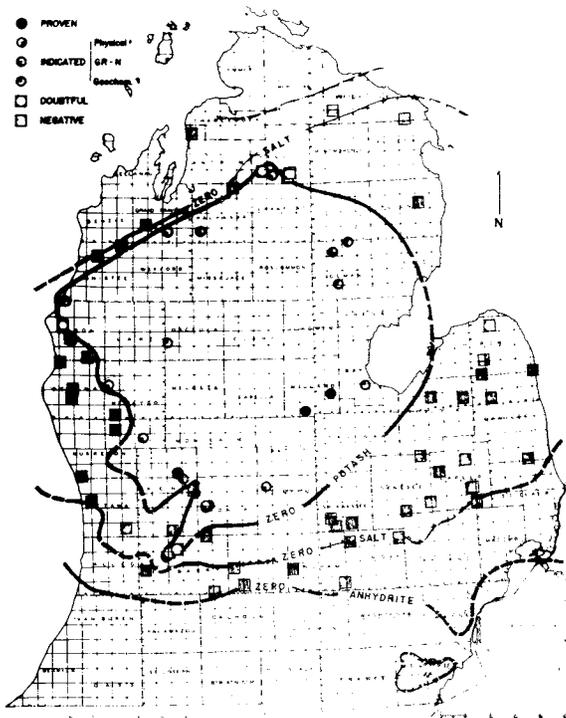


Fig. 3 A-1 Evaporite facies. A list of the wells shown as "Proven", "Indicated", or "Doubtful" is appended.

In the northwest and southwest, where truncation influenced present limits, potash occurs very close to the salt zero line. The northwestern edge of the potash was partially shaped by subaqueous re-solution, but in other places, the potash zero line marks the depositional limit of the most soluble mineral in a classical lateral lithofacies succession for evaporite deposition from bittern salts to halite to sulfates to carbonates (Krumbein, 1951; Sloss, 1953; Briggs, 1958; Stewart, 1963; Shaw, 1964; Holwerda and Hutchinson, 1968).

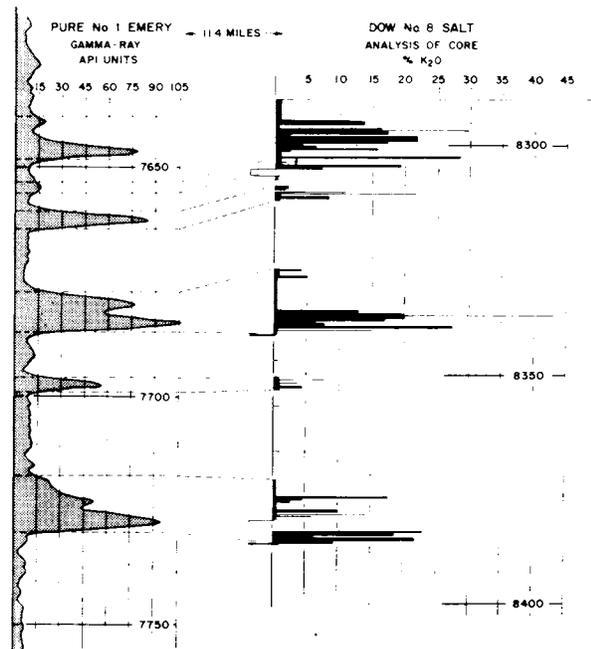
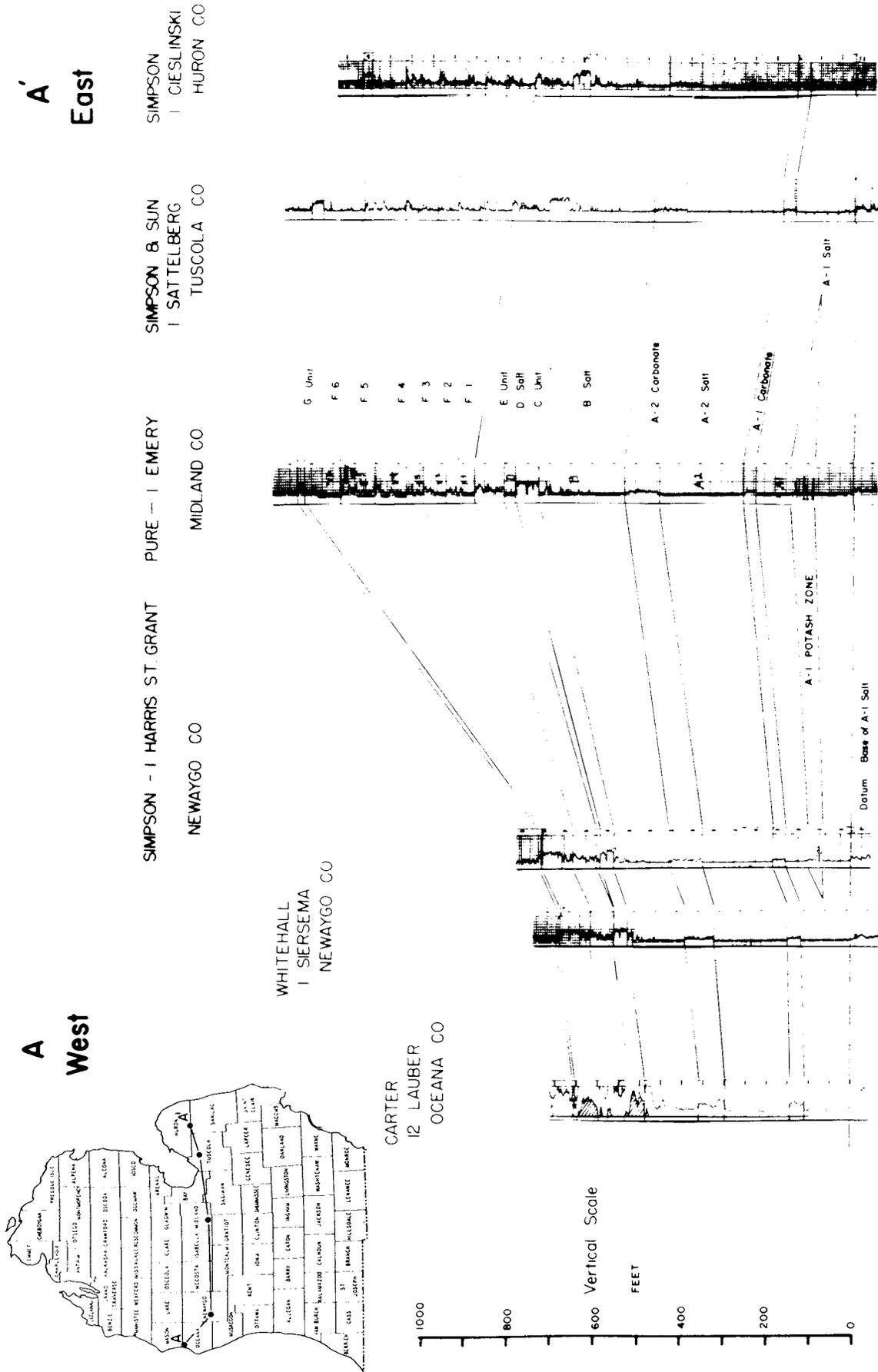


Fig. 4 Correlation of Gamma Ray log with % K₂O present in A-1 Salt core. Distance between wells is 11.4 miles.

In the stratigraphic cross sections (Figures 5 and 6), the base of the A-1 Salt is used as the datum and the total potash-containing interval is outlined. The potash occurs near the middle of the A-1 Salt in most wells, but is found near the top in the north, where salt above the potash was lost by re-solution. The salt beneath the potash is more uniform in thickness than the salt overlying the potash. The variability in thickness of salt over the potash is attributed to subaqueous re-solution before the A-1 Carbonate was deposited.

Some of the control points classified as "indicated" on the potash facies map (Figure 3) were based on radioactive log responses which have been described as "shale or carbonate lenses" in the A-1 Salt in sample logs. Certainly the response of the Gamma Ray curve to something within the A-1 Salt, more radioactive than halite, has been recognized in mid-basin wells, (Ells, 1967) but as "shale or carbonate" it attracted little interest. The shale interpretation is correct for the upper salts; for example, there is no potash in the D Salt in the Midland core, although the Gamma Ray response in that and other salts (upper B and F) is similar to the potash



STRATIGRAPHIC CROSS-SECTION A-A'

Fig. 5

B' South

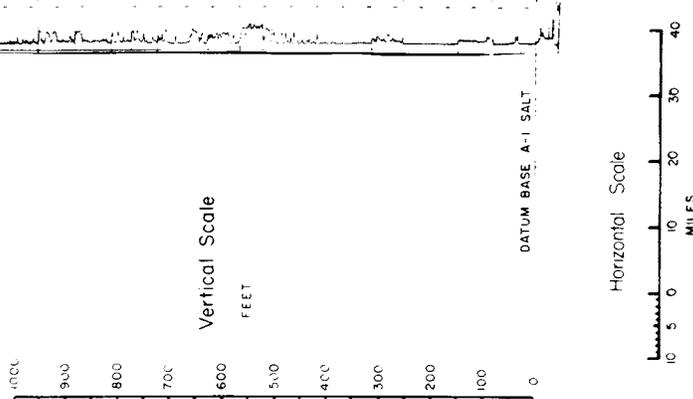
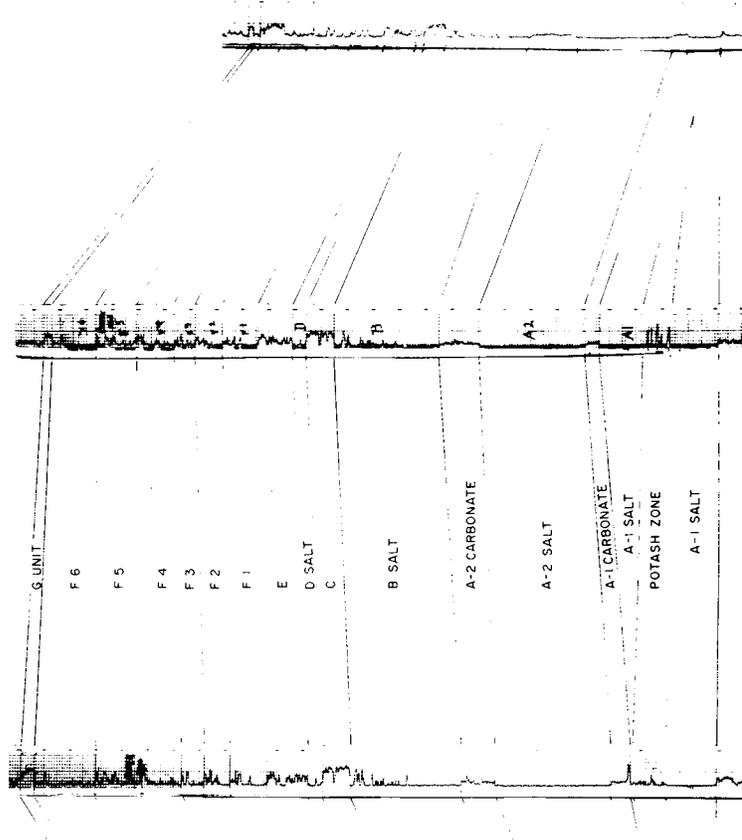
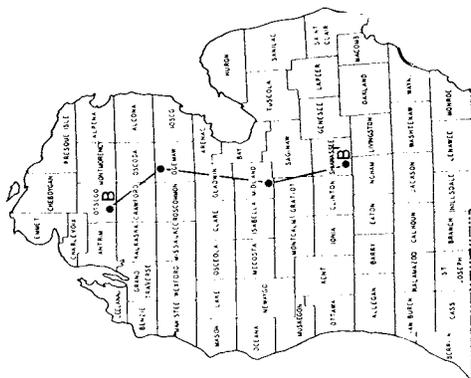
LEE
FERRIS No. 1
SHIAWASSEE CO.

PURE
EMERY No. 1
MIDLAND CO.

BRAZOS-SUN-SUPERIOR
ST.-FOSTER No. 1
OGEMAW CO.

SIMPSON
ST.-OTSEGO No. 1
OTSEGO CO.

B North



STRATIGRAPHIC CROSS-SECTION B-B'

Fig. 6

curve in the A-1 Salt. The dolomite, anhydrite, clay, and quartz found in the middle of the D Salt, mark the midpoint of a single D evaporite megacycle. Analyses of the bromine content of cored salt intermingled with these windblown clastics show higher bromine than the D Salt either above or below.

THE EVAPORITE CYCLE

The presence of bedded potash demands a re-examination of evaporite depositional theories as applied to the Michigan Basin. Previous references to bittern salts were based on trace amounts; the quantities which now must be explained are major. Why potash only in the lowest salt; why in a middle position; why are clastics common in the upper salts and absent in the lower, thicker salts where the potash occurs? Can this potash be associated with deep-basin halite?

Before considering these questions, it will be helpful to review some of the factors concerning evaporite deposition: the nature of the evaporite cycle; the concept of a "transgressing body of brine"; dynamic equilibrium in a cycle when reflux is present; the certainty of potash if reflux is not present; the influence of radial influx on flow patterns and facies; and, the effect of temperature on deposits.

First, evaporite deposition is cyclic. (Figure 7). The early stages of a cycle are dominated by factors which cause increasing brine concentration, the dessication of Stewart (1963). The final stages are dominated by factors which cause increasing dilution, the flooding of Stewart. The peak of a cycle is reached when the brine concentration is at its maximum. Should a cycle proceed to complete dessication, that cycle is at a midpoint and not at the end of a cycle. The most soluble mineral in an evaporite cycle has to be deposited in mid-cycle and as a result, potash should be found in the middle of salt sequences (Peterson and Hite, 1969), except where the deposits of the upper half of the cycle have been re-

dissolved totally or in part. Likewise the highest bromine in halite will be deposited at mid-cycle and in theory should be found in a mid-position in thick salt beds, except for re-resolution. (Unlike Goldsmith, 1969 p. 795).

Second, minerals deposited during the early stages of an evaporite cycle are the result of a "transgressing body of brine" (new term) and in this sense these deposits are transgressive. These are the progressive evaporites of Borchert (1964). These minerals are usually well preserved as they are covered by increasingly concentrated brine. The deposits of the latter stages of an evaporite cycle are the result of a "regressing body of brine" (new term). Such regressive deposits, the retrograde or recessive of Borchert, are often poorly preserved as they tend to be covered by brines capable of redissolving the bottom sediments. Where regressive beds survive without clastic armor, it is due to a thin blanket of insoluble, or less soluble, residues which can develop to hold a protective layer of saturated, interstitial brine on bottom. As used here, the terms "transgressive body of brine" and "regressive body of brine" apply to the sea floor and do not imply changes in shore lines. The terms are not synonymous with "transgressing sea" or "regressing sea". Shore lines need not change as the influence of the brine body changes across the bottom of the basin.

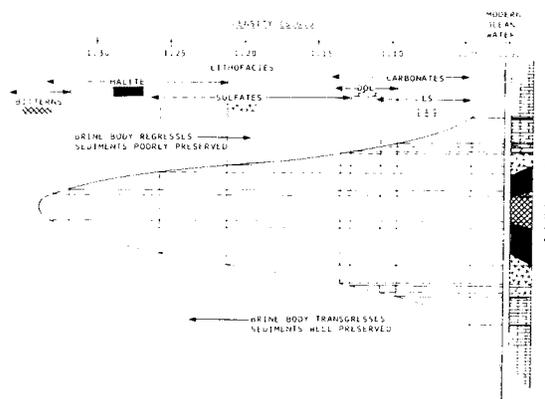


Fig. 7 Idealized evaporite cycle from normal sea water to bittern salt concentrations plotted against the relative time each evaporite lithofacies will deposit in a single evaporite cyclothem.

Third, reversals of a cycle can occur at any point. Most evaporite cycles in the geologic past according to Borchert and Muir (1964) never went beyond the point where limestone and dolomite were being deposited. Dynamic equilibrium conditions can occur at any point in an evaporite cycle, but only if reflux to the open ocean is present (King, 1947). In an isolated basin having no reflux, a complex mixture of ions enters while water leaves by evaporation. Certain ions are removed by precipitation, while remaining ions continue to accumulate in solution. To a minor degree certain volatile constituents, such as iodine, may escape to the atmosphere (Goldschmidt, 1954). The arrest of a cycle would be impossible without reflux because of the increasing number of ions not yet forming precipitates.

Fourth, the reflux of brines carrying ions back to the open ocean is one of the major factors resisting a move of the cycle toward concentration. If no reflux of bittern brines out of the basin is permitted and the other factors favoring increasing water concentration do not change, the cycle must move to the eventual deposition of potash salts. Schmaltz (1969) has calculated that, without reflux, a deep basin would reach late salt concentrations when about half filled with halite, and Borchert and Muir (1964) have said, "We believe that a wide range of depth is still possible even in the last stages of precipitation when the potash salts have started to separate out. There is absolutely no need for this phase to be associated with very shallow basins or with complete dessication." (p. 43-44).

Fifth, the volume of water entering a basin is a major factor controlling whether the cycle moves toward increased concentration, stands still, or becomes more dilute. The number and distribution of inlets exerts a strong influence on the pattern of evaporite facies distribution within the basin (Briggs, 1956; Alling and Briggs, 1961). In some cases influx can be essentially radial, as Briggs

and Pollack (1967) showed was more realistic for Michigan. In a one inlet model, the densest surface water and the most soluble minerals will be found along shore, away from the inlet or open ocean (Briggs, 1956; Shaw, 1964), but with radial inflow the densest surface water will be near center (Lotze, 1957). (Figure 8).

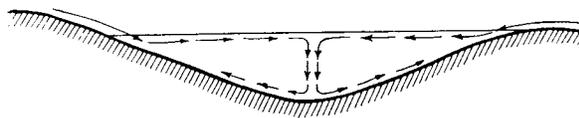


Abb. 48. Ideales Strömungsbild in einem gleichförmig gestalteten Salzsee bei gleichmäßigem Zustrom und Windstille.

Fig. 8 (Ideal circulation pattern in a symmetrical salt lake with radial inflow uninfluenced by wind). From LOTZE: "Steinsalz und Kalisalze", Gebrüder Borntraeger, Berlin/Stuttgart, 1957, p. 96.

Surface water will then slope down to a low area of minimum surface movement in a central position of the basin. This surface low will contain water which is as concentrated as any in the basin. These centrally located brines will sink under the surface low. Bottom currents of this brine will move from under the surface low into any accessible lows in the basin floor. (Figure 9). The extreme vertical

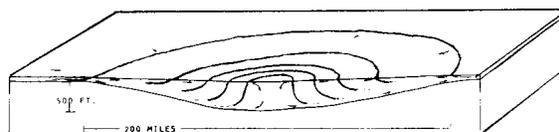


Fig. 9 Circulation in a deep basin restricted by shallow water margins and having radial influx and reflux. The most soluble minerals are deposited in mid-basin.

exaggeration in this sketch must be considered; bottom slopes are only about 1:1000. Minerals precipitating at the surface, where evaporation is taking place, will sink and be redissolved if the lower waters are not yet concentrated in respect to the precipitated mineral. Survival and deposition of the minerals in an evaporite cyclothem deposited in a basin receiving radial inflow will occur first in the deep central part of the basin under the surface low. The densest brine in the system will assume the shape of an inverted mushroom transgressing the basin floor and reaching up to the surface low. As

the evaporite cycle continues in the direction of increasing concentration, this brine body will move across the basin floor and the central column of sinking brine will increase in diameter. The densest brine will be found under the surface low in the core of the sinking column. In this way, the dense bottom brine remains in contact with the solar evaporation process even in deep water.

Sixth, variations in temperature such as an expected cooling at depth, will contribute to the bottom growth of crystals according to Dellwig (1955). It has also been suggested by Borchert and Muir (1964) that cryophilic sylvite would tend to accumulate in the deeper cooler water, while only thermophilic halite might develop in shallower, warmer waters.

CONDITIONS OF EVAPORITE DEPOSITION IN THE MICHIGAN BASIN

As to the specifics of Salina deposition in Michigan, we start with the timing of crustal sag in relation to salt deposition. A similar problem occurs in the Zechstein (Upper Permian) and in that instance, Richter-Bernburg believes it is an illustration of the general principle that no sediments remain to represent the greater part of geologic time (Borchert and Muir, 1964, p.41). Borchert maintains that the salt in Michigan accumulated long after basin

shaping earth movements had ceased.

The Niagaran rocks, on which the Cayugan evaporites rest, thin toward the center of the basin. This thinning has been interpreted by Cohee (1948) as the result of uplift and erosion or by Ehlers and Kesling (1962) as positive crustal behavior and non-deposition. Kay (1965) has commented that Silurian crustal movement in Michigan, "is one of the challenging puzzles of geology" (p.204). In my opinion, Niagaran mid-basin thinning by non-deposition as subsidence continued over a long span of time, compatible with a continuing negative area, is the best explanation and should not be overlooked as a possibility.

As to deep water vs. shallow water origin, it has been my opinion that the thickness and purity of the A-1, A-2, and lower B salts are best explained by the inertia of a large mass of brine found only in a deep basin. This study has led me to conclude that the Michigan Basin was 600 or more feet deep in mid-basin before the first anhydrite of the Cayugan was deposited, deep enough to receive the A-1 Salt without filling. (Figure 10). The deep basin origin of these salts has been proposed by Schmaltz (1966, 1969; Dellwig et al. 1969) and most recently by Rickard (1969); other authors (Holzer, 1966; Sloss, 1969) have questioned some aspects of deep water halite deposition.

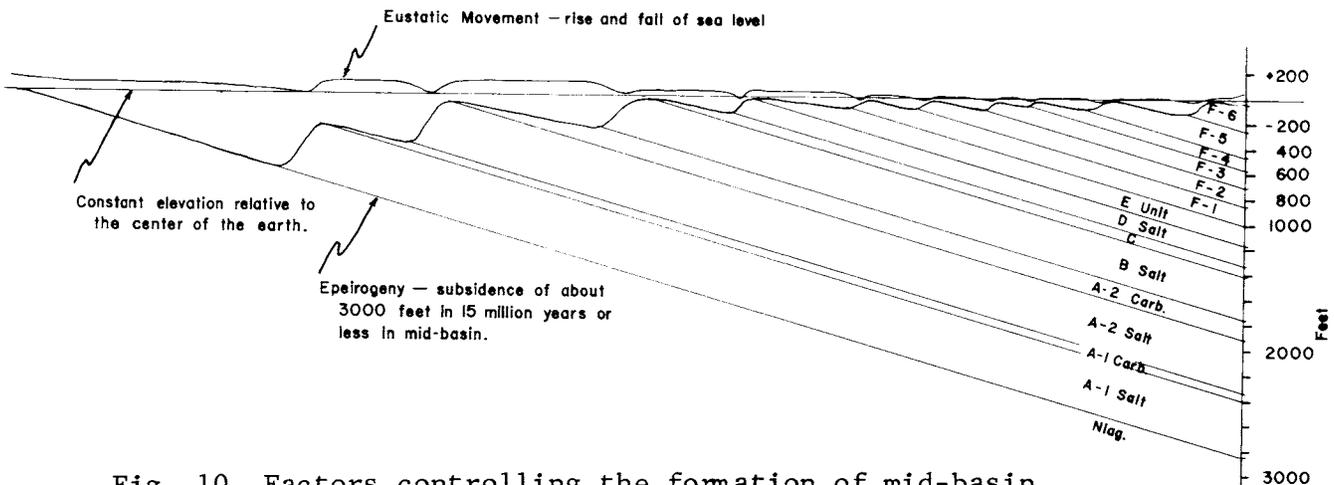


Fig. 10 Factors controlling the formation of mid-basin Salina evaporite cyclothems in Michigan

I picture the basin as a deepening depression in an otherwise relatively flat sea floor during Niagaran time. The bottom slopes of the basin were gentle, in the order of 1:1000 on the average. The New York-Ohio evaporite basin was not yet restricted beyond the point of carbonate deposition, for the oldest evaporite there is not as old as the A-1 Salt according to Ulteig (1963) Fergusson et al. (1968), and Rickard (1969). The water covered approaches to the basin were wide and shallow and the water entering the basin was more saline than open ocean water (Landes, 1963; Sloss, 1969). The influx of water was essentially radial and barriers, when they developed, were more a matter of shallow water margin conditions than one of shore lines.

Evaporite facies within the A-1 Salt represent synchronous deposition in waters of varying concentration. At the peak of the A-1 cycle, while potash and halite were forming in mid-basin, sulfates and carbonates were being deposited around the basin rims and over the flat approaches to the basin. These rim facies have not been identified in this study, but are assumed to be present whenever central basin evidence shows the rims and approaches to be covered with water. The absence of windblown or other clastics in the first salts is evidence that the margins were covered through the first two evaporite megacycles. The first appearance of large land areas near the basin did not occur until the upper part of the B Salt was being deposited. Thereafter, large source areas for windblown clastics were common around both the Michigan and New York-Ohio basins as epicontinental sea bottoms were periodically exposed to wave and wind. Dolomite, anhydrite, and clay bottom muds, along with quartz, were transported by winds over wide areas of both basins during periods of low water. These clastics occur frequently in the many small cycles of the upper B and F salts where they mark the mid-point of individual cycles, as in the D Salt. Adams (1969) has suggested in his paper on the Salado formation that in that area, "It is

more likely that the majority of argillaceous material in the ore zones was carried into the basin by winds." (p. 98).

Water-borne clastics will appear as wedges along the margins of evaporite basins. As the cycle mid-point is likely to coincide with the lowest water stage over the basin margins, these clastics can be expected to occur in a mid-position of edge salt, assuming little or no loss of "recessive" salt deposited during the later stages of the megacycle. (Figure 11-A). Windblown clastics are also to be expected at mid-cycle but these clastics will tend to form thin sheets. (Figure 11-B). These windblown clastics will mark periods of low water over wide areas outside of the basin proper. It is reasonable to expect that as sea level lowers enough to supply source areas for windblown material, both types of clastics will occur together. (Figure 11-C).

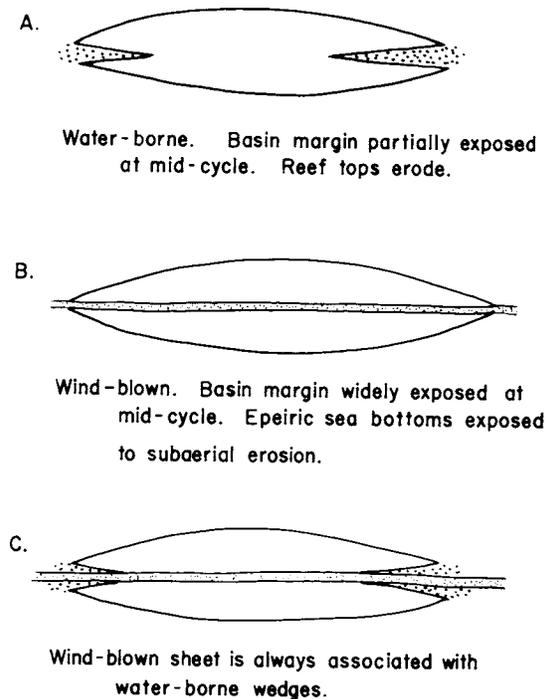


Fig. 11 Clastics in halite lenses.

The great mass of water involved in the first megacycle concentrated very slowly as minor decreases in sea level from Niagaran time tightened the degree of restriction in the basin. During the early stages there was no reflux out of the deep basin. According to Scruton (1953), reflux currents

can flow out of a basin only after, "the slope of pressure surfaces at depth due to excess density creates a potential for flow which exceeds the hydrostatic head." (p.2505). Scruton (1953) has also shown that a number of frictional forces must also be overcome once flow starts, including a dynamic barrier created by the surface inflow of lighter water.

The presence of potash demonstrates that there was no loss of ions by reflux early in the megacycle as the factors combining to concentrate the water continued to the point of potash deposition on the central basin floor. This did not occur in a shallow shrinking sea of the type advocated by Goldsmith (1969), for the absence of clastics shows that the basin rims and shallow margins were still covered by water. If the megacycle reverses slowly enough, most of the recessive salt above the potash will be preserved, no break in sedimentation will occur in the salt and no clastics will be present. (Figure 12-A). If the potash is the result of a shrinking sea or evaporation to dryness, the problem of preserving the highly soluble deposits during the last half of the cycle yet to come must be faced. The most common preservative is a clastic armor, initially windblown, followed by water-borne clastics and brine containing redissolved halite. (Figure 12-B). A very thin layer of undisturbed clastic material can hold an interstitial brine, saturated in respect to the mineral below, so that re-solution of that mineral is prevented.

The long fetches of shallow water outside of the basin proper may have assumed the role of fore-basins in the removal of sulfate and magnesium. Carbonate and sulfate removal before entrance to the basin has been suggested by Dellwig (1955). If this is true, the lack of magnesium-bearing bittern minerals in the core (Mg < 60 PPM) is more easily explained (Anderson and Egleson, 1970)

Any evaporite facies is restricted to the regions of the sea

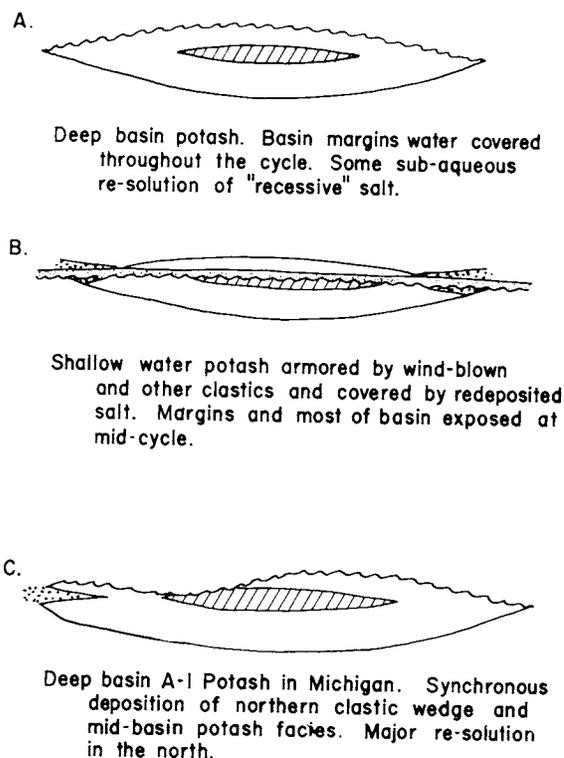


Fig. 12 Potash in halite lenses.

floor covered by solutions sufficiently concentrated to deposit that facies. The zones of facies deposition in the A-1 Salt indicate not a shrinking sea, but rather that a three-dimensional zonation of brine within the basin was maintained. The brine in the basin at the peak of the megacycle did not possess the approximate uniform density suggested by King (1947) for the brines beneath the surface layer of the Delaware Basin sea.

The control over the evaporite cyclothem and other sediments of the Salina was largely one of eustatic change of sea level similar to suggestions by Silver and Todd, (1969) for the Permian and by Peterson and Hite (1969) for the Pennsylvanian. After mid-basin potash deposition had been in progress a relatively short time, a very small rise in sea level over the basin margins increased the influx and reduced the dynamic barriers so that brines, filled to the reflux spill-over point, could move out of the basin for the first time. This gradual start of reflux of bittern brines out of the basin caused the evaporite megacycle of the A-1 to reverse very slowly and potash depos-

ition was interrupted. Three possible early exits for bittern reflux currents are suggested by extensions of potash along the southwestern margin. (Figure 3). Superimposed on the megacycle are numerous smaller cycles indicated by at least five potash zones at the peak of the megacycle (Figure 4) and the several fluctuations in bromine content in the A-1 Salt above and below the potash.

Considerable re-solution of halite above the potash occurred, and an unknown volume of northern potash was lost during the recessive phase of the megacycle. (Figure 6). Thinning of A-1 Salt by re-solution did occur in the north and it is probable that the bulk of the influx during the latter stages of the A-1 Salt megacycle came from the north. There appears to have been some thinning by deposition against a sloping bottom, basinward of the "northern shelf".

The possibility of a small clastic wedge occurring within the A-1 Salt has been heightened by reports of dolomite in the A-1 Salt in Grand Traverse County (Sec 14, T26N R9W). If true, then the schematic diagram of A-1 Salt and potash (Figure 12-C) illustrates a deep water situation with erosion of reef tops in the north and other margins essentially water covered. The thickness of recessive salt in mid-basin is evidence that reversal was slow and that the recessing body of brine on bottom changed slowly as the A-1 Salt above the potash was deposited.

The A-1 megacycle ended abruptly while in a low-bromine halite phase with a rise in sea level sufficient to end the influence of sea floor shape on surface flow. Water depths over the rims may have risen fifty or more feet. The dense mass of brine in the basin, concentrated to the point of halite deposition, was trapped. These heavy brines lay stagnant, removed from surface evaporation, and were no longer mixed with oxygen-laden surface water. Halite deposition stopped. A very slow carbonate deposition began and deposition changed from halite to

carbonate directly without much sulfate. The carbonates, derived from surface waters, settled down through the trapped brine to form the widespread A-1 Carbonate. The A-1 Carbonate deposition required many multiples of the time it took A-1 Salt to deposit. The rate of carbonate deposition was slower than the rate of basin subsidence. Throughout the formation of this inter-cyclic carbonate, the submerged basin remained nearly filled with heavy brine to the reflux "spill over" level.

The end of A-1 Carbonate deposition was caused by a lowering of sea level to earlier evaporite levels with the basins rims remaining water covered as before. In this way, the trapped body of brine - still concentrated to the point of halite deposition - was again rather suddenly exposed to evaporation. Bottom sediments reverted from carbonate to halite with a minimum of sulfate, which might otherwise be expected if a normal concentration cycle had had to start anew. The A-2 Salt megacycle moved quickly to halite deposition without clastics, and shortly thereafter reflux currents began. Dynamic equilibrium was soon established in the halite range and, because of early reflux, due in part to trapped brines, potash concentrations were never reached. The A-1 deposition had caused a partial filling of the lowest parts of what still remained a deep basin, and this partial filling also contributed to early reflux. The second inter-cyclic carbonate, the A-2 Carbonate, was the result of high water as was the A-1 Carbonate. The B Salt began with trapped brines left over from earlier cycles as did the A-2 Salt. Basin subsidence continued throughout the Cayugan but it was not until near the end of B Salt deposition that the basin could be considered a filled basin. Not until near the end of B Salt deposition can one picture a shrinking sea with exposed land areas to supply clastic sediments.

It is unlikely that the A-2 Salt, the B Salt and younger salt cycles in mid-basin ever attained the high mid-point of concentration reached by the A-1 megacycle, because reflux of

trapped heavy brines was an early factor in all but the first megacycle. If late B, D, or F potash deposits exist, they will be found in distinct marginal sub-basins separated from the main basin as in the case of the Lower Rhine deposits, not in mid-basin as is the A-1 Potash.

CONCLUSIONS

Based on geological and geochemical evidence, potash appears to underlie some 13,000 square miles of the Michigan Basin. The potash (sylvinitic) is found in the middle or upper half of the A-1 Salt and is expected to thicken toward the center of the basin.

The cyclic nature of evaporites requires that high-bromine halite or potash be deposited at mid-cycle, and if "recessive" salt from the dilution phase survives, the most soluble mineral will be found near the middle of evaporite sequences. Radial influx causes the densest brines and the most soluble minerals to be centrally located. Lithofacies distribution can be explained by the transgression or regression of a body of brine acting on the basin floor independent of shore lines. Reflux currents are required to hold a cycle in dynamic equilibrium and if reflux is not permitted (other factors remaining constant) potash deposition is certain.

Eustatic changes in sea level controlled the degree of restriction in the deep Michigan Basin. Thus, the evaporite cyclothems and clastics comprising the Salina Group can be used to determine water depths over the basin margins, if individual evaporite megacycles are studied. Shallowing basin depths and trapped brines assisted the development of early reflux currents in all but the first megacycle and prevented later cycles from reaching potash concentrations.

This study was basin center oriented and the problem was considered from mid-basin outward to the margins. Most other workers have studied the shallower rims and looked

inward, the different point of view may explain differences of opinion. Certainly there is much yet to be done on Michigan salt and potash.

Wells shown on Figure 3 as
"Proven", "Indicated", or "Doubtful"

Sec T-R	Well Name	County
2 29N 4W	Lake Haricon	Otsego
16 29N 3W	State-Otsego	Otsego
9 25N 10W	Lemcool	Grand Traverse
10 25N 8W	State-Springfield	Kalkaska
4 24N 3E	State-Rose	Ogemaw
28 24N 2E	State-Foster	Ogemaw
35 22N 2E	Reinhardt	Ogemaw
20N 17W	Mikuta	Mason
20 19N 17W	Timpy	Mason
18N 10W	Stedman	Osceola
20 15N 14W	Thunder-Thompson #1	Newaygo
21 14N 2E	#8 Salt	Midland
21 13N 1W	Emery	Midland
14N 4W	Bateson	Bay
10 11N 12W	Harris	Newaygo
26 9N 10W	Parmeter	Kent
6 8N 9W	Ten Have	Kent
27 8N 4W	Sillman	Clinton
2 7N 9N	Wingeier	Kent
34 7N 8W	Ten Cate	Ionia
35 7N 8W	Essington	Ionia
4 6N 8W	Dieterman	Ionia
34 4N 10W	Janose	Barry
6 3N 10W	Richardson	Barry

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DETECTION OF POTASH ZONES BY DRILLING FLUID ANALYSIS

by

Raymond J. Anderson¹ and E. C. Majeske²

ABSTRACT

By analyzing drilling fluid for percent of potassium, and knowing the drilling and pumping rate, it was calculated that in the Salina A-1 Salt of Silurian age in the Michigan Basin a 6.2 foot bed averaging 7.3% sylvite (KCl) exists at a depth of 5,045 feet in the No. 1 Parmeter, in Section 26, T9N R10W, Courtland Township, Kent County, Michigan, drilled by An-Son Corporation July 7, 1967. Confirmation of these calculations was found on the Gamma Ray log when it was released a few months later.

This inexpensive method for detecting potassium minerals can be used when a well is scheduled to penetrate a salt section. Drilling fluid samples should be taken every two minutes in order that a zone is not missed. To reduce the number of samples sent out for assay a semi-quantitative screening test for potassium can be used.

INTRODUCTION

The search for potash by The Dow Chemical Company in the Midland Basin goes back many years and has encountered the difficulties presented by any search for potash. Few wells drilled for petroleum in Michigan penetrate the Salina Salt. Normally the salt section is not cored and only salt cuttings are available for examination. In these, the potash has been dissolved out by the saturated sodium chloride used for drilling fluid when going through the Salina formation. High bromine content in the salt cuttings indicates only that potash may have been precipitated. Gamma Ray logs, if available and if correctly interpreted, will indicate the presence of potash -- the estimated potassium chloride content from a Gamma Ray log may be as low as half the actual content if the logging speed was not reduced when going through the potash zones.

Following the Dow discovery of potash (Anderson and Egleson, 1970) and the geological study based on gamma logs and geochemical evidence (Matthews, 1970), there was a need for additional direct confirmation in a well which could be sampled (or cored) and logged. Mr. Majeske was asked to arrange for such a test. The An-Son Corporation No. 1 Parmeter (SE SE Sec. 26T 9N R10W Kent County) was the first test to be drilled within the potash outline. The well was not scheduled to be cored in the salt. Mr. Majeske suggested that we sample the drilling fluid and salt samples at short intervals through the zone of interest. The drilling fluid should show an abrupt rise in the potassium content when a potash zone was encountered. At a drilling rate of about one foot per minute in salt, closely spaced samples are necessary in order that a zone not be missed. It was decided the drilling fluid samples on the Parmeter well would be taken every two minutes in the A-1 Salt section. The time was synchronized with the geolograph chart on the drilling rig so all samples could be related back to a drilling depth. The sample lag of ten minutes per thousand feet was checked

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by the first salt returns at the surface after drilling into the A-1 Salt. A Gamma Ray log of a nearby well is helpful in indicating approximately when the potassium zones will be cut. Sampling should bracket the zones to allow for well to well variations. In this test the Gamma Ray log of the Ambassador Oil Company No. 1 Ten Have (Sec. 6, T8N R9W, Kent County) was used to plan the sampling program for the Parmeter well.

PROCEDURE

The An-Son Corporation was contacted and permission was granted to sample the A-1 Salt section in the well. Drilling fluid samples were collected in 200 ml polyethylene bottles and salt cuttings were placed in standard sample bags. It was found by Anderson and Majeske that two men could by constant endeavor secure samples every two minutes. Blank samples were taken before the A-1 Salt was penetrated to establish a background of potassium in the saturated sodium chloride drilling fluid. Sampling continued from six in the evening until eleven o'clock at night. We would recommend that a third person be available during the long sampling session. If it had not been for the cooperation of the drilling crews, we would have had some breaks in the samples. The following information is necessary to the proper use of the system and was obtained from the well site: Sample tops, elevation, mud pump information (operating pressures, liner size, stroke, strokes per minute, type of pump) and the hole size.

Potassium content of the drilling fluid was determined by flame photometry on the settled clears after screening out the low potassium samples by the sodium tetraphenyl boron test suggested by G. C. Egleson. This consists of adding ten drops of 10% solution of sodium tetraphenyl boron to 50 ml. of settled clears. Bromine was determined by x-ray fluorescence on a few of the salt cuttings. Bromine variations are far less indica-

tive of the location of a potash zone than are potassium ions in the drilling fluid.

DATA

An-Son Corp. No. 1 Parmeter, Permit No. 26908; elevation 910 feet K.B. C SE SE Section 26, T9N-R10W, Courtland Township, Kent County, Michigan.

Top of the A-2 dolomite	4262'
Top of the A-1 dolomite	4840'
Top of the A-1 Salt (evaporite)	4897'
Top of the Niagaran (carbonate rock)	5197'

Connections made at:

	Down-time	Drilling Rate-min./ft.
4879'		
4909'	1800-1805	1.5
4938'	1850-1855 (45 min./29 ft.)	1.55
4968'	1940-1945	1.5
4998'	2030-2035	1.43
5028'	2118-2120	1.29
5059'	2206-2210	1.29
5090'	2250-2258	1.29
5121'	2338	

Mud Pump:

1000 psig pressure	60 strokes per minute
5-1/2" liners	18" stroke
	Double action. (Duplex)

Hole size: 7-7/8" diam.
Drill pipe: 4-1/2" diam.

To estimate the average potassium content of a zone, in this case 6.2 feet thick, the potassium chloride in a cylinder 6.2 feet high and 7 7/8 inches in diameter (hole size) is assumed to have been dissolved in the drilling mud volume pumped during the time required to cut the 6.2 feet.

To obtain the average potassium value, potassium content of the fluid is plotted vs time. Integration is obtained by weighing a cut-out of the area under the curve and by weighing a rectangle which includes the peak value. A ratio of these two weights times the peak value gives the average value. In this case the average value is 55.2% of the peak potassium value.

RESULTS

The detailed plot of potassium vs time and depth shows the abrupt rise in potassium content in the

drilling fluid and a slower fall-off, as expected. (Figure 1). Integration of this plot indicates 6.2 feet of 7.3 percent potassium chloride.

The only potassium picked up in No. 1 Parmeter corresponds to the smallest and deepest Gamma Ray kick on

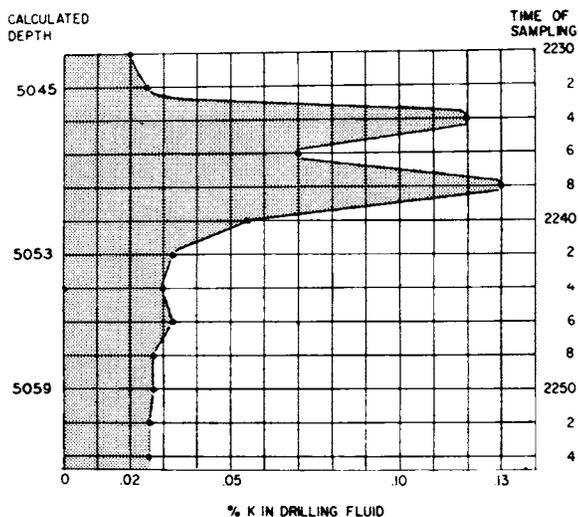


Fig. 1 Percent potassium in drilling fluid vs time of sampling. Drilling rate: 1.29 min/ft. (An-Son Corp. 1 Parmeter, Sec 26, T9N-R10W, Kent Co., Mich.)

the Ten Have log. Confirmation of this potash zone was found on the Gamma Ray log of No. 1 Parmeter when it was released a few months later. (Figure 2). The predicted depth to the potash was within 6 feet of the indication on the Gamma Ray log.

Bromine values in the salt cuttings over the interval of higher potassium ran around 160 ppm, compared to 200-500 ppm bromine in cuttings from wells nearer the center of the basin.

REFERENCES

Anderson, R. J. and Egleson, G. C., 1970, Discovery of Potash in the A-1 Salina Salt in Michigan: 6th Ann. Forum on Geol. of Industrial Minerals, Ann Arbor, Mich., April 2, 1970. (This volume)

Matthews, R. D., 1970, The Distribution of Silurian Potash in the Michigan Basin: 6th Ann. Forum on Geol. of Industrial Minerals, Ann Arbor, Mich., April 2, 1970. (This volume)

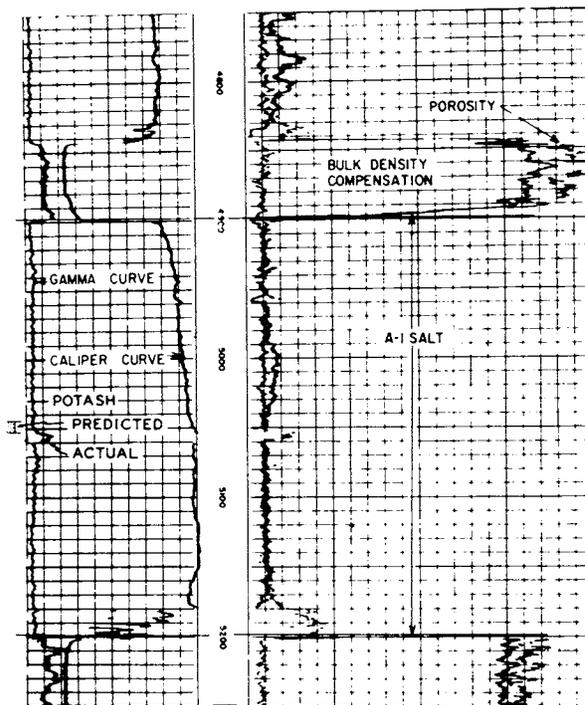


Fig. 2 Partial log of An-Son 1 Parmeter (Sec 26, T9N-R10W, Kent Co.) showing predicted and actual potash within the A-1 Salt.

APPENDIX

Calculations: No. 1 Parmeter.

$$0.552 \frac{\text{Average}}{0.11\% \text{ K (peak of curve)}} = 0.0607\% \text{ K (over 8 min. per ft.)}$$

6.2 ft.) i.e. 607 ppm K in drilling fluid from 6.2 feet of core.

$$\text{Pump piston area} = 0.785 \times 5.5^2 = 23.7 \text{ sq. in.}$$

$$\text{Piston volume} = 18 \times 23.7 = 427 \text{ cu. in.}$$

$$\text{Capacity} = 427 \times 60 = 25620 \text{ cu. in./min.}$$

$$\frac{25620}{1728} = 14.8 \text{ c.f.m.} = 111 \text{ gpm} = 1110 \text{ lb. fluid per min.} \\ \times 2 \text{ (double action pump)} \\ 2220 \text{ lbs. fluid/min.}$$

For 6.2 ft. interval:

$$\frac{2220 \text{ lb. fluid}}{8 \text{ min.}} \times 0.0607\% \text{ K} = 10.78 \text{ lbs. K picked up.}$$

For 7-7/8" diam. cylinder:

$$0.785 \times 7.875^2 = 48.6 \text{ sq. in.} = 0.348 \text{ sq. ft.}$$

$$0.348 \frac{\text{sq. ft.}}{6.2 \text{ ft.}} \times \frac{\text{cu. ft.}}{2.1 \text{ S.G.}} \times 62.4 = 283 \text{ lbs. salt.}$$

$$\frac{10.78 \text{ lbs. K}}{283 \text{ lbs. salts}} \times 100 = 3.81\% \text{ K} = \frac{3.81}{78.2} \times \frac{94.9}{100} = 4.63\% \text{ K}_2\text{O} = 7.27\% \text{ KCl. over 6.2 ft.}$$

by

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Abstract

Mineralogical data indicates that large amounts of potash feldspar occur in some lithic units of the Franconia Formation in numerous areas of Wisconsin and Minnesota, while in the same areas generally less than one percent feldspar is found in underlying lithic units of the Wonewac Formation. These formations consist primarily of various lithic types of coarse- to very fine-grained sandstone with minor amounts of shale.

The Galesville and Ironton Members of the Wonewac Formation are composed of medium and coarse quartz sand, although the Ironton sometimes has a clayey silt matrix. The major minerals composing the Franconia Formation members are quartz, feldspar, glauconite, clay, dolomite, and muscovite. The feldspar content increases with decreasing grain size. The Tomah Member, which is a very fine-grained sandstone, has the greatest feldspar content. It contains at least 35 percent feldspar in several areas of Wisconsin and Minnesota. Feldspar contents of 15 to 20 percent are also quite common in fine-grained, nondolomitic portions of the Birkmose and Reno Members.

Each feldspar grain is composed of a detrital rounded core with an authigenic overgrowth that crystallized in situ. The detrital cores are composed of microcline with some microperthite. The overgrowths probably consist of orthoclase. No plagioclase feldspar has thus far been identified.

Electron probe microanalysis shows that the detrital cores contain 15.5 to 16 percent K_2O and 0.5 to 1.5 percent Na_2O . The overgrowths contain more than 16 percent K_2O and less than 0.1 percent Na_2O .

With the beneficiation techniques now available it is believed that a relatively pure feldspar sand or a quartz-feldspar sand mixture could be produced from these deposits. An added incentive is the favorable geographic location of the deposits to numerous large consumers.

INTRODUCTION

Local occurrences of potash feldspar in Upper Cambrian and in Lower and Middle Ordovician strata in Wisconsin and Minnesota have been described in papers by Tester and Atwater (1934), Goldich (1934), Berg (1952), and Weiss (1954). This paper is an outgrowth of a regional study of the mineralogy of the Franconia Formation in its outcrop area in southwestern Wisconsin and southeastern Minnesota. Its purpose is to call attention to the fact that large quantities of potash feldspar occur in portions of the Franconia

Formation and to suggest that these deposits might be a source of feldspar or feldspar-quartz sand mixtures.

The Franconia Formation occurs approximately in the middle of the sandstone and carbonate sequence composing the Upper Cambrian in the Upper Mississippi Valley.

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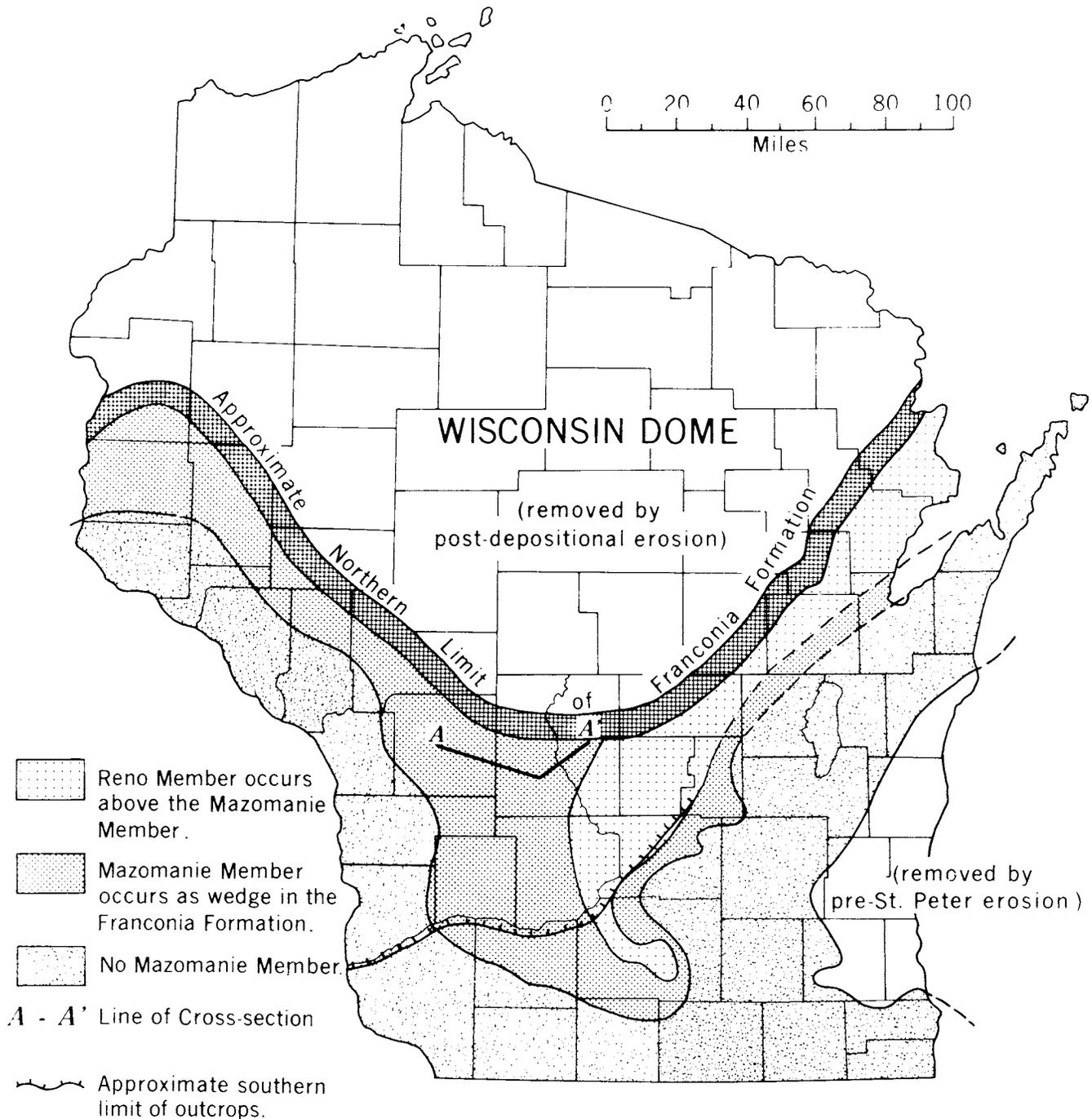


Figure 1. Distribution of the Franconia Formation in Wisconsin (modified from Ostrom, 1966).

OUTCROP AREA

Although the Franconia Formation has a wide distribution in the upper Mississippi Valley, its principle area of outcrop is in southwestern Wisconsin from the Mississippi River to the vicinities of Eau Claire and Wisconsin Dells. It also outcrops along the lower St. Croix River Valley in Wisconsin and Minnesota and in a narrow belt along the

west side of the Mississippi River from Red Wing, Minnesota to near the Minnesota-Iowa border. The regional surface and subsurface distribution of the formation in Wisconsin (Ostrom, 1966) is shown in figure 1. In the region of outcrop the formation is generally confined to streams and valley slopes because it easily erodes due to the poor cementation of the sandstones.

LITHIC SUBDIVISIONS

The Franconia Formation was defined by Berkey (1897) as consisting of a succession of fine-grained sandstones exposed in the St. Croix River Valley near Franconia, Minnesota. Subsequent studies, however, revealed that Berkey's type section was not representative of the lithic character of the formation in most other areas of Wisconsin and Minnesota. For example, Twenhofel and Thwaites (1919) in a study of the Tomah and Sparta Quadrangles, Monroe County, Wisconsin, divided the Franconia into five lithic units (fig. 2). Thwaites (1919) added the sandstone earlier designated as belonging to the Dresbach Formation to the Franconia and named this lithic unit the Ironton.

The rock units defined by Twenhofel and Thwaites (1919) were formally named and given member status by Berg (1954). He also changed the name of the Ironton to the Woodhill Member but retained the Woodhill as the basal rock unit of the Franconia Formation (fig. 2).

Twenhofel and Thwaites 1919	Berg 1954	Ostrom 1965-1966
Upper Greensand	Mazomanie Member	Reno Member
Yellow Sandstone		
Lower Greensand	Tomah Member	Tomah Member
Micaceous Shale		
Basal Beds	Birkmose Member	Birkmose Member
Dresbach Wronstones	Woodhill Member	Ironton Member
		Galesville Member

Figure 2. Comparison of lithic subdivisions of the Franconia Formation.

Ostrom (1965) proposed that the Ironton Member be removed from the Franconia and be considered as a member of a new formation he named the Wonevac (fig. 2). He justified this classification on the basis that the lithic character and heavy mineral assemblage of the Ironton is more analogous to the underlying Galesville Sandstone than to the other members of the Franconia. In addition the contact between the Ironton and Galesville is difficult to distinguish in outcrop and in the subsurface in most areas of Wisconsin and Minnesota. Ostrom (1966) also proposed that the Franconia sandstone succession above the Ironton Member be divided into the Lone Rock and Mazomanie Formations and that the name Franconia be restricted to a stage name (fig. 2).

This study has shown that the mineral composition of the Ironton Sandstone is far

more analogous to the underlying Galesville Sandstone than to any of the overlying sandstones considered to belong to the Franconia Formation (table 1).

LITHIC CHARACTERISTICS

The following brief description of the lithic properties of the Franconia and Wonevac Formations is intended to give the reader a general idea of the nature of the sediments and to illustrate that feldspar abundance is related to some lithic properties, particularly grain size. More complete descriptions of the lithic nature of Upper Cambrian strata in the area under discussion can be found in papers by Twenhofel and Thwaites (1919), Berg (1954), Nelson (1956), Emrich (1966) and Ostrom (1966).

Galesville Member

The Galesville is generally a medium-grained sandstone, but coarse and fine grain sizes are common in numerous areas. A few thin greenish shale layers occur in this member locally. It varies from 20 to over 160 feet in thickness in Wisconsin (Ostrom, 1965).

Ironton Member

The Ironton is a coarse and medium-grained sandstone that also locally contains a few thin greenish shale streaks. Generally the sandstone consists of coarse grains in a medium-grained matrix. In some areas, however, it contains beds several feet thick consisting of essentially coarse or medium-grained sand with some fine sand. It sometimes contains a whitish matrix of fine silica and illitic clay.

The Ironton Member varies in thickness from less than five feet in central Wisconsin to more than 40 feet along the Mississippi Valley near La Crecent, Minnesota.

Birkmose Member

The Birkmose Member (fig. 2), herein considered to represent the basal member of the Franconia Formation, shows considerable variation in lithic character and thickness in southwestern Wisconsin and eastern Minnesota. It is a fine and very fine-grained, dolomitic, argillaceous, and often

conglomeritic sandstone throughout central Wisconsin and along the Mississippi Valley. It is somewhat less dolomitic along the St. Croix Valley. The thickness varies from less than three feet in the Mauston, Wisconsin area near its eastern limit to 35 feet on the Mississippi River near Kellogg, Minnesota. These sandstones often contain worm borings and many beds show extensive evidence of bioturbation by organisms.

Tomah Member

The Tomah Member is the most distinctive and persistent lithic unit in the Franconia Formation. It is a finely laminated, pinkish, thinly bedded, fine and very fine-grained sandstone or coarse siltstone with interbedded shale laminae. It varies from 7 to 28 feet in thickness in southwestern Wisconsin and southeastern Minnesota. Individual sandstone and siltstone beds are usually only a few inches thick but more massive beds ranging up to 5 feet in thickness have been observed near Tomah and Colfax, Wisconsin.

Reno and Mazomanie Members

Figure 1 shows the distribution and regional stratigraphic relationship of the Reno and Mazomanie Members in Wisconsin. These members are differentiated solely on the basis of the abundance of the mineral glauconite. Sandstones that are fine- to very fine-grained and contain generally less than 5 percent glauconite are assigned to the Mazomanie Member, whereas more glauconitic sandstones of similar texture are assigned to the Reno Member. As illustrated in figure 1, these members as so defined show an intertonguing relationship over a broad area in Wisconsin and eastern Minnesota. This stratigraphic relationship in the Mauston, Wisconsin area is shown in figure 3. Ostrom (1966) showed that farther east and south in central Wisconsin the Mazomanie Sandstone also intertongues with lower Franconia members (fig. 2).

The Reno Member is composed of several lithic types of sandstone. Along the Mississippi Valley it contains a large amount of very argillaceous sandstone previously described as "wormstone." Beds of this nature also occur in the Birkmose but with somewhat less argillaceous material. All internal sedimentary structures in these beds have been destroyed by burrowing organisms.

The Reno Member is more than 110 feet thick in southeastern Minnesota and adjacent

Wisconsin. The Mazomanie Member is more than 100 feet thick in central Wisconsin (Ostrom, 1966).

CHARACTERISTICS OF THE FELDSPAR IN THE FRANCONIA AND WONEWAC FORMATIONS

Abundance

The major mineral constituents of the Wonewac and Franconia Formations are quartz, feldspar, glauconite, dolomite, clay minerals, and muscovite. They also contain trace quantities of various heavy minerals and iron oxides. Modal analyses of samples from these formations are given in table 1. The stratigraphic sections and miscellaneous samples included in table 1 were selected from among many studied to illustrate the variations in mineralogy stratigraphically and regionally.

The mineralogic data presented in table 1 as well as unpublished data from other localities show that the Tomah Member is highly feldspathic throughout Wisconsin and Minnesota. Although the percentage of feldspar in the Tomah may vary considerably from bed to bed, there are many sections 20 or more feet in thickness in which the feldspar content averages at least 35 percent. Individual beds in some areas contain as much as 60 percent feldspar. The feldspar is primarily concentrated in the very fine-grained sandstone and coarse-grained siltstone beds.

The Reno appears to be the next most feldspathic member. There are relatively thick sections of the Reno Member which contain an average of at least 15 to 20 percent feldspar. Along the Mississippi and St. Croix River Valleys, nondolomitic beds in the Birkmose Member are similar to the Reno in feldspar content. Birkmose beds with appreciable dolomite usually contain less feldspar.

The Mazomanie Member has not as yet been studied on a regional scale. In the Friendship Mound, Wisconsin area it generally contains less than 5 percent feldspar, while at Goodenough Hill (table 1) near Mauston, Wisconsin a few samples contain over 20 percent. Like the Birkmose, feldspar is less abundant in highly dolomitic units of the Mazomanie Member.

In sharp contrast to the feldspathic Franconia sandstones the Ironton and Galesville Sandstones of the Wonewac Formation seldom contain more than 1 percent feldspar.

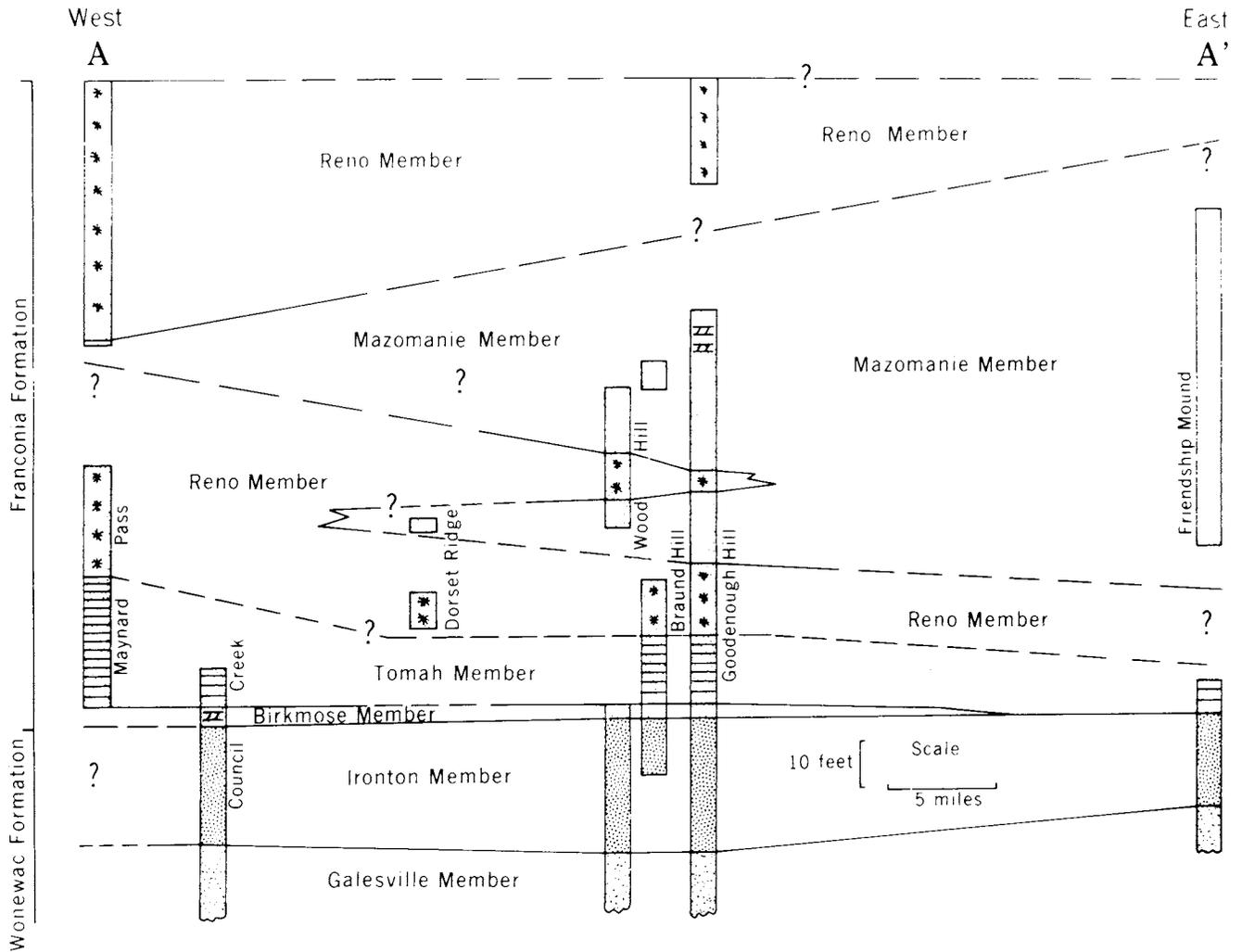


Figure 3. Stratigraphic relationship of members in the Woneewac and Franconia Formations in the Mauston, Wisconsin area.

Grain size appears to be a major factor in the abundance of feldspar in these sediments. This grain size relationship is discussed in a later section.

Mineralogical Composition

The feldspar in the Franconia Formation consists of well rounded detrital grains with varying amounts of authigenic overgrowths (fig. 4A). The authigenic marginal overgrowths form a rim that is clearly definable in transmitted polarized light. The overgrowths tend to develop crystals with euhedral shapes and crystal faces (fig. 4B). The boundary between the detrital nucleus and the marginal material is often marked by tiny inclusions. The authigenic feldspar is completely untwinned.

The detrital grains consist of microcline, microperthite, and perhaps some

orthoclase. No plagioclase feldspar has thus far been observed. Some detrital nuclei show typical microcline cross-hatch twinning (fig. 4C), while others show a complete absence of twinning (fig. 4B). The lack of twinning may be due to optical orientation. Goldich (1934) found that the basal section of some feldspar grains in the New Richmond sandstone did not show twinning.

The feldspar marginal to the detrital cores often penetrates between quartz grains, and in some instances its growth has broken or crushed glauconite grains. These relationships show that the enlargements were developed in situ. The size of the overgrowths vary greatly.

Authigenic feldspar is most abundant in the Tomah Member because of the initial presence of more detrital feldspar. Even in the Tomah the authigenic feldspar probably does not constitute more than 15 percent of the total feldspar.



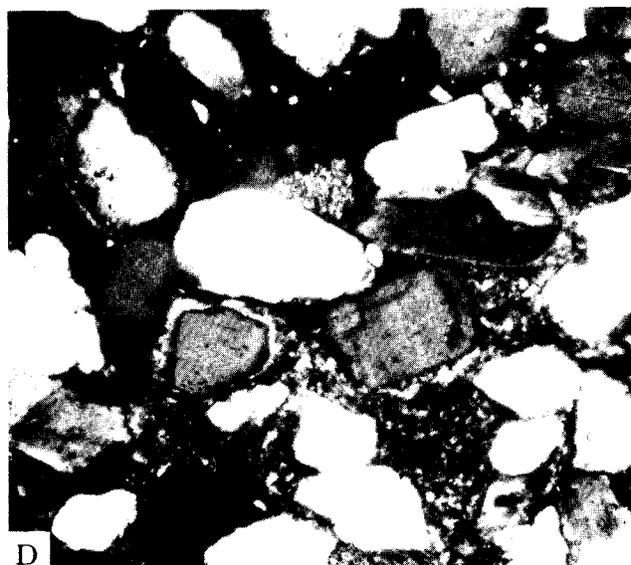
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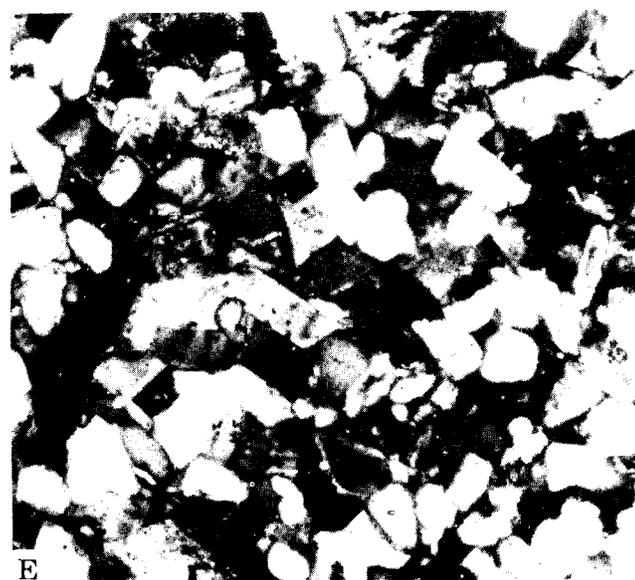
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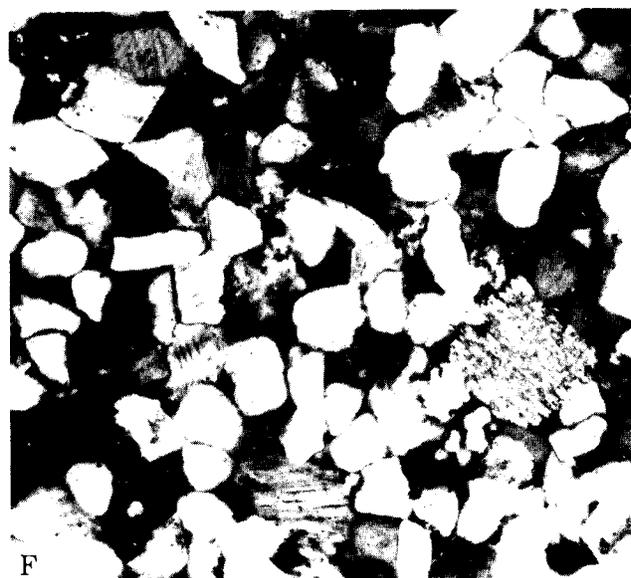
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E



F

Figure 4. (A) Feldspar crystal with detrital core and authigenic overgrowth (360X). (B) Euhedral feldspar crystal (360X). (C and D) Feldspar in fine-grained Reno Sandstone (140X). (E) Feldspar in coarse-grained Tomah Siltstone (140X). (F) Feldspar in very fine-grained Tomah Sandstone (140X).

Table 1. Modal analysis of sandstones from the Franconia and Wonevac Formations.

Stratigraphic Position and Sample Number	Quartz	Feldspar	Glauconite	Clay & Silt	Dolomite	Heavy minerals	Iron oxide	Muscovite
Friendship Mound, NW 1/4, sec. 5, T, 17N., R.6E., Adams County, Wis.								
Galesville Member								
89-30-14	99.3	----	----	tr.	----	tr.	tr.	----
Woodhill Member								
89-30-9	99.8	0.2	----	tr.	----	tr.	tr.	----
Mazomanie Member								
89-30-5	98.6	1.4	----	----	----	tr.	tr.	----
89-30-2	99.0	1.0	----	----	----	tr.	tr.	----
Goodenough Hill near Mauston, SE 1/4, sec. 13, T. 15N., R. 2E., Juneau County, Wis.								
Galesville Member								
1-1	99.5	0.3	----	0.2	----	tr.	----	----
Ironton Member								
1-6	100.0	----	----	tr.	----	tr.	----	----
1-10	99.6	0.4	----	----	----	tr.	tr.	----
Birknose Member								
1-13	57.8	----	4.0	----	38.2	----	tr.	----
Tomah Member								
1-14	29.4	43.0	1.0	4.8	19.0	tr.	2.0	0.8
1-14a	64.8	26.2	2.8	3.0	----	tr.	tr.	3.2
Reno Member								
1-16	58.2	22.8	17.4	1.6	----	tr.	tr.	----
1-19	60.0	30.8	8.4	0.8	----	tr.	tr.	----
Mazomanie Member								
1-17	84.2	11.2	0.4	----	4.2	tr.	----	----
1-18	80.4	18.0	0.4	0.2	1.0	tr.	----	----
1-20	76.2	22.4	0.8	0.6	----	tr.	----	----
1-23	92.8	6.8	----	----	0.4	tr.	----	----
1-26	24.2	1.4	----	----	74.4	tr.	tr.	----
Maynard Pass, NW 1/4, sec. 22, T. 17N., R.2W., Monroe County, Wis.								
Tomah Member								
8-1	33.0	53.4	5.2	3.8	----	tr.	tr.	2.6
8-1	50.2	41.2	3.4	4.0	4.0	tr.	tr.	1.2
Reno Member								
8-7	63.8	26.4	9.2	0.6	----	tr.	----	----
8-10	69.8	24.8	5.2	0.2	----	tr.	----	----
8-11	72.4	3.4	23.8	----	----	tr.	0.4	----
8-13	71.6	15.0	8.8	----	4.6	tr.	----	----
8-14	57.7	12.7	29.4	0.2	----	tr.	----	----
8-16	82.0	9.0	9.0	----	----	tr.	----	tr.

Table 1, Continued

Stratigraphic Position and Sample Number	Quartz	Feldspar	Glauconite	Clay & Silt	Dolomite	Heavy minerals	Iron oxide	Muscovite
8-18	66.0	15.1	12.6	1.8	2.3	tr.	1.7	----
90-45-17	40.4	44.0	5.2	9.6	----	tr.	----	0.8
90-45-13	47.6	23.2	7.0	6.8	15.0	tr.	----	0.4
Mazomanie Member 8-12	92.8	6.8	tr.	0.4	----	tr.	----	----
Ironton Member 89-16-5	Near Lake Deltona, NE 1/4, sec. 24, T.1 3N., R.5E., Sauk County, Wis.							
Birknose Member 89-16-15	75.8	0.8	----	23.4	----	----	----	----
	60.0	0.4	31.6	----	----	----	8.0	----
Birknose Member 90-5-5	Near Lone Rock, SE 1/4, sec. 13, T. 8N., R. 2E, Iowa County, Wis.							
90-5-10	4.6	----	8.2	----	87.2	----	----	----
Tomah Member 90-5-15	55.0	22.4	19.8	2.6	----	tr.	----	0.2
	46.7	46.3	1.2	5.0	0.8	----	----	tr.
Ironton Member 91-20-0-2	Near Ia Crecent, sec. 33, T. 105N., R.4W., Winona Co., Minn.							
91-20-0-4	97.2	2.4	0.4	----	----	tr.	----	----
91-20-0-9	99.2	0.8	----	----	----	tr.	----	----
91-20-0-15	69.6	0.8	----	29.6	----	tr.	----	----
Birknose Member 91-20-1	93.7	5.8	----	0.5	----	tr.	----	----
Tomah Member 91-20-2	39.6	11.4	30.8	----	18.2	tr.	----	----
91-20-3	21.1	23.5	3.6	21.6	29.2	tr.	----	1.0
Reno Member 91-20-5	26.8	59.8	4.0	7.0	0.4	tr.	----	2.0
91-20-6	20.8	10.2	27.4	23.4	16.4	tr.	1.4	0.4
91-20-7	26.2	23.6	10.6	39.0	----	----	0.4	0.2
91-20-8	41.5	26.2	16.5	15.1	----	tr.	tr.	0.7
91-20-20	36.2	10.4	22.6	7.6	7.4	tr.	12.8	3.0
91-20-21	9.5	10.3	23.5	53.9	2.3	----	0.5	----
91-20-22	28.8	24.8	23.6	16.6	3.2	tr.	1.8	1.0
91-20-23	47.0	20.0	21.6	6.2	0.2	tr.	3.8	1.2
91-20-24	24.4	17.0	8.0	46.6	2.2	tr.	0.6	1.2
91-20-28	54.7	9.8	30.1	1.0	----	tr.	1.9	2.5
	46.4	23.3	26.9	1.2	----	tr.	2.0	0.2

Table 1, Continued

Stratigraphic Position and Sample Number	Quartz	Feldspar	Glauconite	Clay & Silt	Dolomite	Heavy minerals	Iron oxide	Muscovite
Near Colfax, sec. 21, T. 29N., R. 11W., Dunn County, Wis.								
Ironton Member								
91-66-35	85.0	0.4	1.0	-----	13.6	tr.	-----	tr.
91-66-30	91.4	0.2	2.2	6.2	-----	-----	-----	-----
91-66-25	96.2	0.2	-----	3.6	-----	tr.	-----	tr.
91-66-20	98.6	1.4	-----	-----	-----	-----	-----	-----
91-66-15	58.4	2.4	-----	38.8	-----	-----	-----	0.4
91-66-10	82.0	2.6	-----	15.0	-----	0.4	-----	-----
Birkmose Member								
91-66-65	38.2	11.8	9.8	16.0	24.0	tr.	-----	0.2
91-66-60	38.2	13.8	11.4	20.6	15.6	tr.	-----	0.4
91-66-55	23.4	13.2	16.2	46.6	-----	tr.	-----	0.6
91-66-50	42.0	14.8	17.0	25.4	-----	tr.	-----	0.8
91-66-45	52.4	39.2	8.2	-----	-----	tr.	tr.	0.2
91-66-40	69.2	19.8	10.2	-----	-----	tr.	-----	0.8
Miscellaneous Samples								
Birkmose Member								
91-80-5	59.2	18.0	3.4	17.6	1.8	tr.	-----	-----
91-2-15	33.0	31.2	14.4	5.4	12.0	-----	-----	-----
Tomah Member								
90-5-15	46.6	46.2	1.2	4.0	0.8	-----	-----	1.2
90-17-1	27.6	50.0	4.0	4.2	11.4	-----	-----	1.0
90-50-15	21.2	34.8	1.6	35.4	5.2	-----	-----	1.8
91-2-26	37.4	46.4	7.0	7.4	1.2	-----	-----	tr.
90-60-15	35.8	53.8	2.6	7.8	-----	tr.	-----	tr.
92-30-20	25.8	61.0	6.0	3.0	-----	tr.	tr.	4.2
Reno Member								
91-2-36	36.0	16.6	11.0	3.0	32.2	-----	tr.	-----
91-3-12	44.4	34.2	11.8	9.2	0.2	tr.	tr.	0.2
91-3-13	33.0	23.0	10.0	20.0	6.3	tr.	6.2	1.5
91-3-20	32.4	23.2	19.4	20.0	4.6	tr.	-----	0.4

Chemical Composition

The chemical composition of the authigenic and detrital feldspar in the Franconia Formation was studied with the electron microprobe. The analyses dealt primarily with K, Na, and Fe contents. Alkali feldspars studied by Smith and Ribbe (1966) were used for standardization.

The chemical data verifies the fact that the detrital cores are composed mostly of microcline and some microperthite. In the several dozen cores studied, the average Na₂O was found to be approximately 0.6 weight percent. These same cores had an average of 15.5 weight percent K₂O. A few microperthites contain blebs with as much as 1.6 weight percent Na₂O.

The authigenic additions are nearly pure potash feldspar. They consistently contain more than 16 weight percent K₂O and less than 0.1 weight percent Na₂O. The iron content in both the authigenic additions and the detrital cores is very low.

No stratigraphic or regional variation in the chemical character of the feldspar was detected.

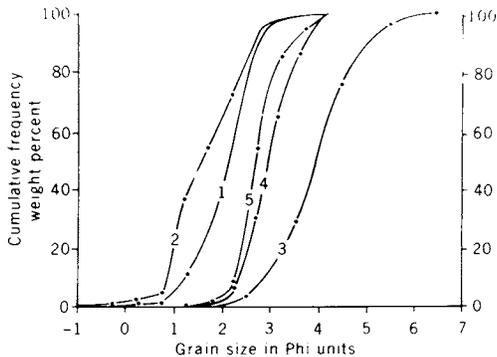


Figure 5. Particle size relationship of members in the Wonewac and Franconia Formations in the Mauston, Wisconsin area. (1) Galesville Member. (2) Ironton Member. (3) Tomah Member. (4) Reno Member. (5) Mazomanie Member.

Grain Size

Feldspar in the Franconia Formation occurs primarily in the fine sand- to coarse silt size fraction, and is almost always more abundant in coarse siltstones and very fine-grained sandstones. The feldspar contents and grain size distributions of Wonewac and Franconia sandstones in the Mauston, Wisconsin area (fig. 5) clearly show this relationship (see Goodenough Hill section--table 1).

In this area the Tomah is highly feldspathic, and its median grain size is approximately 3.8 phi (0.070 mm). The Ironton and Galesville Sandstones in the Mauston area, however, are medium-grained, but the Ironton is coarser than the Galesville (fig. 5). Modal analyses (table 1) of the Ironton and Galesville Sandstones from the above area indicate that they seldom contain more than 1 percent feldspar. Grain size differences between the Reno and Tomah Members are shown in figure 4.

As much as 5 percent feldspar has been found in the Ironton and Galesville Sandstones in a few other areas, but the feldspar occurs only in the fine sand size fraction. Goldich (1934) found that the two to three percent feldspar in the New Richmond Sandstone (Ordovician) at Lake City, Minnesota was primarily concentrated in the fine sand size fraction.

As previously indicated, the Mazomanie Member in the Mauston, Wisconsin area usually has a lower average feldspar content than the Reno Member with which it intertongues. One possible reason for this is that the Mazomanie often contains more dolomite than the Reno. Another possible reason is that the grain size is slightly coarser (fig. 5).

It is believed that the great abundance of feldspar in the fine sand to coarse silt grain sizes as compared to the medium and coarse sand grain sizes is because the abrasion resistance of feldspar is much less than quartz (Hiatt, 1970).

ECONOMIC POTENTIAL

Feldspathic sands for making container glass and glass wool are profitably produced in several areas of the United States (Bowdish, 1967). The economic potential of the feldspathic Franconia sands heavily depends upon whether the feldspar and quartz can be separated from iron bearing minerals present, primarily glauconite and clay. The iron content of the feldspar itself is very low, and there is little iron oxide coating the feldspar or quartz grains. Although the testing of commercial processes that are used to separate feldspar from sands was beyond the scope of this study, it is known that glauconite can be removed easily by electromagnetic separation. There is no obvious reason why the various beneficiation techniques now used in the feldspar industry could not be directly applicable to the Franconia sands.

In addition to the abundance of potash feldspar the Franconia deposits appear to have several additional advantages. First, the deposits are in a more favorable geographic location to numerous large consumers than are the traditional sources of feldspar of similar chemistry. Second, the sandstones are sufficiently friable that grain separation could be achieved at little cost. Mining costs would also be minimal. Third, the sands are virtually free of sand-size feldspathic rock fragments, a common source of impurities. Fourth, in some areas a thick succession of feldspathic Franconia sands occurs within a few feet of the Galesville Sandstone which may be sufficiently pure for glass making purposes. Thus, there would appear to be some potential for the production of several types of sand at a single location.

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LIMESTONE AS RAW MATERIAL

FOR HYDROCARBON FUELS

by

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³
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Abstract

Inorganic hydrocarbons up to and including butane can be formed directly from reactions of calcite, dolomite, siderite and other carbonate species with hydrogen at elevated temperatures and pressures. Experimental evidence indicates that the hydrocarbon compounds form directly by means of a mineral surface - hydrogen reaction rather than via a subsequent reaction between generated gases and hydrogen. In general, the reaction rate proceeds rapidly at temperatures well below the "in air" calcination temperatures of the individual carbonate species. The lower the initial reaction temperature of the carbonate-hydrogen pair, the more complex is the hydrocarbon produced.

The reactions are not only of peculiar pertinence to a number of geological problems, but they possess immense practical and economic potential. These simple hydrocarbons have all the "clean-burning" characteristics of natural gas and thus may be used either directly as fuel or in liquified form in internal combustion engines. They can be converted to more complex hydrocarbons (e.g., acetylene) for chemical uses.

Carbon, converted to CO₂ that is then dissolved in waters of the biosphere, is, to a very large extent, eventually removed by organisms and inorganic reactions to be precipitated as calcite. This fixation-drain of carbon via calcite from the geochemical cycle of carbon throughout geological time has locked much of the world's carbon into a form generally unusable by man. The carbonate-hydrogen reactions provide a practical key for unlocking this carbon storehouse.

Among the implications of the reaction are: 1) The possibility of reserving the relatively limited supply of natural complex hydrocarbons (petroleum, etc.) mainly as a base for chemical raw materials. 2) The possibility of using electrical energy available during excess odd-hour capacity of future nuclear-fueled electrical plants to dissociate water to provide a cheap supply of hydrogen. 3) Raw materials

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are abundant and cheap and their location requires a minimum of technical exploration. 4) By-products of the reactions are CaO or Ca(OH)_2 , both of which are economically useful compounds. 5) The conversion of the inorganic hydrocarbons to fibers is certainly possible. 6) If modification of the process can be made to yield heavy-molecule hydrocarbons similar to those in petroleum, such mixtures would serve equally well as food for yeasts and bacteria that convert petroleum to single-celled protein (SCP), which is nutritionally comparable to meat.

INTRODUCTION

The purpose of this paper is two-fold: 1) To present a description of a laboratory process for the production of inorganic hydrocarbon gases from carbonate minerals and rocks, and 2) To extrapolate from this in order to speculate on the possible implications in the fields of energy and material resources.

FOSSIL FUEL RESERVES

According to some recent estimates and calculations (Hubbert, 1969) if fossil oil fuels (including all types - petroleum, natural gas, oil shale and tar sands) continue to be used mainly for their energy contents and, if they continue to supply, as they do today, the bulk of the world's energy requirements, then: the middle 80% of the ultimate resources of members of the petroleum family will only last a century.

Under the same conditions the time required to exhaust the middle 80% of the world's coal would be 300-400 years. If, however, coal is substituted for petroleum-group fuels and becomes the main energy source, then the middle 80% would be consumed in 100-200 years. Only breeder-type reactors and controlled fusion (if it can be developed at all) offer substantial promise as long-term energy sources.

THE CARBON CYCLE

CO_2 of volcanic (i.e. of juvenile) origin escapes to the atmosphere and is dissolved in its waters and in more

of the hydrosphere. In weathering processes CO_2 allies itself largely with Ca as CaCO_3 and $\text{Ca(HCO}_3)_2$. Eventually CaCO_3 is removed from solution by organisms and various inorganic reactions to be precipitated as calcite or aragonite.

CO_2 removed from the carbon cycle by the deposition of limestone will never be returned totally to the atmosphere, although, of course, it may be reused as CaCO_3 many times within sedimentary cycle. Thus: 1) the formation of limestone represents the greatest "leak" in the carbon cycle and 2) the total quantity of limestone is bound to increase with time.

Estimates of limestone percentages in sedimentary rocks range from 5% (the low for the computed estimate ranges) to as much as 30% (the high for the measured estimate ranges). Using a median figure and an estimate of $2 \times 10^8 \text{ km}^3$ as the total volume of continental sedimentation, one can generate an order-of-abundance figure of $34 \times 10^5 \text{ km}^3$ for the total volume of continental limestone. In contrast to this figure, which represents accretionary accumulation since early Precambrian times, the formation of coal, oil and natural gas are, as Professor Barghoorn of Harvard University has phrased it, only "minor inefficiencies in the carbon cycle."

The deficiency of CO_2 created by limestone formation is covered (or recently more than covered) by new volcanic CO_2 and CO_2 from industrial activity.

The fixation drain of carbon as carbonate throughout geologic time has locked much of the world's carbon into a form unusable by man. The carbonate-

hydrogen reactions described here provide a key for unlocking this heretofore inaccessible storage vault of carbon and for making it available as an energy source.

CARBONATE-HYDROGEN REACTIONS

General

Calcite, dolomite, siderite and other carbonate species under the appropriate conditions react with hydrogen to produce hydrocarbons. These reactions have been studied under various P-T conditions.

The following materials were investigated in the hope that they would have a catalytic effect upon the reactions: metallic nickel, platinum, copper, titanium, magnesium, and iron; commercial mixtures of 0.5% palladium, platinum, and rhodium on alumina; and dried silica gel, activated alumina, hematite, magnetite, chromic oxide, chromium trioxide, and various "kieselguhr" mixtures. The possible autocatalytic effects of product hydrous and anhydrous oxides and pyrolytic carbon also were investigated. None of the above materials had any discernible effect upon the reaction rate. Several of the metals, however, particularly iron, increased the rate of pyrolytic dissociation of the methane generated in the process.

The experimental system is shown schematically in Figure 1. Most of the experiments were carried out in a "cold seal" vessel made from Kelsey-Hayes Company Udimet 500 stainless steel. A 20,000 psi Heise gauge measured the gas pressures. A platinum-wound muffle furnace was used to heat the lower section of the reaction vessel. A stainless steel sheathed Cr-Al thermocouple was inserted into the reaction vessel through the cold seal by means of a pressure fitting to measure the internal temperature. External bottom well thermocouples also were used. A Leeds and Northrup model 60 control unit with a Fincor saturable reactor and later an API digital set-point SCR proportioning controller maintained the temperature automatically. Equilibrium, although approached, was not established in these experiments.

The procedure used for most of

the experiments was:

1. The carbonate mineral was weighed and loosely housed in platinum foil;
2. The sample was placed in the vessel, connected to the pressure system, flushed 2 times with pure helium, at about 1000 psi, then charged with helium to about 1000 psi;
3. Upon reaching the operating temperature, the helium was vented and the system given 3 hydrogen flushes and then pressurized to the desired hydrogen pressure;
4. After the experimental interval the excess hydrogen plus reaction gases were vented (in some experiments a fraction was collected for mass spectographic analysis) and the vessel flushed and pressurized with helium;
5. The furnace was drawn from the vessel and the latter air-quenched under the internal helium pressure;
6. After cooling, most of the samples were opened in air and placed in argon-filled containers. Some experiments were opened in an argon-filled dry glove box (Na dessicant) and samples sealed in glass capillary tubes.

Most of the experiments were conducted at pressures below 10,000 psi. However, one experiment was run to investigate the effect of high pressures. A calcite cleavage rhomb showed no discernible alteration after being held at 228°C under 80,000 psi hydrogen pressure for 23 hours.

Calcite-Hydrogen Reaction

In the calcite-hydrogen system consisting of calcite fragments of 40 to 60 mesh, temperatures between 535-870°C, and 200-8000 psi of initial hydrogen, the following compounds were observed: solid CaO; Ca(OH)₂; graphite; and carbon "soot". Gaseous CH₄; C₂H₆; CO; CO₂; and H₂O also formed.

The experimental results are summarized in Table 1 and in Figures 2, 3 and 4. The weight percent CO₂

in the remaining solid and the mole percent CH_4 formed are plotted against the duration of the run in hours at 2000 psi (P_{H_2}).

Below its dissociation temperature $\text{Ca}(\text{OH})_2$ is the stable solid reaction phase. In runs allowed to cool to room temperature under the reaction gases, $\text{Ca}(\text{OH})_2$, CaO is present if the reaction gases are replaced with helium at the operating temperature. Analyses of the reaction gases indicate that water is the oxygenated product.

Graphite is present chiefly on calcium hydroxide surfaces, with lesser amounts within calcium hydroxide. At runs above 700°C a "soot-like" material formed in the bomb from which it was readily wiped clean. Only rarely was this "soot-like" material ever associated with the solids within the platinum cassette. Examination of the analytical data (Table 1) reveals that at higher temperatures (exp. 81) there is a much larger weight loss of carbon as CO_2 in the solid than can be accounted for as carbon in the generated CH_4 . This discrepancy is beyond analytical error. The "soot-like" material appears to be amorphous carbon formed through thermal dissociation of methane, and higher hydrocarbons if they formed. Any higher hydrocarbons formed by pyrolysis of the methane would be unstable and none were found in the gas analysis. Carbon and hydrogen are the end products of methane pyrolysis, but equilibrium is difficult to attain. Catalysis may have hastened equilibrium. The dissociation of methane is catalytically promoted by platinum, iron, nickel, all of which are present in these experiments.

Analysis of the reaction gases shows that the reaction compounds are restricted in number even though a large population of compounds is possible in the C-H-O system. The gases present are: CH_4 ; C_2H_6 ; H_2O ; CO ; and CO_2 . The latter two appeared in only one experiment (no. 75). This experiment was unique in that the original hydrogen pressure was only 200 psi¹. The appearance of CO and CO_2 at low pressures may be explained, at least in part, through thermodynamic

calculations for a simplified C-H-O gaseous system (French, 1966). These calculations show that decreasing pressure favors the formation of CO_2 and water relative to methane and are in agreement with our experimental findings.

It appears that methane and, if within the stability field, homologues of methane, form directly rather than from reactions between hydrogen and CO or CO_2 . Except at low pressures and high temperatures, the experimental evidence is that CO_2 is not present. Both experimental evidence and thermo dynamic calculations support the contention that the hydrocarbons are direct reaction products between calcite and hydrogen. These data have been presented in detail elsewhere (Giardini and Salotti, 1968, 1969).

Dolomite and Hydrogen

Dolomite and hydrogen were reacted under the following conditions: 1) fragment size 40-60 mesh; 2) 520°C to 835°C ; 3) 2000 to 5000 psi initial hydrogen pressure; and 4) experiments lasting between 2 and 12 hours. Solid reactants observed include: CaCO_3 (calcite); $\text{Ca}(\text{OH})_2$; CaO ; non-crystalline $\text{Mg}(\text{OH})_2$; elemental carbon or graphite, and "soot". Gas analyses show: CH_4 ; C_2H_6 ; CO ; and CO_2 . Water is the oxygenated product from all of the experiments.

Siderite and Hydrogen

The reaction between siderite and hydrogen is more complex than the calcite-hydrogen and dolomite-hydrogen reactions. Reaction begins as low as 345°C . Runs were between 345 to 605°C and 200 to 5000 psi (H_2), all for four hours. A "thermal soak" under helium was used in each case to bring the bomb up to temperature before venting and replacing hydrogen for the reaction gas. Because of the low temperature for thermal dissociation of siderite, in those experiments at

1

Fugacities vary with pressure, consequently the proportion of each substance present in the equilibrium will also vary with pressure.

higher temperatures some siderite undoubtedly decomposed and the decomposition gas, presumably CO_2 , was expelled along with the helium. For this reason the mole percent of gaseous hydrocarbons determined in the reaction gas for these experiments are minimum values.

The solid reaction products for three experiments are iron (Fe) and wüstite (FeO). The solid reaction produced from a low-temperature experiment (400°C , 2000 psi) is magnetite. In all of the experiments the reaction gases were sampled and replaced with helium at the reaction temperature (Table 2).

Summary

Inorganic hydrocarbons up to and including butane form directly in carbonate miner-hydrogen reactions at temperatures as low as 350°C . The experimental evidence indicates that hydrocarbons form directly from a mineral surface-hydrogen reaction rather than from a subsequent reaction between generated gases and hydrogen. In general, the reaction rate is rapid at temperatures well below the "in-air" calcination temperatures of the carbonate minerals.

An inverse relation exists between the complexity of the hydrocarbon formed and the temperature of the experiment. The lower the initial reaction temperature of the carbonate miner-hydrogen pair, the more complex the hydrocarbon.

THE IMPLICATIONS

The implications of these reactions fall into two general categories: geological and economic.

Recent studies by various Russian geologists have demonstrated the existence of primary (i.e. magmatic) hydrocarbon gases during crystallization of alkalic igneous rocks. Studies by Heinrich and Anderson (1965) have shown that similar gases occur in carbonatites and related rocks in Fremont Co., Colorado. Studies by Heinrich (1968) show that hydrocarbon gases from various rocks are of two types: organic and abiotic. The predominant emphasis

in experimental petrology to date has been the study of systems in air; under their own vapor pressures, carbonate and sulfide systems for example; or under an imposed pressure, usually H_2O or CO_2 . The writers believe that the study of natural and synthetic systems under reducing atmospheres will yield information that is pertinent to a number of petrogenetic problems. This study defines a simple process to produce inorganic hydrocarbons under conditions that could reasonably exist within the crust. The data indicate that the reactions are temperature- rather than pressure-sensitive and that the partial pressure of hydrogen is of greater importance than is the absolute pressure of hydrogen in initiating the reaction.

The problem of limestone or dolomite assimilation by a magma is also affected. If the gases associated with a magma are reducing (hydrogen need only be a part of such a reducing gas) then CO_2 need not develop. The water generated in the reaction; carbonate mineral + hydrogen = methane + water + metal oxide or hydroxide; would be the reaction-inhibiting product, not carbon dioxide. This water can, of course, be effectively removed from the system by being incorporated in the rock-forming minerals. The hydrocarbons may or may not leave the system. There is limited field evidence to support such a hypothesis. Petersil'ye (1962) estimates that the rocks of the Khibina alkalic massif of the Kola Peninsula, USSR contain $7 \times 10^8 \text{ m}^3$ of inorganically derived hydrocarbon gases.

Other areas of geological application include:

1. The idea must be considered that planetary atmospheres and hydro-spheres may not represent unaltered solar nebula gas nor result from simple outgassing of unaltered occluded gas, but rather from complex gas-solid reactions within the solid earth prior to liberation of the gas at or near the surface.

2. The process also could provide the carbon, hydrogen and sulfur believed necessary to convert the iron-rich group of chondrite meteorites to the carbonaceous chondrites, thus resolving the problem of the enigmatic "organized elements" in these extra terrestrial rocks. Vac-

uoles in carbonaceous chondrites contain H, CH₄ and CO.

3. Veins of graphite, such as those of Ceylon, represent a unique, monomineralic type of fracture-filling deposit. Reactions similar to those that have been described may serve to explain the origin of such graphite veins as well as to account for the presence of graphite in "hydrothermal" vein deposits of gold, copper and other metals. Much of such graphite may be abiogenic.

The practical and economic potential of the reactions are immense. The simple hydrocarbons generated in H-CO₃ reactions have all the "clean-burning" characteristics of natural gas and thus may be used either directly as fuel or in liquified form in internal combustion engines. Results of tests by the U.S. General Services Administration released in November, 1969 show that internal combustion engines operate efficiently and economically on natural gas as well as on gasoline.

Among the implications of the process are:

1. The possibility of reserving our limited supply of petroleum-family resources as a base for chemical raw materials and eliminating them as direct energy-producing material.

2. One of the problems in converting the process from the laboratory to a state of economic feasibility is insuring a supply of abundant cheap hydrogen. With the development of nuclear-fueled electrical plants, which must operate continuously, electrical energy available during excess odd-hour capacity could be used to dissociate water to provide such hydrogen.

3. The raw materials for the process are abundant, cheap, widespread and have no sharply defined chemical or physical specifications. Their location requires a minimum of technical exploration.

4. By products of the reactions are CaO or Ca(OH)₂, both of which are economically useful. A recent announcement by the U.S. Bureau of Mines envisages the "cleansing" of sea water by utilization of large quantities of Ca(OH)₂.

5. The conversion of inorganic hydrocarbons to fibers is certainly possible.

6. If modification of the process can be made to yield heavy-molecule hydrocarbons similar to those in petroleum, then such mixtures could serve equally well as food for yeasts and bacteria that convert petroleum to single-celled protein (so-called SCP), which is nutritionally comparable to meat.

Imaginative though they may be, the extrapolations we have presented are no more a form of science fiction than were recent speculations on lunar geology. We have tried carefully to delineate between fact and fancy. The facts are that the reaction works and the raw materials for it are cheap, widespread and plentiful. The fancies are that ultimately limestones may be converted to fuel, fabric and food.

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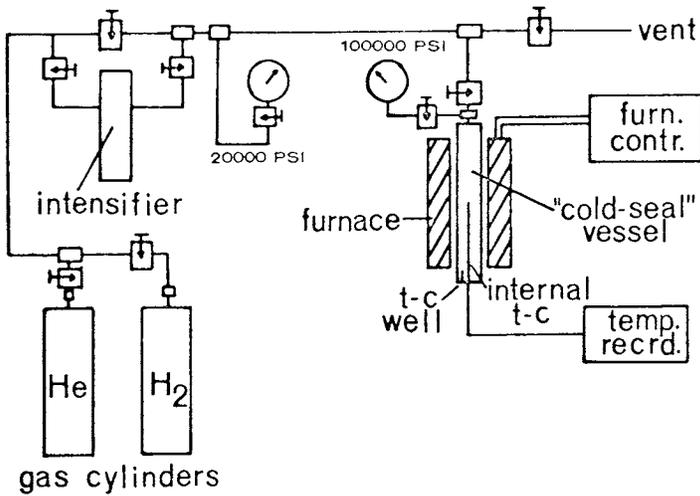


Fig. 1. Schematic drawing of the apparatus used for studies in the calcite-hydrogen; dolomite-hydrogen; and siderite-hydrogen systems.

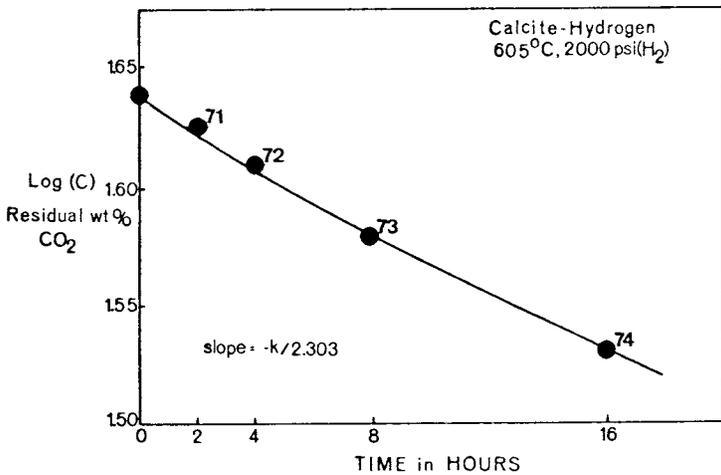


Fig. 2. Linear plot of log C against time for calcite-hydrogen data from experiments 71, 72, 73, and 74; run at 605°C, 2000 psi (H₂) illustrating the pseudo-first-order nature of the reaction.

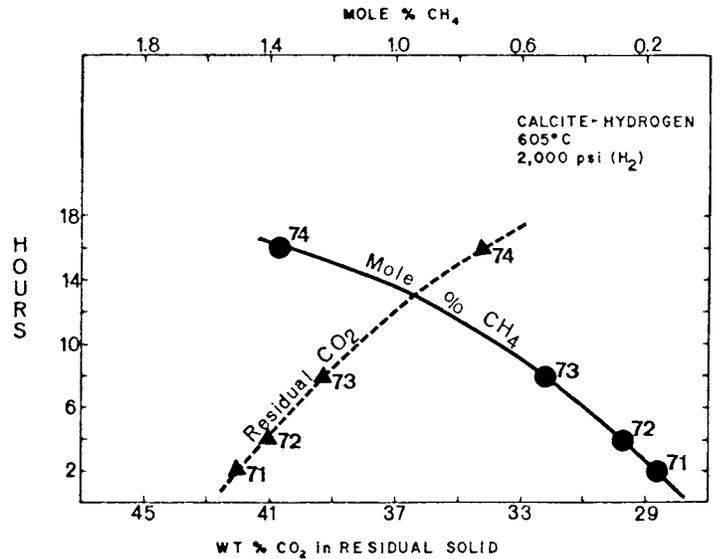


Fig. 3. Plot of mole% CH₄ generated in the calcite-hydrogen system and residual CO₂ remaining as calcite in experiments run at 605°C; 2000 psi (H₂); for 2, 4, 8, and 16 hours.

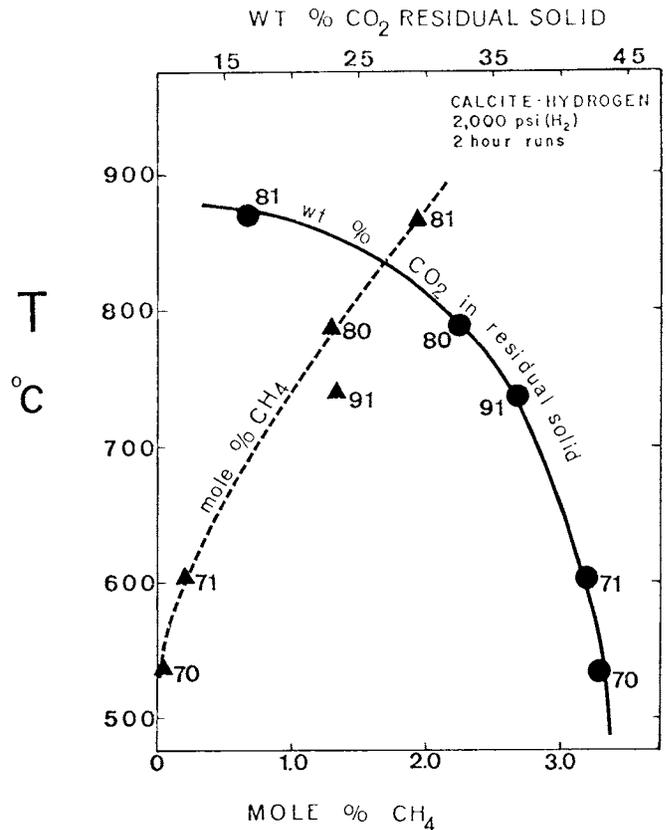


Fig. 4. Plot from calcite-hydrogen system of mole% CH₄ generated and residual CO₂ remaining as calcite in experiments run for 2 hours; 2000 psi (H₂); at 535, 605, 735, 790, and 870°C.

TABLE 1. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES ^{a, b, c} AND WET-CHEMICAL ANALYSES OF RESIDUAL CO₂ IN UNREACTED CALCITE CALCITE - HYDROGEN SYSTEM

Experiment No.	70	71	72	73	74	75	77	78	79	80	81	82	90	91	92	93
Temperature (°C)	535	605	605	605	605	700	700	700	700	790	870	650	610	735	713	700
Pressure (PSI)	2000	2000	2000	2000	2000	200	2000	8000	2000	2000	2000	2000	2600	2000	400	4000
Wt. % CO remaining in solid	43.0	42.0	41.0	39.3	34.2	41.2	26.8	36.0	33.4	34.5	16.3	36.9	N. A. ^d	37.8	N. A. ^d	N. A. ^d
Duration of Run (hours)	2	2	4	8	16	2	8	2	4	2	2	4	12.5	2	2	2
Mole % CH ₄ in Gas	0.02	0.17	0.28	0.53	1.38	1.83	2.67	0.37	1.34	1.43	1.95	0.89	1.64	1.39	2.37	0.99
Mole % C ₂ H ₆ in Gas	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-	-
Mole % CO in Gas	-	-	-	-	-	1.10	-	-	-	-	-	-	-	-	0.31	-
Mole % CO ₂ in Gas	-	-	-	-	-	0.11	-	-	-	-	-	-	-	-	0.04	-
Mole % H ₂ in Gas	99.6	99.8	99.7	99.4	98.5	96.2	97.2	99.6	98.6	98.3	98.0	99.0	98.1	98.6	97.2	99.0
Mole % He in Gas	0.40	0.08	0.04	0.07	0.09	0.75	0.11	0.02	0.07	0.23	0.06	0.10	0.24	-	0.11	20.01

a Analysis calculated on water free basis

b Starting hydrogen impurities given as follows:

less than 5 ppm N₂
 less than 1 ppm O₂
 less than 1/2 ppm CO₂
 less than 1/2 ppm CO
 Dew Point - 100°F

c Detection limit 0.01 %

d Not analyzed

TABLE 2

Mass Spectrographic analyses of reaction gases a, b, c, and wet-chemical analyses of residual CO₂ in unreacted siderite.

Siderite-Hydrogen System

Experiment No.	86	87	89	40	1W	2W
Temperature (°C)	605	455	400	525	345	345
Pressure (psi)	2,000	2,000	2,000	5,000	200	2,000
Duration of Run (Hours)	4	4	4	4	4	4
Mole % CH ₄ in Gas	0.15	4.34	4.45	1.45	0.01	0.01
Mole % C ₂ H ₆ in Gas	-	0.42	0.28	0.12	0.01	0.01
Mole % C ₃ H ₈ in Gas	-	0.23	0.10	0.03	-	-
Mole % C ₄ H ₁₀ in Gas	-	0.05	0.03	-	-	-
Mole % CO ₂ in Gas	-	-	-	0.04	0.68	0.03
Mole % H ₂ in Gas	99.80	94.90	95.10	95.30	99.29	99.95
Mole % He in Gas	0.04	0.08	0.09	3.07	-	-

a. Analysis calculated on water-free basis

b. Starting hydrogen impurities given as follows:

less than 5 ppm N₂
 less than 1 ppm O₂
 less than 1/2 ppm CO₂
 less than 1/2 ppm CO
 Dew point - 100°F

c. Detection limit 0.01%

THE ECONOMIC POTENTIAL OF FERROMANGANESE NODULES IN THE GREAT LAKES¹

by

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Abstract

Ferromanganese nodules occur in all of the St. Lawrence Great Lakes with the greatest deposits found to date in northern Lake Michigan. The Lake Michigan nodules average 20 percent iron and 8 percent manganese and occur as several types based upon physical and chemical properties. Nodules occur as concretionary material around a quartz or feldspar nucleus and ferromanganese oxide coatings on sand grains which are agglutinated into masses usually less than 3 mm in diameter. Chemically, the nodules consist of reddish brown high iron-low manganese material, and dark brown high manganese-low iron masses. The trace element content of nodules is 1 to 2 orders of magnitude lower than marine material. Lake Michigan nodules contain unusually high concentrations of barium and arsenic which appear to be associated with hydrous manganese oxide. Reconnaissance sampling of the Upper Great Lakes revealed the presence of nodules at many localities exhibiting a similar geologic environment. Nodules always occur in oxidized sands that overlay stiff red and gray lacustrine clays. The nodules are extremely sensitive to oxidation-reduction potential and seldom occur in mildly oxidizing sediments. In conjunction with redox potential, sedimentation rates are the other important factor affecting the preservation of ferromanganese nodules. Synthesis of geological and geochemical data permit the evaluation of several parameters that may be useful in exploration for ferromanganese deposits in the Great Lakes.

INTRODUCTION

With the discovery of large deposits of ferromanganese nodules in Green Bay, Lake Michigan (Callender, 1968; Rossmann and Callender, 1969; Moore and Meyer, 1969), interest has renewed in the occurrence and origin of freshwater manganese nodules. Ferromanganese concretions have been known to exist in many freshwater environments but reports of them have been few. Accumulations of iron-manganese oxides have been reported from several Canadian lakes (Kindle, 1932, 1935, 1936; Harriss and Troup, 1969), from several English (Gorham and Swaine, 1965) and Fennoscandian lakes and streams (Ljunggren, 1953), from Lake Champlain (Hunt and Henson, 1969), from Oneida Lake (Dean, 1969), and from the Great Lakes. Besides the occurrence of sizeable deposits in Green Bay, ferromanganese nodules have been found in Lake Superior (E. Callender, unpublished data), in Georgian Bay of Lake Huron and in Lake Ontario (R. L. Thomas, personal communication). The occurrence of freshwater

ferromanganese material appears to be restricted to temperate and subarctic latitudes and is generally associated with glacial deposits.

Although extensive research on the nature, occurrence, and origin of ferromanganese concretions has been conducted on marine material, little sound scientific effort has been expended on their freshwater counterparts. This dearth of freshwater studies probably reflects the lack of widespread, high-grade, nonmarine deposits which, if present, would create an economic impetus for more basic research. With the dwindling supplies of foreign ferromanganese ore and the increased demand for manganese as a structural alloy, once marginal deposits will become more and more economically feasible especially with new technological methods of metal extraction and refining. Undoubtedly this is the view of Deep-Sea Ventures who plan to initiate a pilot study of ocean mining and *in situ* concentration techniques on the Blake Plateau during the summer of 1970. Industry firmly believes that this pilot study will prove economically feasible for the mining and processing of relatively shallow manganese nodule deposits and a group of companies plan to tap deep-ocean reserves in the next few

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years. It seems clear that marine ferromanganese nodules are the future source of industrial manganese and that more emphasis will eventually be placed upon exploration.

Although deposits of ferromanganese nodules are quantitatively much less important in the Great Lakes than in the ocean, these accumulations could eventually become important for local industrial needs. However, of more immediate importance is the value these deposits hold as shallow-water analogs to marine deposits. A unique opportunity exists in the Great Lakes to study the occurrence and origin of ferromanganese nodules and by doing so formulate a general theory that will evolve into a set of operational parameters which can optimize the chances for successful exploration for ferromanganese nodules in any environment, freshwater or marine.

The purpose of this paper is to present the results of our studies on ferromanganese nodules in the Upper Great Lakes and to synthesize geological and geochemical data concerning their occurrence, nature, and origin into a tentative theory that may be useful in future exploration for manganese accumulations of potential economic interest.

GEOLOGICAL OCCURRENCE IN THE GREAT LAKES

General

Accumulations of ferromanganese nodules ranging from 10 to 90% bulk sedimentary material have been reported from Green Bay and northern Lake Michigan (Callender, 1968; Moore and Meyer, 1969). Figure 1 shows the approximate location and concentration of these deposits. Additional localities of ferromanganese accumulations have been reported from north-eastern and western Lake Superior (E. Callender, unpublished data; C. Adams, personal communication), Georgian Bay, northeastern Lake Huron (R. L. Thomas, personal communication), and north-central Lake Ontario (R. L. Thomas, personal communication). The approximate location of these deposits is also shown by Figure 1. In all cases, the nodules occur in medium brown to reddish brown medium sands that overlie stiff glacial lake clays. The ferromanganese occurs as discrete concretions or coatings on sand grains, with concretions varying in diameter from one millimeter to two centimeters. This is contrasted with marine nodules that generally range between 0.5 and 25 cm in diameter (Mero, 1965). The water depths at which nodules occur in the Great Lakes vary from 15 to 60 m, far shallower than

oceanic occurrences of 1000 to 6000 m (Mero, 1965).

Figures 2, 3, and 4 illustrate the three major nodule types found in Lake Michigan. Figure 2 is an incident light photomicrograph of small ferromanganese nodules (0.7 mm average diameter) from northern Green Bay. The light colored bands are iron rich and the dark manganese rich. Generally the nuclei are detrital quartz and feldspar grains. Figure 3 is a photomicrograph of medium-sized nodules (2.5 mm average diameter) from middle Green Bay. Notice the very distinct concentric structure consisting of iron and manganese rich bands about a feldspar or clay nucleus. Figure 4 is an incident light photomicrograph of a polished section from large, clay-cored ferromanganese nodules located in southern Green Bay near the Sturgeon Bay Ship Canal. The nodules average 9 mm in diameter and occur on a stiff red clay. The banding to the left of the mottled clay core is iron-manganese rich and some metal-rich areas occur in the core itself.

Selected Localities

Southern Green Bay

The largest, most concentrated deposits of ferromanganese nodules occur in southern Green Bay. Deposits up to 1 m in thickness have been found near the mouth of rivers entering Green Bay although the average thickness of ferromanganese accumulations is approximately 10 cm. Figure 5 is an underwater photograph taken by SCUBA divers at a depth of 20 m near the mouth of Sturgeon Bay. This is one of the localities where large nodules, up to 2 cm in diameter, occur. Generally the nodules in this area occur in silty sand overlying a stiff red clay. Concentration estimates made on grab samples of bulk material, nodules plus matrix, from several localities in southern Green Bay yield values of from 0.01 to 0.6 grams/cm² with an average value of 0.34 for the southern Green Bay area as a whole (Table 1). This area contains the greatest concentrations of ferromanganese nodules in Lake Michigan with an estimated tonnage of 0.7×10^6 metric tons.

Northern Green Bay

Geographically, this area is larger (600 km²) than southern Green Bay (200 km²) but contains considerably less quantities of nodules. Nodules comprise only 25% of the bottom sediment in contrast to the southern area where nearly 50% of the sediment consists of ferromanganese material. The nodules in

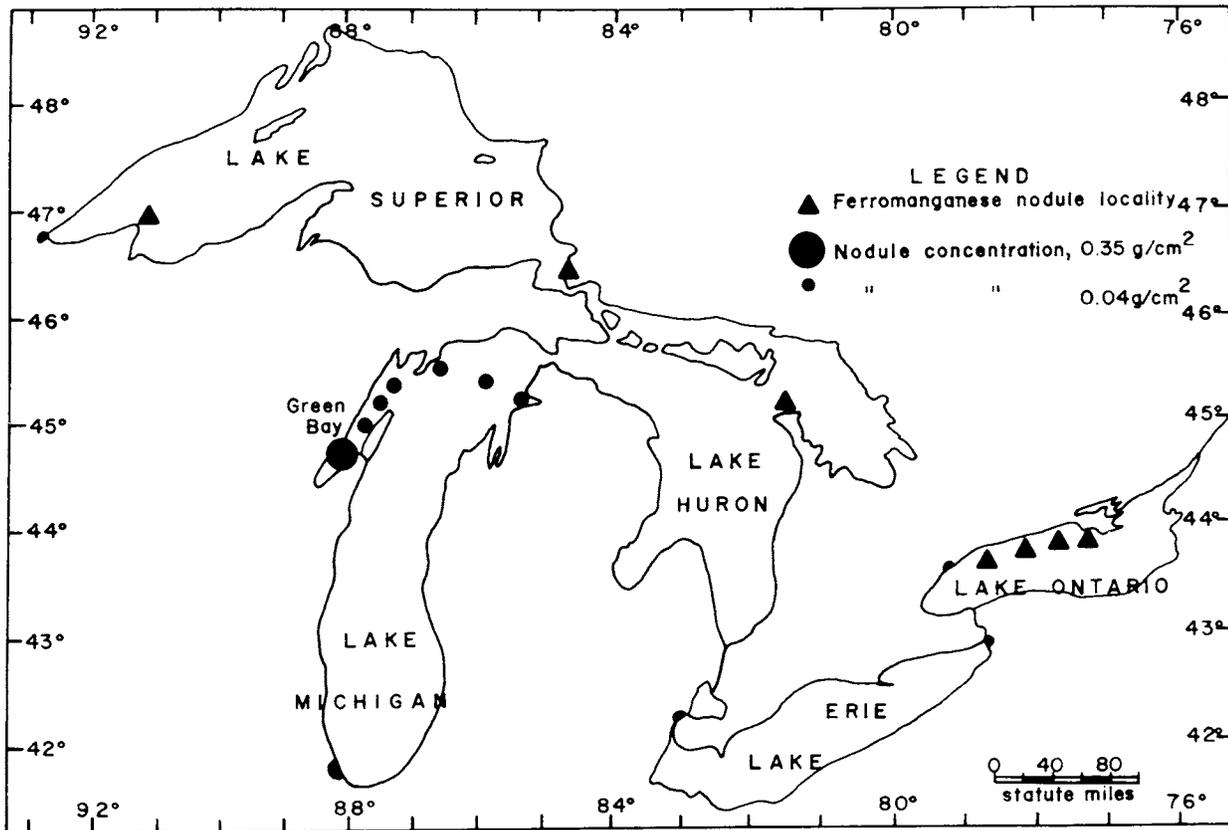


Figure 1. Map of the St. Lawrence Great Lakes showing ferromanganese nodules localities and estimated nodules concentrations in Green Bay and northern Lake Michigan.

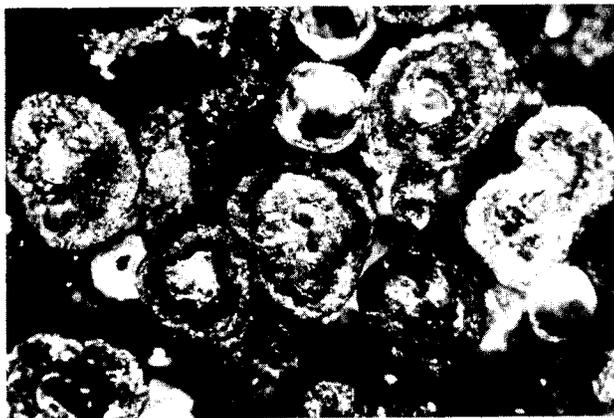


Figure 2. Incident light photomicrograph of polished section of small ferromanganese nodules from northern Green Bay. The nodules average 1 mm in diameter. Note light-colored outer rim which is iron rich and darker inner rim which is manganese rich.



Figure 3. Incident light photomicrograph of polished section of medium-sized ferromanganese nodules from Green Bay. Nodule is 3 mm in diameter. Notice distinct concentric structure.

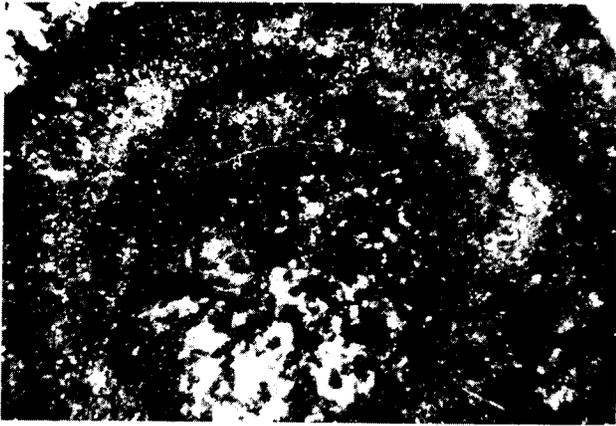


Figure 4. Incident light photomicrograph of polished section of large, clay-cored ferromanganese nodule from southern Green Bay near the Sturgeon Bay Ship Canal. Field of view in the vertical section is 4 mm. Average nodule diameter is 9 mm. The banding to the left of the mottled clay core is iron-manganese rich and some metal-rich areas occur in the core itself.

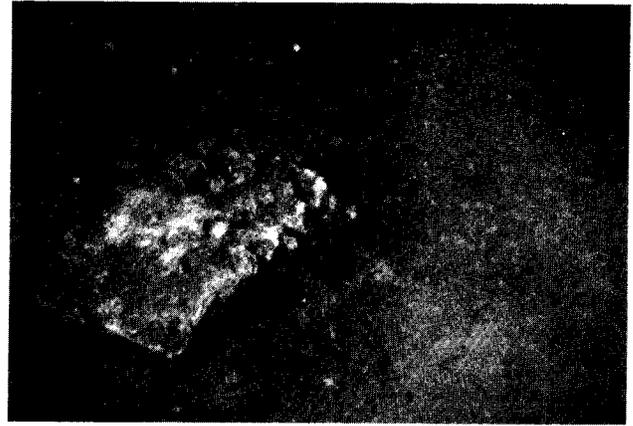


Figure 5. Underwater photograph taken by SCUBA of ferromanganese encrusted limestone boulder and nodules located at a depth of 20 m in southern Green Bay near the Sturgeon Bay Ship Canal. The boulder is 40 by 60 cm and the nodules average 1 cm in diameter. Bottom sediment is silty sand underlain by stiff red clay.

TABLE 1. Concentrations of ferromanganese nodules in Lake Michigan.

Statistic	Southern Green Bay 44°45'N-45°05'N	Northern Green Bay 45°05'N-45°45'N	Northern Lake Michigan 45°20'N-45°30'N
Number of observations	10	33	14
Nodule diameter (mm)			
maximum	10.0	11.0	9.0
minimum	0.5	0.4	1.0
average	5.2	2.1	3.0
Area covered by nodules (%)			
maximum	60.0	90.0	35.0
minimum	5.0	1.0	7.0
average	34.0	28.0	18.0
Concentration estimate (g/cm ²) ¹			
maximum	0.6	0.2	0.1
minimum	0.01	0.01	0.01
average	0.34	0.05	0.03
Estimated tonnage of nodules (millions of metric tons)	0.67	0.29	0.47

¹Estimated using Fig. 62 in Mero (1965).

the northern area are considerably smaller averaging 2 mm in diameter. Invariably the nodules occur in light-brown medium sand which overlies stiff red clay. The sands vary in thickness from 5 to 100 cm and red clay crops out at several localities. Figure 6 is a photograph of these smaller nodules taken at a depth of 25 m in northern Green Bay. Notice that the nodules are restricted to the sands (light gray) and are not present to any significant extent in the darker gray silts that occupy shallow depressions.

Figure 7 illustrates a typical core from northern Green Bay where several centimeters (3 to 5 cm) of dark-colored ferromanganese coated medium sand overlies 10 cm of tan, medium sand that in turn overlies red clay. Concentration estimates of nodules in this area vary from 0.01 to 0.2 grams/cm² with an average value for northern Green Bay being 0.05 grams/cm². The estimated tonnage of nodules based on this concentration is 0.3 x 10⁶ metric tons. The total tonnage of ferromanganese nodules present on the floor of

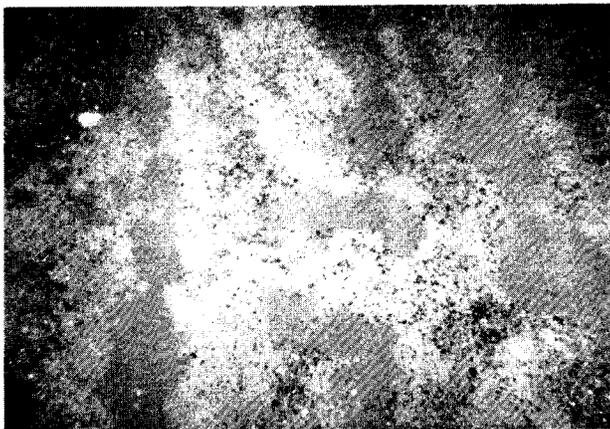


Figure 6. Underwater photograph taken by SCUBA of medium-sized ferromanganese nodules (dark spots) located at 25 m in northern Green Bay. Nodules average 2.5 mm in diameter and occur in light reddish-brown medium sand.

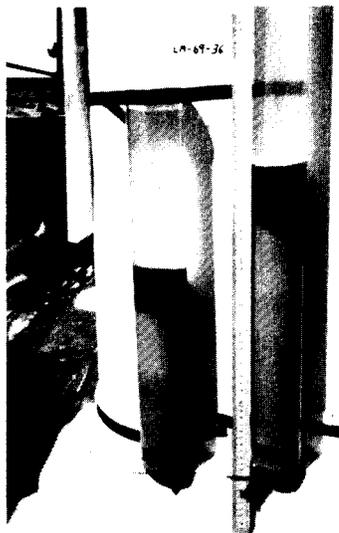


Figure 7. Cores taken by SCUBA diver from medium sands at the bottom of northern Green Bay. Notice sharp contact between dark ferromanganese oxide material and reddish-brown medium sand. The lower, faint contact is between sand and reddish-brown silty clay. Water depth at which core was taken is 30 m.

Green Bay is estimated to be 1 million metric tons. This figure is contrasted with the tonnage of nodules present in an area of comparable size in the Pacific Ocean, 10 million metric tons (Mero, 1965), an estimated quantity that is approximately one order of magnitude greater than the total estimated tonnage of nodules in Lake Michigan (1.5 million metric tons).

Northern Lake Michigan

Concentrations of ferromanganese nodules in Lake Michigan proper are restricted to two major areas. The central region of Little Traverse Bay on the eastern side of Lake Michigan contains quantities of nodules similar to those found in northern Green Bay. Nodules ranging in diameter from 1 to 9 mm occur at water depths of from 40 to 80 m. Again, the nodules are found in light brown and reddish brown medium sands with minor amounts of admixed silt. Other accumulations of ferromanganese nodules in northern Lake Michigan occur in the vicinity of the Fox Islands in water depths of from 30 to 80 m. The average diameter of these nodules is 3 mm and they are similar in size and appearance to those in Little Traverse Bay. Concentration estimates for nodules in northern Lake Michigan range from 0.1 to 0.01 grams/cm² with an average of 0.03 grams/cm². The estimated tonnage of nodules in this area is 0.5×10^6 metric tons.

GEOCHEMISTRY

Environmental Parameters

The precipitation of hydrated iron and manganese oxides is controlled to a large extent by the pH and redox potential (Eh) of the depositing medium, in our case lake water. Eh-pH stability diagrams for the various solid oxy-hydroxide phases that might be in equilibrium with lake water (Rossmann and Callender, 1969) indicate that reduced iron in solution will be oxidized to ferric hydroxide over a normal environmental pH range of from 6 to 9 at redox potentials ranging from 0 to -200 mv. Under these environmental conditions manganese will remain in solution as Mn⁺² and it is not until the redox potential reaches +200 mv at pH 9 that a solid manganese oxide compound is formed. Practically, the redox potential must reach +400 mv at pH 8 to form a manganese oxide compound that is found in manganese nodules. Table 2 gives average environmental data for lake water and sediment pore water (interstitial water) in Green Bay and northern Lake Michigan. Non-nodule areas in Green Bay have lower redox potentials for lake water and interstitial water but interstitial water values are clearly low enough to predict that very little solid manganese oxide should occur in the bottom sediment. Sediment manganese values for samples from this area

TABLE 2. Environmental chemistry of Lake Michigan bottom (BW) and interstitial (IW) waters.

Parameter	Green Bay				Northern Lake Michigan	
	Nodule areas		Non-nodule areas		BW	IW
	BW	IW	BW	IW		
Eh	+385	+158	+321	+28	+378	+168
pH	8.1	7.2	8.1	7.0	8.4	7.5
Oxygen Saturation (%)	75	----	76	----	88	----
Fe (ppm)	0.019	1.14	0.014	2.04	0.015	2.291
Mn (ppm)	0.012	1.48	0.033	1.89	0.003	1.913
Cu (ppb)	4.5	----	2.5	----	5	----
Zn (ppb)	14	81	10	114	22	521
Co (ppb)	1	----	0.5	----	8	----
Ni (ppb)	10	75	5	75	10	81

average 0.1 weight %. One would also predict from Table 2 that the environment immediately above medium sands (nodule areas) would contain sufficient quantities of oxygen to cause oxidation of the manganous ion to a manganese oxide compound. Essentially all environments in Lake Michigan are conducive to some precipitation of ferric iron compounds. The average iron content in bottom sediments is 2%, some 10 to 20 times greater than bulk sedimentary manganese values.

Elemental Composition

The major element composition of freshwater ferromanganese nodules is quite variable. Table 3 gives the transition metal content of nodules from selected freshwater environments. Nodules from several Canadian lakes contain manganese concentrations (Harriss and Troup, 1969) that compare favorably with marine nodules (Mero, 1965). Lake Michigan ferromanganese nodules range between 24 and 1 weight % manganese. Nodules from Swedish Lakes appear to contain the lowest amount of manganese (Table 3). If one combines the major elements with their most naturally occurring oxide, some reasonable estimate of the constituent composition of ferromanganese nodules can be made. Table 4 gives the standard rock analysis constituents and their calculated weight percentages for Lake Michigan and marine nodules. Generally, marine nodules contain twice as much manganese as Lake Michigan nodules but similar contents of calcium, magnesium, and structural water. Although we have not analyzed for silica or alumina as such, the residue remaining from an HCl extract of the nodules consists primarily of these constituents. Thus, Lake Michigan nodules contain approximately twice as much detrital material as marine nodules. This detrital material dilutes the authigenic ferromanganese compounds.

Since ferromanganese oxides are excellent scavengers of various minor elements (Goldberg, 1954), the concentration of these elements in nodules is potentially large enough to be considered a marketable byproduct resulting from the refining process. The minor heavy metal content of Lake Michigan nodules (Table 5) is generally 10 times lower (50 times in the case of copper) than the heavy metal content of marine nodules (Mero, 1965). The minor heavy metal content of other freshwater nodules is comparable to that of Lake Michigan nodules (Table 3). Further inspection of Table 5 points up some interesting differences between Lake Michigan and marine nodules with respect to other so-called minor elements. The average arsenic content of nodules from Green Bay is 0.02% with values as high as 0.05% for nodules located at the mouth of two rivers draining into southern Green Bay. Although arsenic data is not available for marine nodules, arsenic contents of Black Sea manganese nodules range from 0.05 to 0.10% dry weight (Sevast'yanov, 1967). The possibility exists that arsenic in Green Bay nodules is a recent contaminant and may be associated with that part of the nodule formed during the last 100 years. Another interesting element is barium which occurs in ferromanganese nodules from Green Bay at concentrations approaching 2% dry weight. Electron-probe X-ray microanalysis has shown that the barium is associated almost entirely with the manganese-rich phases in the nodules. Marine nodules also contain high barium contents which are usually associated with the mineral barite included within the nodule matrix (Arrhenius, 1963).

Table 5 also gives the average chemical composition of Lake Michigan bottom sediments. One can readily see that the average arsenic value of 0.0026% is nearly ten times lower than that of the nodules. Arsenic values are substantially higher in oxidized sediments relative to reduced sediments. The barium content of bottom sediments is also ten times lower than that of ferromanganese nodules. Similar relationships exist for several other

TABLE 3. Transition metal content of freshwater and marine ferromanganese nodules.

Location	Fe (%)	Mn (%)	Cu (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)
Lake Michigan ¹	20.2	6.1	180	320	200	270
Reddish Brown Nodules ²	26.2	1.2	60	350	80	55
Brownish Black Nodules ²	11.8	15.2	90	800	130	320
Oneida Lake, N.Y. ³	21.2	13.4	40	---	20	60
Canadian Lakes ⁴	18.6	36.6	11	1,245	200	230
Swedish Lakes ⁵	39.4	3.8	40	50	100	40
Deep Ocean ⁵	12.5	19.0	4,000	400-4,000	2,800	5,800

Sources of data:

1. Rossmann and Callender, 1969
2. Callender, unpublished, 1970
3. Gillette, 1961
4. Harriss and Troup, 1969
5. Manheim, 1965

TABLE 4. Average percentages of the major constituents of Lake Michigan and marine manganese nodules.

Constituent	Weight percentages ¹	
	Lake Michigan ²	Ocean ³
Fe ₂ O ₃	26.0	42.0
MnO ₂	13.0	24.3
SiO ₂	----	19.2
Al ₂ O ₃	----	3.8
CaCO ₃	3.1	4.1
MgCO ₃	0.6	2.7
BaO	0.9	----
Organic C	0.9	----
H ₂ O ⁺	15.7	13.0
Insoluble in HCl	<u>43.0</u>	<u>26.8</u>
Total	103.2	109.1

¹Results expressed as weight percent of total dried (110°C) sample.

²Statistics derived from data of Rossmann and Callender (1969) and Callender (unpublished).

³Mero (1965), Table 27.

minor elements such as Cu, Zn, Co, and Ni.

It is also readily apparent from Table 5 that while the manganese content of bottom sediments is at least 40 times lower than that of nodules, the iron content is only 10 times lower. The enrichment of manganese in nodules is clearly a more selective process than that of iron and accounts for the extreme variability of manganese (1-25%) in ferromanganese nodules from Lake Michigan.

Since the nodules are formed by the oxidation of ions in aqueous solutions, the chemistry of this nourishing phase is important

when considering the chemical composition of the nodules. Table 2 gives the average concentration of several transition metals in bottom water immediately above the sediment and in pore water extracted from the sediment. The interstitial water concentrations of iron and manganese are several orders of magnitude higher than concentrations in lake water. This observation suggests that interstitial water is an important source of metals that nourish ferromanganese nodule growth and that as this pore water rises to the sediment surface and encounters a more oxidizing environment, the metals are precipitated as insoluble hydrated oxide compounds. The concentrations

TABLE 5. Concentration of major and minor elements in Lake Michigan ferromanganese nodules, associated bottom sediment, and lake water.

Element	Parts Per Million (dry-weight basis)		
	Ferromanganese Nodules	Associated Bottom Sediment	Lake Water ^{1,2}
Arsenic	185	26	0.0004
Barium	9,200	670	0.050
Calcium	10,100	27,300	36.
Cobalt	150	85	0.007
Copper	40	20	0.005
Iron	124,900	18,100	0.017
Magnesium	2,600	15,500	14.
Manganese	98,500	9,750	0.001
Nickel	750	150	0.007
Uranium	1.3	0.8	0.001
Zinc	270	73	0.030

¹Concentration expressed as mg metal/liter of solution.

²Values for As and U taken from Bowen (1966).

of other heavy metals, Zn and Ni, are also significantly higher in interstitial water and constitute a source of minor metals that are scavenged by the ferromanganese oxides.

ENVIRONMENTAL SYNTHESIS

Geological and Geochemical Data

A large store of data pertaining to the geological occurrence and geochemical nature of ferromanganese nodules in Lake Michigan is now available for synthesis into a general descriptive theory regarding the origin of ferromanganese nodules in the Great Lakes. Associations that are true for Lake Michigan appear to hold true for other of the St. Lawrence Great Lakes based upon data supplied the writer by his Canadian colleagues.

The nodules are generally spherical with distinct to vague concentric bands of iron- and manganese-rich material surrounding a nucleus (Figures 2-4). This nucleus is usually a detrital mineral grain (quartz and feldspar) or red clay. Sometimes the entire inner part of the nodule is permeated with the clay which is intermixed with ferromanganese oxides in a chaotic manner (Figure 4). A second type of nodule, though less important in abundance, consists of detrital sand grains encrusted with and cemented by ferromanganese oxides. The diameter of either nodule type does not exceed 2 cm and generally the nodules exhibit a bimodal size distribution where 8 mm and 1 mm are the dominant nodule diameters.

Ferromanganese nodules in Lake Michigan as well as in other of the Great Lakes occur in tan to reddish-brown silty sands with minor admixtures of clay. The sands are texturally a medium to medium-fine sand. In southern Green Bay, large quantities of medium to large diameter ferromanganese nodules occur in silts that have less than 20% admixed sand. These deposits are often found adjacent to the mouths of the major rivers draining into Green Bay and reach a thickness of 1 m. This association of thick nodule deposits and proximity to the mouths of streams draining the mineralized region to the north must be more than fortuitous.

What determines the presence or absence of ferromanganese oxide accumulations from a geochemical viewpoint is best considered in terms of environmental parameters. Although medium sands that contain little organic and other oxidizable compounds are thought to be generally in an oxidized state, the redox potential of their pore water ($E_h = +160$ mv) is not sufficiently high to cause large-scale oxidation of manganese to insoluble oxide compounds. The sensitivity of manganese to the redox potential is illustrated by limestone boulders embedded in the nodule-bearing sands of northern Green Bay. The surface exposed to oxygenated bottom water is covered with a reddish-brown ferromanganese oxide crust while the portion of the boulder sitting in the sand is devoid of any coating and a very sharp line of demarcation separates the two areas.

The sensitivity of ferromanganese oxides to differing conditions of E_h and pH is so striking that any average combination of these parameters for a given area may determine the relative proportions of iron and manganese as well as associated minor elements. Naturally,

the supply of these metals is also critical to nodule composition, but it is my feeling that the general supply of these metals from streams entering Green Bay and from interstitial water that either dissolves detrital iron and manganese compounds in the sediment column or carries these metals in response to a regional groundwater gradient from other areas in the basin is more than sufficient to nourish the solid ferromanganese phases formed during any given period of time. Therefore, the chemical variation in these ferromanganese nodules may be a result of geochemical parameters affecting the type and rate of solid phase formation and not the availability or supply of metal ions.

Operational Parameters For Exploration

A review of the data given in this paper on chemical composition of ferromanganese nodules in Lake Michigan points out one cold economic fact: with the present manganese mineral economics, ferromanganese nodules in Lake Michigan and other Great Lakes do not constitute an economic mineral resource of manganese. The highest percentage of manganese we at Michigan have found during analysis of nearly 100 samples is 25%, and most of our analyses average out to approximately 10%. The lowest concentration of manganese that would constitute a marketable ore is 35% and even this material must be substantially milled and refined. Therefore, the immediate outlook for a marketable manganese mineral resource in the Great Lakes is dim although future technological advances and waning supplies of high-grade ore may eventually make the nodules a marginal mineral resource. However, even though the nodules have little intrinsic value at this time, they are most valuable as representative examples of more widespread, economically feasible manganese nodule deposits elsewhere. Nodule deposits in the Great Lakes can be studied with comparative ease in order to determine practical parameters for efficient economic exploration. In the future, the demand for manganese will be great enough and the mining economics low enough that manganese nodules will be a prime source of manganese as well as several other minor elements associated with the nodules. Exploration methods that will uncover new deposits in the most efficient, least expensive manner will be essential to the economic recovery of these nodules. The following is a tentative list of operational parameters that might be used to uncover new deposits in the Great Lakes.

1) *Stratigraphic parameter* - medium, well-oxidized sands that overlie stiff lacustrine clays.

2) *Sedimentation parameter* - low rate of

inorganic and organic sedimentation.

3) *Hydrologic parameter* - significant stream inflow that drains partially "mineralized" areas and carries metals as an inorganic and/or organic complex.

4) *Geochemical parameter* - suitable redox potentials associated with normal environmental pH conditions (pH 6 to 9).

We at Michigan have never found or heard of manganese nodule deposits in the Great Lakes occurring in bottom sediments other than sandy silt or silty sand that overlie, at some depth, stiff lacustrine or glacio-lacustrine clays. The exception to this is the occurrence of clay-cored ferromanganese nodules resting directly on stiff red clays at several localities in Green Bay.

Many of the major streams flowing into the Great Lakes drain forested regions underlain by igneous or "mineralized" metamorphic and sedimentary rocks. These streams contain significant quantities of dissolved organic compounds, chiefly humic acids, that complex many transition metals and keep them in solution until the organic complex is "deposited" at the stream's mouth or disrupted in the lake environment proper. Dissolved complexed manganese in several streams draining into Green Bay reaches concentrations of 1 ppm while manganese concentrations in the lake proper do not exceed 0.1 ppm.

Ferromanganese nodules are absent from areas that exhibit significant rates of sedimentation. The rate of sedimentation has a pronounced effect upon redox potential as we have seen that even in relatively clean sand the sediment pore water Eh drops below the equilibrium value for a solid manganese phase just a few millimeters below the water-sediment interface. With low rates of sedimentation, the sediment surface is stable enough to allow slow, continued growth of solid ferromanganese compounds. One might predict that the south shore of Lake Superior would be a likely locality to find ferromanganese compounds. There is an adequate source of metals supplied to the streams by the mineralized rocks in that area and the predominant bottom sediment is a reddish-brown medium sand. The surface sediment pore water redox potentials (Eh = +300 mv) are among the highest in the Great Lakes. Everything is right except one thing; the inorganic sedimentation rate is significant and there is no stable site for slow, continued growth of ferromanganese oxides.

CONCLUSIONS

The four parameters listed in the

preceding section appear to be the major factors governing the presence of ferromanganese nodules in the Great Lakes. Well-oxidized sands may reflect low absolute sedimentation rates where the sand is continuously subject to current action. Sand bodies are easy to identify on fathograms and seismic profiles that are recorded while the ship is underway. Most of the streams draining forested areas in the Great Lakes drainage basin contain humic acids that can complex heavy metals which when transported to the lake proper constitute a source of metals for nodule growth. Both of these conditions, large-scale sand bodies and sources of dissolved heavy metals, exist in many areas of the St. Lawrence Great Lakes. The more critical parameters of low sedimentation rates and high bottom-water redox potentials are not always suitable for formation and preservation of ferromanganese nodules. In general, the open lake environment is well-oxygenated even at the water-sediment interface. Only in isolated bays or other highly eutrophic areas is there insufficient oxygen available to oxidize manganous ions. As a general rule, finer sediments exhibit significant sedimentation rates and redox potentials below the equilibrium value for solid manganese oxides. The exception is the red clay in southern Green Bay where there is essentially no sediment buildup at present and the bottom environment is sufficiently oxidizing.

In summary, what we are looking for is a sandy or stiff clay bottom, swept clean of finer material by currents, where oxidizing (Eh: +200 to +400 mv) conditions exist and the source of dissolved metal ions is nearby either as sediment pore water or organically bound metals in lake water. Such conditions are common in many aqueous environments and all geologists need do is use a few simple criteria during reconnaissance surveys. We must look to the environment for answers to the earth's resource problems.

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GEOLOGY OF GYPSUM IN THE LOWER PENINSULA, MICHIGAN

by

Louis I. Briggs¹

Abstract

Gypsum has been produced in Michigan since 1841, and the production for the last 40 years has ranked second in the U. S. All of the production comes from the Mississippian Michigan Formation, by open-pit strip mining near Alabaster, adjacent to Lake Huron immediately north of Sagina Bay, and by shallow mines near Grand Rapids in the southwestern part of the state.

Extensive thick gypsum occurs elsewhere within both the Michigan Formation (Triple Gyp, Pencil Gyp, and National City Gyp units) and with the Detroit River Group (Massive Anhydrite and Upper Salts). In most of these areas the gypsum occurs under overburden of glacial drift and bedrock of 500-2500 feet, making exploitation economically less favorable than the present areas of mining under present supply and market conditions. Transportation costs are also generally less favorable in the unexploited areas. Future market demands in the next several decades should make these deposits economically attractive to warrant detailed exploratory evaluation.

INTRODUCTION

Exploitation of gypsum in Michigan for use in the plaster industry began in the period 1837-1841, when gypsum quarried from a ledge in Plaster Creek, near Grand Rapids, was ground on a small scale in corn mills (Grimsley, 1904). A crude stone mill was erected here in 1841, and from this beginning, the industry has grown to rank second among the states in domestic production. Exploitation in the Saginaw Bay area at Alabaster began in the 1860's, and has since become the most important in Michigan. There are presently two companies operating in Grand Rapids, and three in the Alabaster area. Most of the ore is processed in Grand Rapids, National City (near Alabaster) and Detroit, and used in plaster board, lath, and plaster. Uncalcined gypsum is used as a cement retarder (Stevens, 1968).

Nature of Study

The object of the present study is to define the stratigraphy of gypsum-bearing formations in Michigan, the location of potential gypsum deposits, and an evaluation of their properties and economic potential. The study is

preliminary in the sense that it evaluates regional and not detailed local characteristics of the deposits. From the information gained, industries interested in exploitation of gypsum may develop more detailed exploration programs to evaluate the nature and extent of economically exploitable gypsum.

The data available for the study originates from electric logs, well cuttings, descriptive logs, and a few cores that are part of the materials resources of the Laboratory of Subsurface Geology, The University of Michigan. In addition the mines at Grand Rapids, National City, and Alabaster provided data on the lithologic characteristics in the mines and pits, as well as relevant stratigraphic and exploitation information.

Subsurface drilling data was selected on the basis of correlated information resources, and only wells having reliable electric logs, drill cuttings, and descriptive logs were used in the stratigraphic and lithologic analysis. For the Michigan Formation, Moser (1963a) utilized 665 mechanical logs for stratigraphic correlation, and 250 in the central grid for purpose of

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mapping of information. To achieve a high level of reliability in sample descriptions, the cuttings from two or three neighboring wells were examined for each control point, over 700 sample sets in all. For the Detroit River Group, Ehman (1954) utilized radioactive logs and cuttings from 119 control wells, following the procedure of Moser. Petrographic and geochemical analysis of the evaporite rocks available from core and outcrop samples was correlated with the other subsurface studies by Haney (unpublished data).

The stratigraphic units defined by regional correlation based on the mechanical logs were analyzed for lithologic and paleontologic properties by the geologists, the data encoded onto Moser's Lithologic Description Card format, and processed by computer. The programs for the stratigraphic analysis and mapping system were developed by Moser (1963b) for his study of the Michigan Formation. Selected formations containing gypsum were analyzed for thickness and depth to the gypsum units, and the data contoured by computer programs developed by Professor Waldo Tobler, Department of Geography, The University of Michigan. Since the algorithm used in the program for calculating rectangular grid values from the somewhat random distribution of well points tends to smooth the data, the maps should be evaluated as generalized illustrations of the distributive properties of the gypsum deposits. This is desirable because of the relative inaccuracy and imprecision of the drilling information for wells outside the control wells. Also, the reader should be aware that drilling depth to the top of the gypsum deposits is locally highly variable owing to the irregularity of the glacial morainal topography. The relief, especially in the northern part of the Lower Peninsula, may range locally more than 500 feet.

The results are presented principally in the form of contour maps of the Lower Peninsula. More detailed maps of the Grand Rapids and Alabaster areas can be had in Stevens (1968).

Acknowledgements

The major part of the investigation was sponsored by the University of Michigan, Institute of Science and Technology. Many persons contributed to the project, in particular Frank

Moser, Donald Ehman, Sumner Hixon and Warren Haney. The Laboratory of Subsurface Geology, The University of Michigan, provided the major geologic resources, and the Computing Center of The University of Michigan the computational resources. We owe particular gratitude to the staff and facilities of the Michigan Geological Survey, Lansing, for their cooperation and advice, and their continuing service to the Laboratory. We also appreciate the courtesy of the management of the company mines visited in Grand Rapids and National City. Many petroleum geologists discussed the problem during phases of its study and offered constructive advice and information.

STRATIGRAPHY OF THE EVAPORITES

The Detroit River Group

In the Michigan Basin the Detroit River Group is a carbonate-evaporite-quartz sandstone association of Lower Middle Devonian (Erian) age. The history of stratigraphic terminology and general stratigraphic framework are detailed by Briggs (1959) and Ehman (1964). Descriptions of the stratigraphic units defined by Ehman were summarized by Briggs and Zigic-Toshich (1958) and will be repeated here only to the degree necessary for clarity of the present discussion. The same principle is used for the Michigan Formation discussed later in this paper.

Although Ehman was able to distinguish and to correlate 13 subsurface units within the Amherstburg-Lucas sequence (Fig. 1), he utilized only 4 in regional analysis. All of the evaporites (including gypsum) occur in the Lucas Formation. The youngest evaporites occur in the Pre-salt Evaporite, unit (A-B), and contain the Massive Anhydrite and Big Anhydrite in the Richfield Member of the petroleum geologist, as well as the Freer Sandstone in west central part of the Michigan Basin. The Massive Anhydrite, largely of anhydrite with interbedded carbonate stringers, can be traced over most of the Michigan Basin (Fig. 2). In southeastern Michigan a core described by Lesperance (1957) contains 7 beds of gypsum/anhydrite beds in an interval of 89 feet which range from 2-7 feet in thickness. The intervening beds are dolomite. Other cores in this area have a similar lithology. (See

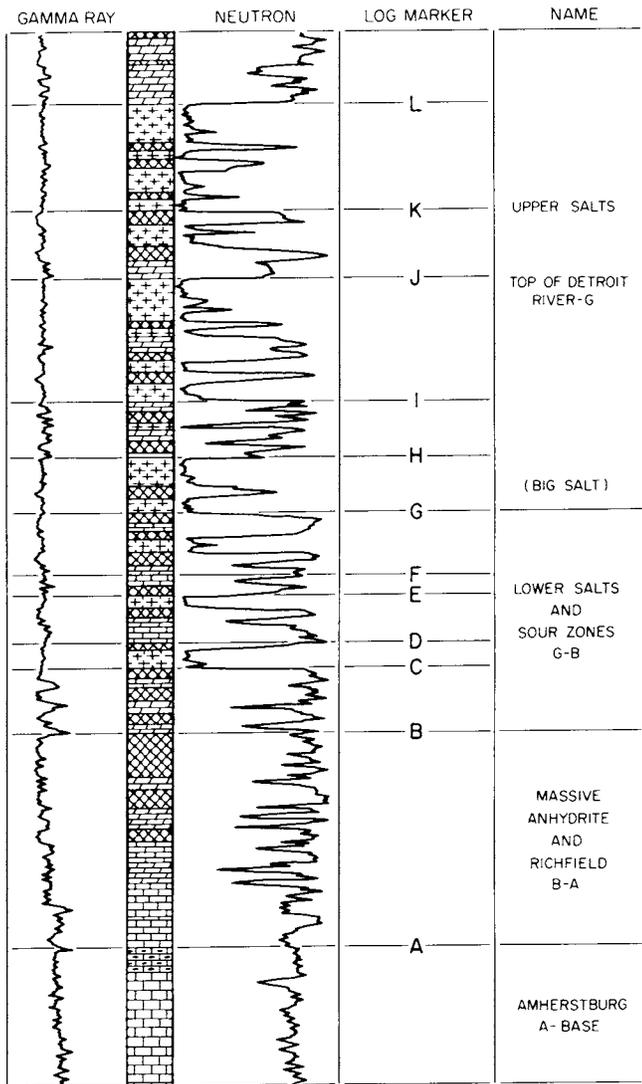


Fig. 1 Stratigraphic sequence of the Detroit River Group, Michigan Basin. (Modified from Ehman, 1964).

Lesperance, 1957). In west central Michigan, sec. 10, T20N, R3W, Franklin Township, Clare County, the Massive Anhydrite in a core from the Allied Investment-Stafford, et. al. no. 4 well (permit 18979) is 89 feet thick and contains 69 feet of anhydrite, 20 feet of limestone, the rest being dolomite. Anhydrite beds range in thickness from 1 to 45 feet. Characteristically, the evaporite units in the Central Basin are thicker much like those in Clare County, and thin on the southern margin, as in the Wayne County Airport well boring described by Lesperance.

The next higher unit in the Detroit River Group (B-G), the Lower Salts and Sour Zones, are much thicker in the Central Basin area (Fig. 3). The lowermost unit, B-C, is typically

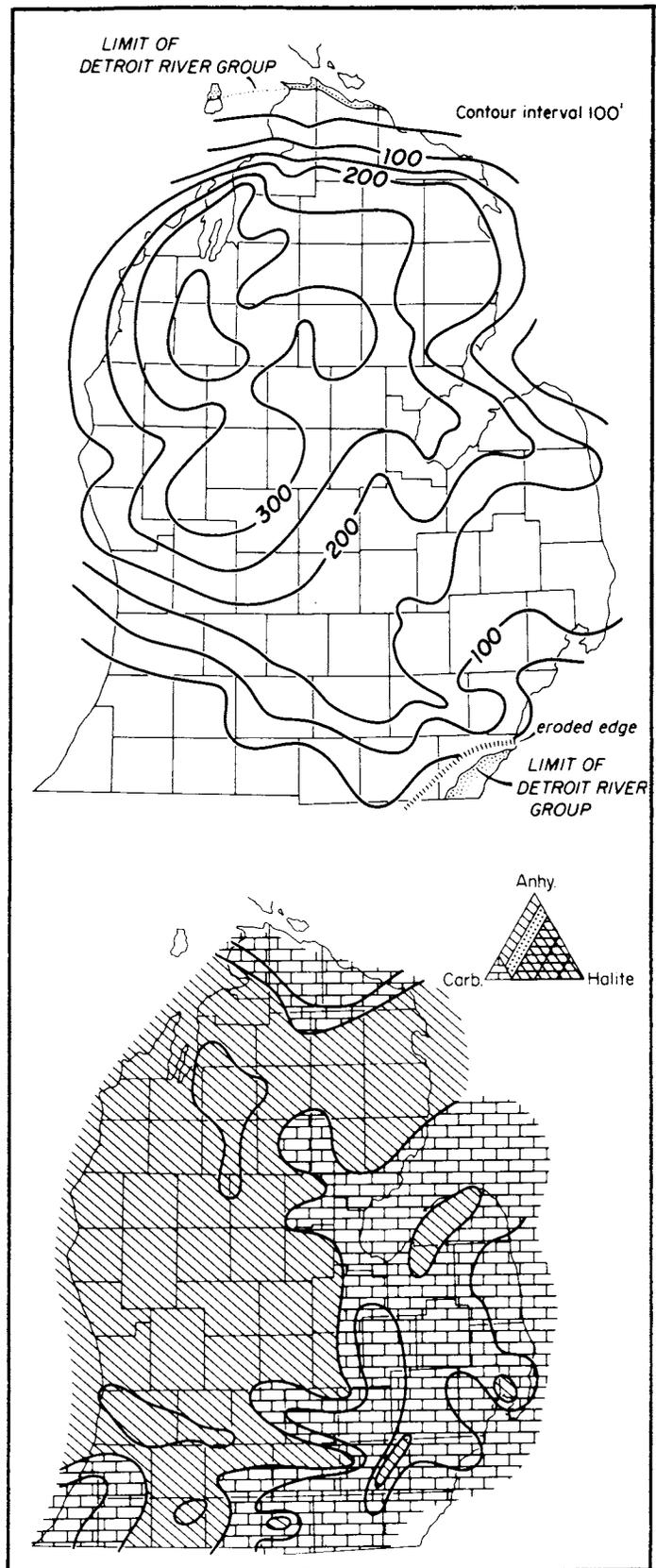


Fig. 2 Evaporite facies and isopachous maps of the Pre-Salt Evaporite of the Detroit River Group, Lucas Formation. (From Ehman, 1964).

a buff, sucrosic dolomite with thickly interbedded anhydrite. South of Saginaw Bay it is highly calcitic. The

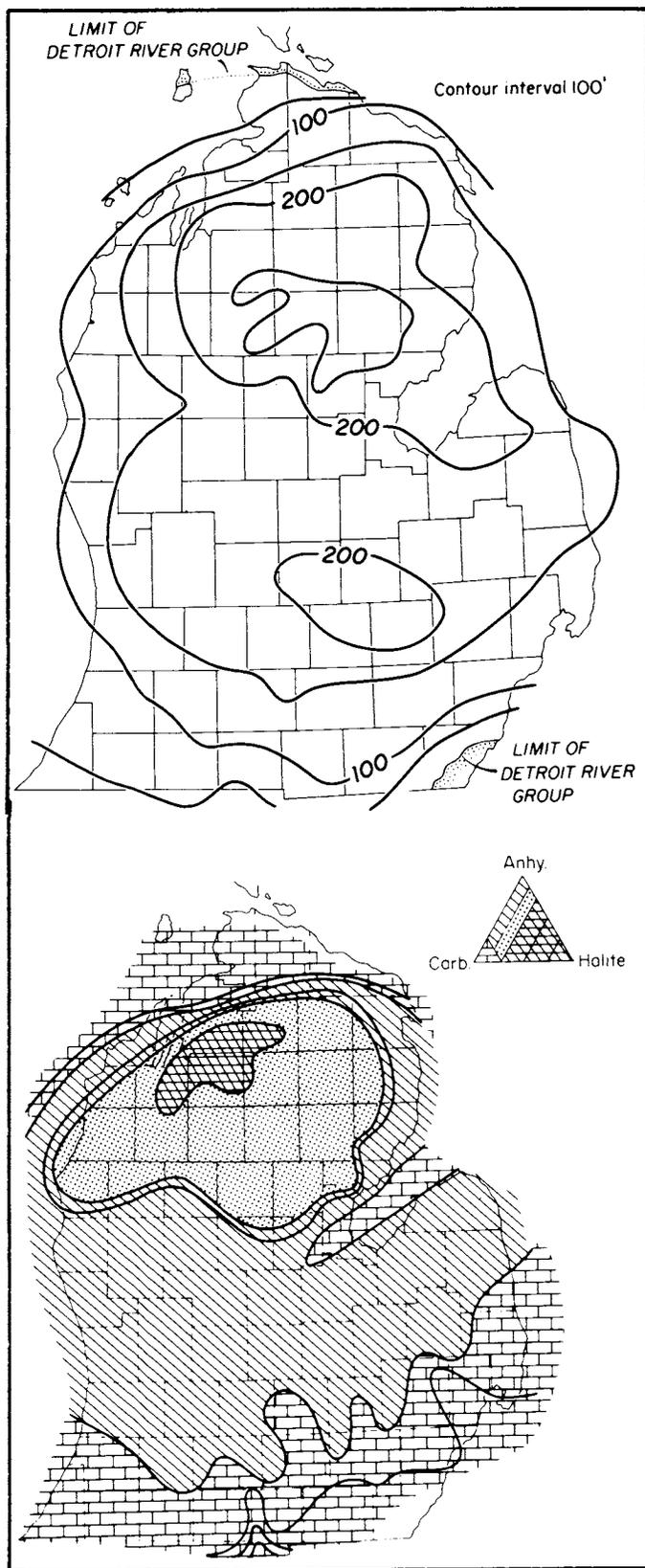


Fig. 3 Evaporite facies and isopachous maps of the Lower Salts and Sour Zones, Detroit River Group, Lucas Formation. (From Ehman, 1964).

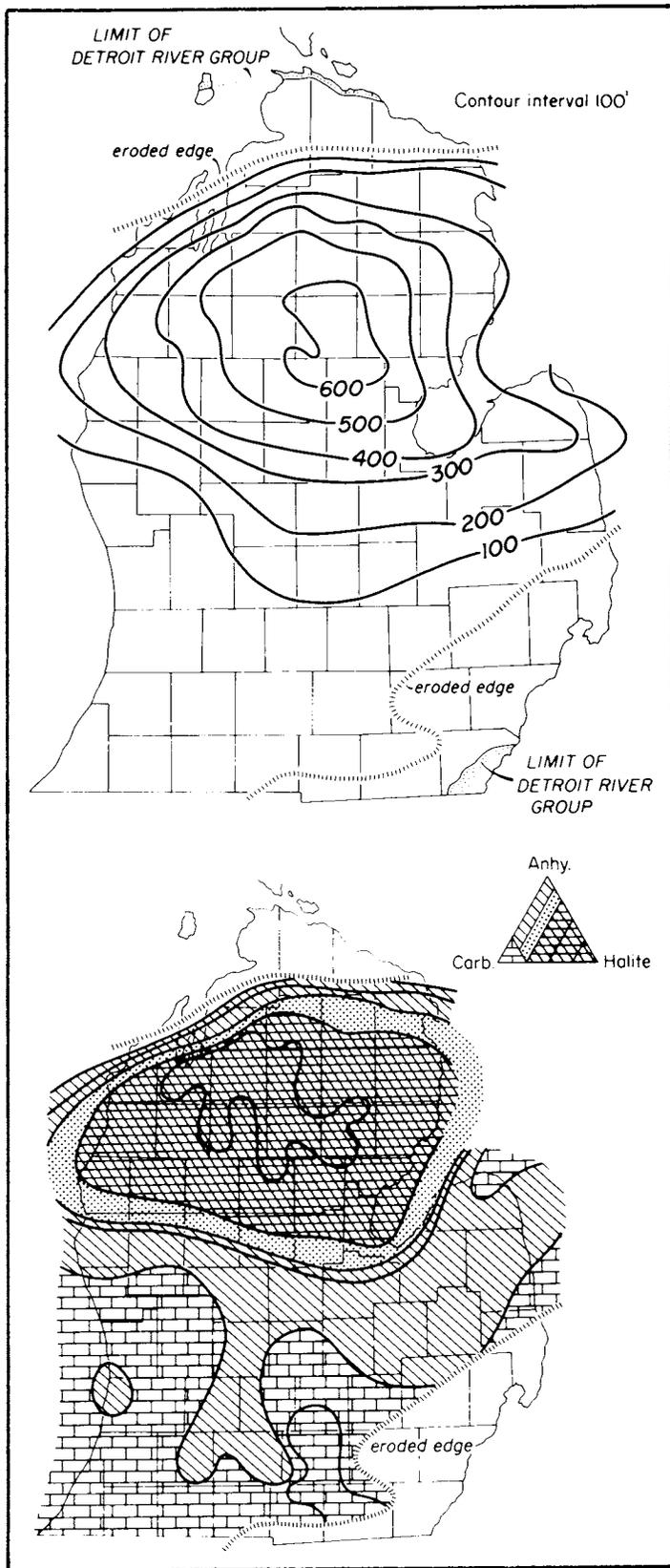


Fig. 4 Evaporite facies and isopachous maps of the Upper Salts and Sour Zones, Detroit River Group, Lucas Formation. (From Ehman, 1964).

C-D member contains the lowest Detroit River salts. In the center of the

salt basin the unit attains a thickness of 90 feet and contains more than 80 percent rock salt. The sequence grades from rock salt and gray anhydrite in the Central Basin to gray and white anhydrite and buff dolomite toward the southern basin margin. The D-E unit contains an upper salt and lower dark brown limestone in the Central Basin, grading to an upper white anhydrite and lower buff sucrosic dolomite toward the southern basin margin. It is 50-70 feet thick in the Central Basin, and thinner elsewhere. The E-F unit is dark brown limestone in the Central Basin, and buff dolomite on the southern margin. It ranges in thickness from 20-40 feet over most of the area. The F-G unit is characterized by interbedded rock salt, anhydrite and dolomite. Toward the southern margin, the sequence grades into interbedded light colored dolomite and white anhydrite. It is thickest (70 feet) in the Central Basin and decreases in thickness uniformly towards the southern margins of the basin.

The Upper Salts of the Detroit River Group is a sequence of interbedded rock salt, anhydrite and carbonate rocks, typically dolomite. Evaporite, principally rock salt, constitute the greatest percentage of the section, and gypsum is present in the northern counties, as well as in Allegan and Jackson Counties (Fig. 4). Unit G-H is 80-100 percent rock salt in the Central Basin and grades into anhydrite elsewhere. The anhydrite facies in turn becomes more dolomitic outward from the basin center. Unit H-I is a double evaporite cycle, the sequence being anhydrite, carbonate, anhydrite, rock salt, anhydrite, carbonate. The I-J unit is a thick salt sequence with interbedded gray and white anhydrite and light brown dolomite which grades and thins towards the basin margin into anhydrite and dolomite. The J-K member has a fairly consistent composition of 40 percent anhydrite, 30 percent rock salt, and 30 percent dolomite, except southeast of Saginaw Bay where limestone is the dominant lithology. The uppermost rock salt in the Detroit River Group is the K-L unit of the Upper Salts. It is confined to the Central Basin and composed predominantly of halite with minor dolomite and argillaceous anhydrite. The top unit of the Upper Salts is also confined to the Central Basin, and is composed of white to gray anhydrite and brown dolomite.

In summary, evaporites occur ex-

tensively in the Lucas Formation of the Detroit River Group in the Michigan Basin, with carbonates and sulfates in the lowermost massive anhydrite (Richfield Zone) and carbonates, sulfates and chlorides in the Lower and Upper Salts. The Upper Salts are largely confined to the Central Basin sector of the Michigan Basin. The evaporites are thick, relatively free of silicate detritus, and are locally gypiferous where the sulfates contact the ground water beneath glacial drift.

The sedimentary framework for the entire Lower Middle Devonian sequence (Briggs, 1959) is represented by three principal phases of sedimentation -- the carbonate-chert phase represented by the Bois Blanc Formation, the quartz sandstone phase of the Sylvania sandstone, and the carbonate-evaporite phase of the Lucas Formation. The sequence of sedimentation was as follows:

The Bois Blanc (Lower Onondagan) sea transgressed across eroded Cayugan (Upper Silurian) rocks into the Michigan Basin from north and east to the southwest border of Michigan. An arid or semiarid climate provided the streams with abundant silica which precipitated as beds in dolomite in the nearshore zones of the basin, and as nodules in limestone offshore (Fig. 5A).

Retreat of the Bois Blanc sea cut off the connection with the Onondaga sea to the southeast, and the primordial Detroit River sea was the southern extremity of a boreal seaway (Fig. 5B). In the paralic zone wind-blown sands (Sylvania sandstone) accumulated while limestones were deposited offshore, and the Sylvania deposition continued as the Detroit River sea transgressed west and south across the Michigan Basin.

Extensive carbonate banks in the phase of carbonate deposition during Amherstburg time developed along the southern and northern borders of the sea (Fig. 5C), and possibly contributed to partial restriction of circulation of the marine waters into the basin.

The continued aridity, restricted circulation and marine transgression initiated evaporite deposition which characterizes the Lucas Formation (Fig. 5D). Regression of the sea during the deposition of the Lower and Upper Salts restricted evaporite rocks of these units largely to the

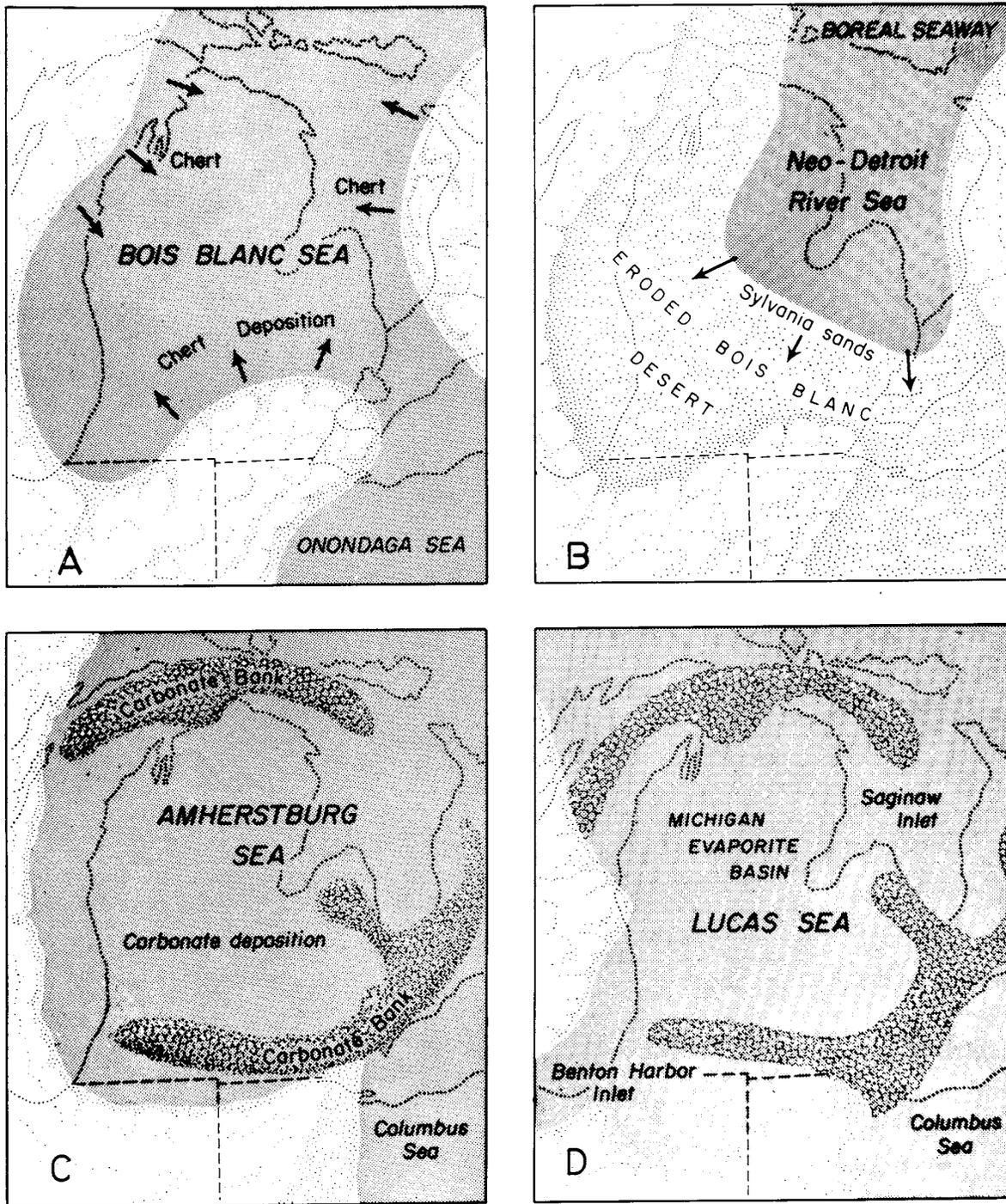


Fig. 5 Paleogeography of the Lower Middle Devonian Sedimentation sequence in the Michigan Basin. (From Briggs, 1959).

central part of the Michigan Basin.

A partial refreshing of the basin brine occurred during deposition of the uppermost unit of the Detroit River Group, although evaporite deposition continued during the deposition of the overlying Dundee Formation which has a significant anhydrite facies in the western part of the

Michigan Basin (Ehman, 1964). There are no reported gypsum deposits in these beds, however.

The Michigan Formation

All of the gypsum exploited in Michigan comes from two members of the

Michigan Formation. The stratigraphy defined by Moser (1963a) is summarized in Fig. 6. There are eleven units, nine of which contain anhydrite beds, however, only three of the units (National City Gyp, Triple Gyp, and Pencil Gyp) contain significant gypsum deposits.

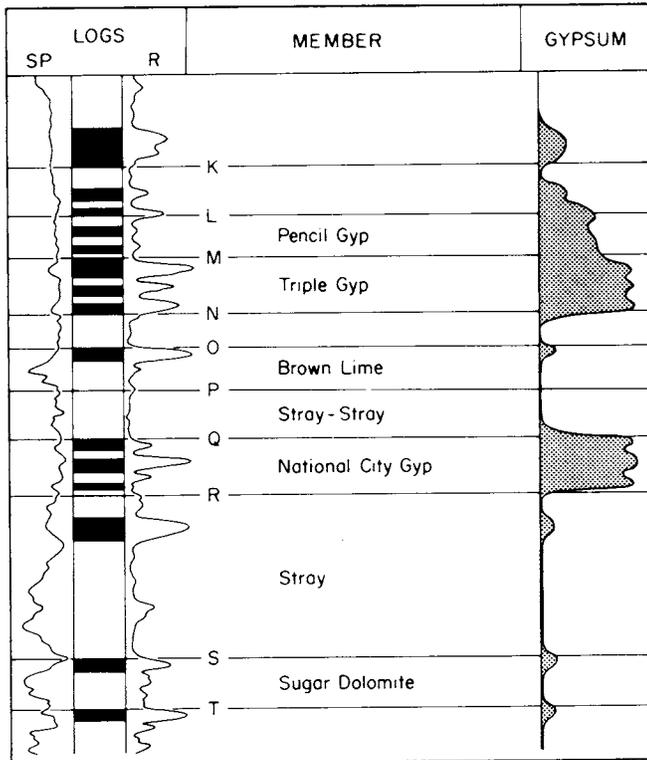


Fig. 6 Stratigraphic sequence and gypsum occurrence in the Michigan Formation, Michigan Basin. (Modified after Moser, 1963a).

The evaporite types and associations in the Michigan Formation contrast markedly with those of the Detroit River Group. Whereas the Detroit River Group rocks are characterized by relatively clean and mature carbonate-evaporite deposits, the Michigan Formation rocks are relatively immature sandstone-shale-evaporite deposits. The latter are principally illitic shale-anhydrite sequences; moreover, no rock salt occurs in the Michigan Formation. Furthermore, the Michigan Formation attains a maximum thickness of only 400-500 feet, whereas the Detroit River Group reaches more than 1400 feet in the Central Basin area. The sedimentary facies within the units of the Michigan Formation are generally very complex. The subgraywacke sandstone, siltstone and shale are intimately associated with chemical and biochemical limestone, dolomite and anhydrite.

The lowermost unit in the Michigan Formation was deposited during the initial advance of the Michigan sea over an eroded "Marshall" landscape. The unit is limited to a small area in the north-central part of the state. Clastics of Unit 1 are fine-grained, shaly sandstone and gray shale. Dark brown, coarse-grained dolomite overlies the clastic sediment and is overlain by anhydrite. Juxtaposition of dolomite and anhydrite indicates that at least part of the dolomite is a primary precipitate.

The areal extent of the Sugar Dolomite (Unit 2) is much greater than that of the previous unit because of continuing transgression of the Michigan sea. The lower part is composed of light and dark brown sucrosic dolomite and black, fissile, dolomitic shale, and the upper part of a thin, continuous bed of fossiliferous limestone overlain by anhydrite. A thin transition zone between the limestone and anhydrite consists of black, calcareous shale containing pockets of crinoids. The upper boundary of the Sugar Dolomite occurs at the end of the second cycle of evaporite deposition and the beginning of a new regressive phase in which the Stray Sandstone was (Unit 3) deposited.

Clastic sediments, predominantly sand, characterize the Stray, being everywhere more than half the section, and over a large area the only component. The non-clastic equivalents of the Stray in the northeast consists of dark, shaly, fine-grained limestone, white massive, anhydrite and light brown, somewhat sandy dolomite. There is a complex relationship between these three lithologic types.

The National City Gyp (Unit 4) is exposed in quarries of the National Gypsum Company at National City in Iosco County, and is correlated to the subsurface by a number of wells in the vicinity. The gypsum at Alabaster is also quarried from the same unit. The conditions of sedimentation during the deposition of National City Gyp were similar to those that existed during the upper part of the Stray. To the north the sediments are composed of massive anhydrite (or gypsum) interbedded with shale. This area was the central portion of the depositional basin. As is indicated on the composite electric log, there are three anhydrite beds of which the middle one is not only the thickest but has the greatest areal extent. In a shoreward

direction there is a gradation from sulfate to carbonate facies. To the southwest a dolomite facies appears followed by a clastic facies while to the southeast the carbonate equivalent is limestone. Both carbonates are sandy as they approach the clastic facies. The limestones are dark gray, shaly and are very different from the light brown, medium grained dolomites.

During deposition of the National City Gyp the size of the basin continued to grow, and the strand line was in the vicinity of the present day outcrop in the southwest. Sand was deposited along the margins of the sea while anhydrite, dolomite and limestone were being precipitated basinward. There were periodic climatic changes on a scale similar to that of the Pleistocene. Successions of arid and humid periods gave rise to interbedded anhydrites and shales. The shale came mostly from the Coldwater Formation which had just been exposed to erosion.

The Brown Lime (Unit 5) is an excellent example of vertical and horizontal development of an evaporite facies. The vertical sequence is shale to carbonate to sulfate. Each bed can be traced horizontally over a large area, indicating very stable conditions of sedimentation. In the near shore environment they all grade gradually into sandstone. The top of the unit is a bed of massive anhydrite which is thickest in the north where it reaches a maximum of 15 feet.

The ingress of Michigan sea onto the land culminated with the deposition of the Triple Gyp consisting of three massive anhydrite beds interbedded with two shale members. The anhydrite beds in the Triple Gyp have the greatest areal extent of any precipitate member in the Michigan Formation. They can be traced to the erosional edge of the formation, where the anhydrite alters to gypsum owing to the action of ground water. The Triple Gyp contains the gypsum which is mined at Grand Rapids. The isopach map of the unit shows a thickening to the north where the center of the subsiding basin was situated. The shale is consistently between 20 and 30 percent of the total, the dolomite increases from its zero isolith line southward to a maximum of 30 percent, and the sulfate decreases from a maximum of 80 percent in the north to 50 in the south. In the direction of the paleoshoreline, some of the anhydrite grades into a brown, anhydritic

dolomite.

The use of the name Pencil Gyp for Unit 7 has a history which goes back to the beginnings of the gypsum industry in Grand Rapids. Grimsley (1940) recounts that the quarrymen in the area referred to a 4 inch red gypsum layer as the pencil rock. Much later the subsurface geologists applied the term "pencil gyp" to any red colored anhydrite or gypsum in the Michigan Formation, irrespective of the stratigraphic position. The present study has shown that although there is a spotty distribution of red anhydrite in most of the upper part of the Michigan Formation, 90 percent is concentrated in a continuous bed above the Triple Gyp. Therefore, the name Pencil Gyp is considered to be appropriate for the unit overlying the Triple Gyp. The unit consists mainly of gray shales intercalated with anhydrite and brown dolomite. To the northeast the dolomite grades into white anhydrite. The isopach map shows the prevalent northward thickening. The percentage of carbonate plus sulfate decreases while the shale percentage increases in the direction of the clastic source.

The basic shale-anhydrite-dolomite alternations, typical of the upper part of the Michigan Formation, continued during deposition of Unit 8. There are, however, important signs both in lithology and in isopach patterns of the impending termination of those environmental conditions which gave rise to the clastic-precipitate cyclicality. Intervals of evaporite deposition increases rapidly from 40 percent in the north to over 70 percent in southern areas. The northern edge was not far from the present day outcrop area and the center had shifted southward.

The top member of the Michigan Formation (Unit 9) can be subdivided into two submembers. The lower is composed of red and white anhydrite which grades into a light brown dolomite. Because this unit is below an unconformity, the anhydrite has been hydrated to gypsum in many wells. The upper submember is predominantly gray and green shale with localized development of anhydrite and dolomite.

In summary, the period of deposition which preceded the Michigan Formation had its climax in a widespread regression of seas from the basin which produced a profound unconformity between the Michigan and the underlying

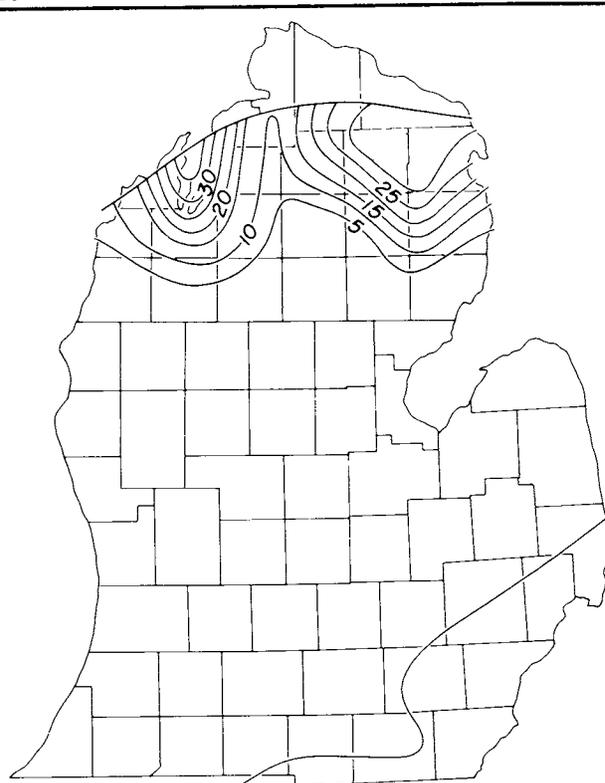
Coldwater Formation everywhere in the basin and a complete hiatus between the two units in southwest Michigan. During deposition of the Michigan Formation the basin was enclosed by land on all sides except to the northeast. In this direction lay the connection with the open ocean. A tectonic sill in the vicinity of the connection was the cause of restricted water exchange between basin and ocean. The sill, combined with climatic changes, resulted in clastic-precipitate cycles of deposition. During the arid phase, evaporites were precipitated while during humid phases sands and shales were deposited. The source of clastic sediments lay mainly in the land margins of the basin. Evaporite deposits of the Michigan Formation consist predominantly of dolomite-anhydrite sequences with some limestone-anhydrite and dolomite-limestone cycles.

The Michigan sea transgressed gradually into the basin from the northeast with only minor regressive movements during deposition of the Stray and Stray-Stray Sandstone units. The transgression reached its apex during deposition of the Triple Gyp unit. This slow shelfward expansion caused the sand-evaporite margin to lie progressively southward. The center of the depositional basin during Michigan times was in the area of the present northern edge of the formation and only the southern half of the deposited sediments remain. Deposition of the Michigan Formation terminated as a result of epeirogenic activity which was strongest in the eastern parts of the state. This eventually resulted in a complete withdrawal of the seas from the Michigan Basin for a short period. Along a series of echelon folds in eastern Michigan much of the Michigan Formation was removed prior to return of the sea and deposition of the overlying Bayport Formation.

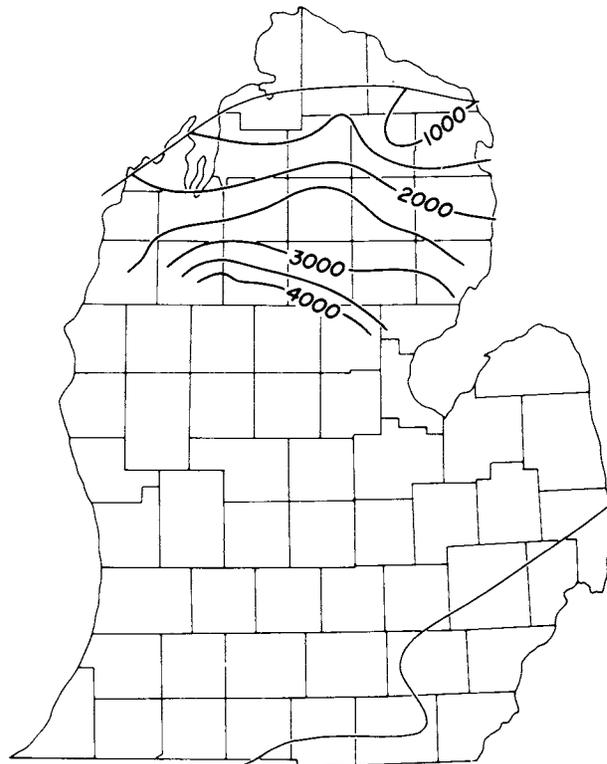
GYPSUM DEPOSITS

The stratigraphic and petrographic studies of core and outcrop samples of the sulfate rocks in the Detroit River Group and the Michigan Formation give no indication as to whether the mineral originally precipitated was gypsum or anhydrite. The nature and distribution of the gypsum-bearing sulfates and the probable depth of burial of these deposits indicate that, whatever the original mineralogy, the

rocks were at some stage entirely anhydritic and subsequently altered to gypsum due to hydration by groundwater.

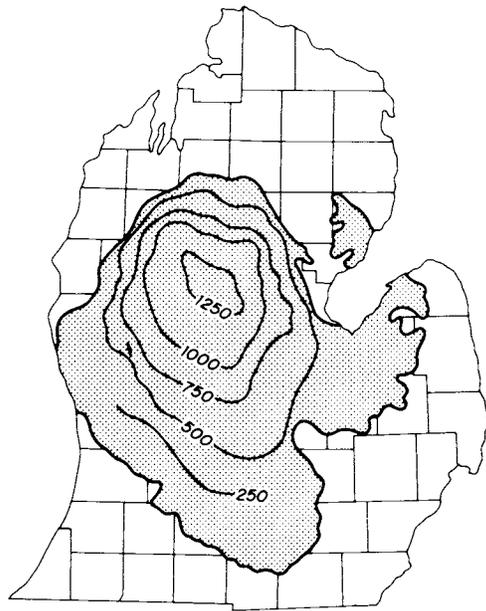


GYPSUM THICKNESS, DETROIT RIVER GROUP UPPER SALTS

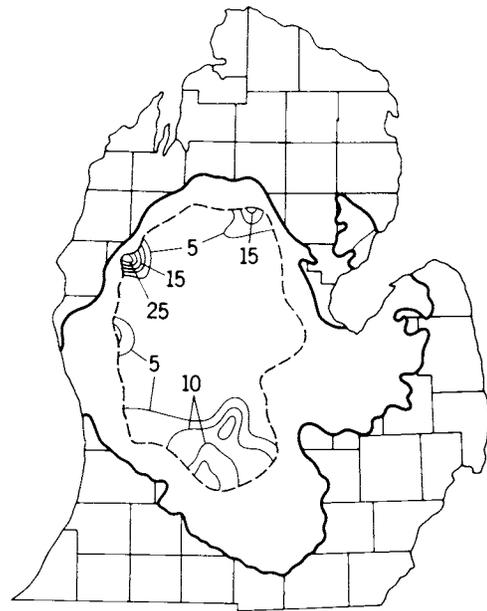


DEPTH TO TOP OF DETROIT RIVER GROUP UPPER SALTS

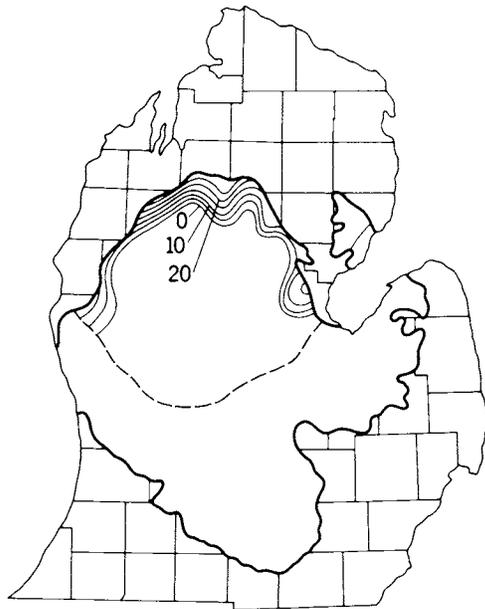
Fig. 7 Depth to top and thickness of gypsum in the Detroit River Group, Michigan Basin.



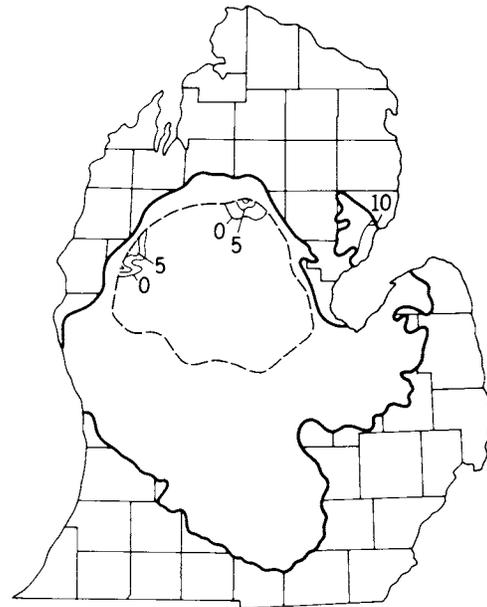
MICHIGAN FORMATION - Depth to top
CONTOUR INTERVAL 250'



TRIPLE GYP - Gypsum thickness
CONTOUR INTERVAL 5'



NATIONAL CITY GYP - Gypsum thickness
CONTOUR INTERVAL 5'



PENCIL GYP - Gypsum thickness
CONTOUR INTERVAL 5'

Fig. 8 Depth to top and thickness of gypsum in the Michigan Formation, Michigan Basin.

Thus potential gypsum exploitation outside of the present are around Grand Rapids and Alabaster should be guided by the nature and depth of ground water circulation in the bedrock and the limits of the sulfate facies in the

geologic formations. Of particular importance are the thickness of the gypsum deposits and the depth to the top of the deposits. Other factors such as purity of the gypsum, gypsum-anhydrite relationships, nature of sur-

rounding beds which affect mining operations, local variations in geologic structure and surface topography must be evaluated by means of detailed coring projects guided by regional analysis showing areas of highest potential. Other economic factors including product market evaluation and transportation cost analysis are subjects best evaluated by the exploitation and manufacturing industry.

The maps (Fig. 7 and 8) show the approximate thicknesses and depths to the top of the gypsum deposits within the Lucas and Michigan Formations. Three units containing the major amount of gypsum are analyzed for each formation; other occurrences are of minor economic importance. Outside of the areas presently being mined, the gypsum occurs under an overburden of glacial drift and bedrock of approximately 500-2500 feet, making exploitation economically much less attractive than in the Grand Rapids and Alabaster areas. In addition, the gypsum that occurs in the massive anhydrite of the Lucas Formation lies virtually beneath metropolitan Detroit, which, although near the largest potential market, raises serious problems for extraction. The relatively small thickness of these deposits within several beds raises further doubts as to their potential value.

There are extensive thick gypsum deposits elsewhere in Michigan, particularly those within the Lucas formation in the northern part of the Lower Peninsula. These deposits are relatively distant from markets and groundwater circulation may create a problem in mining. Numerous drill records in this region report lost circulation while drilling at depths up to 2500 feet, some of which is apparently due to subsurface solution in the evaporite beds (see the well descriptive logs published by the Michigan Geological Survey).

The Grand Rapids area has a very large reserve of gypsum largely within the Triple Gyp member of the Michigan Formation. Likewise there are extensive deposits of potential economic value in southern Michigan between Grand Rapids and Lansing, centered particularly near Ionia. This area warrents more detailed study, particularly for a combined exploitation and processing operation where transportation costs to market are primarily for finished products rather than for gypsum ore.

The results of this study show that there are extensive deposits of gypsum in Michigan other than those exploited in Grand Rapids and Alabaster. Should the quality and cost of extraction of the traditional deposits become economically unfavorable, other deposits within the Lucas and Michigan formations should be tested by detailed exploratory programs. The areas most favorable for exploration shown on the accompanying maps outline the geologically most favorable regions.

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