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GEOLOGY OF SODIUM SULFATE DEPOSITS OF THE NORTHERN GREAT PLAINS

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ABSTRACT

Sodium sulfate (Glauber's salt) is required in the pulp and paper industry and is also widely used in detergents as a replacement for phosphates. Future uses of this industrial mineral include solar energy storage and as an ingredient in glass-making.

Worldwide, there are few commercial deposits of sodium sulfate. North America has major accumulations of this commodity located primarily in Montana, North Dakota, Saskatchewan and Alberta. These northern Great Plains deposits form in shallow ephemeral lakes that range in area from less than one square kilometer to more than 300 square kilometers. There is a wide variety of basin shapes from small kettles to large riverine channels. The basin morphology is controlled primarily by the immediate postglacial history of the area.

The postglacial sediment column within these deposits generally consists primarily of thickly-bedded mirabilite crystal with variable amounts of other evaporite minerals (bloedite, epsomite, natron), organic debris, and clay- to sand-sized clastic material. The mirabilite is both endogenic and authigenic in origin, precipitating from supersaturated intermittent surface brines as well as from pore waters. Variations in mineralogy and brine chemistry occur between basins and through time within a single basin.

The stratigraphic sequence within a deposit is usually complex. Lateral facies changes and post-depositional processes, including solution/reprecipitation of the crystal bed and salt karsting, may modify the sedimentary record considerably.

The origin and evolution of these deposits is still problematic. Their chemistry is likely due to a complex series of reactions including cation exchange and dissolution of subsurface evaporite and carbonate bedrock by circulating groundwater. These playa basins, however, are just one stage in an evolutionary spectrum which also includes the deeper saline lakes of the region.

INTRODUCTION

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Sodium sulfate has been produced commercially from playa lake deposits and brines in the northern Great Plains for over 65 years. Some of man's earliest industrial efforts in the northern Plains region were centered on salt extraction from alkaline sloughs and lakes of southern Saskatchewan. Total composite reserves for this region (North Dakota, Montana, Saskatchewan, and Alberta) are among the largest in the world (Weisman

and Tandy, 1975). Presently, about 500,000 tonnes of sodium sulfate are produced per year from ten "active" deposits. The total annual value of this product normally exceeds \$40,000,000 making this region the world's leading producer.

Despite their economic importance, until recently there has been very little modern sedimentological or geochemical data collected and essentially no stratigraphic information on these deposits. A knowledge of the

sedimentary processes, mineralogy, and postdepositional alterations of the sediment is essential not only to assess the potential of the resource, but also to evaluate both the short-term changes and long-term evolution of the depositional system.

In addition to developing the required knowledge base for exploitation of this resource, investigation of these deposits is important for several other reasons. Saline and hypersaline lacustrine environments are one of the least understood depositional regimes in sedimentary geology. A study of the evaporite mineralogy and its relation to basin morphology, hydrochemistry, and brine evolution will do much to advance our knowledge of terrestial evaporite sequences. Theoretical models of these sequences are becoming increasingly important in both the petroleum and mineral exploration industries. Similarly, diagenetic reactions involving the precipitated

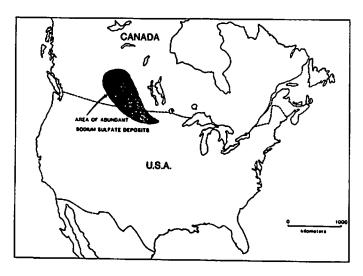


Figure 1. Map of North America showing the location of abundant sodium sulfate deposits in the northern Great Plains.

evaporite minerals and clastic grains are very important in the generation of other saline minerals as well as authigenic silicates (such as zeolites and clay minerals) and carbonates. Details of these reactions, however, are poorly known and infrequently studied.

These lakes are also useful for paleoclimatic studies. The sediments in the playas are a sensitive indicator of any changes in the hydrologic budget within each drainage basin. Thus, the stratigraphic record in the lakes should be a good reflection of both short-term as well as long-term climatic fluctuations.

Finally, elevated levels of heavy metals such as copper, zinc, and lead are present in the sediments of several of these deposits. Mining and extraction of the salts can mobilize these elements, thereby creating a potential environmental problem.

The purposes of this paper are to: (a) review the general geologic and hydrologic setting of the sodium sulfate deposits, (b) briefly discuss the modern sedimentary processes operating in the basins, and (c) examine the evolution of the deposits as suggested by the sedimentary fill in representative basins.

REGIONAL SETTING

Topography, Climate, and Hydrology

The sulfate deposits discussed in this paper are found in the Great Plains physiographic province of North America (Fig. 1). This region is characterized by hummocky to gently rolling topography interspersed with numerous deep, often terraced valleys that have been cut by glacial meltwater. The Missouri Coteau, a distinct 50- to 100-km wide band of knob and kettle topography, is the dominant geomorphic feature of the area.

In general, the northern Great Plains experience a cold, continental, semi-arid climate. Stable, high-pressure continental and Arctic air masses dominate during the winter months giving the region its characteristic cold, clear weather. Continental and Polar air masses also dominate the summer weather resulting in warm and dry conditions. region is south of the main paths of winter summer low-pressure systems. pressure and temperature gradients associated with these systems often lead to the area being influenced by high winds. Mean daily temperature during January over most of the region is about -17°C; during July it is +20°C. However, the most important characteristic of the region in terms of temperature is its extreme variability. There are wide variations in temperature between seasons, between years, and between day and night. This temperature variability has a significant impact on many chemical and physical aspects and processes of the salt lakes of the region.

In addition to temperature, another important climatic factor influencing the region is the high evaporation/precipitation ratio. The mean annual precipitation is about 30 cm; however, more than 125 cm of water can be lost per year through evaporation from open water bodies (CNC/IHD, 1978).

Large areas of the northern Great Plains are characterized by internal drainage. Because of its lack of integrated drainage, the Missouri Coteau contains many individual closed basins which often contain salt lakes. Other large areas of internal drainage also exist in central and western Saskatchewan and eastern Alberta. Together, these basins comprise one of the largest areas of closed drainage in North America.

Bedrock and Glacial Geology

The northern Plains are underlain by nearly horizontal Phanerozoic sedimentary rocks of thicknesses up to 5,000 m (Fig. 2). The Paleozoic section consists mainly of a series of stacked carbonate-evaporite cycles, whereas the overlying Mesozoic and Cenozoic bedrock is dominantly sand-shale sequences. Dissolution of the highly soluble Paleozoic evaporites by groundwater has modified the relatively simple structural relationships of the flat-lying formations and has created collapse structures over much of the area (Christiansen, 1967a, 1971). Grossman (1968) maintains that this evaporite dissolution has provided a source of ions for the many salt lakes of the region.

The bedrock surface has also been strongly modified by preglacial erosion (Whitaker and Pearson, 1972). By the start of the Quaternary Period a mature, dendritic drainage pattern had been established over much of the northern Plains (Stalker, 1961; Christiansen, 1967b). In general, this ancestral pattern is reflected by today's streams, except that much of the upper Missouri River actually flowed northeast into Hudson Bay rather than into the Mississippi River basin (Meneley et al, 1957).

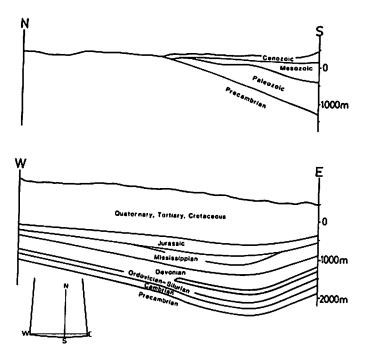


Figure 2. Diagrammatic cross-sections of southern Saskatchewan (modified from Francis, 1974).

The bedrock of the region is mantled by up to 300 m of unconsolidated Quaternary sediment, mainly till and glaciofluvial sands and gravels. During deglaciation, meltwater from the retreating glacier carved numerous ice-marginal channels and spillways in this sediment (Christiansen, 1979). Although now abandoned, or buried under more recent sediment, these valleys are often sites of salt lakes. The hydrodynamic properties of the Quaternary sediments influence, to a major degree, the location and development of the playas by controlling the direction of flow and the quantity of groundwater discharge (Last, 1984).

Origin of the Basins

Unlike many other playas and salt lakes of the world, the origin of the sodium sulfate-rich basins in the Northern Great Plains cannot be attributed primarily to tectonism or deflation. Rather, these lakes occupy closed depressions that were created in association with glacial activity in the region during the past 20,000 years. There are three basic types of basins with combinations and gradations existing between each type: (a) channel/riverine basins, (b) roughly circular "sinkhole" basins or doughnuts, and (c) broad.

flat depressions with no distinctive morphological character.

Most of the sodium sulfate deposits of the region occupy basins that are distinctly riverine in nature (Fig. 3). These basins were created by meltwater cutting a channel into the surrounding glacial material during or immediately after recession of the Wisconsinan ice sheet between 17,000 and 13,000 years The basin is usually floored by well sorted gravels and sands, whereas the channel banks are normally composed of till. Closure of the basin is usually due to a debris slide or an incipient alluvial fan which has prograded across the channel. In channel basins that have a north-south orientation, isostatic crustal rebound has also provided closure by differentially raising the southern end of the basin more than the northern end.

In areas of glacial ice stagnation, such as the Missouri Coteau, the ice sinkholes form the dominant basin type. These sinkhole basins tend to be small and circular, but sometimes can have great thicknesses of postglacial clastics and salt. For example, the lngebright deposit in southwestern Saskatchewan contains up to 50 m of salt in an area less than 0.5 square kilometer (Rueffel, 1968).

Finally, some of the lakes are remnants of much larger postglacial or ice marginal lakes. These basins are simply low spots in the morainic debris and are usually surrounded by old strandlines and lacustrine sediments. The basins can be very large (greater than 300 square kilometers), with most of the reserve in the form of dissolved salts in the brine.

ECONOMIC GEOLOGY

Commercial exploitation of the saline lakes in the region began in 1918 with the extraction of both magnesium and sodium sulfates and carbonates from Muskiki Lake, near Saskatoon, Canada. Production of anhydrous sodium sulfate (salt cake) from some 20 different lakes in the United States and Canada (Fig. 4) gradually increased over the next five decades to a high of approximately 700,000 tonnes in 1973 (Fig. 5). Today, this region supplies nearly 50% of the total North American demand for sodium sulfate with the

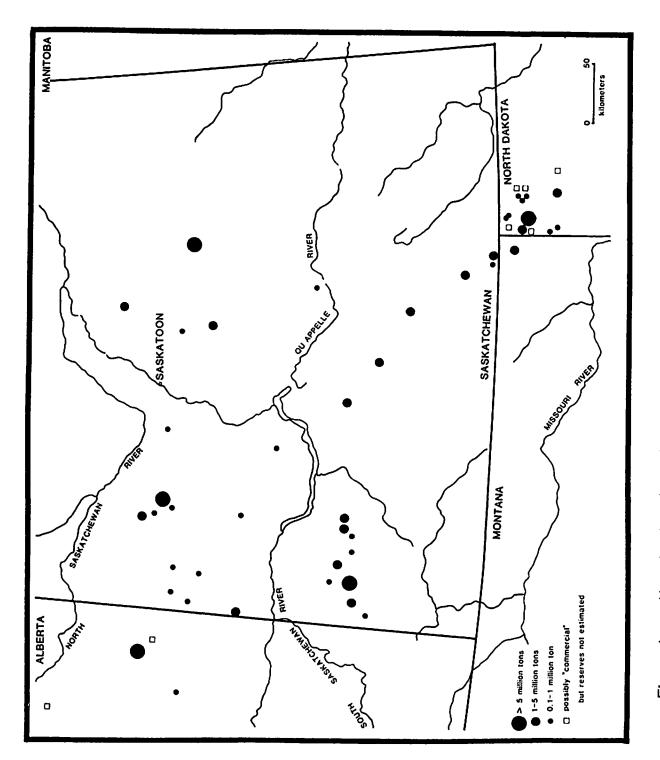
rest coming from deposits in southwestern United States, and as byproducts of various manufacturing processes. A tremendous increase in the price of salt cake during 1973-75 (from \$15 to \$48/tonne) and again during 1980-83 (from \$62 to \$108/tonne) saw a renewed interest in leasing and mining activities in the region during these periods.

Historically, the two largest uses of sodium sulfate have been in producing kraft paper and allied products, and in the manufacture of detergents. More recently, however, the energy industry has been consuming larger amounts of the salt by its use as a conditioner to facilitate fly ash supression in coal-burning power plants (Tremblay, 1984). Another new use of salt cake is in the manufacture of potassium sulfate by the reaction of sodium sulfate with potassium chloride. Other potentially significant applications include use in glass, ceramic, and paint manufacture, and in solar energy collectors.

The sodium sulfate industry in this region is based on reserves of three basic



Figure 3. Aerial view of Ceylon Lake, Saskatchewan, showing typical riverine morphology. Scale bar is 1 km.



Map showing the sodium sulfate deposits of the northern Great Plains. Figure 4.

types: (a) the sodium sulfate that is dissolved in brines that fill the saline lake basins, (b) the hydrated sodium sulfate mineral mirabilite which occurs seasonally on the floor of the salt lakes due to precipitation within the overlying water column, and (c) the bedded salts composed mainly of mirabilite and thenardite that make up the postglacial sedimentary fill in some basins.

Although each of these three sources has been exploited during the past, most production today is from the hypersaline lake waters which are pumped from the basin into holding reservoirs. Upon further concentration by evaporation during summer and then cooling during the fall season, relatively pure mirabilite (Glauber's salt) is precipitated from the solution (Fig. 7). The overlying brine is then drained back into the lake basin, and the salt is removed to stockpiles. Solution mining using hot water (Mac Williams and Reynolds, 1973) and dredge mining of the permanent salt beds are also used.

This harvested Glauber's salt must be

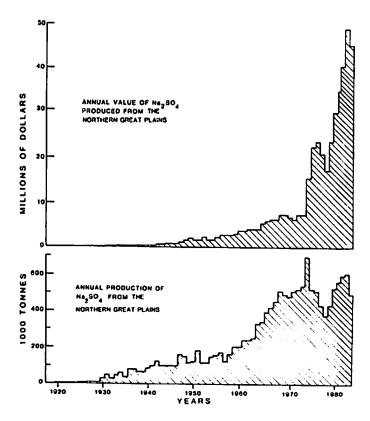


Figure 5. Annual production and value of sodium sulfate mined from salt lakes in the northern Great plains.

CARRONATES

Aragonite CaCO;
CALCITE CaCO;
CALCITE CaCO;
MAGMESIAN CALCITE CaCO;
MAGMESIAN CALCITE CaCO;
DOLONITE CAMP(CO);
Protodolomite CaMP(CO);
Protodolomite CaMP(CO);
Protodolomite CaMP(CO);
Protodolomite CaMP(CO);
Nuntite CaMp(CO);
Nuntite CaMp(CO);
Nuntite CaMp(CO);
Siderite CaCO;
Siderite FaCO;
Scarbroite Alg(CO);
Scarbroite Alg(CO);
Scarbroite Alg(CO);
Scarbroite Alg(CO);
Campium CaSO;
Magnesian CaMp(CO);
SUFFATE;
SUFFIRES AMP CHLORIDES
GTPEUM CaSO;
MAGNESIATE Magnesian
GTPEUM CASO;
MAGNESIATE Magnesian
M

Table 1. Mineralogy of saline playas of the northern Great Plains (taken, in part, from Egan, 1984).

Minerals in uppercase indicate common occurrence.

dehydrated prior to marketing. The methods for this processing vary considerably and are reviewed in detail by Weisman and Tandy (1975), and Rueffel (1968). Most producers simply raise the temperature of the salt to above its fusion point (about 32 C), and then either continue heating to evaporate the water of crystallization or remove the solid anhydrous precipitate from the slurry.

MODERN SEDIMENTARY ENVIRONMENTS AND PROCESSES

General

The salt lakes of the northern Great Plains of United States and Canada show considerable variation in terms of geochemistry, sediment character, and sedimentary processes. Most of these lakes are small (less than 100 square kilometers) and shallow (less than 3 m); nearly all occupy closed hydrographic basins. There are approximately 70 lakes which contain sufficient amounts of sodium sulfate either as dissolved constituents in the

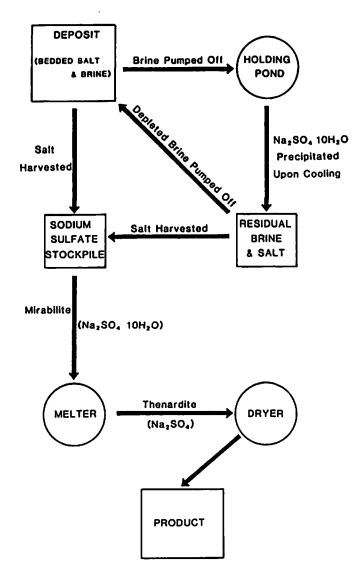


Figure 6. Summary flow diagram of sodium sulfate production from salt lakes of the Great Plains (generalized from Saskatchewan Minerals Information Booklet).

brine or as permanent salt within the sedimentary fill, to be considered economically viable for extraction. Despite some differences, these latter "minable" accumulations simply represent one end-member of a continuum of saline lakes and basins in the Great Plains. It is important to recognize not only the unique features that give rise to a specific deposit, but also the similarities between all deposits in terms of common physical and chemical processes and evolutionary sequence.

Description of Modern Sediments

In their natural state the near-surface

(modern) sediment of these sodium sulfaterich lakes usually consists of a mixture of
very soluble evaporite minerals, sparingly
soluble precipitates, clastic detrital material,
and organic matter (Table I). The soluble
salts, often making up nearly the entire
near-surface sediment mass, are composed of
mainly mirabilite, thenardite, and bloedite,
with secondary abundances of kieserite,
epsomite, burkeite, hexahydrite, and halite.
These salts are clear to white, often coarsely
crystalline, and occur in a wide variety of
habits and morphologies.

The sparingly soluble component, usually amounting to less than 25% of the modern sediment, is composed mainly of gypsum and a wide variety of authigenic carbonates and silicates including: protodolomite, nesquehonite, huntite, natron, trona, and mixed-layer clays. These sparingly soluble precipitates are usually very fine grained and often detectable only by x-ray diffractometry and scanning electron microscopy.

The detrital component of the modern sediment closely reflects the composition of the surrounding glacial material: clay minerals (mainly illite and smectite), dolomite, calcite, quartz, and feldspars (Egan, 1984). In deposits that are actively being mined, this clastic material usually comprises the bulk of the modern sediment. As the soluble sodium sulfate is extracted in mining operations, a layer of this insoluble residue blankets the deposit, thereby greatly decreasing the efficiency of the "brining" extraction process.

The organic matter component of the near-surface sediment is generally quite low (less than 10%), except near the margins of the lake where sheetwash can supply abundant allogenic organics.

Distribution of Modern Sediments

Understanding the occurrence and genesis of the near-surface sediment in these saline lakes is greatly aided by the recognition of distinctive sedimentary facies within the basin. These facies belts are, in general, similar to those identified in saline playa environment elsewhere (e.g., Hardie et al, 1978). Because most of the lakes occupy relatively steep-sided, riverine troughs, the basin margin areas are dominated by poorly sorted colluvium and sheetwash sediments that slope

- Unit E: Silty clay and salt; black to greenish grey; usually highly reducing smell; very soft to frieble but can be well consolidated upon prolonged exposure; very high water content; low to moderate organic matter content with often abundant brine shrimp (<u>Artemia</u>) eggs; usually laminated or banded; often very large salt crystals and crystalline aggregates present; sharp and undulatory lower contact; 5-50 cm thick.
- Unit D: Salt, moinly mirabilite and thenardite, but usually also traces of halite, natroe, trona, spaomite, gypsum, and bloedite; variable clastic content ranging from low (< %) to > 50%; no observable badding except for occasional laminae of black silts and clays; very coarsely crystalline with crystals usually strongly interlocking; sharp but often irregular lower contact; 0.5-50 m thick.
- Unit C: Silty clay; black to dark green; highly reducing smell; abundant intrasedimentary salt crystals up to 4 cm diameter, fewer crystals with depth; high moisture content; soft; low organic content but scattered to abundant <u>Artemin</u> eggs; no observable bedding; elevated levels of some trace metals; gradational lower contact; 0.5-3 m thick.
- Unit B: Silty clay to clayey silt, some sand; becoming coarser with depth; medium grey to greenish grey; generally no observable bedding except for indistinct wispy leminations and occasional thin calcareous wones; low organic content; moisture content higher than Unit A but lower than Unit C; firm; calcareous with occasional to abundant Chara spo., fragmented bivalves, and cladoceran remains identified; sharp lower contact; 0.5-1 m thick.
- Unit A: Coarse sand and gravel; well sorted; 'oxidized' colours; very low organic and moisture contents; sands can be finely laminated; mainly quarts, feldspars and detrital carbonates; very sharp lower contact with firm, pebbly clay (till).

Table 2. Summary of lithostratigraphic units.

down to meet broad mudflats and sandflats (Fig. 7). Classic alluvial fans are not found, and only rarely is there any development of strandline features such as beaches or dunes. The mudflats and sandflats are periodically covered by lake water, and are usually saturated with brine throughout the Exposed mudflats often become encrusted with white, finely crystalline efflorescent salt crusts formed by the evaporation of brine films brought to the surface by capillary action and evaporative pumping. Wind plays an important role in eroding and transporting salts from these dried crusts. The mudflats are also areas of massive intrasedimentary crystallization of salts resulting in destruction of lamination.

Basinward, the mudflat/sandflat grades into the salt pan (Fig. 7). This is the most dynamic zone of the basin in terms of sedimentary processes. As a result of surface runoff and groundwater contribution, water is ponded in this area for several weeks to several months. The concentration of the brine is raised by dissolution of previously deposited salts and by evaporation throughout the season, thereby eventually causing supersaturation and precipitation of a variety of evaporite minerals. Nucleation and precipitation of salts can occur in several forms and at several sites in the brine: (a) at the surface of

the brine in form of hopper-shaped crystals (Fig. 8) which can coalesce to form large floating crystal rafts, and (b) at the sediment-water interface in the form of either rounded accretionary grains (termed "mirabolites") or large, euhedral, bladed to tabular crystals and massive crystalline aggregates (Fig. 8).

STRATIGRAPHIC RELATIONSHIPS AND INTERPRETATIONS

Considering the broad geographic area, it is not surprising that no two playa basins in this region are exactly alike in terms of stratigraphy and evolutionary sequence. Certain stratigraphic associations are recurrent, however, and a generalized evolutionary pattern can be deduced from the deposits investigated to date.

On the basis of preliminary core descriptions and analyses, five lithostratigraphic units have been identified in basins in which there is a full postalacial sequence preserved. In basins that are being altered by mining operations or by other postdepositional destructive phenomena (such as salt dissolution), one or more of these units may be missing. The stratigraphic units observed consist of: (a) a basal coarse clastic (sand and gravel) unit which directly overlies glacial debris, (b) a grey-colored calcareous clay and silt unit. (c) a black, reducing clay with abundant intrasedimentary salt crystals, (d) a massive salt unit, and (e) an uppermost, laminated salt-mud unit. The main characteristics of these units are described in Table 2.

Although detailed interpretations of this lithostratigraphy are not yet complete, the sequence of units suggests the following series of events: immediately after or possibly concurrent with the formation of the basin by meltwater from the retreating glacier or creation of a sinkhole by melting of buried ice, the coarse clastics of Unit A were deposited by fluvial or sheetwash processes. Ponding of water in the basins occurred as the downslope end of a fluvial channel was dammed or by simply accumulation of runoff and meltwater in a topographically low area. Deposition of Unit B and part of Unit C occurred during this time probably in lakes that were considerably larger and fresher than those of today.

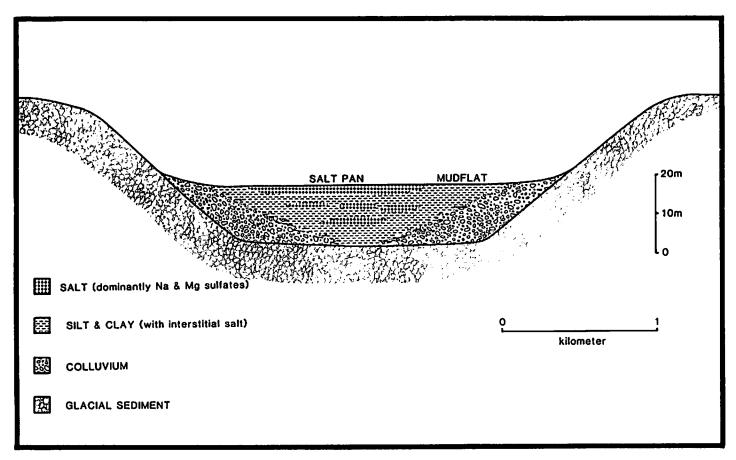


Figure 7. Diagrammatic cross section showing principal sedimentary facies in a typical salt playa of the northern Great Plains.

Gradually, however, in response to the drier and warmer climatic conditions that prevailed over the prairies beginning about 8,000 years B.P., water levels in the basins declined and concentration of the brines in-Although initially relatively deep, creased. chemically-stratified water bodies may have existed in selected basins as suggested by Grossman (1968), it is very likely that climatic conditions soon deteriorated to support only very shallow, playa types of lakes during most of the deposition of Unit D. That is, rather than envisioning a water column several tens of meters deep from which precipitation of the soluble salts is occurring, it is more likely that the thick sequence of massive salt in these basins is due to precipitation in a shallow salt pan/ephemeral lake environment. Prolonged intervals of warm-dry years may have resulted in dry lake conditions, desiccation, and possible erosion of the upper sediments of the salt pan. Wind- and sheetwash-transported clastics periodically blanketed the basin, effectively decreasing the amount of salt dissolution during the next

wet phase. Eventually, about 3,500 years ago, as the climate moderated and a more favorable hydrologic budget existed, shallow (and in some cases relatively deep) water conditions returned to the basins.

ORIGIN OF THE SALTS

The origin and ultimate source of the salts in these lakes has been the subject of considerable discussion in the scientific litera-As summarized by Sloan (1972, p. ture. C22): "Many observations about the occurrence of the salts are valid, but interpretations of their genesis have generally been needlessly complex and unsubstantiated by the observed facts." Certainly much of the high salinity of the seasonally ponded brines is derived from dissolution of previously precipitated salts by the relatively dilute inflow (Last, 1984). Groundwater also likely plays a major role in supplying ions to the basins; however, to-date this groundwater contribution has not been adequately documented.

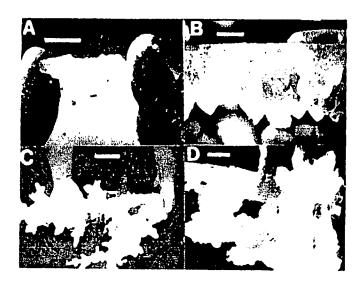


Figure 8. Examples of salt crystals from playas of the region. All crystals shown are mirabilite:

- (a) hopper-shaped crystal (scale bar = 2 cm)
- (b) dog-tooth crystals (scale bar = 2 cm)
- (c) finely radiating and dendritic crystals (scale bar = 10 cm)
- (d) massive crystal aggregate (scale bar = 10 cm)

Many researchers (e.g., Rueffel, 1968; Grossman, 1968; Freeze, 1969) have stressed the close association of major sodium sulfate and magnesium sulfate deposits with buried preglacial valleys, and conclude that these buried valleys act as conduits for groundwater which supplies dissolved components to the lakes. The ultimate source of the ions still remains problematic. It is questionable whether the Paleozoic evaporites, which are known to have undergone extensive dissolution by circulating groundwater, can be a likely source because of an incompatible brine chemistry

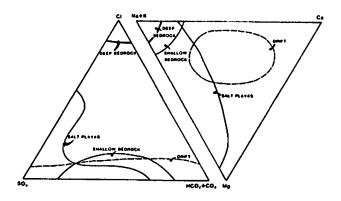


Figure 9. Trilinear diagram showing variation in water composition (in % equivalents) of the salt playas, drift groundwater, shallow bedrock (Cretaceous) groundwater, and deep bedrock (Paleozoic) groundwater in western Saskatchewan (compiled from numerous sources).

(Fig. 9). While such factors as oxidation of pyrite in the Cretaceous shales and dissolution of gypsum in the till and bedrock to provide a source of sulfate are likely possibilities (Wallick and Krouse, 1977), the complicated fractionation characteristics of the sulfur in sedimentary sulfates and sulfides and the presence of sulfate-reducing bacteria make documentation difficult.

ACKNOWLEDGEMENTS

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