

Ceylon Lake, August 16, 2005

EVAPORITE SEDIMENTOLOGY 7.780

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MODERN & HOLOCENE EVAPORITES OF THE NORTHERN GREAT PLAINS

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Field Trip Notes and Guide



Ceylon Lake August 21, 2005 (36 hr after ~6 cm rainstorm)

MODERN & HOLOCENE EVAPORITES OF THE NORTHERN GREAT PLAINS

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Dedication

This guidebook is dedicated to Dr. Bill Williams, who provided much needed leadership, vision and energy to the science of salt lake research for the past 40 years.

1. WELCOME & OBJECTIVES OF EXCURSION

"The scientific exploration of North American salt lakes was relatively slow off the mark." (Williams, 1986, p. 472)

I first want to extend a hearty welcome to the participants of this four-day field excursion associated with the University of Manitoba Graduate Course 7.780 (Evaporite Sedimentology). Welcome to the northern Great Plains! In addition to being one of the most attractive regions North America, the northern Great Plains of the 'prairie' provinces are literally a gold mine of evaporites and evaporitic settings. The most obvious of these are the millions of saline and hypersaline lakes, but the Great Plains also contain saline springs and of course are home to the huge deposits of Devonian evaporites in the subsurface. Certainly for the extant lakes of the region, within a "relatively" short drive from any of the major urban centres of the Prairies in just about any direction it is possible to visit a wide variety of salt lake environments ranging from hypersaline, salt-dominated playas to deep, perennial, chemically-stratified basins. Some of these lakes have been reasonably well studied over the past several decades; many others, however, remain largely untouched from a scientific perspective.

The objective of our activities over the several days is very simple: to provide you with an *introduction* to the wide assortment of salt lakes and modern/Holocene saline environments in this large geographic region known as the northern Great Plains. In addition, I want to familiarize you with <u>some</u> of the major sedimentological and geochemical processes that are operating in these lakes and to review the paleolimnology of selected basins. Finally, a very important purpose of this trip is for you to collect data and samples that can be used in a term project as part of the course 7.780. While it is not absolutely essential to 'do' a term project based on what you see and/or collect during the field trip (i.e., a literature or entirely lab-oriented project is certainly feasible), nonetheless, this trip will provide a unique opportunity for data and sample collection.

Obviously, in the short few hours we have together, many of the important geolimnological details of the lakes and their stratigraphic records will have to be left to the literature; a partial listing of some of the major scientific publications on the geolimnology of the region can be found at the end of these notes. More detailed field guides related to the geolimnology and paleolimnology of the region and covering larger areas of the northern Great Plains, can be found in Christiansen (1973), Last (1991a, 1991b), and Lemmen (1996). Because of time limitations I have also placed most of the emphasis during this excursion on *extant* lakes and their sediment records, and on the physical, mineralogical, and geochemical components, processes and stratigraphies in these basins. Importantly, recent developments at the corporation level (as well on safety perspectives) prevent us from touring many of the commercial operations that exploit the evaporites of these lakes. Likewise and for the same reasons, we can no longer visit or tour the subsurface sequences in the Williston Basin as we have in previous Evaporites field trips.

Overviews of the biological aspects of the lakes, topics which will not be covered in this guide, are provided in Rawson and Moore (1944), Northcote and Larkin (1963), Haynes and

Hammer (1978), Hammer (1981, 1984, 1986), Hammer et al. (1983), Waite (1986), and Adams (1988). The sedimentology, chronology, history, and development of extinct (mainly glacial and proglacial) lakes and wetlands are summarized in Christiansen (1979), Klassen (1989, 1994), Teller and Kehew (1994), Beaudoin (1993), Beaudoin et al. (1997) and others. Unfortunately, with the notable exception of Lake Winnipeg (e.g., Brunskill and Graham, 1979; Todd et al., 1996, 1998; Lewis et al., 2001), there has been relatively little geolimnological research on the few but interesting freshwater basins.

This guidebook is organized into 11 major sections. Following these preface comments/itinerary and several pages of introduction to the physical setting of the region, Section 4 provides an overview of the brine composition of the lakes - a complex and still incompletely understood topic that has held the interest of investigators for over 80 years. Section 5 discusses the modern geolimnology of the basins and summarizes some of the major extrinsic and intrinsic controls that affect the process sedimentology of the lakes. This is followed by a short summary of the spectrum of evaporites in these lakes (Section 6) and the occurrence and formation of a unique sedimentary component: mirabolites. Section 8 provides an overview of the economic aspects of the lakes, and some general comments about several of the major unresolved problems facing paleolimnologists when using these lakes are included in Section 9. Finally, Sections 10 and 11 provide short summaries of the localities we will attempt to visit during the two days of the excursion. Following these is the list of references and several appendices. It is important to realize that at the time of writing this guide we are unable to predict exactly which sites will be visited (because of spring high water levels and possibly limited road/trail access) or in which specific order. Of course, more complete details and discussion will occur at each of the sites

1.1 Acknowledgments

"In comparing various authors with one another, I have discovered that some of the gravest and latest writers have transcribed, word for word, from former works, without making acknowledgment." (Pliny the Elder; Natural History. Book i. Dedication, Sect. 22)

In composing these notes, I have borrowed freely from the work of my past students and postdocs; I fully acknowledge the tremendous efforts that these people have put into advancing our understanding of the salt lakes in this part of North America. Particular thanks go to Wang Li Bao, Doug Bell, Sandra Boden, Alex Carter, Matt Chalaturnyk, Jenny Deleqiat, Martin Egan, Tamara Ewing, Fawn Ginn, Larry Kovac, Susan Lambert, Blair Lockhart, Dana Naldrett, Anne Ross, Lisa Sack, Britta Schuett, Tim Schweyen, Laurie Slezak, Stephen Sun, and Jianyong Wei. I would not be on this trip had these persons not dedicated themselves (for at least short periods of time) to salt lake and geolimnological research. Of course, all publication rights for the unpublished data that are presented in this guide or otherwise provided to the participants during this excursion remain with the original researcher(s).

2. ITINERARY & GENERAL ADVICE TO PARTICIPANTS

Although the region has been experiencing relatively dry conditions over the past weeks, we have to accept that fall is probably the *worst* time of the year to attempt to visit most of these localities. In many respects mid-to late August would be a better time to be touring the lakes from an access perspective because September usually brings autumn rains (and occasionally



snow) and chilly temperatures to the Northern Plains region. Seasonally high water levels in the playas as well as access problems due to waterlogged fields and muddy roads may necessitate substitution of stops or even missed stops. Thus, our itinerary must be flexible. In general, we will take <u>one</u> of two circular routes. The preferred route calls for us to travel west from Winnipeg to Weyburn via Highways 2 and 13. After a series of stops (Ceylon, Coteau, Oro, Willow Bunch, Frederick, Old Wives) in the south-central part of Saskatchewan we will work our way farther



westward toward Maple Creek with stops at Chaplin, Antelope, Mud, Snakehole, Vincent, Corral, Verlo and several other basins. From Maple Creek we go northward toward Macklin (of course with a stop at the world's largest bunnock) with key stops at Freefight, Ingebright, and Manitou lakes. From the Manitou basin we will begin the return trip to Winnipeg via stops at Lydden, Whiteshore, Grandora, Muskiki, Dana, Waldsea, Deadmoose, Lenore, Little Manitou, and the Quill basins. The alternative route (if it looks like we are going to get rainy weather on the southern route) is to simply reverse the direction: head to the Humboldt area first (via Highways 16 and 5) and then west

to Manitou and south to Maple Creek and finally east via Ceylon etc.

We must make every attempt to stay more or less on schedule mainly because of the rather long driving distances between several of the planned stops. However, please do not feel inhibited about asking questions, pointing out inconsistencies, or telling the leader his is full of b.s.!

A few words of caution: many of the lakes we will be visiting are on private property or restricted access public property (e.g., community pasture, etc.). Please respect the rights and wishes of the property owners and pasture managers. Use your best field behavior when on the lakes and crossing the land. Do not unnecessarily climb fences; don't leave your lunch bags or other trash at the lake; do not harass the livestock and wildlife; etc. From a personal perspective,



there are relatively few hazards, but please use caution when walking along the shorelines and across the mudflats of the lakes and when wading in the lakes. The playa basins of the Great Plains, in particular, are infamous for being the "local dump", so everything from abandoned vehicles to dead cattle can be encountered. Be particularly cautious of strands of barbed wire, old machinery, and broken glass. Quicksand and deep dissolution chimneys/springs can pose problems when traversing some of the playa lakes such as Muskiki, Ceylon, and Sybouts/Coteau lakes.

Bugs and various other biting critters are probably not going to be a problem, but be cautious in the southern and southwestern part of the excursion because of snakes. Finally, try to use some degree of restraint when collecting samples: don't attempt to take a shovel-full of foul smelling H_2S saturated mud back to the van if you can get by with just a small vial or sample bag full.

2.1 GENERAL GEOSCIENTIFIC SETTING

We will try for an early take-off on Wednesday morning and drive westward across the fine grained muds of the Lake Agassiz plain. We will get glimpses of Agassiz beaches before

climbing the Manitoba Escarpment and traversing the eastern portion of the Second Prairie Level. After a short stop for snacks or lunch supplies (time limit in Nutters is 30 minutes!) we will approach our first major geomorphic feature of note: the Missouri Coteau, from the east. The Coteau, a 1200 km long and of knob and kettle topography that runs from the Dakotas northwestward into Alberta, is the locale of many interesting saline and hypersaline lakes. At Ceylon Lake we will examine a well-studied salt-dominated playa



having impressive salt karst features, mud diapirism, and a thick sequence of salts evaporites which provide important clues about Holocene paleohydrology and paleochemistry. At Coteau/Sybouts lakes and again at Frederick Lake we will have a chance to visit old abandoned Na₂SO₄ plants as well as discuss mineralogical and geochemical variations. In the Dirt Hills area we will spend a bit of time examining Oro Lake and the particularly well preserved 10,000 year long laminated carbonate record from this basin. On our way back farther westward we will try to make a short visits to Chaplin Lake, one of the largest active Na₂SO₄ plants in Saskatchewan, and Old Wives Lake, one of the largest saline lakes in North America and finally a short stop at a carbonate-precipitating perennial riverine basin, Willow Bunch Lake.

The triangle area between Maple Creek, Swift Current and Leader is home to a large number of saline and hypersaline lakes. Our route will take us to several of the best studied basins in and around the Sand Hills area -Ingebright Lake contains the thickest sequence of Holocene salts in North America; Freefight Lake is the deepest salt lake in Canada; other basins such as Vincent, Corral, Mud, Antelope and Snakehole will show us variations on this basic theme.



North of the South Saskatchewan River Valley the nature and diversity of the lacustrine settings change considerably. At Manitou Lake, a large but poorly studied perennial lake we will be able to see a range of modern and subrecent microbialites as well as discuss the hydrology of



this anomalous basin. Turning eastward from the Battlefords area, our route will take us across glacial lake silts and clays and gently rolling topography, toward the hummocky moraine area of Humboldt. En route to the Humboldt area we will be passing and making brief stops at a number of well-studied salt and mud-dominated playas including Burke, Porter, Patience, Dana, and Berry lakes to discuss short-term temporal water chemistry fluctuations and mineralogical variations. At Lydden Lake, west of Saskatoon, we will once again venture out on to a relatively stable salt

pan to see the acicular sulfate precipitates and sample subsalt gasses. After a stop at Whiteshore Lake, one of the larger active sodium sulfate mines and depending on access, we will try to

spend a bit more time at Muskiki Lake to examine the salt crust of this hypersaline mixed mudsalt playa, and to discuss various aspects of the hydrochemistry and authigenic/endogenic mineralogy. The general geological features include glacial lake Melfort and Elstow plains, solution collapse features, hummocky glacial terrain, and several end member types of salt lakes (e.g., deep, perennial basins, salt-dominated playas, mud-dominated playas). From Humboldt we will head a bit more east to the Wynyard area and finally back southwestward to Watrous.



A short distance north of Humboldt we will visit Waldsea and Deadmoose lakes, two deep-water, perennial and meromictic salt lakes. Discussion will center on the hydrochemistry, modern hydrologic and geochemical budgets, sedimentation rates, modern sedimentary facies and sedimentary processes, sedimentological influence of basin bathymetry, deepwater carbonate and evaporite precipitation, and the late Holocene history of these two contrasting meromictic basins. Lenore Lake (and possibly Basin, Middle, and Sayers lakes) will be visited briefly to examine the stratigraphic sequence of non-meromictic, deep, perennial salt lakes.

Near Wynyard we will stop at the Quill Lakes, which form the 3rd largest inland salt water body in North America, to discuss aspects of deposition in large, shallow saline basins. Finally, we will finish the excursion at Little Manitou Lake to swim and to explore the geochemistry, sedimentology and

stratigraphy of this fascinating perennial hypersaline lake.



2.2 MISCELLANEOUS ADVICE

1. September is a notorious month on the prairies in terms of weather - it can be (hopefully) quite warm and sunny, but rain (or snow) can also be a factor. Because at many of the playa stops we will attempt to traverse the soft mudflats to get out to the relatively 'solid' salt crust, old (throw-away) footwear and clothing are recommended. I note that Tuesday September 6, my favorite clothing store, Value Village, is having a 50% off everything sale. Footwear is always a problem because of the presence of cacti, sharp salts, and wet boggy conditions. I've tried just about everything from

hip waders to surf-shoes and even snowshoes. The best thing I can recommend is old 'lace-up' runners. The old style canvas 'deck' shoes are ideal: cheap (disposable) yet able to stay on your

feet in the soft, thigh-deep mud/salt. I have left more than one pair of sandals and 'gum boots' in the bottom of Muskiki and Vincent lakes.

2. Accommodations: several of the participants work with a very frugal professor (who also happens to be the field trip leader) and were asking about the possibility of tenting. As anyone who has traveled the prairies of western Canada knows, the Saskatchewan regional park system is excellent; simply nothing quite as convenient and inexpensive in all of North America. Unfortunately, many of the regional parks close after Labour Day. My suggestion is that those who are interested in



cutting motel costs (probably around \$70-90 per nite) bring their personal tent and sleeping bag; I am going to. Camping fees at the regional parks are generally about \$10/nite. If there is a regional park conveniently located near whatever village/town we are near at the end of the day, the option for camping will be there. But there is certainly no problem for those who wish to go luxuriously and make use of the local motels/hotels. Indeed, if the rains hit, we all no doubt will be moteling.

3. I am pretty loose about meals, coffee stops, etc. although it might be easiest for things like lunches to stop at a café or Subway and get take-away. Costs of gas/petrol are shared but for the vehicle I am in, it will probably be easiest for me to put the fill-ups on my credit card and then come chasing the others in the vehicle for reimbursement after the trip. IMPORTANT: On my last trip through this region I was really struck with the fact that many of the smaller towns and cities have lost their gas stations (not to mention banks, grocery stores, schools, etc.) – this is particularly the case in the far south and southwestern part of Saskatchewan: other than the everpresent Coop cardlock system, there is ONE gas station in 24,000 km² area bounded by Eastend, Assiniboia, the US Border and Swift Current! The point is: do not let you fuel-tank get too much below half full. Similar advice for snacks, drinks etc.

4. It is not legal to consume or open alcoholic beverages in the vehicle. Please use moderation at other times; drunks will be left on the side of the road.

5. Other than 'general' vicinity, I cannot yet give you specific over-nite locations. A rough guestimate (assuming we that the southerly route going out and northerly route return) is Wednesday: Weyburn or Assiniboia vicinity; Thursday: Maple Creek or Swift Current vicinity; Friday: Battlefords vicinity; Saturday: Humboldt vicinity; Sunday: home.

6. I'm not sure who has cell phones (I do NOT); however, if you wanted to leave Fawn's cell phone number with your family for EMERGENCY situations: it is 613-483-8814. Of course only about half of southern Saskatchewan offers cell phone coverage.

3. INTRODUCTORY COMMENTS: THE NORTHERN GREAT PLAINS

3.1 INTRODUCTION

"...in the central part of the continent there is a region, desert, or semi-desert in character, which can never be expected to become occupied by settlers... Although there are fertile spots throughout its extent, it can never be of much advantage to us as a possession..." Captain John Palliser (British North American Exploring Expedition, 1857-1860), 1862.

We will be traveling in and through the northern Great Plains of western Canada. This region is a land of many contrasts: rolling prairies, deeply incised river valleys, flat, featureless lake plains, sand hills and dunes, hummocky and hilly topography, well-treed uplands and barren, shadeless, wind-swept plains. The region is the agricultural heartland of Canada; Regina, Saskatoon, Swift Current, and Moose Jaw are the major urban areas.



3.2 SCOPE & RATIONALE OF GEOLIMNOLOGY IN THE NORTHERN GREAT PLAINS

"Lakes arise from phenomena that are almost entirely geologic in nature. Once formed, they are doomed. Because of the concave nature of basins, there is a compulsory trend toward obliteration as they fill with sediments... Enormous and deep lakes may be far from death as a result of shoaling, but climatic changes or geologic events leading to desiccation or drainage eventually mark their ends." (Cole; 1979, p. 9).

Among the many sedimentary environments present in the continental regime, the saline lakeclosed basin setting is one of the least studied. In contrast, many regard this environment as being of great importance and interest from both an economic as well as an academic perspective.

In much of the Great Plains of Alberta, Saskatchewan, and Manitoba, saline brines are the *only* surface waters present. In this water-stressed region of North America any changes in lake salinity or chemistry are of major concern. Salinity has a significant impact on the emergent vegetation of the lake's littoral zone and thus influences the value of the area as a waterfowl nesting and staging ground. Equally important is the fact that saline lake sediments often contain a host of unusual evaporitic minerals, sometimes in large enough quantities to be commercially exploited. Some of man's earliest industrial efforts in the Canadian Plains were centered on salt extraction from the playa lakes of southern Saskatchewan. Today, western Canada is the world's leading producer of sodium sulfate. This valuable industrial mineral is extracted by either solution mining or open pit mining of the deposits in the salt lakes of the region. Continued exploitation of this natural resource will, in part, be dependent on our detailed knowledge of the occurrence, stratigraphy, and processes responsible for the deposits.

Saline lakes and their sediments are also of great interest to persons involved in paleoclimate work. Most important is the fact that the salt lakes usually occur in closed basins. Closed basins respond dramatically to environmental changes and, consequently, the sediments contained in these basins often yield a very sensitive record of past conditions. Fluctuations in water chemistry, hydrology, organic productivity, lake levels, drainage basin characteristics, and climate are stored in the "sedimentological library" within the basin. Sometimes this valuable information is easily extracted; that is, the "language" of the library is readily deciphered and understood. Most often it is not. In order to maximize our ability to read the sedimentological record it is of prime importance that we understand the modern reactions and mechanisms which influence the system. Once the present sedimentary and geochemical variables and parameters are evaluated, models may be formulated for representative lake types. These models may then be applied to enhancing our understanding of past environmental conditions and changes, as well as predicting how a given basin will likely respond to future man-induced changes.

A review of the available literature and scientific work done on the saline lakes of western Canada conducted in 1981 (Last et al., 1983) indicated that, although certain aspects of the biology and limnology of the lakes are reasonably well understood, the sedimentological and geochemical characteristics and processes are very poorly documented and virtually unstudied. The past two decades of rather intensive geolimnological and paleolimnological research on the salt lakes of the region has done much to remedy this situation. It is obviously difficult to summarize the advances of twenty years worth of multidisciplinary work on these lakes in a few lines. However, the overall objectives of much of this research was to: (i) Describe the saline lake sedimentary and geochemical environments, and incorporate this information with any available biological and limnological data that already exists. (ii) Identify and evaluate the variability in saline lake types that exist in the region. (iii) Investigate the overall processes responsible for the genesis and diagenesis of the sediment in these saline lake environments by attempting the following: (a) document the aqueous-mineral reactions that occurring; (b) establish the reaction mechanisms and kinetics; and (c) quantify the mass transfer between the lake water and the lake sediment in basins with different salinity types and sediment compositions. (iv) Identify and interpret the physical, chemical, and biological changes that have occurred in selected basins during the postglacial period and relate these changes to the longterm evolutionary sequence of the brine.

3.3 SETTING & PHYSICAL BACKGROUND FOR GEOLIMNOLOGY ON THE NORTHERN GREAT PLAINS

3.3.1 Geomorphology



"A great untimbered, level, dried-up sea of land." (Wilby, 1914)

The saline lakes we will be visiting on this excursion are found in the Great Plains physiographic province of North America. This region is characterized by hummocky to gently rolling topography interspersed with numerous deep, often terraced valleys that have been cut by glacial meltwater.

Within the region, locally separate and distinct subzones or smaller geomorphological

units can be identified as shown in Figure 3.1. The low (< 300 m elevation), swampy area of the Manitoba Lowland extends westward from the Precambrian Shield to the Manitoba Escarpment. This area contains the region's largest lakes - Lake Winnipeg, Lake Manitoba (a saline lake!), and Lake Winnipegosis. With their large drainage basins, generally high sedimentation rates, and early association with extinct giant proglacial lakes, the sediments in these basins reveal long but exceedingly complex developmental histories that are affected by tectonics, evolving landscapes, variable fluvial inputs and regional climate fluctuations.



Figure 3.1. Sketch maps showing the major geomorphic features, and the elevation and vegetation zones in the excursion area (modified from Last, 1991a).

Extending westward approximately from the Manitoba border is the Saskatchewan Plains Region or sometimes referred to as the Second Prairie Level. This is a large area of gentle relief between about 450 and 700 m elevation containing a very large number of mainly small and shallow lakes. Estimates range from 4 to 10 million lakes and wetlands in this region (Gollop, 1963; Adams, 1988) and densities as high as 90-120 lakes km⁻² in some localities (Last, 1989a; Adams et al., 1992). The Saskatchewan River Lowlands in the east give way to the greater topographic diversity of the Central Saskatchewan Plains and the various Uplands areas.

Separating the Second Prairie Level from the western portion of the geomorphic province is the Missouri Coteau and its eastward-facing edge, the Missouri Escarpment. The Missouri Coteau is a distinct, 50 to 100 km wide band of knob and kettle topography that extends for over 1200 km through the Great Plains from central South Dakota northwestward into west-central Saskatchewan. The terrain in this region is rougher and the elevation (550 to 1400 m) greater than in the Central Saskatchewan Plains to the east (Figure 3.1). In some areas "badlands" topography has developed with local relief being as much as 150 m. The Coteau is an important geomorphic feature of the Plains; many of the most important salt lakes of the region are found in the Coteau and Escarpment area. Finally, the Alberta Plains (or Third Prairie Level) continue westward from western Saskatchewan to meet the Foothills of the Rocky Mountains.



3.3.2 Climate

"The Great Plains are a region of temperature and precipitation extremes: a decidedly continental climate that nearly defies generalization. (Wilson and Dijks, 1993, p. 44)

Long-term temperature, precipitation, and other climatic records for the region in which we will be traveling exist for Saskatoon, Regina, and Moose Jaw. In broad, general terms, the northern Great Plains experience a

cold continental, semi-arid steppe to sub-humid continental climate (Figure 3.2). Stable, high pressure continental and Arctic air masses dominate during the winter months giving the region its characteristic cold, clear weather. Most of the region is south of the mean path of winter low pressure systems, but pressure and temperature gradients associated with these systems often lead to the area being influenced by high winds. Continental Arctic and Polar air masses dominate the summer weather, resulting in generally warm and dry conditions. Mean daily temperature during January over most of the region is about -18°C; during July it is 19°C (CNC/IHD, 1978). 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 geolimnology of the saline lakes is the high evaporation to precipitation ratio as shown in Figure 3.2. The region receives an average of about 30 cm of precipitation per year, whereas more than 1.5 m of water can be lost per year through evaporation from open water bodies (CNC/IHD, 1978). Wind is also an important climatic factor that influences the processes operating in the saline lakes. At most times of the year, the average wind speed is moderate to high and mainly from the west and southwest directions. In addition to greatly aiding evaporation of water from the lakes, the high winds can transport sediment and salts into or out of the basin (Wood and Sanford, 1995; Donovan, 1994; Slezak, 1989; Last et al., 1983;) and, in the larger lakes, plays a major role in current and wave generation and, hence, sediment deposition and erosion (e.g., Schweyen, 1984; Kenny, 1985). Wind has also been shown to cause significant local variation in sedimentary facies patterns within some basins (Last, 1994; 1989b; 1987).



Figure 3.2 Sketch maps showing the major climatic regions in the excursion area, the moisture deficit (mean annual evaporation minus precipitation; values in cm), and the major closed drainage basins (shaded) (modified from Last, 1991a).

3.3.3 Hydrology & Geology

"We passed during the day many salt lakes, fringed round the edges with thick encrustations of salt, highly indicative of the rapid evaporation that takes place in these arid regions. (J. Palliser, October, 1857, on the area north and west of present-day Lake Diefenbaker; in Spry, 1968, p. 157)

Large areas of the northern Great Plains are characterized by internal drainage (Figure 3.2). Because of its lack of integrated drainage, the Missouri Coteau contains many individual closed basins. Large areas of internal drainage also exist east of Saskatoon and west of Swift Current. Together, these basins comprise one of the largest areas of endorheic drainage in North America. In total, over 160,000 km² or nearly 45% of southern Saskatchewan and 30% of North Dakota is characterized by internal drainage.

The lack of integrated drainage patterns throughout such a large area makes precise definition of the various watershed and drainage divides somewhat difficult (Figure 3.3). The areas of the northern Great Plains that are not characterized by closed basins are drained by three major river systems. The Saskatchewan system originates in western Alberta and, together with the Qu'Appelle-Assiniboine system, drains southern Saskatchewan to the east and, ultimately, north to Hudson Bay. Runoff in the Dakotas, Montana and parts of southern Saskatchewan and Alberta is directed south into the Missouri River System and the Gulf of Mexico.



Figure 3.3. Sketch maps showing the major drainage basins and the location of buried bedrock channels. Also shown is the Paleozoic salt edge: south and west of this line the Devonian evaporites have been largely removed by dissolution (from Last, 1991a).

The Canadian Plains region is underlain by nearly horizontal Phanerozoic sedimentary rocks of thicknesses up to 5000 m. The Paleozoic section consists mainly of a series of stacked carbonate-evaporite cycles, whereas the overlying Mesozoic and Cenozoic bedrock is dominantly a sand-shale sequence. 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). Several authors have suggested this evaporite dissolution has provided a source of ions for the many salt lakes of the region (Cole, 1926; Sahinen, 1949; Grossman, 1949, 1968; see also comments in Section 4 and reviews in Last, 1988; Murphy, 1996; Garret, 2001).

The bedrock surface has also been strongly modified by preglacial erosion. By the start of the Quaternary Period a mature, dendritic drainage pattern had been established over much of the northern Great Plains (Stalker, 1961; Christiansen, 1967b; Bird, 1980). The most important of these fluvial channels are the Hatfield, Tyner, Battleford, Swift Current and Estevan Valleys (Figure 3.3). 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).

The bedrock of the region is mantled by unconsolidated Quaternary sediment which is over 300 m thick in places. These deposits consist of till, fluvial sands and gravels, and lacustrine silts and clays. During deglaciation, meltwater from the retreating glacier carved numerous ice-marginal channels and spillways in this sediment (Christiansen, 1979; Kehew and Lord, 1989; Kehew and Teller, 1994). Although now abandoned or buried under more recent sediment, these valleys often form modern lake basins. The hydrodynamic properties of the Quaternary fill in the valleys influence to a major degree the character and composition of Holocene sediments in these lacustrine basins by controlling the direction of flow and quantity of groundwater discharge (Witkind, 1952; Rueffel, 1968a; Wood and Sanford, 1990; Donovan, 1992; Donovan and Rose, 1994).

3.3.4 Fauna & Flora

"Mosquitoes have greeted everyone who has had the temerity to set foot on the



central plains of Canada. Anyone venturing outdoors has had to physically protect his face, hands, and body with protective clothing and veils. Working, eating, talking, and even breathing was often nearly impossible when such protection was ignored. Exsanguination is a physical danger to man and beast; Hocking (1952) estimated that an unclothed individual could lose enough blood to mosquitoes in 1.75 hours to be fatal. The psychological effect of buzzand-bite...often caused complete debilitation of man." (Riegert, 1984).

The region supports a tremendously wide variety of plants and animals. Much of the area we will be traveling through originally supported a short grass and mixed prairie. Prairie grasses, creeping juniper, cacti, and small shrubs such as rose, saskatoon, chokecherry, and silver sagebrush are very common. In low areas, small clumps of

aspen, birch, and willow can provide shade on a hot day.

The areas surrounding the lakes can be particularly rich in wildlife, some species of which are rare in western Canada. Large populations of mule deer and pronghorn antelope are usually present. The region is prime birdwatching terrain with frequent appearances of grebes,

pelicans, cormorants, geese, ducks, teals, shovelers, kestrels, grouse, coots, killdeer, sandpipers, owls, swallows, crows, chickadees, nuthatches, wrens, shrikes, warblers, sparrows, kingbirds, and gulls. At least seven different species of hawks can be routinely observed. More rarely, golden eagles and the elusive burrowing owl can be spotted around the lakes. Small mammals also frequent the areas surrounding the lakes. These include: cottontail and jack rabbits, ground squirrels, bats, kangaroo rats, voles, mice, muskrats, porcupines, weasels, badgers, and coyotes.



"...the mere mention of rattlesnakes will be enough to deter some people...The threat was overstated in the old westerns. Rattlesnakes are very shy, not in the least

aggressive....Most spend the summer foraging for food, preferably mice. They use the burrows of gophers and prairie dogs, and ambush their prey as they enter. Because of this tendency to stay underground, there's a good chance you will never see a rattlesnake. Prairie rattlesnakes are the least venomous of all the rattlers. Their bite is rarely fatal. (from "Grasslands National Park", Environment Canada, 1990).

4. HYDROCHEMISTRY OF THE SALT LAKES

4.1 INTRODUCTION

"In this region, there are numerous ponds and small lakes in the hollows among the hills, most of them being more or less brackish or nauseous to the taste from the presence of sulphates of magnesia and soda and other salts. During the dry season of autumn, the water evaporates completely from many of these ponds leaving their beds covered by the dry white salts, which look like snow and are blown about in the wind. Around all the ponds, except those which become completely dry, there is a rank growth of reeds, sedges and grasses, the deep green colour of which forms a strong contrast to the dull grey appearance of the stunted and scanty grass of the hills, which indeed, in many places are almost bare." J. S. Bell (1875). The northern Great Plains of western Canada contain millions of lakes. These lakes show a tremendous diversity in size, basin morphology, hydrology, hydrochemistry, and sedimentary and biological characteristics. As pointed out in the above quote from one of the first scientific efforts in this region, in much of the area ponded saline and hypersaline brines are the only surface waters present. In this water stressed region of North America any changes in lake salinity or chemistry are of major concern to the environmental manager.

Salinity has a significant impact on the emergent vegetation of the lake's littoral zone and thus influences the value of the area as a waterfowl nesting and staging ground. In fact, these lakes, collectively, act as a major breeding ground for over 80% of North America's ducks (Scott and Scott, 1986; Batt et al., 1989). In addition to the importance of this surface water within the realm of wildlife conservation, future agricultural, industrial, and urban development in the Great Plains will likely lead to conflicts and potential environmental problems associated with the lakes in the region (Cameron, 1986; Wood, 1986; Harrington et al., 1997). For example, western Canada is presently the world's leading producer of natural sodium sulfate, with sales of the product contributing over \$50,000,000 annually to the Canadian prairie economy. This valuable industrial mineral is extracted by solution and open pit mining of deposits in the more saline lakes of the region. If the demand for Na₂SO₄ continues to increase, more lakes will be leased and more mining operations initiated. Increased industrial development of this type will have a profound impact on the wetlands resource. If the future industrial and agricultural development that is projected for this region is to take place with a minimum of damage to the natural environment, high priority must be given to the study and understanding of the salinity and chemistry of the lakes and the factors that control their chemical variability.

4.2 SIXTY YEARS OF HYDROCHEMISTRY

Northcote and Larkin (1963) summarized the early limnological efforts in this 350,000 km² area of western Canada. In one of the first systematic lacustrine surveys in the region, Rawson and Moore (1944) reported the water chemistry of 53 lakes from southern Saskatchewan. Although still not as advanced as in some other parts of North America, our knowledge and chemical characterization of the surface waters of the Great Plains has progressed considerably in the last 60 years. Rutherford (1970) showed that Mg, Na, and SO₄ components are the most common solutes in the lakes of Saskatchewan and recognized five main water types on the basis of ionic ratios. He also related spatial variation in water types to the climatic gradients and shallow groundwater composition in the province. More recently, Hammer (1978) reported the water chemistry for 60 saline lakes in southern Saskatchewan and also stressed the importance of Mg, Na, and SO₄ in these brines.

Other important discussions covering smaller geographic areas of the Great Plains include: Govett (1958), and Bierhuizen and Prepas (1985) in central and eastern Alberta; Hartland-Rowe (1966) in southeastern Alberta; Rozkowski (1965) in the Moose Mountain area of southern Saskatchewan; Lieffers and Shay (1983) and Driver and Peden (1977) in central Saskatchewan; and Driver (1965) and Barica (1975) in the Riding Mountain area of western Manitoba. Although not directly included in our excursion, water chemistry of lakes in the United States portion of the northern Great Plains has also been examined. Foremost among these studies are the regional syntheses of Winter (1977) and Gorham et al. (1983).

4.3 GROUNDWATER COMPOSITION

Groundwaters play a pivotal role in the geolimnology of this region. As summarized elsewhere (see overviews in Rutherford, 1967; Brown, 1967; Freeze, 1969; Tokarsky, 1985, 1986; Lennox et al., 1988; Pupp et al., 1991; Betcher et al., 1995) subsurface water compositions in the region are of several main types. Most of the groundwater in unconsolidated "surficial" aquifers is of low to moderate salinity (< 3000 ppm TDS) and dominated by Ca, Mg, and HCO₃ ions. In the areas of lowest precipitation, shallow drift groundwater is usually dominated by the SO₄ ion rather than HCO₃. The shallow bedrock aquifers (Upper Cretaceous and younger rocks) are mainly Na-HCO₃ in southern Alberta, Ca-Mg-Na-SO₄ in Saskatchewan, and Ca-Mg-Na-HCO₃ in western Manitoba. The deeper Paleozoic and Cenozoic bedrock contains higher salinity water (up to 300 ppt TDS) that is usually dominated by Na and Cl ions.

4.4 WHAT DO WE KNOW ABOUT THE CHEMICAL COMPOSITION OF THESE SALT LAKES?

We now have chemical data from about 1000 of the salt lakes in the northern Great Plains (Figure 4.1). Although most of these data represent analyses of single samples, some are averages of numerous samples collected over a period of months or years. In general, the larger lakes (e.g., Lakes Winnipeg, Manitoba, Quill, etc.) have the longest temporal records, in some cases dating back to the early twentieth century. However, no lake in the Canadian prairies has a *continuous* monitoring record of more than four decades in duration. Of the lakes for which there are data, 10% are located in Manitoba, 72% in Saskatchewan, and 18% in Alberta.

4.4.1 Salinity & Composition

"The lakes which fill the hollows are nearly all salt, and even early in the season of the year, the soil is whitened with salty efflorescence." (Hector, June, 1858; in Spry, 1968)

Water salinity, while a very simple concept, is often confusing due to the large variety of methods used to measure this basic parameter (Williams and Sherwood, 1994) and a plethora of nomenclature applied. Biological limnologists and ecologists often use conductivity as a measure of salinity. Conductivity, or specific conductance, is a measure of the ease with which electrical current will pass through the water: in

general, the greater the salinity, the greater the conductivity. This relationship, however, is not straightforward and is controlled by the specific ions present in the solution as well as the level of concentration of the ions. For example, a conductivity of 126 mS₂₀ in a lake such as Bitter Lake in southwestern Saskatchewan, dominated by sodium and chloride ions, would be equivalent to about 100 parts per thousand (ppt or ‰) total dissolved solids (TDS), but this same conductivity value would be recorded in a brine having only about 75 ppt TDS that was dominated by magnesium and sulfate ions (Desai and Moore, 1969). *Clearly, the use of conductivity to quantitatively evaluate salinity in lakes having diverse chemical compositions, such as these basins in western Canada, should be avoided*.



Figure 4.1 Sketch maps showing the locations of lakes with water chemistry, surface sediment and stratigraphic data (modified from Last, 1999)

The quantity or abundance of individual ionic components in the water is usually reported as weight concentration of the ion in solution (i.e., the weight of the dissolved ion in g or mg per kg of solution). This is preferred to the use of weight per litre because of the large increase in density of the solution at high salinities. Care must be exercised in evaluating and comparing published reports using g L⁻¹ units; unless density is taken into account by the analyst, the difference can be substantial at elevated salinities (greater than 7 ppt TDS; Hem, 1985). For example, the bottom water of Freefight Lake, a deep, meromictic lake in Saskatchewan, is 275 ppt (weight/weight) or 340 g L⁻¹. It follows then that the total salinity (total dissolved solids) should be the sum of the measured ionic components.

Those involved with appraising the lake waters from a physical chemistry perspective, and, in particular, examining the thermodynamics of the aqueous/mineral reactions occurring in the lakes, usually report water composition using traditional chemical concentration nomenclature: molal units (m; moles per kilogram of solvent) or molar units (M; moles per litre of solution) and in equivalents. Equivalent, equivalent weight, or combining weight is the formula weight of the dissolved component divided by its valence. Equivalent weight units are particularly useful when comparing ionic ratios of one water with another. In fresh water systems, molal and molar units are essential the same. However, in concentrated solutions, such as those in the lakes of western Canada, differences become significant. Similarly, discussions involving mineral precipitation/dissolution in the lakes usually evaluate thermodynamic activity of the ions (\forall) and ionic strength (I: one half the sum of the product of molality times the square of the valence of each ion). Again, in waters having less than about 30 ppt TDS, there is relatively little difference between thermodynamic activity and laboratory derived molality, but at higher concentrations the electrostatic interactions between the ions greatly reduces their thermodynamic "concentration" and \forall is considerably smaller than m. Like conductivity, ionic strength is also highly dependent on the specific ions in solution: a 1 m NaCl solution has an ionic strength of 1, whereas I of a solution having the same the same analytical concentration but dominated by sodium and sulfate is 3 (Drever, 1988).

Terminology also varies widely for the various levels of salinity, as reviewed by Williams (1967), Carpenter (1978), and Hammer (1986). Most biological limnologists use the classification scheme of: fresh water (less than 1‰), subsaline (1-3‰), hyposaline (3-20‰), mesosaline (20-50‰), and hypersaline (greater than 50‰). Groundwater researchers often refer to fresh water as less than 1‰, brackish water as 1-10‰, saline water as 10-100‰, and brine as greater than 100‰. Finally, most geoscientific literature uses: fresh water (less than 3‰), saline (3-35‰), and hypersaline (greater than 35 ‰).

Even though most of the lakes in the Great Plains of western Canada have similar overall origins, nonetheless, the waters show consider diversity in terms ionic composition and concentration. Early investigators, mainly economic geologists concentrating on the most saline brines, emphasized a strong predominance of Na and SO₄ in the lakes (e.g., Cole, 1926; Tomkins, 1954b). Rutherford (1970) similarly stressed the importance of sodium, magnesium and sulfate components in the lakes of Saskatchewan, and recognized five main water types on the basis of ionic ratios. He also related spatial variation in water types to climatic gradients within the province and to shallow groundwater composition. Hammer (1978) reported the water chemistry for sixty, mainly perennial, saline lakes in southern Saskatchewan, again noting the predominance of Na, Mg, and SO₄ in these brines. However, it was not until the 1980's that the compositional range and degree of diversity of the lakes on a regional basis became evident. We now realize that not only is there a complete spectrum of salinities, but also virtually *every water chemistry type* is represented in lakes of the region (Figure 4.2).

It is hardly surprising that the lake waters of the northern Great Plains show such a considerable range in ionic composition and concentration, considering the enormous geographic area and the varying hydrologic, geomorphic, and climatic settings. The lakes range in salinity from relatively dilute water (0.1 ppt TDS) to brines more than an order of magnitude greater than normal sea water (Figure 4.2). Although it is obviously misleading to generalize by quoting means and averages, the "average" lake water has about 50 ppt TDS and shows: Na>Mg>Ca>K and SO₄>HCO₃>Cl>CO₃ (Table 4.1).

With such a vast range of salinities, it follows that the concentrations of the individual ionic components also vary greatly (Figure 4.3). The frequency distributions of Mg, Na+K, Cl, and SO₄ concentrations in the lake waters tend to be multimodal as opposed to the Ca and HCO₃ ions which show a much narrower distribution pattern.

Sulfate and carbonate-rich lakes clearly dominate the Great Plains, comprising over 95% of the total lakes. This paucity of Cl-rich lakes makes the region unusual compared with many other areas of the world (e.g., Australia, western USA). The cation ratios are much more diverse, with the abundance of all three major types showing approximately subequal proportions.

As would be expected, most of the solutes in the lake waters increase in concentration with increasing total salinity (Figure 4.4, 4.5). Sulfate and sodium + potassium ions show the most statistically significant correlations with TDS, whereas calcium and carbonate concentrations are less directly related to salinity

The proportions of some of the solutes also show a systematic change with salinity. Sulfate increases in relative ionic proportion from less than 30% equivalents in dilute lakes to generally more than 90% in lakes with more than 10 ppt TDS. Calcium and bicarbonate + carbonate proportions show an inverse relationship with salinity, decreasing from over 70% equivalents in the dilute waters to nearly 5% in lakes with more than 25 ppt TDS.

4.4.2 Spatial Variation

The relatively uniform distribution of lakes in the Great Plains for which water chemistry data exists permits examination of the ionic contents on a spatial basis. Spatial analyses have also been undertaken by Winter (1977) and Gorham et al. (1983) for sections of the northern Great Plains in Minnesota, North and South Dakota. Last and Schweyen (1983), Lambert (1989), and Last (1988, 1992a) discuss the regional trends and present isohaline maps for the lakes in the Canadian Great Plains. Figure 4.6 shows these spatial variations in concentration and proportion for the various ions on a regional basis. Lakes with highest Na+K, Mg, and SO₄ concentrations generally occur in the east central Alberta, west central and southern Saskatchewan area, whereas lakes with high HCO₃+CO₃ and Cl contents are found in central Alberta and western Saskatchewan. Lakes with relatively low proportions of Ca and Mg occur in the northern and central parts of the Plains.





Figure 4.2 Ternary diagrams of saline lake water compositions and frequency distribution of average salinities of lakes in the northern Great Plains (modified from Last, 1999).



Figure 4.3 Frequency distributions of ions in the salt lakes of the northern Great Plains. Note that the vertical axes (concentration) are logarithmic. (Modified from Last, 1991a).



Figure 4.4 Scatter plots of cation concentration versus TDS. Note that both axes are logarithmic. (Modified from Last, 1991a.)

Area	TDS (ppt)	Ca	Mg	Na	К	HCO ₃	CO ₃	Cl	SO ₄
Eastern Prairies	3	3	23	4	1	6	1	2	24
Central Saskatchewan	22	19	150	193	5	7	3	54	251
SW Sask. & SE Alberta	81	12	93	1088	4	96	36	29	1073
West-central Sask & East- central Alta	103	3	144	1362	10	268	44	107	1125
Mean	54	8	130	690	5	99	21	56	643

Table 4.1 Average brine compositions of lakes in the northern Great Plains (ion concentrations in mmol L^{-1}) (modified from Last, 1989).



Figure 4.5 Scatter plots of anion concentration versus TDS. Note that both axes are logarithmic. (Modified from Last, 1991a.)

4.4.3 A Statistical Approach: Insight into Water Composition Controlling Factors?



"Statistics are for losers" (Scotty Bowman, 1976)

The major ion composition and concentration of these lakes is the result of: (i) a complex interaction between unconsolidated glacial and nonglacial sediments, bedrock, and precipitation/meltwater in the drainage basin, (ii) the composition and amount of groundwater recharge (and discharge) and streamflow in each basin, and (iii) a wide variety of other physical, chemical, and biological processes operating within the water column itself. In general, several types of geochemical approaches have been taken to help understand the major factors controlling surface water chemistry. These include mass balance calculations, thermodynamic equilibrium considerations, and statistical evaluations (see overview in Drever, 1988). In western Canada, both mass balance and thermodynamic calculations have proved valuable in deciphering many of the intrinsic (within-drainage basin) processes important in water composition on a local scale (e.g., Roskowski, 1965; Wallick and Krouse, 1977; Wallick, 1981; Schweyen, 1984; Last, 1984; Slezak, 1989). In contrast, on a regional scale, various statistical techniques have been successfully applied to help understand the relationships between the water chemistry and extrinsic environmental factors such as climate, bedrock, geomorphology, and till composition (e.g., Dean and Gorham 1976; Winter 1977; Last, 1992). However, these statistical approaches lack the ability to resolve the often important local conditions and processes, however they are essential to our overall understanding of the lacustrine geochemical setting of the region as a whole.

One of the most straightforward ways to analyze the interrelationships within a data set is to examine the simple linear correlations that exist among the various parameters. The concentrations of Na, Ca and Mg in the brines of these lakes are all significantly positively correlated, as are SO₄ and Cl. In addition, the ion pairs of Mg-SO₄, Mg-Cl, and Na-Cl tend to strongly covary. Importantly, the concentrations of Na and SO₄ do not show statistically

significant linear correlation, suggesting different suites of processes affect the abundance of each of these ions. The proportions of Ca and HCO_3 exhibit significant positive covariation, whereas the proportions of Mg and Na, and HCO_3 and SO_4 are inversely related

Using a Q-mode cluster analysis (associations among lakes) Last (1992) subdivided the lakes into two major categories: a group of high salinity (greater than 20 ppt TDS) lakes and a group characterized by relatively lower TDS values. Each of these major clusters was further divided into smaller groups of lakes as related to their major ion composition (Figure 4.7). R-mode analysis (association among the geochemical parameters) indicated the following groups of variables: (i) TDS, Na, and SO4; (ii) K and Cl; (iii) Ca and Mg; and (iv) HCO₃ and CO₃.

By combining a variety of morphological (basin area, maximum depth), geological (bedrock type, depth to bedrock, till type), hydrological (drainage basin area, number of streams entering lake, elevation, groundwater composition), and climatic (mean annual precipitation, evaporation, temperature) variables with a 500-lake water chemistry database, Last (1988, 1992) and Lambert (1989) used R-mode factor analysis to identify a set of seven statistical factors that



Figure 4.6 Maps showing the spatial variation in proportion of ionic concentration in salt lakes of the northern Great Plains. Note that the vertical (z) axes are logarithmic; the numbers on the y axes are degrees latitude. (Modified from Last, 1991a.)



Figure 4.7 Results of Q-mode cluster analysis (modified from Last, 1992).

explained over 90% of the variance in the data. Their interpretation of these statistical factors are that the most important controls of water composition and concentration on a regional basis are: (i) composition of inflowing groundwater, (ii) evaporation/precipitation, and (iii) elevation or position of the basin within the drainage basin. Variables related to bedrock type, glacial drift composition, fluvial input, and lake morphology are statistically less important.



4.4.4 Temporal Variation in Water Chemistry

4.4.4 Short-term Variation

A major complicating factor in characterizing the chemistry of the salt lakes of the northern Great Plains is that many of the lakes exhibit playa characteristics, filling with water during the spring and early summer and drying completely by late summer or fall. Last and Schweyen (1983) estimate that 85% of the salt lakes in this region are influenced by this type of seasonal hydrologic cycle. This strong seasonality of water levels gives rise to dramatic changes in both ion concentrations and ratios, as demonstrated by numerous studies. For example, Ceylon Lake, a salt-dominated playa in southern Saskatchewan that we will be visiting, annually undergoes changes in concentration from about 30 ppt TDS to greater than 300 ppt. This lake also exhibits dramatic fluctuations in ionic ratios on a seasonal basis from a Ma-(Mg)-SO₄-HCO₃ type in early spring to a Mg-(Na)-Cl-SO₄ composition by fall. Hammer (1978, 1986) summarizes the short-term temporal changes in salinity and chemistry of several other saline lakes in the region. Unfortunately, only a few basins in the northern Great Plains have undergone periodic detailed sampling over a period of years.

4.4.4.2 Long-term Temporal Variation

Because lake basins are sinks for sediment they can provide a very important source of information about past hydrochemical conditions in the lake basin, the drainage basin and the surrounding area. The sediment records of topographically closed basins, in particular, offer excellent opportunities to evaluate changes in the chemical nature of the brine and the inflowing waters, and to relate these changes to climatic fluctuations or evolutionary changes in the watershed of the lake. Although the literature on the paleochemistry of saline lakes in the region is small, several examples exist which demonstrate the large potential of salt lake sediment records in terms of deducing past chemical conditions (e.g., Shang, 2000; Shang and Last, 1999; Greengrass et al., 1999; Last, 1995; Last et al., 1994).

However, paleochemical interpretations of salt lake sediments are not without pitfalls. Saline and hypersaline lacustrine environments are amongst the least understood depositional regimes in sedimentary geology. Thus, interpretations of the preserved stratigraphic records are hampered by this incomplete understanding of the modern depositional and diagenetic processes.

Furthermore, we must realize that our database of paleoenvironmental information from this region is discouragingly small. Of the nearly 1000 salt lakes for which water composition data is available we have modern sedimentological data for less than 15% of these and the stratigraphic records of fewer than 10% have been investigated in any type of detail (Last, 1999; Last and Slezak 1988). Although the few lacustrine sedimentary records that have been examined from a paleochemical and brine composition perspective clearly indicate dramatic changes in water levels and brine chemistry, the causal mechanism(s) of these temporal changes

are still largely unknown. Climate has certainly controlled the sedimentation and geochemistry of nearly all of the basins. However, the precise roles of other factors, such as fluctuating groundwater hydrology and hydrochemistry, or postdepositional alteration of the sediments, still remain to be evaluated (Teller and Last 1989).



4.4.5 Source of Salts

"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." (Sloan, 1972).

The origin and ultimate source of the ions in the lakes of the northern Great Plains have been topics of considerable discussion in the scientific literature. Some of the early work suggested that the deeplyburied Paleozoic evaporites which occur in the subsurface could be a possible source for the salts in the lakes. Grossman (1968) shows that there is a correlation between the occurrence of sodium sulfate

deposits in lakes at the surface and the presence and trends of various salt units in the Devonian Prairie Formation in the region. In contrast, shallow Cretaceous and Tertiary bedrock, as opposed to the deep Paleozoic sequence, has been implicated as the source of at least some of the dissolved components in the lakes (Cole 1926; Sahinen 1956; Wallick and Krouse 1977; Wallick 1981).

Finally, rather than invoking bedrock sources, there is considerable support for the source of the ions being largely the Quaternary deposits within which the lakes are immediately situated (Rutherford 1970; Sloan 1972; Rozkowski 1967; Moran et al., 1978; Timpson and Richardson, 1986; Arndt and Richardson, 1992; LaBaugh et al., 1996). Although simply defining flow patterns and groundwater dynamics in a natural system characterized by poorly integrated surface drainage, undulating surface relief, and multiple discontinuous permeable zones is exceedingly complex (Winter, 1978,1995), on a local basis Hendry and Schwarz (1982) suggest that the glacial till is a large "soluble salt reservoir" which can provide salinity to the shallow groundwater systems and, therefore, to the lakes. A variety of physicochemical and biochemical reactions, including cation exchange, dissolution of feldspars and detrital carbonates, oxidation of reduced-S mineral species and organic matter, and precipitation of authigenic sulfate, carbonate, and silicate phases in the tills can be documented which support this latter hypothesis. In assuming a constant local (glacial drift) source and unchanging source water chemistry, Whiting (1974, 1977,1986) and Doering (1982) use the level of salinity to determine the amount
of time required to accumulate the dissolved components in selected closed-basin lakes and wetlands in the region. From this Whiting (loc. cit.) was able to the identify episodes during the Holocene at which the now-closed basins overflowed.

4.4.6 Summary of Water Chemistry Considerations

A large number of saline and hypersaline lakes occur in the northern Great Plains of western Canada. The major ion composition of about 1000 of these lakes is known. While the average brine, consisting of 50 ppt salinity, is Na-(Mg)-SO₄ type of water, it is clearly misleading to refer to the entire region as a sodium-sulfate dominated system. The lakes exhibit a very wide range of salinities and compositions with nearly every water composition type present. Some of the variations display distinct trends, both spatially and with increasing salinity. All the ions increase with increasing TDS, but they do so at different rates. The relative proportions of calcium and bicarbonate+ carbonate show a strong decrease with increasing salinity.



"Professor Last may I be excused? My brain is full."

5. THE MODERN LAKES

5.1 SIZE & SHAPE OF THE LAKES

"The lakes I suppose are not unusual except in numbers alone but if you were able to stand on a great height wherever you are and able to see all the water at once it would still be difficult to find words describing anything but quantity!" (Al Purdy in Brown, 1986)

Basin morphology reveals much about a lake's origin (Timms, 1992) and also exerts a profound influence on the sedimentary processes and resulting spatial distribution of detrital sediments within the lake. In a saline lake, the shape characteristics of the basin similarly help control the distribution of chemical precipitates in lakes (Jones and van Denburgh, 1966; Reeves, 1968, Eugster and Kelts, 1983).

The lakes of the Great Plains region exhibit a remarkably great range in basin size (from small, less than 1 km² prairie potholes and kettles to several of the continent's largest basins), shape (from nearly perfectly circular to linear troughs to highly irregular shorelines), and depth (from playas to mean depths of over 25 m). Hammer and Haynes (1978) provide morphometric details (area, maximum depth, mean depth, shoreline length, shoreline development, volume, and volume development) for thirteen permanent lakes in southern Saskatchewan and summary morphology data (area, shoreline length, shoreline development, and maximum depth) on 47 other shallow basins in the region. Mitchell and Prepas (1990) is a valuable source of detailed morphometric information on about 40 lakes in the prairie region of Alberta. In a morphometric survey of lakes along a north-south (climatic) transect through eastern Alberta, Campbell et al. (1994) and Campbell (1997) demonstrated a strong sensitivity of lake area and volume to a measure of the evaporation/precipitation ratio. Based on a survey of 131 lakes in the northern Great Plains, Last and Schweyen (1983) classified the basins on the basis of size, depth, and degree of permanence. Last (1994a) undertook a similar classification of 360 basins located just within the Palliser Triangle area of the Plains region (Figure 5.1).

Most of the lakes in the northern Great Plains are small and shallow. There are few basins in the region that can be classified as large (greater than 100 km² surface area). Four of the six largest lakes are located in the Manitoba Lowland area in the eastern part of the prairies. Lake Winnipeg, seventh largest lacustrine basin in North America, is also the largest lake in western Canada located off the Precambrian Shield. Lake Manitoba is North America's thirteenth largest lake and Canada's largest saline lake. Of the lakes in southern Saskatchewan and Alberta, two of the largest, Big Quill and Old Wives, are among the six largest inland saline bodies of water on the continent.



Figure 5.1 Classification and relative abundance of salt lake types in the northern Great Plains (from Last, 1994a).

Among the small lakes (less than 100 km²), most are also shallow. Only about 8% of the basins have mean depths greater than 3 m. However, these small, deep basins are very important. They are attractive targets for paleoenvironmental research because their sediment records often contain undisturbed, finely laminated sequences. It is generally held that deposits in these deeper water basins may be less susceptible to wind and current redistribution and to diagenetic changes brought about by either subaerial exposure or subaqueous chemical fluctuations (Richardson, 1969; Teller and Last, 1990). Several of these small, deep basins are also meromictic which further enhances their appeal for paleolimnological study (Schweyen, 1984; Last and Schweyen, 1985; Last and Slezak, 1986).

Of the many small, shallow salt lakes, one further distinction can be made based on the degree of permanence of the water body. The word playa, meaning "beach", "shore" or "coast" in Spanish, has many definitions, synonyms, and, in some cases, contradictory connotations (Reeves, 1968, 1972; Neal, 1975; Bates and Jackson, 1980). Previous researchers on the Great Plains (e.g., Lockhart and Last, 1984; Egan, 1984; Last, 1984a; Osterkamp and Wood, 1987; Gustavson and Holliday, 1992) considered a playa to be any low, seasonally flooded but

intermittently dry basinal area and deemed the term to be generally synonymous with ephemeral lake, slough, or wetland. Rosen (1994b) recommended playa be restricted to continental basin settings characterized by an annual net negative water balance (i.e., more water is lost through evaporation and discharge/seepage than is received through all incoming sources) and in which the capillary fringe is close enough to the surface such that evaporation will cause groundwater to discharge to the surface. About half the lakes with mean depths less than 3 m exhibit playa characteristics in that they fill with water during the spring and summer and usually dry completely by late summer. However, not all of these shallow, ephemeral lakes exhibit groundwater discharge.

5.2 ORIGIN OF THE LAKE BASINS

"Lakes arise from phenomena that are almost entirely geologic in nature. Once formed, they are doomed. Because of the concave nature of basins, there is a compulsory trend toward obliteration as they fill with sediments... Enormous and deep lakes may be far from death as a result of shoaling, but climatic changes or geologic events leading to desiccation or drainage eventually mark their ends." (Cole; 1979, p. 9).



Like the vast majority of lacustrine basins in north-temperate regions of the continent, a glacial origin for most of the lakes of the Canadian Great Plains is evident considering the fact almost the entire area was glaciated during ~23-14 ka. Although only a few lake basins can be attributed to gouging, scraping or scouring action of the glacial ice, many have their origins intimately associated with deglaciation processes. A complex but reasonably clear picture of Late Wisconsinan ice retreat in the Prairie region has emerged over the past decade (Dyke and Prest, 1987; Klassen, 1989, 1994). Ponding of meltwater against the retreating ice margin, due to the regional northward slope and differential isostatic depression, lead to the formation of large proglacial lakes such as Lake Regina, Lake Hind, Lake Saskatchewan, and Lake Agassiz. While

few in number, present-day remnants of these proglacial lacustrine basins, such as Lakes Manitoba and Winnipeg in Manitoba and the Quill Lakes complex in Saskatchewan, are clearly important sources of late Pleistocene and early Holocene paleoenvironmental information. These remnant basins, often simply large but shallow low spots in the glacial deposits, are usually surrounded by old strandlines and glaciolacustrine sediments.

As noteworthy as these extensive ice-marginal lakes were, however, only a small number of the millions of extant lakes in the region have been shown to be direct remnants. Instead, the majority of lacustrine basins in the northern Great Plains are the result of stagnant or dead-ice glacial processes which were not sedimentologically directly related to ice-contact precursor lakes. Slow melting of ice buried beneath a thick superglacial drift blanket resulted in creation of a variety of irregular depressions, ice disintegration trenches, kettles, sinkholes, and donuts, as well as the poorly integrated (i.e., topographically closed) drainage which characterizes much of the region (Gravenor and Kupsch, 1959; Clayton and Cherry, 1967; Clayton and Freers, 1967; Christiansen, 1973). These ice-stagnation basins tend to be small and circular but some have great thicknesses of Holocene and late Pleistocene lacustrine clastics and salts. For example, Ingebright Lake in southwestern Saskatchewan, today a hypersaline playa basin of less than 1 km² area, contains in excess of 50 m of Holocene salts and clays. Similarly, the Deadmoose Lake basin, which we will visit, contains several anomalous troughs and circular depressions up to 50 m deep which are likely due to ice-block melt-out.

In addition to these hollows on the landscape created by stagnant ice melting, many lake basins in the Great Plains have an obvious fluvial origin as evidenced by their long, linear, riverine morphologies. Like the melt-out structures, most of these river-carved basins were created during late Pleistocene deglaciation between about 15 and 11 ka, but some have been shown to occupy older drainage valleys (Rueffel, 1968b).

A number of lake basins in the Plains region owe their existence to several unusual origins. Christiansen (1971) and Gendzwill and Hajnal (1971) demonstrate, through the use of both drilling and seismic geophysics, that Crater Lake, a small, circular lake about 6 m deep located near Yorkton, Saskatchewan, occupies a collapse chimney created by dissolution of the Prairie Evaporite, some 900 m below the surface. Christiansen et al. (1982) describe a basin near Wynyard, Saskatchewan, (Howe Lake) that originated by the process of "hydrodynamic blowout". Downey (1969), Meneley (1977; referenced in Christiansen et al. 1982), and Bluemle (1992, 1993) have identified several other lakes and wetlands in Saskatchewan and North Dakota likely having similar origins. These basins were created when meltwater from the retreating glacier was able to over pressure a shallow groundwater aquifer. The high pressure artesian water exited through a small opening to the surface, in the case of Howe Lake probably a fracture system related to a salt solution-collapse structure. Initially, the extreme pressure was sufficient to expel particles and excavate a basin. Clearly, the geolimnology of these types of basins is controlled, to a large degree, by the dynamics of the continued groundwater flow and the composition of the groundwater solution. In Howe Lake for example, the groundwater aquifer (sandstones of the Cretaceous Mannville Group) contains freshwater, thus Howe Lake is

anomalously fresh despite its closed basin and high evaporation/precipitation ratios. In the case of Kelley Slough, Salt Lake, and Lake Ardoch in North Dakota, the groundwater aquifer contains saline brines and these lakes are, therefore, anomalously saline, in this case in spite of a relatively humid climatic setting.

Finally, tectonic features associated with glacial thrusting of previously deposited glacial sediments and bedrock are well known in the northern Great Plains. Lake basins can be created both within the irregular ridge and furrow topography of the deformed thrust blocks (see, for example, Figure 13 in Aber, 1993, and Figure 3 in Christiansen and Whitaker, 1976) as well as in "up glacier" source depressions adjacent to the ice-thrust ridges (see Figures 31-33 in Bluemle, 1991).

5.3 SEDIMENTS & SEDIMENTARY PROCESSES

5.3.1 Sediment Types

"The study of sedimentary rocks, as compared with igneous rocks, is somewhat hampered by the poverty of terminology." (Moorhouse, 1959, p. 333)

Few of the millions of lake basins in the northern Great Plains have been examined from either a sedimentological or stratigraphic perspective. Of the ~1000 lakes for which water chemistry has been documented, we have knowledge of the sediments in only about 15% of these. Similar to the early brine composition work summarized in section 4, initial sedimentological efforts on these lakes stressed the dominance of sodium sulfate salts, and were directed mainly toward basins with large reserves of economically important industrial minerals. It is now realized that the lakes in the Canadian Great Plains exhibit a complete spectrum of sediment types, from basins dominated by allogenic or clastic material to those in which relatively pure, clastic-free evaporite minerals are forming (Figure 5.2; Last and Schweyen, 1983).

The modern sediments in most of these lakes consist of mixtures of coarse to finely crystalline salts and organic-rich, silty clays/clayey silts in the offshore portions of the basins, grading to somewhat coarser clastics (sands and silts) in the nearshore areas. Due to their small size and negligible fetch distances, most of the lakes have only a very narrow margin of shoreline /nearshore coarse silts and sands. However, in the larger basins and in lakes with long wind-fetch distances, such as characterize the many linear, riverine lakes, coarse clastics can extend farther out into the basin (Veldman, 1969; Sack, 1993). Because of the paucity of fluvial input to most of the lakes, deltas are rare except in the larger basins such as Lakes Manitoba and Winnipeg. Away from the relatively nearshore areas, however, there is usually surprisingly little variation in grain size in any of the basins (Kushnir, 1971; Whiting, 1977; Brunskill and Graham, 1979; Last, 1984b, 1996a, 1996b; Henderson and Last, 1998).



Figure 5.2 Range and examples of salt lake types according to morphology and sediment type (modified from Last, 1991a).

Generally the organic content of the modern sediments is moderate to low, although in some basins organic matter can be as much as 45% (by weight) of the total sediment. The organic content of sediments from playa basins and shallow lakes is not significantly different from that of most of the perennial deep water basins. However, the chemical composition of this organic matter can vary significantly. Playa lake sediments in the region show consistently much lower Rock-Eval hydrogen indices (HI) and somewhat higher oxygen indices (OH) relative to both shallow and deep perennial lakes (Figure 5.3), reflecting a more terrestrial source for the organics in the playas. Similar results are evident for lakes in Minnesota (Dean and Stuiver, 1993).



Figure 5.3 Summary of Rock-Eval data and trends for modern surficial sediment samples from salt lakes in western Canada and elsewhere (from Last, 1999).

5.3.2 Detrital Versus Chemical Sediments

"The union of alkaline earths with carbonate and calcium with sulphate are unlikely in Saskatchewan." (Whiting, 1986, p. 650)

Geoscientists have long recognized three basic genetic types of sediment in most lacustrine basins (Jones and Bowser, 1978): (i) allogenic or detrital: that material derived from weathering and erosion of the soils and bedrock of the watershed and transported to the lake by fluvial, sheetwash, gravity, or aeolian processes; (ii) endogenic: sediment originating from processes occurring entirely within the water column of the lake; and (iii) authigenic or diagenetic: material resulting from processes occurring once the sediment has been deposited. The endogenic and authigenic fractions are sometimes collectively referred to in a non-genetic sense as chemical sediment, as opposed to clastic sediment which is usually dominated by the allogenic fraction.

The allogenic component in most of the lakes of western Canada consists mainly of a mixture of (in decreasing order of abundance): clay minerals, quartz, carbonates, feldspars, and ferromagnesian minerals. The proportions of each of these detrital mineral groups is generally similar to that of the surrounding glacial debris, except sorting by the transporting medium and diagenetic processes operating within the watershed soils can also influence the final detrital mineralogy. The less chemically-stable constituents, such as detrital carbonates and feldspars, are particularly susceptible to loss by weathering processes in the drainage basin (e.g., Ehrlich and Rice, 1955; Mills and Smith, 1971; Teller and Last, 1979). Superimposed on this element of chemical stability of the detrital components is the inherent size fractionation of various minerals caused due to physical abrasion and breakage of grains by the action of glacial ice. For example, because the terminal grade for glacier-comminuted dolomite is medium to coarse silt (Dreimanis and Vagner, 1971), the modern sedimentary facies of the larger lakes in the region show a gradation from dolomite-enriched sediment nearshore to dolomite-depleted deposits offshore (Brunskill and Graham, 1979; Teller and Last, 1979; Last, 1982; Henderson and Last, 1998).

Although the sediments of only a small number of lakes have been examined for detailed clay mineralogy, the most common layered silicates are kaolinite, illite, smectite, and chlorite (Kushnir, 1971; Egan, 1984; Last, 1984b, 1996b; Last and Schweyen, 1985). A variety of mixed-layer clays, most commonly illite-smectite and illite-chlorite species, have also been reported, but at least some of these interstratifed minerals have been attributed to possible authigenic processes within the lake basins (e.g., Slezak, 1989; Last, 1993a). In lakes west of the Manitoba Lowland, the sediments are almost completely dominated by smectitic clays, undoubtedly a reflection of the bentonitic Cretaceous shales which underlie most of the area west of the Manitoba Escarpment. The abundances of kaolinite, illite and smectite in the eastern part of the region tend to be approximately subequal.

The only detrital carbonate minerals identified in the lakes are dolomite and calcite. In bulk (i.e., non-size fractionated) samples $CaMg(CO3)_2$ is usually considerably more abundant than $CaCO_3$, which is most likely a reflection of the relative abundance of these two minerals in

the tills and bedrock of the region, as well as the higher solubility and, hence, lower weathering stability of calcite relative to dolomite (Last, 1982, 1996a; Ghebre-Egziabhier and St. Arnaud, 1983a, b; Henderson and Last, 1998).. Similarly, potassic feldspars are usually more abundant than plagioclase in the lakes due to the partial loss of the relatively unstable Na and Ca feldspars by hydrolysis in the tills and watershed soils.

Considering the great range of water compositions in lakes of the Great Plains as discussed in Section 4, it is not surprising there is an equally significant breadth of endogenic and authigenic minerals found in these lakes. In a study of forty-six playas in the Great Plains, Last (1984a) identified two main types of endogenic precipitates in the modern sediments: (i) very soluble salts, comprising mainly sodium and magnesium sulfates and carbonates, and (ii) sparingly soluble precipitates, including mainly carbonates, sulfates, and silicates. There have now been close to fifty non-detrital minerals identified from the lakes (Section 6). These endogenic minerals can also be subdivided according to their genesis and occurrence within the lake (Last, 1989a): (i) surficial efflorescent crusts and hardgrounds, usually occupying nearshore and seasonally flooded areas; (ii) massive and bedded precipitates, most often found blanketing the floor of the basins from shallow marginal zones down to deep central offshore areas; and (iii) accumulations of salts and precipitates associated with either subaqueous or subaerial springs.

Distinguishing endogenic lacustrine minerals from those formed by diagenetic processes after the sediment has been deposited (i.e, authigenic) is often an exceedingly difficult task. Many times, detailed petrographic and geochemical studies are required to convincingly demonstrate the precise origin for the specific minerals. To date, few lakes and lacustrine sequences in western Canada have been examined in this amount of detail. Although a complete discussion of the genesis (viz. endogenic versus authigenic) of the minerals is beyond the scope of this field guide, some of the more common or noteworthy occurrences will be summarized briefly.

Among the many endogenic and authigenic carbonates identified in these lakes, aragonite, magnesian calcite, and dolomite are the most common. Thermodynamic supersaturation and inorganic precipitation of carbonate minerals is very common in lakes of all types on a global basis; the Great Plains region is no exception. Last and Schweyen (1983) found that nearly all of the 131 lakes they surveyed were strongly supersaturated with respect to these carbonate minerals. Supersaturation and precipitation of carbonates can take place for a variety of reasons, including photosynthetic uptake of CO_2 and consequent increase in pH, concentration changes brought about by evaporation or dilution, temperature changes, and mixing of brines of different compositions. In most of the lakes of the Great Plains, carbonate mineral supersaturation is due mainly to, but not exclusively, the seasonal uptake of CO_2 by primary organic productivity.

The specific carbonate mineral to be precipitated from the supersaturated solution is controlled, to a major degree, by the cations in solution (in particular the ratio of magnesium to calcium in the water). The high Mg/Ca ratios that characterize the lake waters of the Great Plains

give rise to a carbonate mineral assemblage dominated by aragonite (the orthorhombic form of CaCO₃) and Mg-bearing carbonates, such as dolomite, magnesite, huntite and Mg-calcite.

The discovery of non-detrital dolomite in the lakes of the Great Plains has been an important contribution to our understanding of the genesis of this economically important mineral. Dolomite formation and dolomitization in the sedimentary realm are subjects of long-standing interest and study. Probably no other mineral or sedimentary rock has attracted as much speculation regarding its genesis as dolomite (Last, 1990a). The complex "dolomite problem" has been summarized in many recent reviews and in most sedimentary geology textbooks. In its simplest form, the dolomite problem is the enigma that the mineral dolomite (CaMg(CO₃)₂) is a very common component of ancient rocks, but is very rare in modern/Holocene sediment, does not occur as a primary precipitate from marine water of normal salinity and composition, and cannot be readily synthesized in the laboratory at low temperatures and pressures.

The occurrence of penecontemporaneous (i.e., very early diagenetic) dolomite in the surficial offshore sediments of Devils Lake, a 50 km² perennial saline lake in northeastern North Dakota (Callender, 1968; Owen at al., 1973) was one of the earliest documented examples of lacustrine dolomite formation in the world. The Devils Lake dolomite is also very important because it demonstrated, for the first time, dolomitization could take place in solutions of moderate salinities (~20 ppt TDS) and in water with high sulfate contents. Others, working mainly in highly evaporitic marginal marine settings, have suggested that dolomite formation is favored by elevated salinities (>35 ppt TDS) and greatly reduced SO₄ levels (Folk and Land, 1975; Baker and Kastner, 1981; Morrow, 1982).

Modern primary and early diagenetic dolomite occurs in numerous lakes in the Canadian Great Plains (Last, 1990a). Waldsea and Deadmoose Lakes are two adjacent, meromictic saline lakes that will be visited during this excursion. Two distinct types of non-detrital dolomite have been identified in these lakes (Schweyen and Last, 1983; Schweyen, 1984; Boden, 1985; Last and Slezak, 1986). Most is very finely crystalline with subhedral to anhedral crystallites forming aggregates of about 2 :m in diameter. This dolomite, like most Holocene dolomite, is poorly crystalline and poorly ordered (ordering refers to the regular alteration of the layers of cations and anions within the crystal structure), but has a composition close to that of the ideal, stoichiometric mineral (i.e., Ca=Mg). The other type is also poorly crystalline, but is considerably enriched with calcium: $Ca(Ca_{0.2}Mg_{0.8})(CO_3)_2$. Like that of Devils Lake, the dolomite in both Waldsea and Deadmoose is forming subaqueously as a primary inorganic precipitate in sulfate-rich waters.

Another important occurrence of dolomite is in Freefight Lake, a 25 m deep, hypersaline meromictic lake in southwestern Saskatchewan. Detailed examination of this lake by Last and Slezak (19887), Slezak (1989), and Last (1993a) indicates a considerable range of formative environments and dolomitization processes. Calcian (i.e., Ca-enriched) dolomite occurs in the deep-water, offshore sediments and also in the subaerially-exposed mudflats surrounding the basin. Within the mudflat sediments, it is often associated with aragonite and Mg-calcite, and petrographic evidence suggests it may be an early diagenetic product forming in response to the

strong evaporative flux experienced on the mudflats during the ice-free season. In contrast, in the organic-rich, highly reducing offshore sediments, dolomite is associated with a variety of soluble sulfate salts and pyrite. It is forming at the sediment-water interface as a primary precipitate in response to the increased alkalinity brought about by sulfate reduction in the anoxic monimolimnion of the lake.

A final example showing the diversity of Mg-carbonate mineral genesis in these lakes is that of Chappice Lake in southeastern Alberta. Chappice Lake is a small, hypersaline, groundwater-fed playa whose brine is dominated by Na and SO₄ (Vance, 1991, Vance et al., 1992, 1993; Birks and Remenda, 1998). Although endogenic carbonates are not forming in the lake today, the 7000 year long stratigraphic record preserved in the basin contains thick sequences of very finely laminated carbonates. The carbonate crystals and crystal aggregates making up these laminae are euhedral and contain no petrographic evidence of reworking, abrasion, corrosion, or diagenetic alteration, thus suggesting the laminae were generated by inorganic precipitation from within the water column. The lack of detrital grains in these laminae and the absence of rhythmicity indicates relatively rapid and non-annual precipitation events. As shown in Figure 5.4, it is clear from the detailed mineralogical composition of the sequence that the brine underwent striking compositional changes in both carbonate alkalinity and cation ratios.

The mineralogy of the endogenic and authigenic sulfates in the Great Plains' lakes is complex. Not only is the stable sulfate mineral suite controlled by the ionic composition and cation ratios in the brine, but the temperature at which the precipitation occurs is also very important. For example, in a simple binary salt system (e.g., Na-SO₄-H₂O, Mg-SO₄-H₂O, or Na-Cl-H₂O) the solubility of mineral phases such as mirabilite (Na₂SO₄ · 10H₂O), and epsomite (MgSO₄ · 7H₂O) show enormous ranges over temperatures normally encountered by the brine on a diurnal and seasonal basis. In contrast, common non-sulfate salts, such as halite or bischofite (MgCl₂ · 6H₂O), exhibit comparatively little solubility change over these near-surface temperature ranges. In more complex aqueous systems, such as Na-Mg-Cl-SO₄-H₂O, prediction of the stable phase(s) becomes somewhat more complicated, but the influence of temperature remains important.



Figure 5.4 Carbonate mineralogical variation in a laminated sequence from Chappice Lake. Width of core is 3.2 cm (modified from Last and Vance, 1997).

The effect of temperature on the mineral suite in these lakes is most obvious in the playas (Last, 1984; 1987, 1989b) and shallow lakes/wetlands (Timpson and Richardson, 1986; Timpson et al., 1986; Skarie et al., 1987) where the annual cycle of sediment accumulation (precipitation) and dissolution is readily apparent. However, the deep perennial salt lakes are also strongly influenced by the annual (and diurnal) temperature regime. For example, in Freefight Lake, the surficial waters become supersaturated with respect to mirabilite and epsomite during the winter due to low temperatures of the upper part of the mixolimnion (-10 to -15°C depending on salinity) and the formation of an ice cover which increases the brine concentration in the upper meter. The precipitated Na₂SO₄ · 10H₂O and MgSO₄ · 7H₂O crystals undergo corrosion and dissolution as they settle through the understaturated (-5 to 5°C) mixolimnion below the ice cover. Dissolution of these sulfate salts in the mixolimnion is of sufficient magnitude to, in turn, affect the temperature of the water. The dissolution of mirabilite is a strongly endothermic reaction. When 1 mol of mirabilite dissolves the reaction absorbs over 4 MJ of heat. This heat must be acquired from the surrounding water, thereby lowering the temperature. However, at the chemocline sulfate salt precipitation begins anew, despite a still higher temperature, due to the greater salinity. Gypsum shows a similar pattern of precipitation from the surficial waters, dissolution within the mixolimnion, and precipitation through the monimolimnion, except the supersaturation at the surface is usually brought about during the ice-free season due to evaporative concentration of the brine. Thus, the petrography of the resulting deep-water sulfate salts in this basin records a complex series of multiple precipitation and dissolution events that are controlled largely by seasonal temperature fluctuations within the water column.



5.3.3 A Spectrum of Sedimentary Processes

"I often say that if you measure that of which you speak, you know something of your subject; but if you cannot measure it, your knowledge is meager and unsatisfactory." (Lord Kelvin)

The lakes of the northern Great Plains offer an excellent opportunity to examine the processes of lacustrine sedimentation on both a local and regional scale. As is the case with most other depositional settings, these lakes exhibit a continuous spectrum of sedimentary regimes. This continuum exists in terms of nearly every parameter that can be evaluated for the basins: morphology, hydrology, degree of permanence, brine salinity and ionic composition, sediment character, composition, etc. This great diversity presents somewhat of a problem in studying and discussing the lakes.

In an effort to subdivide this continuum, several "end member" types of lakes can be recognized. A fundamental sedimentological distinction must be made between those basins whose brines are shallow enough to permit periodic drying and those whose brines are deep enough to maintain a relatively permanent water body. The most significant processes operating in shallow intermittent basins (playas) include: cyclic flooding and desiccation of the playa surface, formation of salt crusts, efflorescent crusts, hardgrounds, spring deposits, and intrasedimentary salts, formation of solution pits and chimneys, and periodic detrital sedimentation by sheet flow and wind. Discussions and comprehensive summaries of these basic playa processes can be found in Eugster and Hardie (1978), Handford (1981), Lowenstein and Hardie (1985), Smoot and Lowenstein (1991), and Rosen (1994b). However, it must be emphasized that most of these overviews deal with lacustrine systems occurring in warm and dry climatic regimes. The five to six months of sub-freezing temperatures experienced in western Canada, as well as the occurrence of snow and high seasonal runoffs associated with snow melt, dictate some modifications and additional processes be considered when studying the playas of the northern Great Plains (Last, 1987, 1989a, 1994a).

The large number of individual playa basins in the Great Plains, the tremendous diversity of chemical and hydrologic settings, and the variable impact of humans are the main factors that have given rise to the complex suite of interrelated sedimentary processes in these lakes. To better understand the relative importance of the many and diverse processes, Last (1984) used Q-mode cluster analyses to help quantitatively group various classes of playas in the region. This analysis identified five groups of playa basins. One group of lakes, typified by the Chaplin, Bigstick, and the Quill Lakes complex, are characterized by having large areas, moderate salinities but high Cl contents, and high detrital to endogenic sediment ratios. Mudflat and sand flat sedimentary processes dominate. In contrast, basins such as Snakehole, Whiteshore, and Muskiki are marked by brines with very high salinities that are almost completely dominated by sodium and sulfate ions. Sedimentation in this group of lakes is controlled largely by chemical processes also dominate in lakes such as Ceylon, Ingebright, and Vincent, but they

exemplify a third group of playas distinguished by their relatively small areas, and high shoreline length and development indices (i.e., very irregular shorelines or very long, linear basin morphologies). Lakes belonging to the final two groups include those whose brines are characterized by calcium, magnesium, and bicarbonate ions rather than sodium and sulfate. Sedimentation is controlled by either mixed chemical/physical (e.g., Verlo, Corral, Lydden) or mainly chemical processes (e.g., Metiskow Lake).

Despite the great range of sediment types and hydrologic settings, the processes in these basins create a discrete suite of modern sedimentary facies. Although significant variations in the development of these facies do exist from basin to basin, a basic facies pattern common to most of the playas in western Canada can be recognized. An outer shoreline/nearshore complex, comprising colluvium, mudflat/sand flat, and beach facies, grades basinward into a pan complex. This basic pattern shares many of the same features recognized by Renaut and others in British Columbia (Renaut and Long, 1989; Renaut, 1994; Renaut and Stead, 1994a, 1994b; Renaut et al., 1994) and is broadly similar to the facies distributions in playas in Spain (e.g., Pueyo Mur and Inglés-Urpinell, 1986; Ordóñez, et al, 1994).

The colluvium facies consists of a chaotic mixture of coarse to fine detrital material derived from the adjacent glacial deposits by mass wasting and creep. The mudflats and sand flats are characterized by a mixture of sandy to silty detrital sediments often capped by efflorescent crusts and occasionally hardgrounds. Unlike efflorescent crusts on mudflats in playas elsewhere (e.g., Australia, southwestern United States), these crusts are not monomineralic. They usually consist of a complex mineral assemblage of both hydrated and anhydrous Na, Na+Mg, and Ca sulfate and sulfate-chloride salts (Keller et al., 1986a, 1986b; Last, 1989a). In some basins carbonate hardgrounds and crusts are also present. The mudflat/sandflats are areas of active shoreface and beach processes during seasonally high water levels, but for much of the year evaporation is the dominant process. Intense evaporation during the warm dry summer months results in upward capillary movement of shallow groundwater, ionic concentration, and intrasedimentary and crust mineral precipitation. Once efflorescent crusts have formed, further evaporation is hindered, and the mudflats can maintain a high moisture content throughout the dry season.

In some basins the mudflats are colonized by extensive areas of vegetation and cyanobacterial mats. The sediments in these areas are distinctively laminated (Last and Vance, 1997), organic-rich, and often sites of intense carbonate mineral genesis and diagenesis. Many of the more exotic carbonate mineral species found in the Great Plains (e.g., hydromagnesite, psuedohydromagnesite, kutnahorite, siderite, tychite, huntite) have been identified in these biolaminated algal flat sediments. To date, the biology and biogeochemistry of these mats have undergone only cursory examination (Lieffers, 1981; Slezak, 1989; Lyons et al., 1991).

The salt pan complex usually comprises over 50% of the playa basin. Depending on weather and drainage basin conditions, it can covered by brine for much of the ice-free period, but is often exposed by late summer or early fall. Overall, the facies is usually characterized by high endogenic to detrital sediment ratios, although a complete gradation exists from salt

dominated to mud dominated pans. The most distinctive feature of the pan facies is its annual cycle (Lockhart, 1983; Last, 1984a, 1989b). During spring, relatively dilute inflow from melting snow and rainfall can dissolve much of the very soluble salt that was precipitated in the pan during the previous dry episode. This results in a rapid increase in water salinity and dramatic changes in ion ratios. These brine compositional changes drive many of the penecontemporaneous diagenetic reactions (Egan, 1984; Last, 1992b). Throughout the summer, brine salinities continue to increase due to evaporative concentration. As discussed above, even relatively minor diurnal temperature changes will cause massive salt precipitation and dissolution. If brine remains in the basin after the onset of freezing conditions, considerable thicknesses of salts can occur due to freeze-out precipitation.

Several subfacies can be recognized in most playa pans on the basis of mineralogy and crystal morphology (Last, 1989b). Near the margins where pan sediments interfinger with the mudflat/sand flat facies, a zone of large dog-tooth mirabilite crystals develop. These crystals grow displacively downward into the soft, water-saturated mudflat sediments. Further basinward the floor of the pan usually consists of a mosaic of large, interlocking, bladed crystals. The specific sulfate and/or carbonate mineralogy is controlled by the cation content of the brine and the diurnal and seasonal temperature fluctuations experienced. Warm temperatures favor species such as thenardite, hexahydrite, anyhydrite, and thermonatrite; cooler temperatures encourage mirabilite, epsomite, natron, and gypsum.

Superposed on these salt pan evaporites or clastics can be zones of mirabolites and/or sediments associated with spring openings. Mirabolites are rounded accretionary grains (analogous to carbonate pisolites) composed of Na₂SO₄ · 10H₂O or MgSO₄ · 7H₂O that form in the shallow, supersaturated, and wind agitated brine. These mirabolites can be moulded into bedforms, shoals, and ridges on the pan surface or form beach deposits on the marginal mudflats. Spring openings are often sites of very rapid and massive salt mineral precipitation because these are areas where water of different temperatures and compositions mix. Frequently the springs continue to discharge onto the playa floor to form large, low mounds and ridges after the pan has been completely desiccated (see extensive descriptions of these large salt and mud mounds in Cole, 1926, 1930).

In summary, present-day sedimentation in the playa basins of the Canadian Plains region is controlled by the interplay of: (i) flooding of the playa which causes dissolution of soluble minerals of the salt pan facies and efflorescent crusts of the mudflat and sand flat facies; (ii) evaporative concentration of the brine which results in supersaturated conditions and precipitation of various soluble and sparingly soluble salts; (iii) detrital influx by streamflow, wind, and spring discharge; and (iv) organic productivity. In addition, evaporative pumping of shallow groundwater in the mudflats and sand flats causes growth of intrasedimentary displacive and poikilitic salt crystals in the near-surface clastic sediment.

In contrast to this complex assortment of interrelated sedimentary mechanisms operating in the playa basins, deposition in the perennial lakes appears to be controlled by a much smaller array of important processes (Brunskill and Graham, 1979; Last, 1994a). Most of these processes, such as shoreline erosion and deposition, wave and current distribution of sediments, river inflow and deltaic sedimentation, pelagic fallout sedimentation, and slumping, turbidity flow and interflow, are basic sedimentological processes common to any aqueous medium. Numerous papers and compilation volumes already provide excellent summaries of these processes in perennial lakes (e.g., Sly, 1978; Håkanson and Jansson, 1983; Lerman et al., 1995; Talbot and Allen, 1996), as do most current introductory geoscience textbooks (e.g., Friedman et al., 1992; Boggs, 1995; Prothero and Schwab, 1996). However, several processes are either unique to the perennial basins of western Canada or are of such fundamental importance that they will be introduced here briefly.

One of the most critical of these processes is development of stratification of the water column. The influence of seasonal temperature stratification on carbonate mineral saturation and equilibria in these lakes is well known (Last and Schweyen, 1983, 1985; Last, 1984b). The superposition of thermal stratification on an already chemically stratified (meromictic) water column greatly complicates mineral precipitation-dissolution reactions. For example, in Deadmoose Lake both evaporitic and biogenically-induced carbonate precipitation occurs in the upper, well mixed epilimnion. Much of this carbonate material, however, is dissolved upon passing through the thermocline into the anoxic, lower pH water of the hypolimnion, such that modern carbonate-rich muds are found only at water depths of less than 8 m (Boden, 1985; Last and Slezak, 1986). In contrast, gypsum precipitation occurs in the water column below about 12 m depth and is preserved in the sediments of the monimolimnion. Although the surface waters become supersaturated with respect to CaSO₄ · 2H₂O during the winter and gypsum precipitation occurs, sediment trap data indicate this gypsum is re-dissolved before reaching the chemocline (Last, 1994b). Similarly, mirabilite precipitation occurs at the chemocline and in the surface water during winter. However, it is only preserved in the sediments of the monimolimnion at water depths of greater than 20 m. Although this inhomogeneity can be relatively easily modeled once sufficient details are known about the chemical budgets of the stratified brine (e.g., Sloss, 1969; Schmalz, 1969; Imboden and Lerman, 1978), any interpretation of the stratigraphic record is made much more obscure because even subtle chemical and/or temperature changes can result in substantial changes in mineral precipitation and preservation.

Two other important aspects of deposition in these perennial lakes of the Great Plains are the generation and accumulation of deep water soluble salts, and the extraordinarily high rates of sedimentation experienced by some basins. Many of the non-playa lakes in the region are characterized by either mixed endogenic-allogenic sediments or entirely allogenic deposits (Last and Schweyen, 1983). However, it has been shown that in some basins soluble and sparingly soluble salts are forming in deep water, offshore environments (Boden, 1985; Slezak, 1989; Last and Slezak, 1987b; Sack, 1993; Last, 1993b, 1994b; Sack and Last, 1994). Sedimentologists have recognized for some time there are very few examples of modern sedimentary environments in which deep water evaporite mineral formation is occurring. This paucity of modern deep water settings is problematic because many ancient evaporitic sequences have been interpreted as forming in deep water (Kendall, 1984; Peryt, 1987; Warren, 1989). Thus, the perennial lakes in the Great Plains in which deep water salts are forming today provide a critical analogue in helping to understand the sedimentology, geochemistry, and stratigraphy of these ancient deposits.

Deadmoose, Little Manitou, and Freefight Lakes all have soluble evaporite minerals forming and accumulating in their deep, offshore areas. Subaqueous salt precipitation by freezeout mechanisms have been reported from other lakes in the region (Cole, 1926; Hammer, 1978b; Last and Schweyen, 1983), but presumably these salts are seasonal and re-dissolve during the ice-free period or during annual overturn of the water column. Both Deadmoose and Freefight are hypersaline and meromictic, whereas Little Manitou experiences 'temporary' meromixis. All three lakes are dominated by sodium, magnesium and sulfate ions, but the mineralogy of the modern offshore precipitates is somewhat different in each lake as controlled by the specific ionic ratios in the brines. The mechanisms by which these salts form also vary. As outlined above, the diurnal and seasonal temperature fluctuations of the mixolimnions in Freefight and Deadmoose Lakes and the elevated salinities of their monimolimnions lead to a complex multi-site source for the precipitates within the water columns of each basin. In Little Manitou, which is considerably shallower than Freefight or Deadmoose, it appears that brine mixing associated with both subaqueous spring discharge as well as aperiodic breakdown of the chemically stratified water column initiates precipitation.

In addition to the occurrence of these deep water salts, the rate at which they are accumulating is extraordinary. For example, sedimentation rates at the sediment-water interface in the deepest part of the basin in Freefight Lake have averaged nearly 30 kg m⁻² yr⁻¹ over the past 15 years. Although it must be emphasized that this these data are determined by sediment traps and therefore do not represent net accumulation, nonetheless the stratigraphic sequence recovered in the offshore areas of the basin similarly suggest linear accumulation rates of more than of 2 cm yr⁻¹. As discussed by Holser (1979), Warren (1989) and Einsele (1992), such high rates of chemical sedimentation should be expected in an evaporitic regime. However, until the discovery of these salt lakes in western Canada, such rates were not adequately documented in modern deep water environments.

Several facets of this offshore, deep water precipitation should be emphasized. Firstly, although the mechanism of precipitation in all the basins appears to be temperature driven, in fact crystallization ultimately depends only upon evaporation (or more precisely, the ratio of inflowing water to evaporation). Mineral genesis will continue as long as the climatic/hydrologic regime in each basin maintains the present P/E. Any positive increase in the hydrologic budget of these lakes (i.e., any combination of increased runoff, increased meteoritic precipitation, or decreased evaporation) will terminate mineral formation. If, however, the current hydrologic budget is maintained for some time (approximately 500 years in the case of Freefight Lake) precipitation will also cease due to shallowing of the basin and breakdown of meromixis. Secondly, once thermodynamic saturation (or supersaturation) has been reached by evaporative concentration of the brines in these basins, the high rates of mineral formation and deposition, and the relative abundances of the various salts are controlled by the striking differences in solubilities of the minerals within the ranges of temperatures experienced by the brine. In other

words, the amount of salt precipitated (i.e., sedimentation rate) is controlled by the temperature differences rather than the specific mineral solubility.

6. THE SPECTRUM OF EVAPORITES IN THE SALT LAKES

"Sodium sulphate is said to have been known as a secret medicine as early as the middle of the 16th century but the credit of its first description rests with J. R. Glauber who described it in his treatise De Natura Salium, 1658. He ... called it sal mirabile on account of its ascribed medicinal virtues. Probably the first use of sodium sulphate was for medical purposes, it being employed as an aperient." (Cole, 1926)

Of the approximately 1000 basins in the northern Great Plains for which water chemistry has been documented, we have knowledge of the sediments in less than a quarter of these. Similar to the early brine composition work, initial sedimentological efforts on these lakes (e.g., Cole, 1926; Grossman, 1949, 1968; Binyon, 1952; Tomkins, 1953, 1954) stressed the dominance of sodium sulfate salts and were directed mainly toward basins with large reserves of economically important industrial minerals. We now realize that the lakes exhibit a complete spectrum of sediment types, from basins dominated by allogenic or clastic material to those in which relatively pure, clastic-free evaporites are forming.

The evaporite minerals found in the modern surficial sediments of the salt lakes are listed in Appendix B. Sulfates and evaporite-related carbonates dominate the modern endogenic component of most of the basins, although more rarely silicates and chlorides have been identified. Our limited knowledge of the postglacial sequences in these evaporitic basins reveals a much more diverse mineral assemblage.

Four basic types of evaporite mineral occurrences can be differentiated on the basis of stratigraphic and genetic criteria: (a) crusts and hardgrounds, (b) massive and bedded salts, (c) spring deposits, and (d) subsurface and groundwater-related accumulations.

6.1 CRUSTS & HARDGROUNDS

Surface efflorescent crusts and hardgrounds are mineralogically and texturally the most complex occurrences of salts in the region. Efflorescent crusts (Figure 6.1) are found associated with virtually all of the salt lakes but can also form on hillsides and in other non-lacustrine depositional settings. When associated with the salt lakes they are most frequently found covering the marginal mudflats and sandflats of the basins. They are usually thin (1-5 mm), but can vary greatly from less than a millimeter to several tens of centimeters in thickness. The exposed surface is the crusts are often soft, friable and ragged, and easily eroded by wind and rain-wash. Internally, the thicker crusts are very porous and often quite hard.



Figure 6.1 Example of efflorescent crust with a complex mineralogy (Corral Lake, Saskatchewan).

Unlike the monomineralic efflorescent crusts reported from salt lake environments elsewhere (Eugster and Hardie, 1978), the crusts of the northern Great Plains' lakes are seldom composed of only one evaporite mineral. In any single salt efflorescence associated with the lakes, a variety of Na and Mg sulfates can commonly occur. Mineralogical characterization of these crusts is further complicated by seasonal changes brought about by the dramatic temperature and humidity fluctuations throughout the year, which significantly affect mineral solubilities (Keller et al, 1986; Timpson et al, 1986; Timpson and Richardson, 1986).

Hardgrounds or lithified surface crusts are not as common as efflorescent crusts in the salt lakes of the Great Plains. Where they do occur they tend to be thin and easily broken up into small cm-sized plates. These plates can then be re-cemented to form lithified breccias. Both cemented and uncemented coarse clastic units composed mainly of fragmented hardgrounds occur as modern shoreline deposits in the lakes and have been reported from the mid-Holocene of Waldsea and Deadmoose lakes in central Saskatchewan (Last and Schweyen, 1985; Last and Slezak, 1986).

The most commonly precipitated cement in the hardgrounds is carbonate. Depending on the specific Mg/Ca ratio, sulfate content, and salinity of the pore water, these carbonate cements range from calcite and high magnesium calcite to aragonite, dolomite and, more rarely, magnesite. Similarly, crystal size and morphology are highly variable. In addition to carbonate cemented hardgrounds, surface crusts and lithified horizons composed of other authigenic precipitates such as gypsum and mirabilite occur in association with some of the salt lakes. The modern hardgrounds are not associated with any specific facies within the saline lakes. They have been found in both subaerial (exposed mudflats, sandflats, and beaches) and subaqueous (water depths from less than one meter to greater than 20 m) environments. It is evident that these hardgrounds are not all genetically related. Some appear to be formed by straightforward inorganic cementation due to evaporative concentration of pore water in the vadose environment. Others are obviously related to organic (cyanobacteria and blue green algae) processes, while still others may be forming in response to mixing of different water types or to pH-Eh changes at the sediment-water interface.

6.2 MASSIVE & BEDDED SALTS

Because of their importance as a source of industrial minerals, the massive and thickly bedded evaporites of the playas of the Great Plains have been extensively drilled and studied (Govett, 1958; Ruffel, 1968; Broughton, 1984; Slezak and Last, 1985). The salts which form this resource base are dominantly Na and Mg sulfates (mainly mirabilite, thenardite, and epsomite; Figure 6.2). In detail, however, the mineralogy of individual deposits can be quite complex. Other than indistinct bedding features, the salts record little original (primary) depositional fabrics or textures. They tend to be uniformly coarsely crystalline and equigranular, and show an interlocking crystalline mosaic texture. Individual crystals usually have few inclusions. Even in very muddy sections of the salt column the insoluble material is concentrated at the crystal boundaries, suggesting repeated dissolution-reprecipitation. Crude horizontal bedding in these otherwise massive salts is most frequently brought about by changes in concentrations of clays and other insolubles. In some cases bedding can also be due to compositional differences, changes in crystal morphology and orientation, or variation in degree of compaction and crystal intergrowth.



Figure 6.2 Example of massive, relatively pure salt from Ingebright Lake (from Shang, 2000).

These evaporites, which can attain thicknesses in excess of 45 m, are generally viewed as originating from shallow water, playa-salt plan environments. Recently, a second type of

depositional setting has been recognized - the deep, meromictic salt lake. While it has been known for some time that many perennial salt lakes of the region exhibit massive Na and Mg sulfate mineral precipitation due to freeze-out phenomena (Rawson and Moore, 1944; Hammer, 1978), it has been tacitly assumed that these soluble salts were put back into solution upon warming of the lake brines during summer. Indeed, this type of freeze-out precipitation - resolution does seem to be operating in many of the "intermediate" depth (1 to 3 m) perennial salt lakes of the region today (Table 3 in Last and Schweyen, 1983). However, in some of the deeper lakes and particularly in hypersaline meromictic basins, seasonal salt precipitation does occur but not all of the precipitate is re-dissolved, thereby giving rise to a deep water, subaqueous salt accumulation.

Compared to the shallow playa basin salts, relatively little is known about these deep water deposits. Freefight, Deadmoose, and Little Manitou lakes all have deep water salt deposits. We will be visiting each of these during the next several days. In contrast to deep water gypsum and halite accumulations reported elsewhere, the Na and Mg sulfate salts that are accumulating in these deep lakes are coarsely crystalline and only poorly bedded. Individual euhedral crystals up to 10 cm in diameter have been retrieved from the modern bottom sediment at depths greater than 20 m in Freefight and Deadmoose lakes. From limited core recovery, these evaporites exhibit both large scale, indistinct bedding and irregular fine lamination. The coarse banding, represented by regular cm-scale alteration of light and dark coloured crystal, is due to variable mud and organic matter contents. The fine, irregularly spaced laminae are composed mainly of organic debris and clay minerals with minor gypsum and aragonite.

In addition to these very soluble salts, some of the deep saline lakes also contain a variety of evaporite-related sparingly soluble carbonate and sulfate minerals. Precipitation of calcite and high magnesium calcite due mainly to evaporative concentration is well known from numerous lakes in the region (Callender, 1968; Last, 1981; Forbes and Hickman, 1981; MacDonald, 1982; Ghebre-Egziabhier and St. Arnaud, 1983a and b; Hickman et al, 1984). The generation of mm-scale aragonite-organic clay couplets in Waldsea and Deadmoose lakes have been attributed to periodic carbonate whitings in lakes of moderate salinity (40-60 ppt TDS). In contrast, the gypsum-carbonate laminae (which include aragonite, magnesite, and dolomite) in these two lakes probably originated from brines of considerably higher salinity (Last and Schweyen, 1985; Last and Slezak, 1986).

Post-depositional modification of these massive and bedded salts appears to have been extensive but little work has been done to document the diagenetic processes. Large scale salt solution and karsting has been identified in numerous basins (Cole, 1926), as has mud diapirism (Last and Slezak, 1987a). On a smaller scale, diagenetic alteration and replacement of metastable hydrated salts (often with equally metastable minerals) is common (Schweyen, 1984).

6.3 SPRING DEPOSITS

Although not strictly evaporites, travertine and tufa deposits do occur in several saline lakes of the Great Plains. Unfortunately, one of the best occurrences/outcrops of a groundwater discharge buildup (tufa mound and terrace) along the eastern margin of Muskiki Lake in central Saskatchewan is no longer accessible. Large tufa deposits have also been reported from Metiskow Lake, Alberta (Cole, 1926). Last and Schweyen (1985) and Last (1987b) identified sections of the early and mid-Holocene sediment records in Waldsea and Ceylon lakes having tufa-like fabrics and microtextures.



Figure 6.3 Example of spring orifice salts, Ceylon Lake.

Somewhat more common than these carbonate mound and tufa accumulations are spring orifice and sheet-flood deposits composed of very soluble salts which occur in many of the salt lakes. Groundwater discharge is a very important component of the hydrologic budget of these saline lakes. Lake bottom springs are quite visible in most of the playa basins (Cole, 1926; Last, 1984) and equally evident in some of the perennial lakes. Because of temperature differences between the lake brine and the discharging groundwater, saline springs can build sinter-like ridges and large cones (up to 3 m high) composed of soluble Na and Mg salts. Similarly, cold freshwater springs entering a sodium or magnesium sulfate lake can cool the brine sufficiently to produce massive spring orifice deposits of mirabilite and epsomite (Figure 6.3). Finally, in a playa setting, if the springs remain active during winter, laterally extensive sheet flood deposits of soluble salts (mirabilite, epsomite, hydrohalite) can be precipitated on the frozen lake surface.

6.4 SUBSURFACE ACCUMULATIONS

Salt mineral precipitation in each of the previous three types of evaporite occurrences takes place either subaerially or within a saturated water column of the lake. Although the resulting mineralogies can be complex (as is the case for desiccation of near surface groundwaters to form efflorescent crusts), in general these precipitates form rapidly and do not require any unusual mechanism other than simple evaporative concentration. A final type of evaporite mineral accumulation associated with the salt lakes occurs in the subsurface. Unfortunately, relatively little is known about the characteristics and genesis of this type of occurrence. There appears to be a gradation from single, isolated, salt crystals growing displacively in the unconsolidated clastic sediments of playa mudflats to thick, laterally continuous beds of salt underlying entire basins.

Individual intrasedimentary crystals can vary in size from less than a micron to magnificent blocky to pyramidal crystals up to 10 cm in length. Occasionally clusters or pockets of crystals can be found, but most often they occur individually scattered throughout the muddy matrix. The mineralogy of these salts is dominated by mirabilite-thenardite, epsomite, and bloedite, although more rarely other precipitates can be found including scarbroite, dawsonite, kieserite, burkeite, and halite. Our knowledge of the vertical and lateral mineralogical distribution of these intrasedimentary salts is still incomplete. In Lydden Lake, a small salt playa in central Saskatchewan that we will visit, gypsum seems to be concentrated in the mudflat sediments at the basin margins, whereas the more soluble sulfates decrease in abundance with increasing depth until at about 5-6 m the muds are dominated by carbonate minerals and allogenic components (Lockhart and Last, 1984).

At the other end of the subsurface spectrum, laterally continuous and, in some cases, thick "sheets" of salts can be found within the stratigraphic sections of many of the playas of the region. These extensive, sheet-like accumulations differ from the previously described subsurface intrasedimentary salts in several ways: (i) They are always composed mainly of mirabilite with few other ancillary evaporites. (ii) The deposits are usually clastic-rich; insoluble contents can be as high as 85%. (iii) The salt is compact and hard, and shows a poikilotopic fabric. (iv) The upper surface of the accumulation usually occurs between 0.5 and 1 m below the surface of the playa and is constant across a given basin.

These subsurface salt beds can be in excess of 2 m thick and sometimes extend laterally beyond the margins of the present-day lacustrine basin. They appear to be relatively common in the lakes of the Great Plains, but mapping of these features is difficult because of the lack of any surface indicators. Of the 25 sodium sulfate deposits described by Cole (1926), only four contained subsurface salt beds. In contrast, our reconnaissance drilling of mud-dominated playas in the Tompkins-Verlo area of southwestern Saskatchewan showed 8 out of 12 basins examined had this type of accumulation. Similarly, data supplied by Grossman (1949) and Binyon (1952) suggest that many of the playas in North Dakota have buried salt deposits. The genesis of this mode of salt occurrence is not yet resolved. It is possible that the subsurface salt units were

formed at the surface of a playa and subsequently buried by non-evaporitic playa muds. Alternatively, these salts may represent precipitation associated with a particular water table level or groundwater condition. Finally, the possibility that they are the result of illuviation by downward percolating playa waters must be considered.

6.5 PROCESS-PRODUCT CONTINUUM IN SALT LAKES

The salt lakes of the northern Great Plains offer an excellent opportunity to examine the processes of continental evaporite deposition and diagenesis on both a local and regional scale. However, as is the case with most other depositional settings, the salt lakes exhibit a continuous spectrum of sedimentary regimes. This continuum exists in terms of nearly every parameter that can be evaluated for the basins: morphology, hydrology, degree of permanence, brine salinity and ionic composition, sediment character, etc. This great diversity presents somewhat of a problem in studying and discussing the lakes.

In an effort to divide up the continuum, several "end member" types of salt lakes can be recognized. A fundamental distinction must be made between those basins whose brines are shallow enough to permit periodic drying and those whose brines are deep enough to maintain a relatively permanent water body. The most significant processes operating in the shallow intermittent basins (playas) include: cyclic flooding and desiccation of the playa surface, formation of salt crusts, efflorescent crusts, hardgrounds, spring deposits, and intrasedimentary salts, formation of solution pits and chimneys, and periodic detrital sedimentation by sheet flow and wind. These processes are discussed in detail in Last (1984 and 1987b).

In contrast, in the perennial lakes one of the most important features controlling sedimentation is stratification of the water column. The influence of seasonal temperature stratification on carbonate mineral saturation and equilibria in these lakes is well known (Last and Schweyen, 1983). The superposition of thermal stratification on an already chemically stratified (meromictic) water column greatly complicates mineral precipitation-dissolution reactions. For example, in Deadmoose Lake both evaporitic and biogenically-induced carbonate precipitation occurs in the upper, well mixed epilimnion. Much of this carbonate material however, is dissolved upon passing through the thermocline into the anoxic, lower pH water of the hypolimnion, such that modern carbonate-rich muds are found only at water depths of less than 8 m. In contrast, gypsum precipitation occurs in the water column below about 12 m depth and is preserved in the sediments of the monimolimnion. Although the surface waters become supersaturated with respect to CaSO₄ · 2H₂O during the winter and gypsum precipitation occurs, sediment trap data indicate that this gypsum is re-dissolved before reaching the chemocline. Similarly, mirabilite precipitation occurs at the chemocline and in the surface water during winter. However, it is only preserved in the sediments of the monimolimnion at water depths of greater than 20 m. Although this inhomogeneity can be relatively easily modeled once sufficient details are known about the chemical budgets of such a brine (Imboden and Lerman, 1978; Sloss, 1969; Schmalz, 1969), any interpretation of the stratigraphic record is made much more obscure

because even subtle chemical and/or temperature changes can result in substantial changes in mineral precipitation and preservation.

7. NOTES ON MIRABOLITES

Accretionary grains composed of mirabilite $(Na_2SO_4 \cdot 10H_2O)$ are a common occurrence in saline playas and shallow lakes of the northern Great Plains. They can be particularly abundant during the late summer and fall on the shores of many of the basins we will be visiting on this excursion. These particles, termed mirabolites, form on the floor of the basin when the overlying brine is supersaturated with respect to mirabilite and is shallow enough to permit windinduced agitation of the lake bottom. Once formed, the loose mirabolites can be molded into various bedform features including ripples, dunes, shoals, and beach ridges. The relatively large size (up to 4 cm diameter; Figure 7.1) and rough surfaces of the particles are consistent with the high viscosity of the saturated solution and the very small difference in density between the mineral and the brine. Although these accretionary grains and their sedimentary structures are easily destroyed by rain, wind, or subsequent higher water levels in the playa, preservation can occur, resulting in a distinctive lens-shaped deposit of relatively pure salt surrounded by clayrich mudflat sediments.



Figure 7.1 Mirabolites from Ceylon Lake.

7.1 CARBONATE ACCRETIONARY GRAINS VERSUS MIRABOLITES

The occurrence of spherical accretionary grains composed of calcium carbonate is widespread in a variety of modern environments including: shallow open marine settings

(Newell et al, 1960; Bathurst, 1975), hypersaline lakes and lagoons (Kahle, 1974; Risacher and Eugster, 1979; Freeman, 1962), freshwater streams and lakes (McGannon, 1975; Geno and Chafetz, 1982; Wilkinson et al, 1980), and subaerial exposure surfaces and caves (Esteban, 1976; Baker and Frostick, 1951). In contrast to the extensive literature on carbonate forms and textures, there is only a small number of references to non-carbonate primary accretionary grains in the modern record. Direct precipitation of phosphatic oolites has been reported to occur in shallow restricted lagoonal environments (Birch, 1980). Iron-rich oolitic and pisolitic grains can be found in modern lake and swamp sediments (Blatt et al, 1980). Weiler et al (1974) describe the formation of halite oolites (halolites) in the shallow near-shore areas of the Dead Sea.

7.2 THE MIRABOLITE GRAINS

Mirabilite pisolites and spherulites (termed mirabolites) have been found in the modern sediments of saline playas and lakes in the northern Great Plains region (specifically Ceylon, Coral, Lydden, Little Manitou, Vincent, Verlo, Sybouts, Ingebright, and Whiteshore lakes). These accretionary grains occur in a variety of sizes, with most ranging from 5 mm up to 15 mm in diameter. Most of the mirabolites are ellipsoidal to spherical, with occasional elongate and irregular forms. The surfaces of the grains typically exhibit a rugose to coarsely blocky, platy, or bumpy texture; rarely are the grains smooth. Most of the accretionary grains are relatively fragile and can be easily crushed by hand. Some, however, are quite stable and are capable of withstanding shallow burial (to 3 m) with deformation.

A variety of internal structural morphologies and fabrics are present in the mirabolites. Most of the grains examined have a nucleus composed of a single mirabilite crystal. Other nuclei include allochthonous sand-sized quartz and carbonate grains, gypsum and calcite crystals, organic debris, and mud clasts. Some of the grains lack any observable nucleus. The individual mirabilite crystals making up the accretionary grain are usually unoriented with respect to the center. Occasionally, a very indistinct tangential arrangement of crystals has been observed. Concentric lamination is not present.

Although mirabolites can occur over the entire subaqueous playa lake floor, they are usually found in greatest concentrations in the shallow nearshore areas. Wave action along the shoreline creates beaches, bars, and spits composed of mirabolites. Although these shoreline features are frequently destroyed by rain and wind, in some cases preservation has occurred creating a lens of salt up to several tens of centimeters thick within the clastic mudflat sediments.

In addition to shoreline accumulations, the mirabolites can be found concentrated as offshore bars and shoals. When present, these subaqueous deposits are low relief (25-50 cm), relatively narrow (5-15 m), and very well-sorted accumulations. Most offshore bars examined show a decrease in grain size from coarsest particles at the crest to finer particles at the margins. Small wave and current ripples often cover the surface of the offshore bars.

7.3 HOW & WHY DO THEY FORM?

Crystallization of Na₂SO₄ 10H₂O in the salt lakes and playas of the northern Great Plains takes place in several ways: (a) as large dendritic crystals and aggregates in the lake floor; (b) in the form of encrustations, sinter-like ridges, and platforms; and (c) as hoppers and acicular crystals at the brine surface. In a calm water and low wind situation, the floating hoppers and crystals enlarge and coalesce to form rafts which eventually sink to the bottom or are grounded on the lake's edge. In windy conditions, however, the floating crystals are quickly mixed into the brine and, with continued agitation in the supersaturated brine, rapidly accrete by further mirabilite growth around the original crystal. Non-mirabilite grains such as gypsum and quartz, derived from agitation of the lake bottom sediment, also serve as nuclei.

The distinctive solubility and crystallization properties of sodium sulfate play a major role in the process of mirabolite formation. Because mirabilite shows a very strong positive temperature coefficient of solubility, both diurnal and seasonal temperature changes are extremely important. Once the brine is concentrated by evaporation to the point of saturation, massive mirabilite precipitation can readily occur with only a slight drop in temperature. Thus, active mirabolite formation is most often observed during the late summer-fall season and during late afternoon-evening hours when lower temperatures give rise to supersaturated brine conditions.

Similar to the halolites of the Dead Sea (Weiler et al, 1974), the mirabilite accretionary grains are much larger than CaCO₃ ooids. This is most likely due to the combined effects of: (a) a much smaller density difference between the mineral and the precipitating solution, and (b) less grain abrasion caused by the higher viscosity of the concentrated brines. The small density difference between mirabilite (1.49 g cm^{-3}) and the brines $(1.15 - 1.30 \text{ g cm}^{-3})$ means that the accretionary grains in these lakes have smaller equivalent diameters, implying that the mirabolites can attain a larger size for a given current velocity relative to normal marine water and aragonite ooids. Furthermore, the viscosity of a saturated Na-SO₄ solution at 20°C is approximately twice that of normal sea water. Thus, it is reasonable that there is less physical abrasion by grain interaction in the hypersaline brines relative to the marine setting, resulting in the generation of larger accretionary particles.

8. ECONOMIC ASPECTS OF THE LAKES

"The brine...is ladled into the kettles, and the salt scooped out as it forms, and allowed to remain for a short time to drain before it is packed in birch bark roggins for transportation to Red river, where it commands twelve shilling sterling a bushel.... The brine is very strong. From one kettle two bushels of salt can be made in one day in dry weather." (Hind, 1861)



The lakes and wetlands of the northern Great Plains serve a great variety of uses. Many studies have documented the importance of these terrestrial environments on surface runoff and flow stabilization, erosion control, waste assimilation, agriculture, irrigation, and wildlife habitat (see, for example, Waite 1980, 1986; Adams 1988; Batt et al., 1989; Richardson and Arndt 1989; Wood, 1996; Environment Canada, 1997). One of the most important economic aspects of the lakes is they are a source of

valuable industrial materials, minerals, and compounds.

Exploitation of the lakes in western Canada probably started well before the arrival of Europeans. Journals and diaries of nineteenth century European settlers commonly refer to Aboriginal use of the lacustrine salts and brines for medicinal purposes, tanning, and food preservation. These salts also provided the basis for several of the earliest commercial industrial efforts on the northern Great Plains (Hind, 1861; Cole, 1930). Large scale mineral production (Figure 8.1) from the lakes began in 1918 with the extraction of magnesium and sodium sulfates and carbonates from Muskiki Lake (Cole, 1926). Production of anhydrous sodium sulfate (salt cake) from some 20 different lakes gradually increased over the next five decades to a high of approximately 700,000 tonnes in 1973. Today, the 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 artificial byproducts from various manufacturing processes. A large increase in the price of salt cake during 1973-1975 (from \$15 to \$48 tonne⁻¹) and again during 1980-83 (from \$62 to \$108 tonne⁻¹) saw renewed interest in leasing and mining activities in the region during these periods. Despite softening markets and production declines during the last several years, price stabilization at about \$90 tonne⁻¹ has lead to an average of over \$40,000,000 worth of sodium sulfate produced annually from the lakes (Figure 8.2)

Historically, the two largest uses of sodium sulfate have been in producing kraft paper and allied products, and in the manufacture of detergents (Broughton, 1984; Murphy, 1996). More recently, however, the energy industry has been consuming larger amounts of the salt by its use as a conditioner to facilitate fly ash suppression in coal burning power plants (Tremblay, 1984). Another new use of salt cake is in the manufacture of potassium sulfate by the reaction of Na₂SO₄ with KCl (Barry et al., 1985; Barry, 1986; Eatock, 1987). Other potentially significant applications include use in glass, ceramic, and paint manufacture, and in solar energy collectors.



Figure 8.1 Sodium sulfate mining, Saskatchewan.



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(baking soda; Cole, 1926; Templeton, 1968; Alberta Sulfate Limited, 1981), and sodium chloride (Cole, 1930). Finally, coarse clastics (sands, gravels) deposited on beaches, along shorelines, and in deltas of both proglacial and modern lakes are utilized by many of the urban communities in the region (e.g., James F. MacLaren Limited, 1980; Groom, 1985; Mollard and Mollard, 1987).

Figure 8.2 Historical production and value of sodium sulfate from lake in the northern Great Plains (modified from Last 1991a)

9. SALT LAKE PALEOLIMNOLOGY IN THE NORTHERN GREAT PLAINS

"It has long been my feeling that when a geologist gets into trouble, he changes the climate." (Beaty, 1971)

9.1 INTRODUCTION

Because of the great diversity in lake types, brine chemistries, and depositional processes, the sediments in these basins offer a tremendous opportunity to examine past environmental conditions and changes in the region. Despite the sensitivity of these deposits to environmental change, interpreting the records in terms of paleoclimate, hydrology, and chemistry is fraught with difficulty. Factors that complicate these interpretations include: diagenesis of the evaporites, post-depositional physical disruption of the sediments, and a lack of proper understanding of the depositional processes operating in lakes of this type. Furthermore, an active and growing industrial minerals industry based on the deposits of the salt lakes has obliterated, and will likely continue to adversely affect, the stratigraphic records of some of the salt lakes provide the best and, in some cases, only record of past environmental conditions in this semi-arid region. Paleolimnology in the northern Great Plains is poised for a rapid expansion, fueled by the combination of significant technological breakthroughs, improvements in methodology, and a more positive view of the importance of paleolimnological research in environmental management.

At nearly any time during the last several decades it was commonly stated that "*the past few years have witnessed the most explosive growth in interest and research in paleolimnology seen to date*". Accepting Frey's (1988) definition of paleolimnology as "*the interpretation of past limnology from changes that occurred in the ecosystem of the lake, and their probable causes*", there, indeed, can be little argument that this multidisciplinary science has undergone, and is continuing to experience tremendous progress. Paleolimnology has emerged from the past several decades to form an important and even pivotal role in applied limnology and natural resource management. As outlined by Smol (2002) and Smol and Cumming (2000), much of this striking advance of paleolimnology can be directly related to the great surge of interest in lakes from an environmental perspective.

However, not all areas of paleolimnology have experienced this rapid and sustained level of activity. Despite the fact that salt lakes occur on every continent and, on a global basis, contain nearly the same volume as fresh water lakes and rivers combined, the paleolimnological literature of salt lakes is small compared to that of fresh water environments. About 15 years ago, Hammer (1986) remarked: "*Extensive palaeolimnological studies have been carried out although the effort spent on saline lakes has been minimal except in Australia and the United States*." (p. 165). With some exceptions, this statement is still true today!

At first glance, this deficiency seems incongruous: because saline lakes often occupy topographically-closed basins, they should provide the most detailed physical and chemical

paleoenvironmental records of all terrestrial environments. Unfortunately, the very aspects that make salt lake sediments so potentially attractive for paleolimnological, paleohydrological, and paleoclimatic analyses also give rise to significant interpretation problems.

We have repeatedly emphasized the great number of lacustrine basins and diversity of lake types within the 350,000 km² region of the northern Great Plains of western Canada. The comments and discussion in Sections 4-6 emphasize the features of the Great Plains that are of major importance to the occurrence of the salt lakes and briefly summarize the lakes' key sedimentological and geochemical characteristics that make them so attractive to paleolimnologists. To re-emphasize these major points: (i) The northern Great Plains is a large semi-arid to arid region in which geology, climate, and hydrology have interacted to form many saline lakes. (ii) Although there is a wide spectrum of basin morphologies, sedimentary characteristics, and water compositions and concentrations, the modern lakes can generally be pigeon-holed into one of several basic types. (iii) The level of understanding of the physical, chemical, and biological processes operating in these lakes, and the resulting sedimentary facies in the basins, has advanced considerably in the past decade but is still incomplete and uneven.

Our intent in this section is to discuss some of the more serious difficulties that must be faced in attempting to interpret the Quaternary stratigraphic records of the basins and to highlight future paleolimnological research directions and opportunities in this region. Importantly, this is not intended to be either a review or synthesis of salt lake paleolimnology in the Great Plains; numerous other publications have already done this (e.g., Last and Slezak 1988; Teller and Last 1990, Last, 1992, 1994; Vance and Last, 1994; Vance et al., 1995; Fritz, 1996; Sauchyn, 1997; Last and Gosselin, 1997). Finally, the emphasis of our comments here and on the field excursion is from a geoscience perspective; much of Smol's (1990; and Smol and Cumming, 2000) discussion on recent advances and future developments of biological paleolimnology are very much applicable to the study of the lacustrine records in the Great Plains.

9.2 MINING INDUSTRY ACTIVITY

Although mining of the valuable industrial minerals from the salt lakes occurs in various ways, the end result of the extraction process(es) on the basin is, from the standpoint of paleoenvironmental research, overall undesirable. Because the lakes that are the most economically attractive for mineral exploitation are often also those whose sediments provide some of the best evidence for geochemical and brine compositional changes through time, the mining of nearly forty of the salt lakes, and the likelihood of expanded mining efforts in the near future, becomes a major concern for paleolimnological work in the Great Plains. At present, the lakes affected by mining are all playa basins. This may not be the case in the future; several perennial, deep water lakes in the region have salt reserves which rival that of the playas.

9.2.1 Metiskow Lake Example

An example of irretrievable loss of valuable paleolimnological data due to mining activities is that of Metiskow Lake, Alberta. The economic potential of Metiskow was first recognized by Cole (1926) who calculated a sodium sulfate reserve in the lake of about five million tonnes. Cole (1926) also suggested that Metiskow was unusual in that its hypersaline brine was dominated by carbonate ions rather than sulfate. Subsequent drilling and bulk chemical analyses of the sediments in the lake by various companies during the 1960's confirmed that the 17 meter thick lacustrine salt sequence contained some 250,000 tonnes of sodium carbonate in addition to the large sodium sulfate reserve.

Before mining operations obliterated the stratigraphic record in the basin, Wallick and Krouse (1977) and Wallick (1981) were able to decipher the groundwater flow and likely water-rock chemical reactions that gave rise to this unusual deposit. These two studies, as important as they are in providing quantitative information on the source of the salts, merely serve to accentuate the tremendous potential of the paleolimnological record in Metiskow. The basin contained a thick sequence of alternating sodium carbonate salts, sodium and calcium sulfates, and detrital material; similar mineral assemblages have been used very effectively in other salt lake sequences to reconstruct the details of paleohydrochemical conditions and changes (e.g., Eugster and Smith 1965). The magnitude of this lost opportunity is further emphasized by the report of a single ¹⁴C date of 10,250 yr BP (Wallick 1981) from the base of the salt section, which indicates that Metiskow was one of the few saline lakes cored in the region to date that may have provided a complete record of Holocene and late Pleistocene environmental change.

9.3 POST-DEPOSITIONAL CHANGES

Numerous summary and overview papers have already stressed the susceptibility of salt lake sediments, particularly evaporites, to post-depositional changes. In the salt lakes of the northern Great Plains, three major types of diagenetic alteration have been documented: (i) saline mineral diagenesis; (ii) salt dissolution and karsting; and (iii) diapirism. As a generalization, the playa basins are most prone to post-depositional changes because of the periodic desiccation and subaerial exposure. However, as shown in many examples elsewhere, diagenetic alteration under subaqueous conditions can be equally severe.

9.3.1 Mineral Diagenesis

"The other day, as I will swear I saw some salt that wasn't there. It wasn't there again today -How do I prove it went away?" (John Van Couvering; quoted in Schreiber, 1978 p. 61) Evaporites of salt lakes of the Great Plains have a distinct and characteristic mineralogy. It is this mineralogy that can be so useful in helping to decipher paleochemistry of the brines and paleohydrology of the basins (Teller and Last 1990). Regardless of precisely how a certain evaporite formed (e.g., by "simple" concentration of lake water via isothermal evaporation, by a temperature increase or decrease of the brine, by mixing of brines of different compositions, by biologically-induced precipitation, etc.), the presence of that particular salt mineral in a stratigraphic sequence implies the formative brine was saturated (or supersaturated) with respect to that precipitate. Thus, a given suite of evaporite minerals can be used to calculate, in considerable detail, the thermodynamic conditions of the evaporating solution (e.g., Shang and Last, 1999). Problems arise, however, if it cannot be assumed that the minerals are either endogenic or at least very early diagenetic (formed essentially at the sediment-water interface). In many salt lakes, very dense, hypersaline surface brines can percolate downward into subsurface sediments. Because these dense brines are late stage residual products, they often have dramatically different chemical compositions than the normal lake or groundwater. The ability of these descending brines to radically alter the original mineral composition of large sections of the subsurface sediments has been well documented (Sonnenfeld 1984; Warren 1989).

9.3.2 Salt Dissolution and Karsting

In addition to conversion of one evaporite mineral to another, undersaturated groundwater or surface water can completely dissolve the most soluble components of the stratigraphic record of a salt lake. The formation of deep karst chimneys and large dissolution pits is occurring today in numerous saline lakes in the Great Plains. For example, in Ceylon Lake, a salt-dominated playa that we will be visiting, saline karst chimneys (Figure 9.1) up to 9 m deep have been identified (Last 1989b). In Lydden Lake, another salt playa located west of Saskatoon, Saskatchewan, solution pits up to 30 m wide and 3 m deep are present. The occurrence of buried mud "mounds", highly irregular salt thicknesses, and abrupt compositional changes over short distances in some basins indicate that the process of salt removal has also taken place in the past. It is especially important to recognize this when attempting to interpret the stratigraphic record of the lakes because large vertical sections of the lacustrine sediment can be affected.



Figure 9.1 Example of a dissolution chimney, Ceylon Lake.

9.3.3 Mud Diapirism

Diapirism, or the process of piercing of an overlying geological unit by an underlying mobile core material, is a phenomenon commonly described in several modern and recent sedimentary environments. Mud diapirs, or mudlumps, are particularly abundant in birdfoot type of deltas, where, for example in the Mississippi River delta, they can penetrate 100 m of delta front sands (Coleman and Prior 1980). Features of similar origin also occur in saline lakes of the northern Great Plains (Last 1984). Although the precise mechanisms of the diapirism are not yet known, these features in the salt lakes are likely the result of instability brought about by the loading of a thick section of dense and non-permeable salt on top of relatively low density, water saturated lacustrine muds. This instability causes the muds to flow upward through the salt to the surface of the lake. At the surface, this clastic sediment is redistributed by wave action and incorporated into the modern deposits of the lake thereby leading to potential contamination.



Figure 9.2 Example of a mud diapir, Verlo Lake.

9.4 SEDIMENTARY & GEOCHEMICAL PROCESSES AND CONCEPTS

As discussed above, a complete understanding of the sedimentary processes operating in the entire spectrum of salt lakes of the Great Plains is still far off. Because virtually all geological interpretations of the stratigraphic records in these basins depend on a knowledge of the modern environments and modern sedimentary processes, it is important that these deductions be made with great care. Following are several of the more important, but unresolved "conceptual" problems that continue to obscure the interpretation of the paleolimnological record in these salt lakes.

9.4.1 Significance of Fine Grained Clastic Units

In a sedimentary basin strongly influenced by physical factors such as wind generated waves and circulation, currents, and river inflow, the distribution and character of the accumulating sedimentary material is controlled to a major degree by the level of energy at the depositional site. Thus, coarse grained sediments (sands, gravels) are generally interpreted to have been deposited under relatively shallow water, high energy conditions (for example a beach or delta), whereas very fine grained sediment (clay sized material) requires settling through a deep, essentially motionless water mass. As stressed by Sly (1978), Håkanson and Jansson (1983), and Teller and Last (1990), many other factors can interfere with this simple grain size-water depth-energy relationship, including flocculation of fine grained material, basin morphology, weathering and erosion characteristics of the watershed, and vegetation cover.

Thin beds and laminae of fine grained siliciclastic material commonly occur interbedded with evaporites in the stratigraphic records of the salt-dominated playas of the Great Plains. Their paleolimnological significance and sedimentological interpretation are particularly problematic. They may represent periods of relatively deep and fresh water conditions in which increased runoff from the surrounding watershed, due to a more humid climate, brought an increased influx of clastic material to the lake. Conversely, the fine silt and clay units could be residual products, the end result of dissolution and downward leaching of the salts due to prolonged desiccation of the playa and a lowered groundwater table brought about by a more arid climate. Finally, the fine clastics may have been deposited during periods of increased aeolian activity, also possibly associated with increased aridity.

9.4.2 Significance of Carbonate Mineralogy

Carbonate minerals are among the most common and also most useful inorganic constituents of lakes sediments. Many studies have documented the suitability of calcite and aragonite in paleolimnology (e.g., Kelts and Hsü 1978; Dean 1981; Eugster and Kelts 1983; Dean and Fouch 1983; Behbehani et al. 1986). The application of other carbonate mineral species, such as dolomite, magnesite, and siderite, which commonly occur in salt lake sediments, has been less widespread.

Based mainly on observational data provided by Müller et al. (1972), conventional wisdom holds that the mineral sequence of: low-Mg calcite Ψ high-Mg calcite Ψ aragonite Ψ dolomite Ψ magnesite/huntite reflects increasing Mg/Ca ionic ratios in the precipitating solution and, very likely, increasing salinities. Thus, it has become commonplace to use the stratigraphic variation of these species in a lacustrine basin to deduce past ionic ratios and salinity of the lake water (e.g., Last 1982; Last and Schweyen 1985). Unfortunately, there are many pitfalls associated with this cookbook approach. The application of the sequence to paleochemical interpretations implies that the minerals being used are endogenic precipitates. Talbot and Kelts (1986) provide an example of the complexity of the interpretations if any of the carbonate components are diagenetic in origin. It is often very difficult to distinguish primary endogenic
carbonates from either primary or secondary diagenetic precipitates. Furthermore, it is likely that other factors besides, or in addition to, Mg/Ca and salinity have a major influence on the specific carbonate species being precipitated. For example, both the alkalinity and the sulfate concentration of the water are thought to be key controlling factors in the formation of dolomite (Morrow 1982; Baker and Kastner 1981; Kastner 1986). Temperature of the solution, in addition to the Mg/Ca ratio, plays a major role in dictating how much Mg⁺² is incorporated into the calcite lattice in the formation of high-Mg calcite (Müller and Wagner 1978).

9.4.3 Importance of Saline Mineral Metastability

The two fundamental assumptions that allow paleolimnologists to deduce the composition of a brine from the mineral record preserved in the sediment are that: (a) the composition of the mineral suite has not been significantly altered by post-depositional changes, and (b) the mineral suite that is ultimately preserved is a true reflection of the water composition that existed in the basin at the time of deposition. Problems associated with (a) have been discussed above. If the salt lake is viewed simply as a container of water in which relatively dilute inflow is concentrated by evaporation to the point of saturation with respect to the minerals present, assumption (b) is valid: the mineralogy is a reasonable reflection of the brine composition at the point of precipitation.

Unfortunately, this view of a salt lake as a container of water undergoing evaporation is an oversimplification of the real world. Apart from ignoring the role of biological processes in mineral formation, this approach is inadequate for at least two major geochemical reasons: Firstly, the newly formed minerals are not necessarily isolated from the brine immediately upon precipitation. This ability of the salts to react with a changing brine composition on a seasonal basis (as is the case in many playa basins) or as the precipitate settles through a deep, chemically stratified water column greatly increases the likelihood of mineral alteration even before being incorporated into the sediment record. Secondly, this simple view does not take into account metastability of the salts. The formation of metastable phases is a common phenomenon in low temperature geochemistry, particularly in late-stage evaporation of brines (Krauskopf 1979; Holser 1979; Drever, 1988). Although with time, the metastable phases should transform to thermodynamically stable phases, this transformation can be slow enough to allow the metastable material to persist in the geological record, thereby muddling the interpretation of the mineral suite.

To summarize some of the more important problems facing paleolimnologists working with lakes in the northern Great Plains: (i) The salt lakes of the region support an active and growing salt minerals industry. Unfortunately, often the lakes that are most attractive for mining are also the ones that contain the best potential for paleolimnological research. (ii) A variety of post-depositional changes can significantly alter the composition and nature of the preserved stratigraphic records in these lakes, thereby obscuring the paleorecord. (iii) Our incomplete understanding of several basic sedimentary processes and genesis of some commonly occurring stratigraphic units in these basins is limiting the precision of our interpretations.

9.5 THE PALEOLIMNOLOGICAL FUTURE

During the 1990's the Geological Survey of Canada coordinated a major multiorganization, multidisciplinary research project whose main objective was to decipher the timing and severity of postglacial climatic changes and their geomorphic impact on the prairie landscape (Lemmen et al., 1993; 1999; Vance, 1997). Investigation of the Holocene and late Pleistocene stratigraphic records preserved in the lakes of the region formed a pivotal role in accomplishing this objective. This very successful project resulted in increasing by nearly 300% our lacustrine stratigraphic coverage and data. As of 2001, the stratigraphic records of about fifty basins in the northern Great Plains have been investigated in any type of detail (Figure 4.1). Clearly interest in the paleoenvironmental records of these lakes is high and growing, from both a geological as well as biological perspective (see also Fritz et al., 1999; Wilson and Smol, 1999; Wilson et al. 1997). Some of the more obvious physical, mineralogical, and geochemical tools that will continue to help advance our understanding of the paleoenvironmental records preserved in these lakes are summarized below.

9.5.1 Texture

The texture of lacustrine sediments has been a mainstay for paleolimnologists since the early works of Russel (1885) and Gilbert (1890), and will likely continue to provide important information about water depths and sediment distribution in clastic dominated sequences in the Great Plains. Allogenic particle size is usually used to interpret water depth by deducing the level of energy being imparted to the sediment-water interface at the sampling site. Coarse grained sediments (sands, gravels) are generally interpreted to have been deposited under relatively shallow water, high energy conditions (e.g., a beach, shoal, or delta), whereas very fine grained sediment (clay sized material) requires settling through a deep, essentially motionless water mass. The textural maturity of the sediment, usually evaluated by how well sorted the particle sizes are, is also useful for interpreting the effectiveness (consistency) of the mechanical energy at the depositional site.

Because grain size is such a basic descriptive sedimentological parameter, examples of its use in paleolimnology of the northern Great Plains abound. Nearly all of the approximately fifty Holocene lacustrine stratigraphic sequences examined in the region have recorded grain size, although at considerably different vertical resolutions and degrees of precision. To cite one well-studied example, Teller and Last (1979, 1981) use a general upward increase in mean grain size in the 14 m long offshore record of Lake Manitoba to indicate an overall shallowing of the basin as this lake progressed from part of a giant, deep (200 m) proglacial lake 12,000 years ago to a large but shallow (4 m) remnant today. Periodic incursions of a major fluvial system (the Assiniboine River) and delta formation in the basin are recognized by the occurrence of relatively coarse, well sorted clastics superposed on this overall coarsening upward trend.

Of special interest to researchers studying the stratigraphic records of the more saline lakes is the occurrence of thin beds and laminae of fine grained detrital material which commonly occur interbedded with the evaporites. While their hydrologic significance and sedimentological interpretation are, at present, enigmatic, these allogenic interbeds offer great potential for supplementing our paleolimnological interpretations in these salt-dominated basins. For example, if these thin beds represent periods of increased influx of clastic material from the surrounding watershed, this would imply increased runoff and probably relatively deep and non-hypersaline conditions (i.e., more humid conditions). Conversely, the fine silt and clay laminae could be residual products, the end result of dissolution and downward leaching of the salts due to prolonged desiccation of the playa and a lowered groundwater table brought about by a more arid climate. An increase in aridity could also be interpreted from these fine clastics if they were deposited during periods of increased aeolian activity.

One of the most promising but, to date, untested avenues of future particle size research on Canadian Plains' lakes is that of high resolution textural analysis of finely laminated sediments. With the advent of laser particle size analysis instrumentation (Agrawal, et al., 1991), it is now possible to analyze, rapidly and on a statistically valid basis, complete size spectra of individual sub-millimeter laminae from small diameter cores. This type of 'event' stratigraphy has been used successfully on much thicker varves and rhythmically bedded sediments of glacial and proglacial lakes in central and western North America for many years and should be applied to the finely laminated Holocene sequences in the Prairies.

As important and promising as the examination of allogenic particle size trends are in a lacustrine stratigraphic sequence, it must be emphasized that the interpretations of these data are not straightforward. Indeed, the basic relationship between grain size and water depth must be used with caution. As stressed by Sly (1978), Håkanson and Jansson (1983), and Teller and Last (1990), many other factors can interfere with this simple grain size-water depth-energy relationship, including flocculation of fine grained material, basin morphology, weathering and erosion characteristics of the watershed, and vegetation cover.

9.5.2 Quantitative Paleochemistry

Obviously, in lacustrine systems that are dominated by inorganic endogenic mineral formation, as are most of the lakes in western Canada, the composition of the inorganic fraction is a foremost paleoenvironmental parameter. The composition of the precipitated material is one of the most direct and unambiguous indicators of past chemical composition of the lake water available to paleolimnologists. Several aspects of the usefulness of these data must be emphasized. As pointed out by Shang (2000), the theoretical basis and our knowledge of the thermodynamics of the reactions responsible for most of these minerals has improved dramatically in the past few decades. Remarkably explicit chemical paleo-reconstructions are now possible for saline lake waters once the detailed equilibrium mineral assemblage is known. The importance of collecting mineralogical data versus bulk sample elemental geochemical data cannot be overemphasized. To quantitatively reconstruct brine composition, it is absolutely

essential that mineralogical rather than elemental data be used. Knowing a sample contains quartz, plagioclase, hexahydrite, and halite is much more meaningful than a chemical analysis identifying the analytical proportions of Si, Na, Ca, Mg, Al, S, and Cl.



Although literature on the paleochemistry of these Great Plains lakes is discouragingly small due mainly to the large database that must be collected for each site, numerous examples do exist outside of western Canada and the Great Plains region which demonstrate the great potential of the Canadian lake sediment records (e.g., Eugster and Smith, 1965; Smith 1979; Smith et al., 1983; Wasson et al., 1984; Spencer et al., 1984; Teller and Last, 1990; Renaut and Last, 1994b). Despite its infancy in western Canada, this brine reconstruction research has already lead to important insights into the chemical history and evolution of the lakes.

The basic principles of long-term nonmarine brine evolution have been known and discussed for over thirty years (Jones, 1966; Jones and Van Denburgh, 1966; Garrels and MacKenzie, 1967; Eugster, 1970). Probably the best known conceptual model of brine evolution is that of Hardie and Eugster (1970), which interprets the composition of closed-basin waters in terms of a series of chemical divides. While the basic principles of chemical divides as described by these early researchers are valid, only recently have we begun to understand the limitations and complexities of brine evolution (Drever, 1988; Herczeg and Lyons, 1991; Bryant et al., 1994). It is clear that the salt lakes of western Canada will provide addition important information on the principles of brine evolution.

Because the salt minerals are thermodynamically and kinetically responsive to even relatively minor changes in brine composition (Braitsch, 1971; Sonnenfeld, 1984; Sonnenfeld

and Perthuisot, 1989), the basins in the Great Plains that are most adaptable to interpreting longterm chemical changes in the lakes are those having relatively thick, continuous sequences of evaporites. Using interpreted major ion ratio changes as deduced from the evaporite mineralogy in twenty-four hypersaline lakes, Last (1995) provided a glimpse at a complex series of some nine different evolutionary sequences present in the Great Plains lakes. The most commonly occurring cyclicity in these lakes was that of CO₃ 6 CO₃-SO₄ 6 SO₄ for the anions and Ca 6 Ca-Mg 6 Na 6 Na-Mg-Ca for the cations. It should also be noted that more than 20% of the lakes examined exhibited no statistically significant cyclicity. In a similar study on Ceylon Lake, Last (1990b) identified a somewhat more complex cycle in the 7000 year long record of chemical precipitation.

While lacustrine sequences dominated by soluble evaporites are most suitable for these kinds of brine reconstruction efforts, valuable information about past lake water compositions can be derived even from the endogenic minerals of marginally saline and fresh water systems. Carbonate minerals are among the most common endogenic constituents in these lakes. Many studies, both in the Great Plains and elsewhere, have documented the suitability of calcite and aragonite in paleolimnology (e.g., Kelts and Hsü 1978; Dean 1981; Eugster and Kelts 1983; Dean and Fouch 1983; Dean and Megard, 1993; Haskell et al. 1996) although the application of other carbonate mineral species, such as dolomite, magnesite, and siderite, which commonly occur in marginal saline lake sediments in the Great Plains, has been less widespread.

Based mainly on observational data provided by Müller et al. (1972), it is generally held that the mineral sequence of: low-Mg calcite 6 high-Mg calcite 6 aragonite 6 dolomite 6 magnesite/huntite reflects increasing Mg/Ca ionic ratios in the precipitating solution and, very likely, increasing salinities. Thus, it has become routine to use the stratigraphic variation of these endogenic species in the lacustrine basins of the Great Plains to help deduce past Mg/Ca ionic ratios and salinity of the lake water (e.g., Last 1982; Last and Schweyen 1985; Vance and Last, 1996; Last and Vance, 1996).

9.5.3 Isotopic Studies

The mineralogical data of these lakes can provide particularly useful information when interpreted in conjunction with stable isotopic analyses. Investigation of the stratigraphic variation in stable oxygen and carbon isotopes of lacustrine sediment has lead to important paleohydrological observations and paleoclimatic interpretations in many modern and ancient lakes in the world (see reviews in Ito, 2001; Talbot, 2001; Pearson and Coplen, 1978; Buchardt and Fritz, 1980; Kelts and Talbot, 1989; Swart et al, 1993). Stable isotope analyses have also been instrumental in helping understand the complex genesis and diagenesis of endogenic and authigenic minerals in lake sediments (e.g., Talbot and Kelts, 1986; Rosen et al., 1989; Perkins et al., 1994). Historically, inorganic carbonates (mainly calcite and aragonite) and biological endogenic carbonates (ostracode shells) have been the main targets for the paleoenvironmental approach as summarized in numerous synthesis papers (e.g., McKenzie, 1985; Siegenthaler and Eicher, 1986; Talbot, 1990; Lister, 1988; Talbot and Kelts, 1990). More recently oxygen isotopes of non-carbonate organic components have been shown to be valuable in supplementing the

paleoenvironmental information that can be deduced (Wolfe et al, 2001; Edwards and Fritz, 1986; Edwards and McAndrews, 1989; Edwards, 1993; Wolfe et al., 1996; Wolfe and Edwards, 1997). These combined approaches, together with trace element measurements, now offer a particularly powerful avenue to deducing information about past water levels, salinities, temperatures, and organic productivity in lake basins.

The general principles of use of oxygen and carbon isotopes are reasonably well known and straightforward, however interpretation of the data from nonmarine settings can be complex. The oxygen isotopic composition of an oxygen-bearing endogenic mineral depends on the isotopic composition and the temperature of the solution at the time of precipitation. The isotopic composition of the lake water, in turn, depends mainly on the composition of the inflowing waters and the residence time of the water in the lake basin. In lakes characterized by open or 'flow-through' hydrologic systems, residence times are generally low, the waters have not been subjected to isotopic evolution within the basin, and the isotopic composition differs little from that of the inflowing waters. In closed hydrologic settings, however, residence time increases and the lake waters can undergo significant enrichment of the ¹⁸O isotope because the lighter ¹⁶O is preferentially incorporated into the gaseous phase during evaporation. Because fractionation of *¹⁸O is also temperature dependent between the mineral phase and the aqueous phase but is independent of temperature between the aqueous phase and endogenic organic matter, by examining the ratios from both mineral and organic matter it is possible to infer lake water paleotemperatures.

Although factors controlling the ratio of ¹³C to ¹²C in the precipitated carbonate are not directly related to hydrology and evaporation/precipitation ratios in the lacustrine basin, the preferential uptake of ¹²C by aquatic vegetation and the preferential outgassing of ¹²C-rich CO₂ from the lake surface during long residence times lead to a marked covariance of *¹³C and *¹⁸O in closed basins.

Despite these demonstrated applications to paleolimnology, there have been surprisingly few isotopic studies on lake sediments in the Canadian Prairies. Last et al. (1994) used the *¹³C and *¹⁸O of endogenic inorganic magnesian calcite and ostracode shells to track the hydrologic fluctuations of the 12,000 year long record in the Lake Manitoba basin. These results show a complex hydrochemical and hydrologic history due to multiple and shifting water sources, regional climate changes, and repeated alternations of open and closed basin conditions. Further stable isotope examination of these carbonates combined with Mg/Ca and Sr/Ca analyses are currently underway (Ito et al., 1996). Boden (1985) and Last and Slezak (1986) summarized the isotopic record of endogenic aragonite in Deadmoose Lake. They found relatively minor hydrologic variations but identified several periods of increased primary organic productivity during the past 2500 years in this saline, meromictic lake. Van Stempvoort et al.(1993) was similarly able to identify episodes of enhanced aridity, increased productivity and/or warmth in the 2500 year long aragonite-laminated record from Redberry Lake, another deep water saline lake northwest of Saskatoon. Padden (1996) examined the stable isotopes of both carbonate and cellulose in the sediments of Chappice, Oro, and Killarney Lakes. While the complex endogenic

carbonate mineralogies of Chappice and Oro lake records and the occurrence of relatively large proportions of allogenic carbonate in Killarney Lake hampered her use of quantitative paleothermometry in these lakes, she recognized periods of hydrologic aridity generally consistent with other lithostratigraphic parameters investigated in these basins. Finally, most recently Kelley and Holmden (2001, 1999a, b; and Kelley et al., 1998) have demonstrated the successful application of H, O, and Sr isotopes in fingerprinting the complex groundwater input to the hydrologic budget of these saline lakes.

9.5.4 Laminae & Other Bedding Features

Laminated lake sediments are a great untapped wealth of information for paleolimnologists working in western Canada. Last and Vance (1997) recently summarized the range of bedding and lamination types found in these lakes and provide several examples of how various types of mineralogical, textural, and geochemical analyses can provide information about past water levels, brine compositions, ionic ratios, hydrology, and water-column stratification. They also stressed that although most of the extant lake basins cored to date exhibit some degree of bedding and lamination, only a few such sequences have been studied.

9.5.5 Summary

Where does salt lake paleolimnology go from here? As pointed out by Smol (1990), the multidisciplinary nature of paleolimnology makes it difficult to predict future development of the science. However, within the geographic constraints of the northern Great Plains, the axiom "more, better, faster" does apply. We should not be too cynical about attempting to "do" paleolimnology without first knowing everything about the modern lakes. Sedimentologists have long accepted the fact that much of what is known about some depositional settings is based not on the modern environments but rather on the preserved ancient record. But certainly a high priority must be placed on overcoming the most crucial deficiencies in present sedimentological and geochemical concepts/knowledge as summarized in the previous section: quite simply, more modern sedimentological data must be collected from the lakes, especially from the deep, non-stratified basins and the clastics-dominated playas. At the same time, however, many more salt lake basins have to be cored, with particular emphasis in areas where there is little data today (i.e., most of western and southwestern Saskatchewan and eastern/southern Alberta) and in strategically significant areas, such as near present-day climatic/vegetational boundaries.

The quality of sedimentological and geochemical data has to be improved. This is particularly important in the collection of mineralogical data: it is much more useful from a paleolimnological perspective to know that the stratigraphic unit contains bloedite than merely that it contains traces of magnesium. Our understanding of the evolution of salt lakes in the Great Plains may be quite different today had the large amount of data collected in conjuction with industrial development of the Metiskow Lake sodium carbonate-sulfate deposit been placed in a mineralogical framework, rather than a bulk chemistry context. Finally, there has been no better time than now to begin this new wave of paleolimnological investigation. Regional climatic change, drought, salinization, sustainable development have all become "buzz words" of the new millennium. Local, provincial, and federal governments as well as international scientific bodies have suddenly become aware of the need for documentation of past environmental changes in order to properly evaluate present-day trends and fluctuations.

In many ways our study of salt lake sediments has remained relatively simple and traditional, more or less unchanged from the 1960's and 70's. It is likely that the next decade will bring a great increase in sophistication of methodology as well as technology. Already it can be seen how high technology will undoubtedly play a pivotal role in dictating the future direction of paleolimnological research in the Great Plains (Figure 9.3). Just a decade ago many of these techniques did not exist and such detailed investigations would have been unthinkable. Many of the recent advances in geochronology and sample acquisition (Last and Smol, 2001) have yet to be applied to Great Plains lakes; these will almost certainly revolutionize the paleolimnological efforts in the region.

The few paleolimnological studies that we will be highlighting on this field excursion demonstrate the usefulness of saline lake deposits in helping to gain an understanding of postglacial changes in brine chemistry on a regional basis. These salt lakes are particularly attractive for such studies because there are a large number of basins located in a wide variety of modern hydrologic, climatic and vegetational settings, and there is a great diversity of lacustrine chemical and sedimentological systems within this large geographic area.

The scientific study of salt lakes in the northern Great Plains is ripe for an explosive expansion. The paleolimnological problems are difficult but not intractable. The tools are available. The potential pay-offs are big. However, we must guard against resorting to excessive use of comparison and analogue study. The sedimentary realm of the lacustrine environments of the Great Plains is, in many ways, unique. What is fashionable in Australia or what "works" in southwestern United States, for example, may not necessarily be applicable in the Great Plains. Finally, to use the advice of Loehle (1990): "Don't be an expert." and "Don't read the literature." The most pressing need of paleolimnology in the Great Plains is for creative and courageous research, not study.



Figure 9.3 Summary of the interrelationships of major physical and geochemical paleolimnological tools (Last and Smol, 2001).

10. NOTES ON SOME OF THE LAKES VISITED

10.1 PORTER-BURKE LAKES

The Porter-Burke lakes are two small mud-dominated playas very typical of this region of the Great Plains. Examination of topographic maps reveals that there are literally hundreds of such playas in the vicinity of Saskatoon. These two lakes were the subject of one of the most intensive sedimentary geochemical studies in the entire Great Plains region (Lieffers, 1981) to determine the seasonal changes in salinity and ionic ratios and the movement of salts between the water and sediments. Over a two year period 60 cm cores were taken <u>biweekly</u> (during the ice free season) from several stations in the basins. Pore water, lake water, and dried sediment were analyzed for major ions. Unfortunately, sediment mineralogy was not examined at the time, but is now being analyzed. The following is the abstract from an unpublished manuscript ("The Seasonal Salinity Regime of Three Shallow Saline Lakes in Saskatchewan") by V. Lieffers and J. Shay:

"Seasonal changes in water volume and water and sediment salinity were monitored at three shallow, closed, saline wetlands in Saskatchewan in 1978 and 1979. Porter Lake, the main study site was dry in 1978 and flooded in 1979. When dry, the salinity of surface sediments was higher than sediments 50-60 cm deep and those in the lake centre were more saline than at the shoreline. Upon reflooding in 1979, there was a large, immediate decrease in surface sediment salinity, also surface layers were less saline than sediments 50-60 cm deep. Sediments in the lake centre were still more saline than those at the shoreline. Over the summer in 1979, the water salinity showed a continuous increase and the mass of dissolved salts within the water volume increased fivefold. This increase in mass is thought to be derived either from large deposits of salts in the deep sediments or from inflow of salinized groundwater. The ionic proportions of the major salts within the water remained relatively constant during this rise in salinity. Differences in the ionic proportions of salts within the sediments at various basin positions and depths appear to be related to differences in the solubility of the salts and where they are precipitated as the lake water levels recede "

10.2 PATIENCE LAKE

Patience Lake is located about 20 km east of Saskatoon. It occupies an elongate channel basin similar to many other salt lake basins that we will see during the excursion. Since the late 1970's Patience Lake has been receiving the runoff from a tailings pile associated with a potash mine at the south end of the basin. This influx has lead to a dramatic increase in salinity and changes in ionic ratios. If conditions are right, large, magnificent zoned halite crystals can be collected (Figure 10.1). Patience Lake also is of note because it is one of only two lakes in the

entire northern Great Plains to regularly precipitate hydrohalite (NaCl · 2H₂O). The following comments are abstracted from Hammer and Parker (1984).

Patience Lake has increased in salinity from 175 (15 June 1970) to as high as 428 (14 May 1981) g/l as a result of dissolved potash mine tailings added to the lake. Over two decades it has changed from a sodium-magnesium sulfate lake to one that is dominated by sodium chloride. This change in salinity and salt type has resulted in ice formation only during extremely cold conditions. In January 1982 ice formation occurred only when air temperatures below -30°C persisted. Under 15 cm of ice in late January water temperature was -24°C.



Figure 10.1 Halite from Patience Lake.

10.3 MUSKIKI LAKE

Welcome to the birth place of Canada's sulfate minerals industry!

Muskiki Lake is a large (~12 km²) salt playa located about 90 km east of Saskatoon that is interesting for a variety of reasons. It is the site of the first successful commercial sulfate salt extraction effort in the Great Plains. Originally staked at the turn of the century by prospectors in the mistaken belief that the salts were potash, by 1915 the lake was being exploited for both sodium and magnesium sulfates and carbonate salts. Furthermore, it is surprisingly welldocumented. Until Shang (2000) and Lieffers (1981) undertook their sedimentological and geochemical research on Ingebright Lake and Porter/Burke lakes, respectively, Muskiki was the single most intensively studied and sampled playa basin in the Canadian portion of the northern Great Plains. Another interesting and somewhat unusual feature of Muskiki is the presence of many springs (and spring deposits) in the basin.

Unfortunately, an extensive mudflat, which is usually very soft, makes access to the main salt body difficult during the ice-free season. We have done only very limited sampling and

coring of Muskiki (Figure 10.2; see Egan, 1984; Last et al., 1983). The extensive mapping of the basin by Cole in the early 1920's still stands as the most complete documentation of this lake.

Muskiki Lake brine is particularly interesting because it is one of the most Mg-rich waters in the Prairies region. The surface salts are composed of a complex mixture of mainly mirabilite, bloedite, epsomite, with (in some years) smaller amounts of hexahydrite, halite, vanthoffite, kieserite, loeweite, d'ansite and gypsum. The mineralogical details of the subsurface salts are not known, but from bulk chemical data presented in Cole (1926), the evaporites are clearly similarly complex and multi-mineralogic. The non-soluble fraction of the sediment is dominated by quartz, feldspars, and clay minerals and carbonates. Some of the carbonate fraction of the sediment is diagenetic in origin, consisting of huntite, Mg-calcite, protodolomite, and various carbonate-apatite minerals. Egan (1984) also suggested that some of the clay minerals of the clay-sized fraction are authigenic/endogenic and identified the rare authigenic Alcarbonate mineral scarbroite (Egan, 1986).

We will attempt to make only one stop at Muskiki Lake (access permitting): on the west side of the basin to examine the mudflat sediments and (hopefully) the permanent salt bed a short distance offshore. Unfortunately, access to the east side of the basin at Paint Point and Muskiki Springs to examine a late Pleistocene-early Holocene spring deposit and a mud chimney is no longer possible.





Figure 10.2 Composite stratigraphy of south basin, Muskiki Lake (from Last, 1991a).

10.4 DANA & BERRY LAKES

In the vicinity of Muskiki Lake are two other localities that we will try to visit: Dana Salt Lake and Berry Lake. However, during the fall access is usually poor.

Dana is a small ($< 0.5 \text{ km}^2$), circular lake about 10 km south of Muskiki. The surrounding area is quite hilly and extensively farmed. Although the lake contains a "permanent" salt bed, extensive soft mudflats surround it. These mudflats have been examined in detail by Egan (1984). Vegetation mats (Figure 10.3) and intrasedimentary evaporite crystals are very common on and in these mudflats. The evaporites in Dana are somewhat unusual in that they are mainly bloedite with lesser amounts of mirabilite. An authigenic (endogenic?) carbonate-apatite mineral is also found here. Finally, Dana Lake is one of the few lakes in the entire western Canada and northern Great Plains regions to contain sepiolite. Organic matter content of the mudflat sediment as well as the salt is high (15-50%). Unfortunately, we have only limited stratigraphic information on this interesting basin (Figure 10.4).

Berry Lake is a somewhat larger ($\sim 2.5 \text{ km}^2$) salt-dominated playa also set among the undulating ground moraine hills south of Muskiki. Like Muskiki, it was the site of some of the earliest mineral extraction efforts on the Prairies. The brine is Na dominated and under good evaporating conditions (usually during late summer) large floating rafts of mirabilite and thenardite can be observed covering the shallow saturated brine. Egan (1984) also noted several distinct morphologies of gypsum in the surface and near-surface sediments, probably related to the origin of this Ca-sulfate mineral.



Figure 10.3 Vegetation mat at Dana Lake.



Figure 10.4 Composite stratigraphy of Dana Lake (from Last, 1991a).

10.5 WALDSEA & DEADMOOSE LAKES

10.5.1 Why are we here?

Waldsea Lake is probably one of the most intensively sampled and studied salt lakes in Canada. As of 2000 it has been the subject of eight M.Sc., 3 Ph.D. theses, and at least five honors B.Sc. theses; a total of more than thirty reports and scientific contributions have been published on this lake. The basin is attractive for detailed study because of its small size, excellent accessibility, and interesting meromictic character. Similarly, nearly Deadmoose Lake is presently undergoing detailed sedimentological and geochemical study.

In many respects the two lakes are quite similar. They are both saline and meromictic; they both contain phototrophic bacterial plates; they both precipitate aragonite and contain finely

laminated stratigraphic sequences. However, other aspects of the basins are quite different. The Deadmoose Basin is much more complex in terms of morphology, modern sedimentary facies, and processes than Waldsea. The Holocene history of Deadmoose also appears to be less 'straight-forward' than that of Waldsea.

10.5.2 The Modern Lakes

10.5.2.1 Setting

Waldsea and Deadmoose lakes are located ~100 km northeast of Saskatoon. The lakes are part of a chain of basins that occur in a large area (14,000 km²) of internal drainage. Nearly all of the larger (> 1 km²) lakes in the area are brackish to hypersaline, with concentrations ranging from about 3 g L⁻¹ to over 300 g L⁻¹.

The mean annual temperature at Humboldt is 1°C; average annual precipitation is a rather we 40 cm. The natural vegetation of the area is aspen parkland - transitional between the prairie grasslands a short distance to the south and west and the pine-spruce forests to the north. However, much of the natural vegetation cover has been cleared for agricultural purposes, and most of the area immediately surrounding the two lakes is cultivated.

10.5.2.2 Limnology & Hydrogeology

The limnologic and biological characteristics of the two lakes have been discussed in Hammer and Haynes (1978), Hammer (1978), and Haynes and Hammer (1978). In order to provide some background information, a brief synopsis of the main morphometric and chemical parameters of these lakes is given in Tables 10.1 and 10.2. Waldsea Lake has relatively steeply sloping sides and a flat bottom. Deadmoose Lake has a much more irregular basin morphology with several deep (> 35 m) troughs and holes (Figure 10.5).

The groundwater hydrology and resources of the area have been reviewed by Meneley (1967) and Rutherford (1967). Sands and gravels within the unconsolidated Pleistocene section and sandstones at the top of the Cretaceous bedrock form the most continuous and abundant aquifers in the area. The groundwater nearest the surface (shallow glacial drift) is relatively dilute (<1000 mg L⁻¹ TDS) and dominated by calcium and bicarbonate ions. The lower glacial drift contains higher salinity water (1000 to 3000 mg L⁻¹) of the Ca-Mg-HCO₃ type, whereas the shallow bedrock groundwater is of similar salinity but sodium and sulfate-rich. The formation waters of older sediments (pre-Cretaceous) rapidly increase in salinity with depth to greater than 300 g L⁻¹, and are of the Na-Cl type. Detailed groundwater hydraulic and flow analyses have not been published for the area.

Morphometry		
Surface Area	4.65 km ²	
Drainage Basin Area	47.2 km2	
Drainage Area/Lake Area	10.2	
Shoreline Length	10.7 km	
Shoreline Development	1.3	
Maximum Depth	14.8 m	
Mean Depth	8.1 m	
Relative Depth	0.63%	
Volume	0.04 km3	
Volume Development	1.7	
Volume in Mixolimnion	87%	
Volume in Monimolimnion	13%	
Total Salt	700 x 106kg	

 Table 10.1 Morphometric characteristics of Waldsea Lake.



Figure 10.5. Morphology of Waldsea (left; perspective from campground) and Deadmoose (right; perspective from Launch Bay) basins (Last, 1991a, 1991b).

Both Waldsea and Deadmoose lakes are saline, with average surface water salinities of about 30 g L⁻¹. Both are also meromictic, having monimolimnions with approximately twice the salinity of their mixolimnions. Both lakes contain phototrophic bacterial plates located at their chemoclines (Lawrence et al, 1978; Parker et al, 1983). In Waldsea the dominant species in the plate is Chlorobium; in Deadmoose Thiocapsa roseopersicina dominate (Appendix A). The lower layers of these two lakes are typically strongly reducing (Eh values of -300 to -400 mv.), high in H_2S (150-200 mg L⁻¹), and slightly less alkaline than the surface waters. The mixolimnions also exhibit seasonal temperature stratification. The ionic composition of the water in Waldsea and Deadmoose lakes, as well as that of many of the other salt lakes in the immediate area, is dominated by Na, Mg, and SO₄. Although higher in total dissolved solids, the bottom waters of the lakes have major ion ratios similar to their surface waters. These lakes are saturated or supersaturated with respect to various carbonate minerals at all times of the year and at all depths in the water columns, although the degree of supersaturation decreases considerably beneath the chemoclines and during winter. The monimolimnions of Waldsea and Deadmoose lakes are at or near saturation with respect to gypsum, while in winter their surface waters come close to saturation with respect to mirabilite.

Hydrochemistry			
	Mixolimnion	Monimolimnion	
	(Average concentration: mg L ⁻¹)		
Ca2+	320	441	
Mg 2+	3939	5616	
Na+	4414	6988	
K +	156	273	
HCO ₃ -	231	427	
so4 ²⁻	12488	30067	
Cl-	4471	8863	
TDS (ppt)	25.4	67.2	
Ionic Strength	0.61	1.03	
pH (pE)	8.7 (3.4)	7.8 (-5.3)	
S H2	0	590	

Table 10.2 Hydrochemical characteristics of Waldsea Lake.

10.5.2.3 Modern Sedimentology

The modern (upper 2 cm) sediments of the two lakes consist mainly of organic-rich, silty clay and clayey silt in the offshore portions of the basins grading to coarser clastics (sands and gravels) in the nearshore areas. In Waldsea Lake the shoreline and nearshore sands are restricted to a very narrow, 50-100 m wide perimeter of the basin, whereas in Deadmoose Lake sands and coarse silts extend farther out into the basin. Away from the relatively nearshore areas, however, there is little variation in grain size in either of the basins.

The modern mineral suite in each lake is roughly similar: mainly clay minerals, carbonate minerals, and pyrite. Waldsea sediment has up to about 15% gypsum, whereas this sulfate mineral is less abundant in Deadmoose surface sediment. The clay-sized fractions of the sediment in each basin are likewise similar, consisting of a complex mixture of clay minerals, non-clay mineral silicates, carbonates, pyrite, and inorganic amorphous material. The proportions of major clay mineral constituents (illite, kaolinite + chlorite, and expandable lattice clays) do not vary significantly from basin to basin. In Deadmoose Lake mirabilite is found in the surface sediments in water depths greater than 25 m.

Three genetic types of sediment can be recognized in the modern offshore deposits of these lakes: (a) detrital, (b) endogenic, and (c) authigenic. The detrital component, consisting of clay minerals, quartz, dolomite, feldspars, and low-Mg calcite, is derived from shoreline and stream erosion of the surrounding glacial sediments. The endogenic component, or that portion of the sediment originating from within the water column, consists of aragonite, high-Mg calcite, gypsum, mirabilite, and organic matter. Both the aragonite and high-Mg calcite are precipitated inorganically in response to supersaturated conditions brought about by uptake of CO₂ by primary organic productivity. As shown in studies of numerous other saline lakes (e.g., Muller et al, 1972; Callender, 1968; Last, 1982), the high Mg/Ca ratio of the lake water (5 to 50), is the reason that aragonite and magnesian calcite are generated rather than low-Mg calcite. The two sulfate minerals (gypsum and mirabilite) likely originated by inorganic precipitation from the hypersaline monimolimnion. The only authigenic component recognized in the modern sediments is pyrite, which is likely derived as a very early diagenetic product of H₂S, organic matter, and dissolved iron in the near surface sediment.

10.5.3 Stratigraphy of the Lacustrine Sediments

The relatively simple modern facies assemblage present in these two basins does not persist into the Holocene record. Rather, the stratigraphic sequences preserved in the basins reflect significant fluctuations in lake levels and chemical conditions (Figure 10.6). Last and Schweyen (1985) used the distinctive mineral suite (gypsum, dolomite, mirabilite), and the morphologies and textures of these components in the lower part of the lacustrine record from

Waldsea Lake to demonstrate that deposition occurred in a saline, clastic-dominated playa, where water levels fluctuated on a seasonal basis. When there was ponded water in the basin, it was dominated by Na and SO₄ ions. Concentrations in the shallow playa probably exceeded 200 g L^{-1} as indicated by the pore water chemistry, and seasonal precipitation of mirabilite and other evaporitic salts occurred. The mudflats surrounding this shallow lake were sites of abundant gypsum and carbonate precipitation. The intense evaporation on the mudflats created a dynamic diagenetic environment and much of the original calcium carbonate was quickly altered to dolomite in response to the high Mg/Ca ratios of the pore water. When water levels were even lower, algal mudflats and vegetation mats covered most of the basin.

An overlying unit of fine, undisturbed carbonate laminae alternating with organic-rich muds suggests deposition in a relatively deep, probably meromictic lake, as the hydrological budget became increasingly more positive. High pore water salinities indicate that the lake was still hypersaline during this high water phase. Deposition of pure aragonite laminae was most likely related to carbonate "whitings" which were triggered by dilute inflow water periodically entering the basin and mixing with the highly alkaline and Mg-rich saline lacustrine brines. In addition to this endogenic precipitation of aragonite, high but fluctuating Mg/Ca ratios in the lake are recorded by the complex assemblage of early diagenetic carbonates including high-Mg calcite, dolomite, and magnesite.

The lake became shallow once more between 2800 and 2000 yr B.P. and mudflat-playa conditions returned to the basin as evidenced by gypsum laminae, dolomite crusts and organic fiber mats. During the last 2000 years, deposition in the Waldsea basin was dominated by finely laminated aragonite-clay couplets, which probably formed in a relatively deep water, stratified basin. Either a lowering of the lake or a loss of vegetative ground cover occurred about 1000 years ago as indicated by the occurrence of a thin but basin-wide coarse silt-sand unit.

Because of its irregular basin morphology, the stratigraphic sequence and facies relationships in nearby Deadmoose Lake are more complex. Conditions within the main (deep) part of the basin were probably roughly similar to that to that of today for much of the mid to late Holocene. Fine, undisturbed laminae of aragonite and the lack of carbonate-cemented crusts, intraclasts, and fiber mats suggest the existence of a permanent, relatively deep, stratified water body. The presence of aragonite throughout this deep water facies points toward high and probably stable Mg/Ca ratios. Stable oxygen isotope data on this endogenic aragonite indicate a warmer, more evaporitic regime at the base of the section grading upward to cooler conditions at the top of the sequence. A sandy facies found at the northern end of the basin was part of a shoreline/delta complex that was active about 1500 years ago, when the lake was 10 m lower and much smaller than today. The presence of coarse clastics, carbonate-cemented laminae, vegetation mats, and gypsum beds in the relatively shallow margins of Deadmoose also confirms this lower lake level. Last and Slezak (1986) show that several satellite basins, which are now part of Deadmoose, were probably separate lakes during much of the mid to late Holocene. With higher water levels and a transgressing shoreline beginning about 1000 years ago, the nearshore

coarse clastics and mudflat deposits were drowned, and deeper water (aragonite laminated) sediment was deposited on top of shallower water clastics.



Figure 10.6. Summary of stratigraphic fluctuations, Waldsea Lake (Last et al., 2002).

10.5.3.1 Aragonite Laminae Petrography

With this backdrop of geolimnological and paleoenvironmental work, work on several aspects of the Waldsea Lake sequence is continuing on the endogenic mineralogy and detailed carbonate petrography in order to better understand the changes that have occurred during the most recent millennium. The mineralogical and petrographic results discussed here are part of a larger on-going effort to better understand and resolve the most recent history and paleolimnology of both Waldsea and Deadmoose Lakes through the use of multiple proxies, including stable isotope and trace element geochemistry, organic Rock-Eval geochemistry, palynology, and ostracode biostratigraphy.

Detailed petrography of the aragonite in the deep-water laminated sequence of Waldsea Lake offers considerable new insight into the paleolimnology of the basin. Although as discussed above, the entire recovered stratigraphic sequence from Waldsea Lake is finely laminated, the following comments and observations here apply just to the sediments deposited during the past \sim 2000 years (approximately the upper 2 m of sediment).

The aragonite laminae range in thickness from about 0.2 mm to just under 2 mm. Overall, the laminae are widely spaced (two to three laminae per centimeter) but much closer spacing does occur (Figure 10.7). Upper and lower contacts are invariably sharp and horizontal. The laminae are usually white (Munsell: 5YR 8/1) to pale yellow (2.5Y 8/4) with occasional red

(2.5YR 5/8) to pink (5YR 7/4) colors. The pink and red colors rapidly fade upon exposure of the core, and are presumably associated with deposition of organic material from the red to purple colored bacterial plate at the chemocline or staining by pigments. Individual laminae and sets of laminae



staining by pigments. Individual laminae and sets of laminae take. Top is to the left; scale bar is 1 cm. (From Last et al., 2002).

can be readily correlated from core to core thus confirming that these rapid precipitation events are basinal in extent. There is no apparent periodicity in the frequency or thickness variation of the laminations within the upper 2 m of section, although the detailed image analysis and statistical evaluation necessary to properly identify a non-random occurrence have not yet been completed.

Individual laminae are composed entirely of extremely well-sorted, euhedral, micronsized CaCO₃ crystals (Figures 10.8 and 10.9). There is an almost complete absence of biological and other non-carbonate grains, suggesting that the layers represent rapid inorganic precipitation and accumulation without dilution by non-carbonate endogenic minerals, siliciclastics, or organic debris. These aragonite crystals show considerable variation in both size and morphology. Individual CaCO₃ crystals range in shape from acicular to ellipsoidal, but are usually uniform in any single layer. Most of the laminae have fine, needle-like crystals that are typical of the aragonite formed in many other perennial saline lakes in the northern Great Plains region (e.g., Valero-Garcés and Kelts, 1995; Sack, 1993; Van Stempvoort et al., 1993; Slezak, 1989). The aragonite in some of the laminae, however, has a distinctive wheat grain or rice grain morphology. This ellipsoidal aragonite has been noted in other deep water saline lakes in Canada and Australia , as well as from the Black Sea, and is indicative of newly-formed CaCO₃ crystals settling through a relatively deep, stagnant, somewhat undersaturated water column (Sack and Last, 1994; Last and De Deckker, 1990; Stoffers and Müller, 1978; Hsü, 1978).



Figure 10.8. Examples of acicular (r) and ellipsoidal (l) aragonite.



Figure 10.9. Examples of size spectra of aragonite crystals from laminae in Waldsea Lake (from Last et al.,2002).

Conditions in Waldsea Lake today are such that ellipsoidal aragonite does not form and the modern bottom sediments contain only acicular CaCO₃. This is because both the mixolimnion, where the aragonite is forming, and the monimolimnion are very close to saturation with respect to aragonite. However, geochemical modeling (Schweyen, 1984) indicates that shallowing of the chemocline by about 4 m would produce undersaturated conditions in the lower water mass and, in turn, create conditions favorable for the generation of rice-grain aragonite crystals. Thus, laminae with ellipsoidal aragonite crystals indicate the presence of a stratified water column in which the chemocline was considerably shallower than that of the modern lake, or, alternatively, the monimolimnion was less saturated (more undersaturated) with respect to CaCO₃.

The proportion of euhedral acicular aragonite crystals relative to other shapes in laminae from one of the cores near the basin center increased dramatically at about 500 years B.P. This suggests that the depth to the chemocline increased significantly in the lake about that time possibly due to the influx of more freshwater via precipitation and steam runoff, increased wind mixing of the mixolimnion, or an increase in the degree of saturation with respect to $CaCO_3$ of the monimolimnion.

The crystals in individual laminae are extremely well sorted (average $\Phi < 1.0$:m) and have a mean size ranging from less than 2 :m to more than 26 :m. There is a general trend toward increasing crystal size upward in the cores. Although many geochemical and environmental factors combine to determine the size of precipitated inorganic crystals, one of the most important is the length of time the crystal resides in the supersaturated solution. Thus, the stratigraphic variation in aragonite crystal size in the laminae is a reflection of the depth of the supersaturated water column. In the modern lake, this is essentially the depth of the mixolimnion (or the depth to the chemocline). Using aragonite crystals collected in sediment traps from modern Waldsea Lake and other aragonite-precipitating basins, it is possible to calibrate the stratigraphic variation in crystal size in terms of approximate depth to the paleochemocline (or, more correctly, the vertical extent of the supersaturated water column). Other factors, such as the degree of supersaturation and the amount of crystal size modification that may take place during settling through an undersaturated monimolimnion may affect these estimates, but this crystal size parameter should offer a reliable means of estimating past chemocline depths.

Figure 10.10 shows the fluctuation in interpreted chemocline depth of Waldsea Lake over the past 2000 years based on the mean crystal size of aragonite crystals in two cores in the basin. Core 6, the same core on which the detailed aragonite shape analysis was done, is located near the deepest part of the basin. Core 23 is located about a kilometer north of core 6 in ~10 m water depth. Although the fluctuations do not match precisely, there is good general correspondence between the two cores. Both cores show a significant increase in interpreted chemocline depth during the most recent 500 year period and generally shallower chemocline depths between about 500 and 1700 years B.P. This corresponds well with the changes in water column conditions interpreted from the aragonite crystal shape analyses.

10.5.3.2 Detailed Carbonate and Evaporite Mineralogy

Although the stratigraphic sequence recovered from Waldsea Lake is dominated by aragonite, pyrite, and clay minerals, a wide variety of other endogenic, authigenic, and allogenic minerals have been identified in the cores. As pointed out above, the paragenesis of specific mineral phases and suites of minerals identified in Waldsea Lake is exceedingly complex. In a saline meromictic water body that is dominated by groundwater influx such as Waldsea Lake, the distinction between true endogenic sediments (material generated from within the water column) and authigenic components (minerals originating either by diagenetic alteration of previously deposited material or minerals precipitated from solution within the pore space of the

sediments) becomes obscure. Nonetheless, a basic tenet of chemical sedimentology is that in a hydrologically closed system undergoing evaporative concentration, the assemblage of nondetrital minerals must have the same bulk ionic composition as the original water (Hardie, 1984). As discussed elsewhere (Wasson et al., 1984; Torgersen et al., 1986; Teller and Last, 1990; Last, 1994), there are many assumptions and limitations that must be accepted in the application of this straightforward principle to paleolimnology. However, Waldsea Lake, a topographically and hydrologically closed basin having a relatively small catchment and a long, continuous record of chemical sedimentation from saline and hypersaline brines, is ideally suited for paleochemical reconstructions from such types of thermodynamic and mass balance calculations.



Figure 10.10. Interpreted variation in chemocline depth (from Last et al. 2002).

Fundamental to our understanding of past chemical conditions in the basin is the fact that regardless of how a particular mineral formed (i.e., whether it is endogenic or authigenic), its presence (rather than abundance) implies that the formative brine was saturated (or supersaturated) with respect to that mineral. In other words, the product of the chemical activities of the ions of which the mineral is composed must have exceeded the solubility product for that mineral. For example, a sample with an endogenic mineral assemblage composed entirely of

gypsum implies that the lake or pore water had a minimum equimolar concentration of Ca^{2+} and SO_4^{2-} of 5.0 x 10⁻³, or a minimum salinity of ~2 ppt TDS, whereas the formative brine responsible for a sample with both mirabilite and gypsum had a minimum salinity of about ~40 ppt and concentrations of 5.2 x 10⁻³ m Ca²⁺, 6.3 x 10⁻¹ m Na⁺, and 3.1 x 10⁻¹ m SO₄²⁻. This conceptually simple approach becomes more complex as the ionic strength of the solution increases because the salts become increasingly dependent on the co-solutes in the water.

Figure 10.11 shows the variations in relative thermodynamic activity for the major cations and anions in the formative brines over the past 2500 years interpreted from core 32. Clearly, Waldsea Lake brine compositions have fluctuated significantly over the past several millennia. Similar to the results of the aragonite petrography discussed above, it is evident a major change occurred at about 500 years BP in which the chemistry of the water became strongly depleted in calcium and relatively enriched in magnesium. Likewise, a similar Mg-enrichment/Ca-depletion phase occurred for several centuries immediately before 1500 BP which corresponds well with a relatively deeper chemocline interpreted from the aragonite petrography of core 6.



Figure 10.11. Interpreted fluctuations in brine composition, Waldsea Lake (from Last et al. 2002).

10.6. LENORE LAKE

Compared to the very well studied and well cored Waldsea and Deadmoose Lake basins, very little is known about the sediments and stratigraphy in the large Lenore Lake basin. Cores have been acquired from two sites in the basin. The sediment is uniform very organic rich, nonlaminated, black to dark brown silty clay and clayey silt. Although the sediments show a distinct coarsening upward in the upper three meters, there are not obvious lithologic breaks or sharp contacts. Preliminary dating of these cores indicates very high sedimentation rates.

10.7 QUILL LAKES

"Traveling through the vast prairie province of Saskatchewan, one marvels at the immense stretch of flat land bordered only by the horizon. As a traveler, you can be easily lured into thinking that the endless stretch of flat land is all that exists. This is until you reach the area surrounding the community of Wynyard. As you approach the community, you will begin to notice an increase in bush land and rolling hills. Already, your excitement mounts with the expectation that there is obviously more to come. And how right you are! There, before you very eyes, will stretch a vast body of water known as the Quill Lakes.

You will take a second to see if you eyes deceive you when you are confronted by such a surprising spectacle. Now, your curiosity is extremely aroused and you will want to know exactly what you are viewing. To assist you in understanding this unique marvel, we will give you a sample of what you will find. The Quill Lakes are spoken of as the largest inland body of salt water in North America. As you find your way to the edge of Big Quill Lake, you will look out and try to pick the area where you think the giant meteor landed in 1922. This meteor, which has yet to be recovered, splashed down and when it did, it shook the land for miles around. Imagine, vast clouds of steam that rose out of the lake as it boiled from the heat of the meteor and its impact.

(from "Wynyard, Saskatchewan" tourist brochure)

The Quill Lakes together form the third largest inland salt water body in North America. Although little basin analysis work has been undertaken on these lakes, they have received considerable hydrometeorological study. In fact, the Quill Lakes Basin is one of the most intensively instrumented and monitored saline environments in North America.

In the early part of the century Big Quill Lake was the site of a viable commercial fishing industry (suckers, cisco, whitefish) and a popular resort area. These activities ceased by the 1930's with increasing salinity and decreasing water levels of the lake. More recently the lake complex has been investigated for possible zooplankton harvesting and the recovery of sodium and magnesium salts. The following is the abstract and conclusion sections from the final Saskatchewan Research Council Report (SRC Report E 77-12) on the 12 year study of the Big Quill Lake Basin by J. M. Whiting.

The Big Quill Lake basin is one of the largest internal drainage basins in Saskatchewan, covering 2500 square kilometers. The brine in the lake contains about nine million metric tons of magnesium sulfate and about seven million metric tons of sodium sulfate. These salts at current market prices would have a gross sales value of half a billion dollars.

Since 1966, the water balance of this large, shallow lake has been investigated in sufficient detail to make sound conclusions and to enable future planning of the development of its resources such as recovery of salts in the brine, and use of freshwater for municipal, agricultural, wildlife, and recreational purposes.

Basic data have been obtained on the volume of water entering the lake from spring runoff, groundwater inflow and precipitation. Estimates of these parameters have been made from 1920 to 1966 to assist in predicting future lake conditions. It has been determined that the salts in the lake have been dissolved from surface and subsurface soils and tills by water moving towards the lake. The water which arrives in the lake is then concentrated by evaporation. Analysis of lake bottom sediment cores has shown that the ratio between salts has been constant for 10,000 years.

The 12 year study of Big Quill Lake has produced conclusions on which the future potential of the lake should be based. Statistically it is improbable that man could force a major change in the water and salt balance of the lake. It is estimated that man will increase the drained area by 15 percent but will add a further ten percent storage in the channels. In fifty years, this change in basin conditions will increase the lake level by 0.31 meters. This is in part due to the fact that the water budget is controlled by basin characteristics and not directly from climatic input. The salt balance is therefore the end result and is the best estimator of the basin's history. For example, if the lake is to be controlled in its present state, the runoff would have to be decreased by 40 percent and this water injected into the groundwater regime to increase the groundwater by 300 percent. The annual level fluctuation has been calculated to be composed of 10 percent winter precipitation, 53 percent net evaporation, 24 percent spring runoff and 13 percent groundwater. Over the last 10,000 years, the average ratio between these parameters has remained the same. Annual precipitation falling on the basin has been shown to be divided into the following apportionment: 24 percent runoff, 13 percent groundwater, 45 percent evaporation and 18 percent lake level change.

The study of Big Quill Lake has produced seven conclusions on which the future potential of the lake should be based. Statistically, it is improbable that man could force a major change in the water and salt balance of the lake. This is in part due to the fact that the Big Quill Lake water budget is controlled by the characteristics of its basin and not by direct input from climatic factors. The history of the lake is therefore best described by analysis of the salt balance. Analysis of the salt balance history should be pursued further.

It is were necessary to ensure that the lake would remain static at its present state, under the same climatic conditions, 40 percent of the runoff would have to be prevented from reaching the lake (i.e., stored) and this water injected into the groundwater regime to ensure a 300 percent increase in groundwater. The static level could then be maintained with a decreased runoff by inducing a constant groundwater inflow with an accompanying lag for greater stability. Or on an annual basis, net evaporation and runoff are the most important parameters in the lake's balance and they also vary the most. Therefore, inducing a higher ratio in the groundwater component increases the stability of the lake balance.

Big Quill Lake, because of its large size relative to its shallow depth, experiences extreme changes. The lake balance components vary up to twentyfive percent of its present depth. An extreme drought would decrease the lake by thirty-three percent of its depth. In the opposite direction, an extreme flood would increase the lake by twenty-two percent of its depth. The salt balance is proportionally changed. The percent of salt (by weight of water) undergoes an annual cycle of thirty-eight percent due to evaporation during the summer and disproportioning of salts by freezing of the water in the winter. Under extreme drought conditions the salt concentration would increase by eighty-five percent over the present maximum.

An imbalance between the components of the water balance causes relatively large fluctuations of lake level in proportion to its depth. Thus, the continued existence of the lake appears to be dependent upon a balance between these components. Two hypotheses were introduced. One was that the lake is relatively independent of groundwater discharge, but not on the absence of a persistent flow. This hypothesis would indicate a sensitive dependence on climatic factors from year to year. The second was that groundwater is much more directly a reflection of lake level changes and the hydrostatic pressure exerted by the lake and the connecting aquifer system which reflects a change of balance between climatic factors of more than one particular year. From the information presented, it would appear that both are occurring and that they occur because there is more than one aquifer system. The connection between precipitation and lake level change was shown to exist. The size and distribution of a major part of the groundwater inflow was shown to be independent of the basin's annual climatic condition. It is recommended that satellite remote sensing be used to measure the change in volume outflow on a regular basis, in particular to investigate when and how the groundwater changes from inflow to outflow and what this change does to the lake.

Under the above criteria, the basin and lake are suited to agricultural production and mineral salt production. Community pastures and waterfowl impoundments are two other viable considerations outside of the lake boundary. There are about nine million metric tons of magnesium sulfate and about seven million metric tons of sodium sulphate dissolved in the lake basin. These salts at current market prices would gross one half a billion dollars. Sodium sulphate is used in Kraft paper pulp, detergents, animal feeds, ceramics, sponges, textile dyes, bleach, and photographic products. Magnesium sulphate can be used directly as Epsom salts or in pulp production, sizing and fireproofing agents, or as magnesium oxide in reflectors, insulation, abrasives, vulcanization of rubber, and printing inks. Other products which could be produced are magnesium metal, magnesium carbonate, magnesium silicate, potassium hydroxide, sodium sulphate, and carbon disulfide. Lithium is the only other element which is of economic potential and above oceanic concentrations.

Municipal effluent is presently being dumped from two towns (Wynyard and Watson) into the lake and if this continues, the heavy metals from the sewage will begin concentrating just as the salts have. The sewage will also increase the chlorophyll concentration which will support more water life such as brine shrimp. The Israelis are presently researching the possibility of using dunaliella (algae) to produce oil using hydrogen under pressure. Brine shrimp in Big Quill Lake were tested at 15% oil (fat).

There is therefore both immediate and long term economic potential to be derived from the lake. Already, a pilot plant has been built by SRC on the shores of the lake to concentrate magnesium salts and prove the feasibility of concentrating the lake water from four percent up to levels from which economic recovery is possible.

In review, the seven conclusions are:

1. Man cannot affect the long term water and salt balance of the lake;

2. The water balance is controlled by the basin's characteristics and not by direct climatic input;

3. The salt balance is the result of the water budget;

4. The magnitude of the parameters are known for both drought and flood conditions;

5. Groundwater inflow to the lake is induced from two effects: (a) long term effect due to percolation of groundwater from recharge areas; (b) short term effect due to the imbalance between the hydrostatis head of the lake and that of the Hatfield Valley aquifer and immediate aquifers;

6. The contribution of precipitation and its apportionment is known;

7. Over 10,000 years, the average ratio between parameters has remained the same.

10.7.1 Sedimentology and Stratigraphy

In striking contrast to the excellent hydrometeorological study by SRC, very little is known about the postglacial sediments or the sedimentary processes operating in this lake. Sampling efforts both by SRC and us have been largely unsuccessful. The following quotes summarize the state of knowledge:

"A drilling program was started in 1966 and during the following three years test holes were drilled in the region of the lake with a view to establishing the stratigraphy. The kinds of material encountered are classified by texture and other properties, but basically there are two kinds of material encountered: gyttja and glacial drift...."

"A geological analysis of the material that was not obviously till was not carried out..."

"There are a variety of limitations and problems relating to the method of sampling that was adopted. For example, the gyttja is of such a soft texture that usually no auger samples were obtained..."

"The glacial drift has a very variable composition and for this reason it is not easy to produce any stratigraphic continuity between nearby holes."

"...the gyttja is of such a soft texture that usually no auger samples were obtained until about 2 ft. into this material. The depth to the gyttja was measured using a flat disk fixed perpendicularly to the end of a staff. The staff was lowered through a hole before the drilling on the bottom was started and the bottom surface of the lake determined just by feel. Clearly under these conditions it is very difficult to describe exactly what is meant by the bottom of the lake."

"This work has given some first information on the nature of the lake bottom, and it certainly produced some surprises on the maximum depth of sediment. It also provided some information on the nature of the lake bottom n relation to the regional geology... However, the samples that were taken were relatively few and did not cover any very large area of the lake."

Langham, SRC Report E 70-12.

10.8 LITTLE MANITOU LAKE

"The water has been compared to 7% solution of Epsom Salts and is reported to perform very well as a fast and effective laxative..." Appleby & Green (1986). Little Manitou Lake, located about 100 km southeast of Saskatoon, occupies a relatively large, steep-walled glacial meltwater outwash channel. Despite the fact the communities immediately surrounding the basin have a long history of intensive recreational development dating as far back as 1910, surprisingly little is known of the limnology, hydrology, or geology of the lake. Although the number of resort facilities adjacent to the lake has declined since the 1950's, the area is still a popular and attractive tourist destination. Historically, the lake has also been the site of mineral salt and brine shrimp harvesting. Until 1981, the sulfate salts of mirabilite, bloedite, and epsomite were collected, bagged, and shipped to Winnipeg, Manitoba, where they formed the major ingredient in the 'curative and therapeutic' waters of Uhlman's Health Spa on Main Street.

10.8.1 Water Chemistry

Perhaps one of our first tasks at this stop should be to dispel some of the erroneous beliefs, exaggerations, and outright fabrications that surround Little Manitou Lake. The water does *not* have a "density greater than that of the Dead Sea" (Leader-Post, 1990) nor is the chemistry even remotely similar to either the Dead Sea (Saskatchewan Tourism tourist brochure) or the ocean (The Great Saskatchewan Vacation Book, 1992). The lake basin is *not* "glacier-carved" and, although groundwater plays an important role in the hydrochemical budget, the lake cannot be classified as "spring-fed". Finally, the lake is *not* the "saltiest in western Canada" (or even in Saskatchewan), nor is it the "deepest" (or "shallowest") saline lake in the region.

The long-term average water composition of Little Manitou Lake brine is shown in Table 10.3. The water of the lake is, indeed, difficult to characterize, not because of any unusual or unique properties but rather because the lake has experienced dramatic fluctuations in both concentration and composition during historic times. Since the first published analyses in the early 1920's, the salinity has varied by nearly 200%. During the period 1921-1949, the brine increased in concentration from less than 70 ppt TDS to over 200 ppt; since the early 1960's the lake has been artificially freshened by diversion of Saskatchewan River water. However, even with this freshening, the bottom waters during most of the past decade have been about 200 ppt. Furthermore, pre-diversion seasonal fluctuations in composition were dramatic. Cooling of the brine during periods of relatively high concentration resulted in massive subaqueous precipitation of hydrated Na and Mg sulfate salts, such as epsomite (MgSO₄ \cong 7H₂O), mirabilite $[Na_2(SO_4)_2 \cong 10H_2O]$, and bloedite $[MgNa_2(SO_4)_2 \cong 4H_2O]$. This seasonal precipitation of salts was so great that the lake regularly alternated between a Na-SO₄ and a Mg-Cl brine type. This annual sulfate salt precipitation is further enhanced by freeze-out concentration and precipitation of salts during the winter under the thin ice cover. The annual layer of salts precipitated can be as much as 50 cm thick. Most of this very soluble material is re-dissolved upon melting of the ice (causing dilution) and warming of the brine during spring. However, our coring and monitoring of Little Manitou indicates a substantial thickness of salt has been preserved in the central part of the basin, and that in any given year not all of the seasonally precipitated salts are necessarily taken back into solution. This seasonal precipitation - dissolution process also has interesting and profound effects on the stratification character of the brine and on the heat budget characteristics of the lake.

TABLE 10.3: Little Manitou Lake Vital Statistics		
Surface Area (A)	13.9 km ²	

Drainage Basin Area		169 km ²
Maximum Length (L _{max})		20.1 km
Maximum Width (W _{max})		1.1 km
Maximum Depth (z _{max})		6.1 m
Mean Depth (z _{mean})		4.0 m
Volume (V)		169 10 ⁶ m ³
	mg L ⁻¹	mmol L ⁻¹
Ca ²⁺	882	22
Mg ²⁺	17091	703
Na ⁺	11035	480
K^+	782	20
HCO ₃ -	1098	18
SO4 ²⁻	71181	741
Cl	16131	455
TDS	179.1 ppt	
Ionic Strength	1.86	
pН	9.1	
Total Alkalinity	20.43 meq	
Carbonate Alk.	20.41 meq	

10.8.2 Modern Sediments and Stratigraphy

The basin is flat bottomed with very steeply sloping sides. The modern bottom sediments exhibit a simple facies pattern: a narrow band of poorly sorted, coarse (sandy gravel to silty sand) siliciclastics in the near-shore area grades basinward into clayey salt and salt in the deep water (>3 m depth) offshore area. The offshore sediments are composed mainly of soluble evaporitic minerals dominated by epsomite, bloedite, and mirabilite. The offshore areas of the lake are presently experiencing very high rates of sedimentation of these salts, with annual rates (measured by sediment traps) of up to nearly 30 kg m⁻². In detail, the paragenesis of these

endogenic salts are complex and the modern sediments include a wide variety of Ca, Mg, Na, and Fe sulfates. The lake contains about 2 million tonnes of industrial grade Na and Mg sulfates.

Our knowledge of the Holocene stratigraphic sequence preserved in this lake is still incomplete. We have recovered sediment cores of up to 3 m in length from 11 sites in the offshore area of the basin. The oldest sediment penetrated to date is only about 2000 years old. All coring sites were in water depths greater than 4 m, so we still have no understanding of how these deep water sedimentary facies relate to the coarse clastics of the near-shore areas. This offshore sedimentary sequence ranges from fine-grained, organic-rich mud and poorly sorted, clayey, sandy silt to coarsely crystalline, well-indurated salts. Five lithofacies can be recognized as shown in a typical composite lithostratigraphic section in Figure 10.12. The basal structureless clay (Facies E) is firm and non-bedded, and passes sharply upward into about 50 cm of gypsum $(CaSO_4 \cong 2H_20)$ and indistinctly laminated gypsiferous mud (Facies D). Interfingering with this gypsum-rich facies is a black, organic-rich, highly reducing mud (Facies C). Overlying Facies C and D is a carbonate-rich mud (Facies B) characterized by irregularly-spaced packages of finelylaminated sediment alternating with nonbedded material. The carbonate is mainly aragonite and this aragonite often has a distinctive "rice grain" crystal morphology. Occasional large granules and pebbles, probably of dropstone origin, also occur in Facies B. Finally, the uppermost sedimentary facies in the offshore area of the lake consists of soluble salt. This salt is generally clear, colorless, and nonbedded, but even small amounts of mud and organic matter can give a grey to black coloration. Although Facies A is, overall, dominated by Na sulfate minerals, the proportions of the major compositional groups (i.e., Na sulfates, Mg+Na sulfates, and Mg sulfates) show consistent stratigraphic variation: the lower third of the facies has a relatively high proportion of Mg sulfates. These salts grade upward into several tens of cm of mixed Na and Na+Mg salts, and, finally in the uppermost part of the facies, back into more Mg sulfate-rich precipitates.



Figure 10.12. Composite lithostratigraphy, Little Manitou Lake.

The sediments recovered in our coring to date show the lake has undergone significant changes in salinity, composition, and water depth during the past several millennia. The oldest sediments (Facies E) were deposited in a relatively deep and freshwater lake that existed in the basin about 2000 years ago. Soon after 2000 BP, hydrologic conditions in the basin changed abruptly, water levels dropped, and the lake became a shallow to ephemeral mudflat/salt flat or playa basin. The water in this lake was compositionally complex and reflected a varying mixture of shallow, hyposaline Ca-SO₄ groundwaters and more alkaline, highly concentrated hypersaline surface brines. These low water/playa conditions existed in the basin until about 1500 BP, at which time the lake gradually deepened and eventually a perennial lake was re-established. Water depths for the next 500-700 years may have been as much as 20 m, and the lake was probably chemically stratified (meromictic). The rice grain aragonite indicates that the precipitated carbonate crystals settled through a relatively deep and slightly undersaturated monimolimnion. Water salinity began to increase about 1000 BP, probably associated with an overall lowering of lake levels. For the past millennium conditions in the Little Manitou Lake basin have likely been similar to that of today (e.g., a perennial lake about 5-6 m deep with moderate seasonal fluctuations and occasional meromixis).

11.1 BLACKSTRAP LAKE

Blackstrap Lake is a narrow, riverine lake occupying a 50 m deep postglacial river valley. We have only a very approximate idea of the fill in this valley. Christiansen (1973) suggests that the valley originated approximately 12,500 years ago as an ice marginal channel which drained meltwater from glacial lake Saskatoon (to the south) northeastward into glacial Lake Elstow. Lake Elstow, in turn, drained southward into the large Last Mountain Lake. A re-advance of the ice dammed the northern end of the Blackstrap channel and initiated lacustrine sedimentation.

The carbonate mineral fraction of the sediments was studied by Ghebre-Egziabhier and St. Arnaud (1982). They showed that the modern bottom sediments of the lake contain high-Mg calcite. This fine grained endogenic calcite is readily distinguished from the coarser grained detrital calcite that is derived from the surrounding calcareous tills. The high magnesium content of the endogenic calcite is the result of the slightly elevated Mg/Ca ionic ratio of the lake water. The stratigraphic variation in carbonate content has not yet been examined.

Ghebre-Egziabhier and St. Arnaud (1983) also suggest an interesting recent brine evolution scheme for Blackstrap Lake: prior to flooding the waters were hypersaline and dominated by Ca and SO4 ions resulting in gypsum precipitation. Following inundation from the South Saskatchewan River in 1969, the water was diluted and dissolution of soluble salts and gypsum occurred. This dilute phase was short-lived and passed quickly into the lake's presentday saline phase in which both normal (low-magnesian) and disordered, high-magnesian calcite are being precipitated. This study also shows that these authigenic carbonates are cementing fines into sand-sized particles.

Just two kilometers to the south of this stop is Mount Blackstrap. The mountain was constructed from till of the Battleford Formation to provide a ski hill for the 1971 Canada Winter Games. The conical shaped hill rises about 40 m above the surrounding till plain, and together with the 50 m adjacent Blackstrap valley, provides a 350 m long ski run.

11.2 LAST MOUNTAIN LAKE

This stop gives us a striking panorama of two major meltwater spillways: the Qu'Appelle valley (to the east and southwest) and the Last Mountain Lake valley (to the west and north). A short distance to the west, a third valley, the ice-marginal, 60 m deep Arm River Valley, connects to Last Mount Lake. All of these valleys are incised into shales of the Cretaceous Bearpaw Formation. Several small Na₂SO₄ deposits occur near Regina Beach. Cole (1926) reports that the deposit at section 25, township 20, range 22 was one of the first commercially exploited lakes.

11.3 CEYLON LAKE

11.3.1 Introduction

Within the context of the geolimnology and paleolimnology we have been examining so far, Ceylon Lake offers us an excellent opportunity to examine the stratigraphic record of a saline lake for which the modern sedimentary processes are already reasonably well documented. The specific aims of this stop are to summarize and interpret the postglacial lacustrine stratigraphic record of Ceylon Lake, a typical salt-dominated playa basin in the northern Great Plains, and to emphasize some of the contemporaneous and postdepositional processes that can significantly affect the stratigraphic records in basins like this. We will also have the opportunity to view many of the important modern sedimentological and geochemical processes operating in typical salt playas.

11.3.2 What Data Do We Have and How Did We Get Them?

Most of what we know about the stratigraphic record of Ceylon Lake is based on analysis of a total of approximately 40 meters of sediment core taken from the basin during the period 1983 to 1986. Cores up to 12 m in length were acquired during the summer (ice-free) season using a motorized rotary drill and a modified hand-driven Livingstone piston sampler (Cushing & Wright, 1965). Most of the interpretations are based on cores and samples from nine locations in the basin. Supplementary stratigraphic and isopach data from numerous other locations were acquired using a hand-operated auger.
11.3.3 The Modern Lake

11.3.3.1 General Setting

Ceylon Lake is located 120 km directly south of Regina, Saskatchewan, and about 30 km north of the Canada-United States border. The lake occupies a long, narrow, riverine basin located in the Missouri Coteau, a distinct, 50 km wide linear geomorphic feature consisting of hilly or 'hummocky' topography. Because the Missouri Coteau has such poorly integrated drainage, there are many salt lakes in the area. Commercial extraction of the brines and evaporitic minerals has taken place from several of these basins, including Ceylon Lake (Last & Slezak, 1987a).

A small area of finely laminated and cross-stratified sandstone (quartz arenite and subarkose)belonging to the Paleocene Ravenscrag Formation is exposed on the west wide of the valley wall above Ceylon Lake. Whitaker (1974a) shows that the Ceylon basin occupies a tributary of one of these bedrock valleys. Hammer seismic surveys over the main southern basin of the lake show depths to bedrock of between about 10 and 30 m.

11.3.3.2 Hydrogeology

The modern hydrology and hydrochemistry of Ceylon Lake and surrounding drainage basin have been discussed in Last (1984, 1989a). Rutherford (1967) and Whitaker (1974a) also provide groundwater data for the area.

Ceylon Lake exhibits playa characteristics, filling with water during the spring and early summer and usually drying completely by late summer or fall. Maximum water depth recorded in the lake since 1981 is 2.1 m. Conversely, even when the basin appears to be dry, a considerable amount of water is usually present within and below a thin salt crust. This water is derived from sub-bottom springs. Seasonal development of the salt crust greatly reduces water loss from the lake by evaporation.

Ceylon Lake water is usually hypersaline with salinities normally in the range of 100 to 300 g/l total dissolved solids (TDS). Because of the large area of "exposed" soluble salts in the center of the basin, high salinities are quickly reached as the lake floods with relatively fresh inflow water during early spring. The lake brines are usually dominated by magnesium, sodium, and sulfate ions, however large variations in ionic ratios and concentrations exist both seasonally and spatially within the basin (Last, 1989a). During early spring the water is a Na-(Mg)-SO₄-HCO₃ type. By late summer any remaining brine is normally of a Mg-(Na)-Cl-SO₄ composition.

Because of the elongated riverine morphology of the basin, water circulation is often restricted, resulting in more concentrated brine at the south end of the lake relative to that at the north end. This north-south variation in brine chemistry and concentration is also reflected in the

modern sediments being deposited in the lake (see below), and is due mainly to differences in the amount of stream inflow and spring discharge in the two parts of the basin (Last, 1984).

The largest components of the hydrological budget of the modern lake are influx by groundwater and loss by evaporation. There are no major perennial streams entering the lake, however there are over twenty ephemeral streams. The basin is topographically closed. The inflowing groundwater is relatively dilute (< 10 g L⁻¹ TDS) with Na and HCO₃ as the major ions, although high salinities are readily achieved as this fresh water passes through and over the thick sequence of soluble salts in the basin. Unfortunately, details regarding the groundwater flow and dynamics within the basin are unknown.

11.3.3.3 Modern Sedimentology

The modern sediments and sedimentology of Ceylon Lake have been described in detail Last, 1989a. Ceylon Lake is presently a salt dominated playa. The modern sediments in the basin consist of (in order of abundance): (a) very soluble evaporitic magnesium and sodium sulfate and chloride salts (mainly bloedite, mirabilite, thenardite, epsomite, and halite), (b) sparingly soluble carbonates and sulfates (high and low-Mg calcite, aragonite, dolomite, and gypsum), (c) silicates and ferromagnesian minerals, and (d) organic matter. Three genetic types of sediment can be recognized: (a) allogenic (i.e., derived from weathering and erosion of the surrounding glacial drift, soils, and bedrock in the watershed), (b) endogenic (i.e., originating from processes occurring entirely within the water column of the lake), and (c) authigenic (i.e., originating from processes occurring once the sediment has been deposited). All of the soluble salts and some of the sparingly soluble carbonates and sulfates are interpreted to be either endogenic or authigenic. Most of the silicate and ferromagnesian minerals and some of the sparingly soluble carbonates are allogenic. This detrital material is composed mainly of clay minerals (kaolinite, smectite, and illite), guartz, and feldspars. The organic matter, which can comprise up to 40% of the total sediment in some parts of the basin, is both endogenic and allogenic in nature.

Several major environmental zones can be easily recognized in the basin, giving rise to two basic modern sedimentary facies assemblages: (a) a clastic-sediment-dominated shoreline and nearshore facies group which consists of colluvium, mud flat, sand flat, and beach subfacies; and (b) an offshore chemical-sediment-dominated salt pan facies. The salt pan facies covers most of the area of the southern part of the basin (Figure 11.1), whereas the clastic sediment facies are more dominant in the north.

Present-day sedimentation in the basin is controlled by the interplay of: (a) flooding of the playa which causes dissolution of soluble minerals of the salt pan facies and efflorescent crusts of the mud flat and sand flat facies; (b) evaporative concentration of the brine which results in supersaturated conditions and precipitation of various soluble and sparingly soluble salts; (c) detrital influx by wind, streamflow, and spring discharge; and (d) organic productivity. In addition, evaporative pumping of shallow groundwater in the mud flats and sand flats causes

growth of intrasedimentary displacive and poikilitic salt crystals in the near-surface clastic sediment.

11.3.4 Stratigraphy

11.3.4.1 General

The stratigraphic sequence recovered from Ceylon Lake is quite variable in terms of sediment type, thickness, and distribution depending on the location in the basin. The sediment varies from loose, unconsolidated sands and gravels to massive, indurated salt. In general, cores from the northern half of the basin and from nearshore areas of the southern part of the lake consist of up to 8 m of soft to firm silty and clayey sediment overlying coarser sands and gravels of undetermined thickness. Sediment colors are generally dark gray (2 Y 2.5/1, Munsell) to dark greenish gray (5 Y 2.5/2) and brownish black (5 YR 2/1). Overall, the sequence is very poorly bedded with occasional laminae composed of organic fiber mats or coarser/finer clastics. Large, clear, euhedral salt crystals are common in the upper, finer grained part of the sequence. These salts are mainly mirabilite and bloedite, and show displacive intrasedimentary growth. Lenses and beds of mirabilite and bloedite up to several tens of centimeters thick are sometimes encountered in the upper part of the section. The coarse clastics at the base of the section are generally well sorted. Moisture content is high (50-80%) in the clavey part of the section and low (20-30%) in the sandy material. Unlike other lacustrine sequences in the Great Plains (e.g., Teller & Last, 1982; Last & Schweyen, 1985), distinctive zones of low moisture content are not present in Cevlon. Organic matter ranges from less than 2% in the lower, coarse grained sediment to about 20% in the overlying finer grained material, but does not show any specific trend with depth. Mineralogically, the sediments are composed mainly of clay minerals, feldspars, quartz, and minor carbonates.



Figure 11.1. South basin salt pan, Ceylon Lake.

In contrast, the sediment fill in the main southern portion of the basin, away from the nearshore areas, consists of a thick sequence of salt overlying the fine grained clastics which, in turn, overlie coarse grained clastics. A poorly sorted, very compact pebbly clay was encountered at the base of one of the cores near the southern end of the lake.

11.3.4.2 Lithostratigraphy

Based on sediment texture, mineralogy, moisture content, color, sedimentary structures, and organic matter content, six subsurface sedimentary facies units can be recognized in the Ceylon Lake basin. Three of these facies are interpreted to be lacustrine, one is fluvial, and one is ice-laid (till). The main sedimentary and mineralogical features that characterize each facies are summarized in Table 3. Not all of the facies were encountered in all of the cores.

Facies A: Poorly sorted clayey sand. Facies A is a gravelly clay loam diamicton. It is characterized by: (a) low moisture and organic matter contents, (b) dark yellowish brown color, and (c) poor sorting. Textural analysis of a single sample indicated it is a heterogeneous mixture of clastic material with a wide range of grain sizes: 43% sand, 28% silt, and 29% clay, with a mean grain size of 0.2 phi. The sediment is composed mainly of clay minerals, quartz, and feldspars, with minor amounts of ferromagnesian minerals and carbonates. The small amount of carbonate material is composed of calcite and dolomite. The CaCO₃ is low-Mg calcite (less than 4 mole percent MgCO₃); the dolomite is approximately stoichiometric and appears to be well ordered, although the small amount of CaMg(CO₃)₂ throughout the entire stratigraphic section in Ceylon Lake prohibited detailed crystallographic study of the mineral. Both carbonates are interpreted to be entirely detrital in origin.

Because of the dry, firm nature of the sediment, penetration and core recovery were very poor. Facies A was recognized in only one core so its thickness and lateral extent within the lake proper are unknown. However, similar material can be found underlying present-day colluvium and soils on the slopes of the basin. Where observed, Facies A sediment has a sharp upper contact with the overlying facies.

Facies A is interpreted as being composed of either ice-laid sediment or poorly sorted colluvium. The relatively coarse but wide range of grain sizes, the lack of bedding, the low moisture content, and the oxidized color are all compatible with deposition by ice or possibly accumulation by downslope mass movement.

Facies B: Well sorted sand. Facies B consists predominantly of well sorted, fine to medium grained sand with minor amounts of coarse grained sand and gravel. Colors are generally light brown to brownish gray. The sediment has very low moisture and organic matter contents. Textural analysis of three samples showed mean grain sizes of 2.6 to 1.9 phi. The sediment is composed mainly of quartz and feldspars with minor ferromagnesian and carbonate

minerals. The carbonate minerals in Facies B are similar to those of Facies A: calcite (low-Mg) and dolomite, and are, likewise, interpreted to be detrital.

Although core recovery was generally poor, where available for observation of the sediment of Facies B exhibits both massive bedding and indistinct, flat, parallel lamination. Facies B immediately overlies Facies A in the core from location 1 in the southern part of the basin. The maximum thickness of Facies B is 2.5 m at location 2. The unit is present in the northern part of the basin, but was not completely penetrated. Facies B shows a sharp to interfingering contact with Facies C and a sharp contact with Facies A.

The well sorted nature of Facies B sediment and the relatively coarse grain size indicate deposition in a high energy environment. This could be in a variety of sedimentary settings such as in a fluvial channel, in a delta, beach or shoreline environment of a deep perennial lake, or even in the offshore area of a shallow lake. The indistinct sedimentary structures and the inconsistent vertical trends in grain size within the facies provide little conclusive evidence as to the specific setting. The long, linear basin that Ceylon Lake occupies is part of a larger glacial meltwater spillway system that operated between about 16,000 and 15,000 years ago (Christiansen, 1979; Witkind, 1952). This spillway system cut several deep valleys (which are now abandoned) in glacial drift and bedrock in the area (Whitaker, 1974a, b). The coarse, well sorted clastics of Facies B were most probably deposited in the Ceylon valley during the waning stages of this fluvial episode.

Facies C: Calcareous mud. This facies encompasses a range of lithologies. The dominant lithologies of Facies C are calcareous silty clay and clayey silt. Thin beds of slightly coarser sediment (silt and sandy silt) are also present. Mean grain size ranges from 4.1 to 7.2 phi. Colors range from dark gray to dark greenish gray. In general, the sediment is characterized by: (a) high moisture and carbonate mineral contents, (b) the presence of ostracod and gastropod fragments, and (c) the presence of irregularly spaced laminae and thin hardgrounds/cemented crusts. Organic fibers and laminae composed of organic fiber mats are present but are not so abundant as in Facies E. The carbonate minerals consist mainly of calcite and aragonite. The calcite contains up to 8.6 mole percent MgCO₃. Most of this carbonate material is biogenic in origin. The unit also contains some tufa-like material consisting of calcite coated plant fragments and calcareous intraclasts. The hardgrounds, crusts, and laminae, which are irregularly spaced throughout the facies, are composed of aragonite- and calcite-cemented clastic material. The calcite in these lithified laminae and crusts is both low-Mg and high-Mg CaCO₃. A small amount of dolomite also occurs in Facies C. This dolomite appears to be slightly Carich as evidenced by the displacement of the X-ray diffraction peaks (Goldsmith & Graf, 1958). However, the small quantity of the $CaMg(CO_3)_2$ prohibited more detailed crystallographic and ordering investigation. Thicknesses of Facies C typically range from 10 to 40 cm; Facies C is more common in cores in the center and southern parts of the lake than near the basin margins. The unit shows gradational and interfingering lower contacts with Facies B and is intimately interbedded with Facies D.

The fine grain size and occasional thin bedding and lamination of Facies C are indicative of quiet water deposition. Although sedimentation may have been in overbank floodplain areas associated with the fluvial channel deposits of Facies B, the narrow width and steep sides of the Ceylon valley would suggest that extensive areas of poorly drained floodplains were not present. Thus, the more likely environment for deposition of Facies C is a lake.

The presence of endogenic and authigenic carbonates indicates that the lake and sediment pore waters were supersaturated with respect to at least calcite and aragonite, and that this precipitation was taking place from a relatively low Mg/Ca ratio solution. The MgCO₃ content of the non-detrital calcite suggests Mg/Ca ratios of less than 5. Similarly, the paucity of Mg-bearing carbonates and other salts indicates that the lake water was relatively fresh with Mg/Ca ratios of less than about 10. However, if the small amount of Ca-rich dolomite is interpreted to be non-detrital (that is, derived from precipitation within the lake or pore water), this would indicate at least sporadic occurrences of higher Mg/Ca brines. The high organic matter content and the abundant shell material point toward high levels of organic productivity in the lake. The occasional presence of fine, undisturbed laminae suggests that conditions were unsuitable for burrowing organisms, possibly due to periodic development of a stratified water body and anoxic conditions at the sediment-water interface.

Water depths in the lake during deposition of Facies C are difficult to estimate. The present-day basin has a spill-over point approximately 10 m above the surface of today's lake floor. Thus, if Facies C sediments are interpreted to represent deposition in a relatively low salinity, hydrologically open basin, water depths in excess of 15 to 20 meters may have existed in the lake.

Facies D: Gypsiferous mud. Facies D is similar to Facies C in appearance and texture, except that Facies D sediment contains gypsum and a relatively low amount of carbonate material. The gypsum occurs both as irregularly spaced laminae and as finely crystalline material disseminated within the structureless fine grained siliciclastics. The gypsum shows a variety of morphologies and textures, including euhedral lenticular plates and rounded, silt sized grains. Sediment colors are variable, including dark greenish gray, dark gray, and dark olive gray. The gypsum laminae are light gray, and composed of relatively pure silt sized gypsum grains and crystals (gypsite as defined by Warren, 1982). Individual units of Facies D are normally less than 20 cm thick. The sediment is interbedded with Facies C, but the contacts are gradational.

The fine grain size and overall relatively poor sorting indicate quiet water sedimentation similar to that of Facies C. However, the presence of both disseminated gypsum and gypsum laminae in Facies D shows that the lake/pore water did, at least occasionally, undergo evaporative concentration to the point of saturation with respect to CaSO₄ · 2H₂O. These high salinities may have been spatially limited and associated only with evaporative concentration of pore waters in nearshore mud flat/sand flat areas of the basin. Thus, the complex interfingering relationship with Facies C reflects transgression/regression cycles and lateral migration of

shoreline (Facies D) and offshore (Facies C) environments. Alternatively, the gypsum-rich Facies D may represent elevated salinities in the entire lake, which would be a consequence of basin-wide lowering of water levels. In this case, the interbedding of Facies C and D would point toward dramatic and possibly rapid fluctuations in lake level and brine composition. The array of gypsum crystal forms, fabrics, and textures which occurs in Facies D further points toward fluctuating hydrological (and possibly compositional) conditions. Although there are many environmental factors that have been shown to influence the morphology of $CaSO_4 \cdot 2H_2O$ in saline lake settings (see, for example, discussion in Bowler & Teller, 1986; Warren, 1982; Carenas et al, 1982), the presence of laminated gypsite indicates subaqueous precipitation and relatively high water conditions, whereas the occurrence of the larger, non-abraded euhedral gypsum crystals dispersed within a detrital clay matrix suggests displacive precipitation from saturated pore solutions, probably under subaerial (low water) conditions.

Facies E: Structureless black mud. Facies E consists of black, fine grained silty clay and clayey silt. The sediment is recognized by: (a) very high moisture contents, (b) abundant intrasedimentary salt crystals, and (c) dark gray to black color. Mean grain size ranges from 6.9 phi to over 8 phi but does not exhibit any trend with depth. Facies E shows gradational lower contacts with Facies C/D and a sharp to interfingering upper contact with Facies F. The freshly cored sediment has a strong hydrogen sulfide odor suggesting reducing conditions. Although the sediment does contain abundant plant fibers, there is no observable bedding. The inorganic component of the sediment is composed mainly of clay minerals, quartz, and iron sulfides. The carbonate mineral content is very low compared with Facies C. The intrasedimentary salts are mainly mirabilite and bloedite with minor gypsum. As much as 35% of the sediment can be authigenic precipitates.

Similar to Facies C and D, the fine grain size of the detrital sediment of Facies E suggests deposition in a quiet water (lacustrine) environment. The presence of soluble Na and Na-Mg salts in the form of intrasedimentary precipitates often showing displacive fabrics indicates saline to hypersaline pore water solutions. The low gypsum content and absence of other Ca-bearing precipitates suggests that this brine was dominated by sodium and magnesium cations. Similarly, the lack of endogenic and authigenic carbonates indicates lower carbonate alkalinities relative to that of Facies C deposition; the low gypsum content suggests lower Ca activities relative to Facies D. The strong H₂S odor and the presence of pyrite and other poorly crystalline iron sulfides is the result of dissimilatory sulfate reduction by microbial activity at or just below the sediment-water interface: $2CH_2O + SO_4 ---> H_2S + 2HCO_3$ and $2H_2S + Fe ---> FeS + 2H$.

The water level in Ceylon Lake at the time of deposition of the black mud of Facies E is difficult to evaluate because similar sediment is forming today in both perennial (deep water) and ephemeral (shallow water) saline lacustrine basins. For example, the modern sediments of both Waldsea Lake and Deadmoose Lake consist of black, organic-rich, highly reducing, structureless silty clay with occasional large, euhedral intrasedimentary mirabilite crystals (Last & Schweyen, 1985; Last & Slezak, 1986). In contrast, the surficial sediments of many of the saline playas of the northern Great Plains region are characterized by black, nonlaminated silts and clays very

similar to that of Facies E (Last, 1984). Finally, the sediment of Facies E may represent a residue: a concentration of mainly insoluble clastic material remaining after dissolution of the more soluble evaporitic minerals. Clearly, the paleohydrological interpretation of Facies E is equivocal; without independent evidence the sediment could have been deposited under any of a wide range of hydrological conditions from deep water to shallow water to complete basin desiccation.

Facies F: Salt. The sediment of Facies E interfingers laterally and upward with well consolidated, massive, coarsely crystalline salt of Facies F. Volumetrically, this salt is the most abundant stratigraphic unit within the basin. It can reach up to nearly 9 m in thickness in the center of the southern part of the lake. It thins laterally toward the edges of the basin and to the north. The unit is also the most mineralogically complex facies in the basin. Similar to the modern salt pan sediments, the salts of Facies F are dominated by bloedite, mirabilite, and thenardite but there are also appreciable amounts of epsomite and gypsum. In addition, a wide range of other sulfates, carbonates, and halides occur in minor amounts.

Overall, the proportion of sodium sulfate salts (mirabilite and thenardite) decreases upward in the section from about 80% to 55% of the total soluble salt fraction. In contrast, the amount of Mg-bearing evaporites (mainly bloedite and epsomite) increases from less than 5% at the base of the unit to 25% near the top.

The salts of Facies F are generally clear and colorless when fresh and white when dry, although even minor amounts of fine grained clastic material and organic matter can give a black to dark grey coloration. The sediment is equigranular and uniformly coarsely crystalline. In situ, the sediment shows an interlocking crystalline mosaic texture, however this is rarely observed because the coring tends to cause fragmentation and disaggregation of the crystalline material. Individual crystals usually have few inclusions and even in very muddy sections of the facies, the insoluble material is concentrated at the crystal boundaries. The bedding characteristics of Facies F are difficult to evaluate and describe. Because of the coarsely crystalline nature of the salt, undisturbed core samples were rarely recovered such that small scale bedding features cannot be identified. On a large scale, Facies F is interbedded with relatively thin (1-10 cm) zones of Facies E sediment.

When examined and analyzed in detail, the sediments of Facies F can be further subdivided into 37 individual subfacies based on the composition of the soluble salts. As discussed by Hosler (1979), the use of "facies" in this context is somewhat different from other uses of the term: in evaporite sediments, "facies" is used to characterize the mineralogical-chemical composition of the deposit. Each facies is distinguished by a particular suite of chemical precipitates. Thus, it is important to realize that the facies are identified, not by the proportion or amount of certain salts, but rather by the simple occurrence (in any proportion or amount) of a particularly evaporite mineral(s).

The sediment of Facies F was deposited in a hypersaline lacustrine environment. However, as is the case for Facies E, the depth of water in which the salts of Facies F accumulated is difficult to determine. Because the salts record little original (primary) depositional fabric, there is no a priori evidence within the sediments themselves to conclusively point toward either shallow or deep water deposition. The coarsely crystalline texture, the presence of appreciable amounts of insoluble clastics, the thick bedding and lack of thin, laterally persistent laminae all suggest deposition in a shallow water lake probably similar to the modern Ceylon basin. A shallow water, ephemeral lake environment like that of today's basin also helps account for the extensive recrystalization evident in the salts which would obliterate most finescale shallow water sedimentary structures such as cross-bedding, ripple marks, and mud cracks. In contrast, as demonstrated elsewhere (Last, 1989b; Last & Slezak, 1987b), thick, coarsely crystalline salt much the same as Facies F can be found in some deep saline lakes of the region. As indicated above, water depths of as much as 10 to 15 m may have existed in the still hydrologically closed-basin lake. This shallow water versus deep water enigma is not uncommon in evaporite studies and has been the source of long-standing controversy in geological literature (see, for example, discussions in Schreiber, 1986; Sonnenfeld, 1984; Kendall, 1984). Indeed, there is considerable evidence indicating that water depth has relatively little to do with the actual processes of evaporite formation (Sonnenfeld & Perthuisot, 1989), thus suggesting that interpretation of lake levels and depth fluctuations on the basis of the preserved salts is inconclusive.

In contrast to these enigmatic paleohydrological interpretations, the evaporites of Facies F do provide the basis of less ambiguous interpretation regarding brine composition. The systematic stratigraphic variation in the major evaporite composition within Facies F reflects changing brine composition. The overall upward increase in Mg-bearing salts and a concomitant upward decrease in mirabilite/thenardite suggests a shift in brine chemistry from a sodium dominated solution to one of mixed sodium and magnesium. As discussed later, the occurrence of compositional variation exhibited by the minor and ancillary evaporites in Facies F (i.e., the various subfacies indicates a rather complex interplay of primary crystallization and diagenetic processes within this overall trend.

11.3.4.3 Radiocarbon Dates & Pollen Stratigraphy

Organic matter in the sediment at 480 cm depth in core 6 (Facies C) has a ¹⁴C date of 6400 years B.P.; the organics in the sediment of Facies D at 300 cm depth in this core is 5690 ¹⁴C-years B.P. In both cases, finely disseminated organic matter was dated. The pollen spectrum from the dated samples showed no pre-Quaternary microfossils, suggesting little contamination by old carbon (cf., Nambudiri et al, 1980).

A reconnaissance-level investigation of the pollen preserved in the section was also done on the 6 m long core taken at location 6. The upper meter of sediment in this core is salt (Facies F) with very poorly preserved pollen grains. Similarly, the lower meter of the core (Facies B) is relatively coarse grained (sandy) material with little pollen. The sequence between about 1 m and 5 m depth contained abundant and well preserved pollen grains. Because of the reconnaissance nature of this palynological investigation, the stratigraphy and interpretations presented below must be regarded as preliminary.

Based on a sampling interval of approximately every 35 cm, the part of the section between 1 and 5 m depth can be divided into three zones: the lowermost unit, Zone I, is dominated by a mixture of Pinus, Gramineae, Artemisia, and Chenopodiaceae. Ambrosia is present whereas Selaginella is absent. Pinus shows a gradual increase upward in the Zone. This zone is interpreted as representing a relatively warm and dry climate. Zone II is marked by high values of Pinus and Gramineae. Compositae and Cyperaceae maintain their proportions, but Chenopodiacae, Artemisia, and Sarcobatus decrease, suggesting a somewhat cooler and wetter climate (relative to that of Zone I). The uppermost unit, Zone III, is dominated by Pinus, Gramineae, and Artemisia with appreciable amounts of Chenopodiaceae, Compositae, Sarcobatus, Cyperaceae, and Selaginella. This zone is interpreted to represent a mixed grass prairie and probably a warm and slightly more humid climate relative to that of the present.

11.3.5 Postdepositional Modification of the Stratigraphic Record

A number of postdepositional processes have modified the sediments preserved in Ceylon Lake and changed the stratigraphic relationships of the deposits. The most important of these processes, mineral diagenesis, salt karsting, and mud diapirism, are summarized below and described in detail in Last (1989a, b, and 1984). In some places in the basin, these processes significantly alter or disrupt large sections of the postglacial sediment fill, thereby creating difficulties in using the recovered stratigraphic sequence as a paleoenvironmental tool.

11.3.5.1 Mineral Diagenesis

The soluble salts of Ceylon Lake are extremely susceptible to dissolution and reprecipitation. Other than indistinct bedding features, the sediment of Facies F has few original depositional fabrics or textures preserved. The salts tend to be uniformly coarsely crystalline and equigranular, and show an interlocking crystalline mosaic texture suggesting repeated episodes of dissolution and reprecipitation. This lack of preservation of original fabric and textures in the salt makes interpretation of the unit difficult, particularly with respect to whether deposition of the salts occurred in a shallow or deep water lake. Both types of salt deposition (i.e., deep water and shallow water) can be found in modern saline lakes of the Great Plains.

Diagenesis can also affect the mineralogy of the deposit. The most common diagenetic alteration in Ceylon Lake sediment is simple dehydration. The mirabilite to thenardite transformation is the most readily observed dehydration reaction, and is also the most difficult to evaluate because either of the two sodium sulfate phases (i.e., Na₂SO₄ · 10H₂O or Na₂SO₄) can be primary precipitates in the modern lake under certain conditions. A similar situation likely exists in the Na-Mg-SO₄ phase assemblage as shown by Keller et al (1986a, b), Timpson et al (1986), and Skarie et al (1987) in wetlands in North Dakota: konyaite [Na₂Mg(SO₄) · 5H₂O] is

the most likely primary Na-Mg sulfate precipitate at the temperature and humidity conditions of Ceylon Lake. This primary but metastable double salt readily loses one water of crystallization to form bloedite within a matter of several days to a few weeks. Other simple dehydration reactions taking place in the Ceylon Lake sediment include the alteration of: (a) magnesium sulfates: e.g., epsomite (MgSO₄ $^{-}$ 7H₂O) to hexahydrite (MgSO₄ $^{-}$ 6H₂O) and kierserite (MgSO₄ $^{-}$ H₂O), (b) sodium carbonates: e.g., natron (Na₂CO₃ $^{-}$ 10H₂O) to trona (NaHCO $^{-}$ Na₂CO₃ $^{-}$ 2H₂O) and nahcolite (NaHCO₃), (c) sodium-calcium carbonates: e.g., gaylussite (Na₂CO₃ $^{-}$ CaCO₃ $^{-}$ 5H₂O) to pirsonite (Na₂CO₃ $^{-}$ 2H₂O), and (d) sodium-calcium sulfates: e.g., hydroglauberite Na₄Ca(SO₄) $^{-}$ 2H₂O to glauberite Na₂Ca(SO₄)₂. In contrast to the sodium and sodium-magnesium sulfate salts, the dehydration of the magnesium sulfates does not offer any interpretive ambiguity because hexahydrite and kieserite do not occur as primary precipitates in the modern lake.

Because of the salts' metastability with respect to the formative brine, any change in ionic ratios or concentrations can significantly alter the mineral composition beyond just the hydration-dehydration phase changes discussed above. Last (1989b) describes one such reaction from Ceylon Lake: bloedite and halite were found to be pseudomorphically replacing thenardite in the upper part of Facies F. Furthermore, as discussed above, it is possible that the thenardite itself was not primary, but rather a dehydration product of mirabilite. Considering the dramatic fluctuations in ionic ratios exhibited on a seasonal basis in the lake today and the striking influence of temperature on many of the most common evaporites in the basin (see Last and Schweyen, 1983), it is likely that other similar reactions are commonplace.

11.3.5.2 Salt Karsting

Dissolution of soluble salts and crystal beds by relatively dilute groundwater is likely a common occurrence in many evaporitic sequences (Coode, 1987; Sonnenfeld, 1984), however its impact on interpreting a preserved stratigraphic section has generally been ignored.



Figure 11.2. Solution chimney, Ceylon Lake South Basin.

Postdepositional dissolution of soluble evaporites has created local solution pits or chimneys in the sediments of Ceylon Lake. At least seven such chimneys have been identified in the modern lake on the basis of their surface expression (Figures 11.2 and 11.3). The occurrence of pre-modern dissolution pits and chimneys which have subsequently been filled in have also been identified on the basis of isopach irregularities in Facies F and dramatic compositional changes over short distances in the basin. The modern chimneys and pits do not affect spatially large areas of the basin; in total they are less than 150 m. However, the chimneys can be up to 9 m deep. This type of postdepositional dissolution of stratigraphically large sections of the soluble salts of Facies F and the deposition of new salts or perhaps clastic material has a significant and obvious impact on the resulting paleolimnological interpretations.

11.3.5.3 Mud Diapirism

The deposition of a thick sequence of relatively high density and low permeability salt (Facies F) on top of the lower density, high water content muds of Facies C, D, and E has led to instability of the underlying sediments. The liquefaction and fluidization of the underlying muds results in a variety of diapiric intrusions of mud into Facies F. Although these dykes and mud mounds are small in areal extent and spatially limited to areas having low to moderate thicknesses of Facies F (i.e., salt pan margin areas), wave reworking of the intruded sediment at the surface of the playa can redistribute this older sediment over broad areas of the basin. This provides a source of "old" palynomorphs, "old" carbon, and compositional/textural characteristics not compatible with the present hydrological and geochemical setting.

Figure 11.3. Air photo showing chimneys, Ceylon Lake.



11.3.6 Brine Compositional Changes During Deposition of Facies F

A fairly detailed record of compositional changes that have occurred during the most recent 5000 year history of Ceylon Lake can be deduced from the occurrence and distribution of the saline evaporitic minerals comprising Facies F. Although, as discussed above, the specific mineral species have probably changed in much of the deposit as a result of postdepositional dehydration and/or recrystalization, it is likely that the overall chemical composition of the various subunits of Facies F are approximately the same as they were at the time of deposition because of the very low permeability of the thick salt sequence. Furthermore, the kinetics for most of the diagenetic reactions are sufficiently rapid such that an equilibrium mineral assemblage is likely achieved well within the time span represented by even the smallest sampling interval. While seasonal, monthly, and diurnal temperature variations can significantly affect the mineralogy of the salts at the sediment-brine interface in the modern lake (Last 1989a), thereby likely obliterating any primary crystallization assemblage and making stratigraphic interpretation apparently difficult, Smith & Friedman (1986) and Smith et al (1987) have shown that the maze of early diagenetic transformations occurring in salt lakes such as this makes relatively little difference in the net result of salt crystallization once the material is buried to depths beyond the influence of significant seasonal temperature variations. Indeed, the fact that there are relatively abrupt stratigraphic compositional changes within the salts of Facies F confirms that the unit has not been completely homogenized by postdepositional processes.

Both the detailed fluctuations in salt mineral assemblage (i.e., Facies F subfacies) and the more general overall decrease in relative abundance of Na-bearing sulfates and complementary increase in Mg salts upward in the stratigraphic column are almost certainly due to fluctuations in brine composition of Ceylon Lake. Interpretation of the latter is straight forward: the brine of Ceylon Lake has changed from a mainly Na-SO₄-dominated solution about 5000 years ago to one with a considerably higher Mg content today. This increase in magnesium activity with time is not unique to Ceylon Lake but has also been identified elsewhere in the northern Great Plains (see, for example, Jones & van Denburgh, 1966]; Owen et al, 1973; Hammer, 1978; Last, 1982; Timpson et al, 1986). Although a wide range of mechanisms can be suggested to account for this long-term temporal change in brine composition, probably the most reasonable and straight-forward hypothesis for Ceylon Lake is that the higher magnesium content is a reflection of a more humid climate. Under a higher rainfall regime, it is likely there would be more dissolution of Mg-bearing minerals, such as dolomite, within the tills and soils of the watershed, thereby increasing the Mg/Na ratio of the lacustrine brine.

Examination of the subfacies sequence within Facies F reveals much more complex compositional variations with time. As expected considering the overall mineralogy of the evaporitic components in Ceylon Lake, the dominant subfacies present in Facies F sediment are (in order of abundance): (i) Ca-SO₄, (ii) Ca-SO₄ + Ca-Mg-CO₃, (iii) Na-SO₄, (iv) Na-SO₄ + Na-Mg-SO₄, (v) Ca-SO₄ + Na-Mg-SO₄, (vi) Ca-SO₄ + Na-Mg-SO₄, (vi) Ca-SO₄ + Na-Mg-SO₄, and (vii) Ca-SO₄ + Na-SO₄ + Na-Mg-SO₄ + Na-Mg-SO₄ + Mg-SO₄ + Mg-S

the evaporite sequence preserved in Ceylon Lake, the mineralogical subfacies reflect, in general terms, relative proportions of ionic components in the formative brine. Thus, the subfacies can be used to suggest the composition of the lake/pore water. For example, the magnesium sulfate salts of Subfacies F1 indicate that the brine had high proportions of magnesium and sulfate ions, but relatively low proportions of calcium, sodium, potassium, carbonate/bicarbonate, and chloride ions. In contrast, Subfacies F11 (Na-SO₄) indicates a high proportion of Na+ and SO₄, and low proportions of the other ions. In this generalized interpretive scheme, double salts (such as bloedite, pirssonite, and glauberite) indicate medium (or mixed) ionic proportions.

A cursory examination of some sections of several of the cores may suggest a cyclic or preferred order of vertical transition from one subfacies to another, however, most of the subfacies in the salt section appear to have a random vertical distribution. In an effort to objectively describe any preferred facies succession or sequence within the salts, th stratigraphic section was subjected to Markov chain analysis. Markov analysis has been used with considerable success by numerous investigators to help identify and interpret cyclic (or nonrandom) facies successions in a number of sedimentary settings.

Two transition frequency matrices were constructed from the raw core data: one evaluating the cation composition of the subunits of Facies F and the other summarizing the anion composition of the salts The expected transition frequency matrices for each data set were then calculated assuming a model of quasi-independence according to the method outlined by Powers & Easterling (1982). A chi-square test rejected the hypothesis of statistical quasi-independence for both matrices (at the 95% confidence level), suggesting a non-random vertical distribution of facies. The facies relationship diagrams shown in Figure 11.4 were drawn with the most significant non-random transitions identified using the binomial probability method of Harper (1984).



Figure 11.4. Markov chain geochemical facies analysis, Ceylon Lake (from Last, 1990).

Figure 11.4a shows that two anion facies associations occur more often than random: (i) a carbonate subfacies tends to be overlain by units with both sulfates and carbonates, which then pass upward into one of the sulfate subfacies, and (ii) the carbonate subfacies can be overlain by sulfate + chloride salts, which also pass back into sulfate units. The Markov analysis of cation composition shows a somewhat more complex vertical transition pattern (Figure 11.4b). One association comprises the cycle:

Ca + Na + Na-Mg ==> Na + Na-Mg ==> Mg ==> Ca + Na + Na-MgThis simple upward increase in magnesium cycle can then be overlain by two other associations: (i) a Ca + Na subfacies passes upward into first Ca facies, followed by Ca + Mg, then Na, and finally back into Na + Na-Mg, and (ii) a Ca + Mg + Na + Na-Mg subfacies grades into Ca + Mg + Na-Mg, then into a Na unit, and finally back to the Na + Na-Mg. As shown in Figure 11.4, the statistically most significant non-random transitions include: (a) Ca + Na ==> Ca, (b) Ca + Na-Mg ==> Ca, (c) Ca + Mg ==> Na, (d) non-salt facies ==> Na, and (e) Ca + Mg + Na + Na-Mg ==> Ca + Mg + Na-Mg.

11.3.7 Take-home Message from Ceylon Lake

The physical and chemical nature of the stratigraphic record preserved in Ceylon Lake indicates that the basin has experienced significant fluctuations in water levels, water chemistry and salinity, and sedimentary-depositional setting (Table 11.1). Because of the mainly erosional regime during much of the late Pleistocene and early Holocene, the early history of Ceylon Lake is largely unknown. The long, riverine morphology of the basin and the presence of fluvial sands and gravels at the base of the section suggest that the basin probably originated as a river channel. The flow required to erode the Ceylon valley (as well as numerous other linear valleys in the region) came from meltwater and extraglacial runoff associated with a retreating glacier martin. Christiansen (1979) contends that deglaciation in the Ceylon area took place about 15-16,000 years ago.

The earliest lacustrine sediments preserved in the basin are laminated calcareous muds which indicate that the lake water was probably relatively fresh with a low Mg/Ca ionic ratio. Although there is no direct sedimentological evidence of high water levels (such as beach ridges or wave cut scarps), the lake at this time was most likely hydrologically open, which would suggest water depths of possibly as much as 20 m. By about 6000 to 7000 years ago, however, there is evidence of increasing salinity and a change from mainly carbonate-rich water to sulfate-dominated brine. This change is likely associated with lowered water levels and development of hydrologically closed-basin conditions. Preliminary pollen data indicate the occurrence of an initially warm and dry climate followed by a brief period of relatively cool conditions, and then a return to a warmer but more humid environment (relative to that of today) by mid-Holocene time.

Despite this palynological indication of relatively humid climate, hypersaline, evaporitic conditions began in the Ceylon basin during mid-Holocene, and have, in general, existed

throughout the past 5000 years. Although it is difficult to reconstruct bathymetry on the basis of the preserved sediments, the lake has most likely been continuously shallow with a saline to hypersaline water body during this entire time. There is no evidence that the basin was ever dry for extended periods.

Even though a number of postdepositional physical and chemical processes have disrupted the late Holocene sequence in the basin, the relative abundances of the various salts do indicate changing brine composition from an initially sodium sulfate-rich system about 5000 yr B.P. to a mixed sodium-magnesium system now. Furthermore, the composition of the salt mineral assemblages that occur in this sequence provides considerable insight into changes in cation and anion ratios in the brine with time.

10.4 SYBOUTS-COTEAU LAKES

"Silence and solitude - the finest gifts Saskatchewan has to offer the bedeviled modern man." (McCourt, 1968).

The Na₂SO₄ deposits in the Sybouts-Coteau Lakes originally had reserves of about 15 x 10^6 tonnes in the form of bedded salts. Much of this reserve has now been depleted from the eastern basin (East Coteau Lake) by the mining operations. Salt thicknesses of up to 12 m were present. The western group of lakes (West Coteau Lake, Coulee Lake) have also been extensively modified by the mining process but have not been specifically exploited. A small reserve of sodium sulfate also exists in Alkali Lake which straddles the Canada-USA border.

The Sybouts-Coteau deposits were evidently very difficult to work successfully due to the presence of large karst features, mud plugs, and active springs. Mining operations were suspended in the mid-1970's. In 1981 Saskatchewan Minerals purchased the deposit and upgraded the facilities. There is an estimated 5×10^6 tonnes of marketable sodium sulfate remaining. On our route back to Saskatoon we will be passing several other active or abandoned salt mining operations and will visit these as time permits (Figure 11.5).

¹⁴ C YR BP	North Ingebright Mean Relative Humidity	Chappice Water Level & Salinity	Clearwater Water Level & Salinity	Ceylon Water Level & Salinity		
Present		FLUCTUATION FROM LOW TO		LOW & HYPERSALINE		
	HIGH	HIGH & FRESH TO SALINE		HIGH & FRESH		
1000		LOW WATER		STABLE CONDITIONS		
	LOW		DEEP & FRESH WATER	LOW WATER &		
2000	_		STABLE CONDITIONS			
	_	WATER		HIGH & FRESH		
3000	_			STABLE CONDITIONS LOW WATER &		
	HIGH					
4000	_					
	_	STABLE CONDITIONS		VERY LOW TO DRY & HYPERSALINE		
5000		LOW WATER & HYPERSALINE				
	VERY LOW		MISSING SECTION			
6000		REPEATED				
	HIGH	FLUCTUATION FROM DRY TO		REPEATED FLUCTUATION FROM SHALLOW TO DEEP & FRESH TO HYPERSALINE		
7000		DEEP & FRESH TO HYPERSALINE				
	FROM LOW TO HIGH		DEEP & FRESH WATER			
8000		Base of Record				
9000	HIGH		DEEP TO SHALLOW (DRY AT 8200 BP) & SALINE TO HYPERSALINE			
			SHALLOW & HYPERSALINE	DEEP & FRESH		
10,000	VERY LOW TO LOW		SHALLOW & FRESH WATER	WATER		

 Table 11.1 Comparison of Holocene paleolimnological conditions at Ceylon, Chappice, Clearwater and North Ingebright lakes.



Figure 11.5 Satellite mosaic showing some of the lakes that will be visited.

11.5 ORO LAKE - HOLY GRAIL OF THE NORTHERN GREAT PLAINS?

Despite the dramatic increase in interest, paleolimnological research in the northern Great Plains of Canada still lags behind that of other areas such as the Foothills and Rocky Mountain areas to the west and the boreal forest region to the north and east (Sauchyn, 1997). Ritchie and Harrison (1993) identify only one site in the prairie region of western Canada having a limnological record extending back to 10,000 BP. To date only very few of the extant lakes in the region have provided complete, uninterrupted sequences spanning the past 10 kyr. Oro Lake is one of these. Our objective at this stop is to summarize the lithostratigraphy of this lacustrine sequence and to discuss the changes in physical and chemical limnology that have occurred during the Holocene as interpreted from the mineralogical and lithostratigraphic record. Investigations of the biological, magnetic susceptibility, and isotopic aspects of the record are ongoing and reported elsewhere (e.g., Stuart, 1999; Stuart et al., 1998; Padden, 1996; Vance and Last, 1996; Cywinska and Delorme, 1995).

11.5.1 Setting & Geolimnology of Modern Oro Lake

Oro Lake is located 80 km southwest of Regina, Saskatchewan, and about 80 km north of the Canada-USA border. The lake occupies a small, elongate basin just south of the Dirt Hills area on the Missouri Coteau. The Dirt Hills are a series of parallel, deformed bedrock ridges mantled by about 100 m of glacial sediment. They were formed about 11,000 years ago by several surging ice lobes during deglaciation (Aber, 1993; Parizek, 1964). The Oro Lake basin likely formed shortly after this, probably as an ice-block melt out kettle depression. The terrain around Oro Lake is hummocky, typical of the disintegration morainal topography of the Missouri Coteau.

The Oro basin is small (0.5 km^2) and relatively shallow (mean depth: 2.8 m; maximum depth: 6.1 m). The hydrology and modern limnology of the basin are poorly known. Several small, ungauged ephemeral streams drain the small (< 10 km²) catchment. There is no surface outlet. Presumably the modern hydrologic budget is dominated by groundwater inflow and loss by evaporation during the ice-free season. Like many other perennial prairie lakes, Oro Lake has experienced a marked reduction in lake-level over the past several decades. Once a popular recreation site, with a small regional park and day-use facilities located at the north end of the basin, declining lake levels and deteriorating water quality now restrict use of the lake.

Although there has been no neolimnolological or modern sedimentological research yet done, the Oro Lake water column was chemically stratified during sampling visits to the lake in 1994, 1995, and 1999 (Table 11.2). The surface water averaged ~30 ppt (parts per thousand) salinity and the monimolimnion was about 45 ppt TDS. Unlike many of the other salt lakes in the vicinity (e.g., Shoe, Willow Bunch, Frederick, Old Wives), Oro Lake brine is dominated by Mg²⁺ rather than Na⁺. Oro Lake has the highest meq% magnesium of any salt lake in the Great Plains (cf., Last, 1992). The origin of this strong Mg²⁺ signature has not yet been resolved although it is clear the Oro brines represent a complex mixture of shallow (Ca+Mg+HCO₃), intermediate and deep (Mg+SO₄) groundwater contributions modified by evaporative concentration and mineral precipitation.

The entire water column of Oro Lake is strongly supersaturated with respect to many magnesium and magnesium+calcium carbonates and, during winter, is also saturated to supersaturated with respect to a variety of Mg and Na-bearing sulfate salts. The surficial offshore bottom sediments (0-1 cm; see Table 11.3) consist of a complex mixture of aragonite, Mg-calcite, disordered dolomite, hydrated magnesium sulfates (epsomite and hexahydrite), magnesium+sodium sulfates (konyaite and bloedite), calcium sulfate (gypsum), magnesium carbonate (magnesite), and detrital components (quartz, feldspars, clay minerals, calcite, and dolomite).

	9/1994		1/1005	5/1005	6/1997		3/1999		Groundwater					
	Surface	5 m	Surface	Surface	Surface	Surface	Surface	Surface	5 m	Surface	5 m	Shallow Drift	Deep Drift	Bedrock
Ca ²⁺	91.9	128	126	59			99.2	123	83	390	334			
Mg ²⁺	4500	6640	5950	2120			5100	6540	279	313	230			
Na ⁺	1940	2820	2680	1150			2190	2760	5.5	445	427			
K^+	369	530	397	127			398	512	8	13	13			
HCO3 ⁻ +CO3 ²⁻	1033	1860	1398	585			1117	1800	369	959	1030			
SO ₄ ²⁻	22200	31100	29000	12400			26100	30900	28.8	2080	1570			
Cl ⁻	600	812	814	313			680	798	8.2	136	135			
3Alkalinity	20.2	31.9	31				1010	1210	5.8	15.8	16.9			
Si	3.12	14.1	6.73	2.25			4.01	13.9	0.01	0.08	0.07			
F	6.4	7.4	7	10.3										
Li	2.56	3.74	3.44	1.5										
Ionic Strength	0.51	0.75	0.68				0.6	0.7	0.01	0.08	0.07			
TDS (ppt)	33.5	46.6	44.4	17.8	11	20	39.2	45.9	0.5	4.4	3.7			
pН	8.7	8.1	8.4	8.6			9	8.8	7.9	7	7.3			

Table 11.2. Oro Lake hydrochemistry (ionic concentrations in mg L^{-1}). Data from 6/1997 are from Stuart (1999). Total alkalinity is expressed as milliequivalents. Blanks indicate no data.

	Lithostratigraphic Unit									
	Diamicton	Unit 1	Unit 2	Unit 3	Unit 4	Surface Sediment Average	Overall Average			
% Total Siliciclastic Fraction	81.6	76	22.6	41.6	23.4	65.1	36.1			
% Total Clay Minerals	25.9	50.5	16.8	26.3	20	59.8	24.8			
% Quartz	25	10.1	3.1	8.1	2.1	0.8	5.7			
% Total Feldspar Minerals	38.8	14.6	2.6	7.1	1.4	4.5	5.5			
% Plagioclase	34.4	10.1	2.2	5.8	1.1	2.8	4.7			
% K-feldspars	9.4	4.5	0.4	1.3	0.3	1.7	0.8			
% Amphibole Minerals	1.9	0.9	0.1	0.1	0.1	< 0.1	0.1			
% Total Detrital Carbonate Fraction	18.4	11.6	16.5	23.9	10.8	6.1	20.8			
% Calcite	3.2	6.9	1.4	5.2	3.7	< 0.1	3.8			
% Dolomite	15.2	2.3	5.8	13.7	8.8	6.1	10			
% Total Endogenic & Authigenic Fraction	np	12.4	60.9	34.5	65.8	28.8	43.1			
% Magnesian Calcite	np	1.3	0.4	0.1	0.4	1.8	0.4			
Mol% MgCO ₃ in Mg-Calcite	nd	11	11.9	12.6	10.4	6.2	11.4			
% Disordered Dolomite	np	6.2	0.2	0.8	1.1	5.6	0.9			
Mol% CaCO3 in Disordered Dolomite	nd	66.1	70	65.5	68.1	64	68			

Table 11.3. Summary of average mineralogical characteristics of lithostratigraphic units. nd = not determined; np = not present

% Aragonite	np	2.5	3.4	30.3	19.8	2.5	21.9
% Total Mg Carbonate Minerals	np	np	np	0.1	2.7	2.5	< 0.1
% Total Sulfate Minerals	np	2.4	56.9	3.2	41.8	16.4	27.2
% Gypsum	np	2.4	56.5	3	27.9	7.7	26.4
% Total Mg Sulfate Minerals	np	np	<0.1	np	4.3	2.9	< 0.1
% Total Mg + Na Sulfate Minerals	np	np	np	np	3.4	2	< 0.1
% Total Na Sulfate Minerals	np	np	0.1	0.2	6.2	3.8	0.2
% Total Na + Ca Sulfate Minerals	np	np	np	np	< 0.1	< 0.1	< 0.1
% Total Other Sulfate Minerals	np	np	<0.1	np	< 0.1	< 0.1	< 0.1
% Total Phosphate Minerals	np	np	<0.1	np	< 0.1	< 0.1	< 0.1
% Total Chloride Minerals	np	np	< 0.1	np	< 0.1	np	< 0.1
% Pyrite	np	<0.1	np	<0.1	< 0.1	np	< 0.1
% Moisture	15.1	57.4	42.2	51	69.1	82.3	53.6
% Organic Matter	2.1	30.9	20.3	12.4	21.8	20.6	16.2
% Sand	5.5	16.9	4.6	1.8	5.7	6.5	4.5
% Silt	74.9	76.7	81.5	70.3	88.6	90.2	80.8
% Clay	19.6	6.4	13.9	28.9	5.7	3.3	15.1
Mean (µm)	17	38.1	21.3	15	29.9	29.9	21
Median (µm)	8.2	30.6	14.7	8.8	24.8	35.7	16.1

Sedimentation Rate ¹ (cm 100 yr ⁻¹)	nd	nd	8.2	8.3	7.9	nd	8.2
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¹Calculated on the basis of a best fit line of depth versus time for Core OR1 and assuming no interruption in deposition.

11.5.2 Lithostratigraphy

The Holocene stratigraphic sequences recovered from the three core sites in the basin generally consist of massive to well-bedded, slightly organic-rich, clayev silt. The upper meter of sediment is very soft with high moisture contents, whereas the lower ~20 cm recovered in each core are very firm and relatively dry. Moisture contents decrease gradually downward from greater than 80% at the surface to less than 50% in the lower half of the sections. Organic matter content is remarkably constant through most of the section ($\sim 15\%$), however thin zones of organic-rich sediment overlie the basal dry zones in each core. Sediment colors are generally dark olive grey (Munsell: 5Y 3/2) to dark yellowish brown (10YR 3/6) and dark grey (2.5 Y 2.5/1). Texturally, the sediment is mainly clayey silt. Mean grain size ranges from less than 4 :m to greater than 40 :m, with an overall average of ~ 20 :m. With the exception of the upper halfmeter of sediment and the lower 20 cm of the sections, parallel lamination is prominent. Most of the laminae consist of millimeter-scale light coloured (10YR 8/4 to 5Y 6/2) beds. Composition of individual laminae is usually monomineralic or strongly dominated by one mineral. However, the composition can vary considerably over relatively short (cm-scale) stratigraphic distances. Often these laminae occur in cm-scale packages or bundles of regularly spaced laminations alternating with massive or poorly bedded sequences. In addition, more indistinct, cm-scale light-dark banding is also common.

As shown in Table 11.3, the inorganic fraction of Oro Lake sediment, which comprises generally greater than 85% of the total sediment, consists of a mixture of soluble and sparingly soluble salts, carbonate minerals, and clay minerals, with minor amounts of quartz, plagioclase and potassic feldspars, ferromagnesian minerals, and pyrite. Although the paragenesis of this complex mineral suite is still being investigated, the high solubility of the sulfate salts and the lack of a source for most of the carbonate minerals within the drainage basin precludes their origin as clastic detrital material. It is likely that the clay minerals, quartz, feldspar minerals, calcite and dolomite are detrital in origin (i.e., allogenic), being derived from erosion of the sulfates, pyrite, aragonite, Mg-calcite, nonstoichiometric dolomite, magnesite, and other soluble salts have most likely been derived from within the basin itself, either by direct precipitation from the water column (i.e., endogenic) or by postdepositional authigenic/diagenetic precipitation processes.

The carbonate minerals in Oro Lake sediment, comprising about 40% of the inorganic fraction, are dominated by aragonite, dolomite, and calcite, with smaller amounts of magnesian calcite and disordered, nonstoichiometric dolomite (subsequently referred to as "protodolomite" in this paper), and sporadic occurrences of hydromagnesite [4MgCO₃Mg(OH)₂ $\overset{*}{}_{=}$ 4H₂O], magnesite (MgCO₃), and natron (Na₂CO₃ $\overset{*}{}_{=}$ 10H₂O). Soluble evaporitic sulfate minerals dominate the lower and upper third of each sequence, and make up an average of about 30% of the sediment overall. The soluble salt assemblage consists mainly of gypsum with irregular occurrences of thenardite (Na₂SO₄), bloedite [Na₂Mg(SO₄)₂ $\overset{*}{}_{=}$ 4H₂O], konyaite [Na₂Mg(SO₄)₂ $\overset{*}{}_{=}$ 5H₂O], epsomite (MgSO₄ $\overset{*}{}_{=}$ 7H₂O), and hexahydrite (MgSO₄ $\overset{*}{}_{=}$ 6H₂O). Endogenic and/or authigenic phosphate minerals and very soluble halides occur in a small number of samples.

Among the phosphates identified, brushite (CaPO₄), rockbridgeite [(Fe, Mn)Fe₄(PO₄)₃ (OH)₅], and strengite (FePO₄ \cong 2H₂O) occur most frequently. Halite was the only halide mineral identified.

The allogenic fraction of the sediment comprises mainly siliciclastic material (average 36%), with smaller proportions of carbonates (~20%). The siliciclastics are dominated by clay minerals but quartz, plagioclase, and potassic feldspars also occur in small amounts in nearly all samples. The detrital carbonates are dolomite and calcite. The ratio of these two minerals remains relatively constant throughout the sequence and compares well with the ratio of detrital carbonates in the tills and glacial deposits of the region (Teller and Last, 1981; Sun, 1996; Egan, 1982). The ratio of siliciclastics to detrital carbonates is also relatively constant throughout most of the sequence. This ratio, which reflects the relative chemical stability of siliciclastics versus carbonates (see Last and Sauchyn, 1993; Teller and Last, 1981), suggests little overall change in the intensity of chemical weathering processes within the Oro Lake watershed.

Based on the mineralogical composition, organic and moisture contents, and bedding features, the Holocene sequence recovered from Oro Lake can be subdivided into five lithostratigraphic units (Figure 11.6).



Figure 11.6. Composite lithostratigraphic section, Oro Lake (Last and Vance, in press).

11.5.2.1 Diamicton (pre-9700 BP)

The lowermost unit (diamicton) is a firm, compact, structureless, siliciclastic-rich sandy, clayey silt with very low moisture and organic matter contents. Large (cm-scale) rounded carbonate pebbles are present in a matrix of finer grained material. The mineral suite consists of subequal proportions of detrital feldspars, quartz, clay minerals and carbonates. The carbonate fraction of the sediment consists entirely of stoichiometric, well-ordered dolomite and calcite of detrital origin. Endogenic and authigenic minerals, which dominate the overlying sediment, are absent in this lowermost unit.

11.5.2.2 Unit 1 (9700-9300 BP)

Sharply overlying this basal diamicton is a thin (10-20 cm thick), massive to faintly bedded, calcareous, organic-rich clastic unit (Unit 1). Organic matter content is as high as 75% and the inorganic sediment is dominated by fine-grained siliciclastic material. The detrital carbonate mineral fraction is unusual in that it is dominated by calcite with smaller amounts of dolomite; the entire rest of the sequence in Oro Lake and in most other lakes of the region show a dominance of dolomite as the detrital carbonate component. This suggests that some of the calcite may be endogenic in origin rather than detrital material derived from the surrounding drainage basin tills and soils. However, the detailed petrography required to differentiate the detrital CaCO₃ from endogenic low Mg-calcite has not yet been completed. Although Unit 1 is dominated by organic matter and fine grained detrital material, aragonite, Mg-calcite, protodolomite, and pyrite all exist in small amounts (Table 11.3). The core taken in the shallowest part of the basin (OR3; 3 m water depth) contains the greatest abundance of these endogenic carbonate precipitates (~40%) suggesting a likely facies composition change from relatively pure organic matter+siliciclastics in the more offshore areas of the basin to more carbonate-rich sediment in shallower water environments.

11.5.2.3 Unit 2 (9300-7400 BP)

Immediately overlying the thin organic-rich clastics of Unit 1 is a relatively thick unit of laminated gypsite (Unit 2; Figure 11.7). Maximum thickness of Unit 2, approximately 2 m, occurs in core OR1 in the most offshore part of the lake, with progressively thinner sequences shoreward. The sediment of Unit 2 is moderately organic-rich (~20%) and shows increasing organic contents in the shoreward direction and decreasing contents upward in the unit. Composition ranges from nearly pure (>95%) CaSO₄ \cong 2H₂O to a mixture of gypsum, detrital clay minerals and detrital carbonates. Endogenic carbonate content is low except in the most shoreward core, in which gypsum-rich zones alternate with aragonite-dominated sediment. Although most of the nondetrital sediment is gypsum, the unit also contains small to trace amounts of sodium and magnesium sulfates, halite, and phosphates. In core OR1, the lower contact is sharp but the upper contact is gradational over 20-30 cm into the overlying carbonate-rich sediment of Unit 3; in the other two cores both the upper and lower contacts are sharp.



Figure 11.7. Unit 2, Oro Lake.

11.5.2.4 Unit 3 (7400-4000 BP)

Unit 3 (Figure 11.8) is finely laminated to indistinctly bedded and color-banded, aragonitic clayey silt. It is distinguished from the underlying sediment mainly by the relatively low abundance of sulfate and other soluble evaporitic minerals and high proportion of endogenic carbonates, detrital carbonates and siliciclastics. Thickness of the unit is greatest (~3 m) in the most offshore location (OR1) but thins to 1.6 m in the other two cores. With an average mean grain size of 15 :m, Unit 3 is also the most clay-rich unit of the entire sequence, averaging about 30% finer than 4 :m material. Aragonite is the dominant nondetrital mineral, but protodolomite and magnesite also occur in small amounts throughout the unit. Many samples from Unit 3 in OR3, the most shoreward core, also contain Mg-calcite. Like Unit 2, this thick aragonitic unit is also well laminated, with a dominance of very thin to thin (< 1 mm to 3 mm) monomineralic laminae. However, the unit also contains numerous centimeter-scale zones of massive to indistinctly bedded and banded material as well as convoluted and minor graded bedding.

11.5.2.5 Unit 4 (4000-present)

Unit 4 (Figure 11.9), the uppermost lithostratigraphic unit in Oro Lake is characterized by a decrease in endogenic carbonates and detrital components, and a significant increase in grain

size and soluble evaporite mineral content relative to Unit 3. The lower contact of Unit 4 with Unit 3 is readily delineated by the change in texture (decrease in clay, increase in sand and increase in mean size) and gypsum content. Organic matter shows a gradual increase upward in the unit, as do moisture content and mean grain size. The evaporite mineral suite is dominated by gypsum but also contains smaller proportions of bloedite and epsomite. Aragonite is the dominant endogenic carbonate and, unlike the gypsite of Unit 2, can comprise a significant proportion of the inorganic material (Table 11.3). Although both Units 3 and 4 contain Mgcarbonates, magnesite, hydromagnesite and protodolomite occur more commonly in Unit 4. Similar to the older sections of the cores, there is a facies composition change in Unit 4 from the basin-center core to the more shoreward locations. In OR1 and OR2, the nondetrital components are dominated by CaSO₄ 2H₂O, whereas in OR3 the endogenic fraction is mainly aragonite with smaller proportions of gypsum. Similarly, Unit 4 in the core from the most nearshore position in the basin (OR3) contains no Mg-carbonates. Bedding in Unit 4 ranges from finely laminated to massive and is dominated by alternating packages of well laminated sediment and poorly bedded material. The upper 60 cm of this youngest stratigraphic unit is non-bedded, with gradually increasing levels of hydrated sodium and magnesium sulfate salts and decreased gypsum upward in the section.



Figure 11.8. Unit 3, Oro Lake.

11.5.3 Interpretations & Discussion

Although only a relatively small proportion of the lakes in the prairie region of western Canada have been cored, the Oro Lake record is unique. Oro Lake contains the longest uninterrupted laminated lacustrine sequence in the Canadian Great Plains. With the exception of the organic-clastics of Unit 1, the mineralogical record of Oro Lake suggests the water has been saline to hypersaline throughout most of the Holocene. The ubiquitous occurrence of gypsum, a soluble evaporitic mineral, in Units 2-4 requires that brines of salinities *at least* ~15 ppt TDS occupied the basin continuously since early Holocene. In fact, concentrations were probably considerably higher than this minimum value for long periods in the lake's history. Today every lake in the region in which gypsum is present in the modern sediments has salinity greater than about 30 ppt (Last and Schweyen, 1983; Last, 1989). Furthermore, the occurrence of other soluble evaporites in Units 2 and 4, such as thenardite, bloedite, and epsomite, points toward at least temporary episodes of much higher salinity (>75 ppt) conditions at the sediment-water interface.



Figure 11.9. Unit 4, Oro Lake.

The thick accumulation of laminated and bedded sediments, and the absence of exposure horizons, unconformities and pedogenic zones, features which are common in other Holocene lacustrine sequences in the Prairies (Teller and Last, 1982; Last and Vance, 1997), indicate the Oro basin never experienced extended periods of dry or very low water conditions during the Holocene. The generation and preservation of laminae and the fine-grained nature of the sediment imply relatively deep water conditions persisted throughout the past ~10k yr. However, more precise estimates of past water depths cannot be deduced on the basis of the physical or mineralogical records alone. In western Canada, fine-grained, laminated offshore sediments occur in salt lakes with mean depths as shallow as 3 m and as deep as 24 m. While it is difficult to reconstruct water depths on the basis of only three cores in a stratigraphic section, it is evident from the elevation differences that depths in the central part of the basin were at least greater than 7-8 m during deposition of Unit 2 and 3 and greater than 4-5 m during Unit 4.

The lack of disruption of bedding in Oro Lake (see Figures 11.7-11.9) by bioturbation suggests that anoxic conditions prevailed at the sediment-water interface. These relatively deep water and anoxic conditions, particularly if taken in context with the continuous record of saline to hypersaline brines, imply that Oro Lake may have been meromictic during much of the Holocene. However, it must be emphasized that presently there is no evidence to indicate long-term accumulation of annual laminae or varve couplets, nor is there any other apparent regular rhythmicity in the Oro record.

The complexity of sedimentary facies resulting from the diverse array of geochemical, biological, and physical processes operating in high salinity and meromictic lakes has been well illustrated in numerous other studies in the Great Plains (e.g., Valero-Garcés et al., 1997; Valero-Garcés and Kelts, 1995; Last, 1999, 1994; 1993; Van Stempvoort et al. 1993; Last and Slezak, 1986; Schweyen and Last, 1983). Although comparable detailed modern sedimentary facies analyses in Oro Lake have not yet been completed, it is most likely both the carbonate and sulfate laminae represent short-term, aperiodic basinwide inorganic precipitation events. As shown in other perennial saline lakes in the region (e.g., Waldsea Lake, Deadmoose Lake, Freefight Lake, Redberry Lake, Medicine Lake), aragonite and other carbonate mineral laminae can be generated by various intrinsic and extrinsic triggering mechanisms, including changes in streamflow, surface runoff and groundwater input, or pH and concentration changes brought about by evaporation or dilution, brine mixing, and organic productivity. In addition to carbonates, in these and other deep water lacustrine environments, gypsum and other soluble minerals can precipitate as (i) seasonal salts from the upper part of the water column (due to both summer evaporative and winter "freeze-out" concentration mechanisms), (ii) travertine and spring discharge encrustations, and (iii) true subaqueous evaporites from the saturated monimolimnion or from the chemocline.

In contrast to this overall stable and relatively complacent record of deep water and high salinity during most of the Holocene, the endogenic mineralogy implies the precipitating brine underwent dramatic changes in composition during the past 10,000 years. Again with the exception of the lowermost lacustrine unit (Unit 1) and the basal diamicton, the most striking fluctuations within the stratigraphic record are in aragonite and gypsum: Units 2 and 4 are dominated by CaSO₄ ¹/₂ 2H₂O, with relatively little endogenic CaCO₃, whereas Unit 3 shows a dominance of aragonite and only minor amounts of gypsum. This inverse correlation between the abundances of gypsum and aragonite $\mathbb{R} = -0.71$; significant at $\forall = 0.001$) points toward alternation between a sulfate-dominated brine and one more enriched in HCO₃. However, because Oro Lake was likely meromictic throughout much of the Holocene, this need not necessarily imply dramatic changes in water sources or significant variations in hydrology. For example, during deposition of the gypsite of Unit 2 the endogenic components were likely derived mainly from a calcium-sulfate-saturated monimolimnion or from the chemocline, with relatively little contribution of material from the mixolimnion. In contrast, during deposition of the carbonate-rich Unit 3, the upper water mass became the dominant source of most of the endogenic sediment with little or no subaqueous salt precipitation. The lateral gradation from almost entirely aragonite in Unit 3 in the most offshore core (OR1) to mixed aragonite-gypsum

in the more nearshore cores suggests that the seasonally-flooded mudflat areas of the basin were likely sites of intense evaporative concentration and salt precipitation.

Thus, throughout most of the Holocene, Oro Lake held a relatively stable, deep and probably chemically stratified water body, with a monimolimnion at or just slightly above saturation with respect to evaporitic sulfate salts and a mixolimnion at or near carbonate mineral saturation. Although the gypsum-aragonite-gypsum sequence of Units 2-4 suggests deposition from significantly different brine compositions, this is most readily accounted for simply by alternating the loci of endogenic mineral precipitation within the water column between the mixolimnion and the monimolimnion. Alternatively, occasional breakdown of meromixis, giving rise to the infrequent massive and poorly laminated sections of the sequence that occur mainly in Unit 3, would also account for a dilution of the saturated bottom waters, reduction in CaSO₄ \bigotimes 2H₂O generation, and a relative increase in CaCO₃ contribution to the sediment of Unit 3. However, the prevalence of fine, undisturbed laminae indicates that non-stratified water conditions did not persist for long periods of time.

The lateral trends toward more evaporitic salt content in the nearshore direction within each unit likely reflect the presence of seasonally-flooded saline evaporitic mudflats surrounding the basin. The predominance of aragonite and the secondary occurrences of Mg-bearing carbonates such as magnesite, protodolomite, and magnesian calcite throughout the section not only reflect the high pH and alkaline conditions but also emphasize the overall elevated Mg/Ca ratio of the waters. The Mg/Ca molar ratios in the lake were never less than about 2 (corresponding to Mg-calcite deposition) and at times were approaching 100 or more (protodolomite and magnesite precipitation).

Deposition of the thin organic-rich Unit 1 and the basal diamicton are exceptions to this general statement of elevated salinity and meromixis throughout the Holocene. The basal diamicton was deposited either directly by glacier ice or, more likely, represents debris slumped from the unstable basin slopes during the lengthy period of postglacial disintegration of buried ice. The thin organic-rich lacustrine sediments immediately overlying this basal diamicton (Unit 1) were deposited in a fresh to hyposaline but highly productive lake or slough with water depths in the central part of the basin more than about 5 m. Cywinska and Delorme (1995) note that this basal lacustrine sediment in OR1 is particularly rich in ostracodes. Thus, the unusually high calcite/dolomite ratio may reflect the very high ostracode shell content. The lateral change in composition of Unit 1, from organic-detrital sediment in the basin-center core to sediment with a higher endogenic mineral content toward the more nearshore areas suggests that the shallow water and shoreline areas of the lake may have been evaporitic carbonate mudflats.

11.5.4 Synopsis of Oro Lake History

The late Pleistocene and earliest Holocene was a period of rapid environmental change in the northern Great Plains. Although the active margin of the glacier retreated from the Missouri Coteau in southern Saskatchewan about 11,000-12,000 years ago, disintegration of stagnant ice buried beneath the thick glacial sediment of the Coteau continued for several millennia. This

gradual melting initiated a wide variety of topography reversals, and caused rapid evolution of drainage systems and other landscape features (Bluemle, 1991; Christiansen, 1973; Clayton and Freers, 1967). In addition to creating the thousands of small lake basins ("prairie potholes") that characterize the hummocky collapsed topography of the Coteau, the melting ice provided a large and constant source of water to the local hydrologic systems during the early phases of these lakes.

Studies of early postglacial vegetation elsewhere in the region suggest a relatively cool but wet climate prevailed during the late Pleistocene, which allowed a boreal forest type of vegetation to become established over much of the area (e.g., Yansa and Basinger, 1999; Yansa, 1996; 1995; Grimm and Clark, 1998, 1995; Klassen, 1989). At the Andrews site, a small sediment-filled "kettle" situated on the Coteau about 40 km northeast of Oro Lake, lacustrine sedimentation began about 10,200 years ago in a relatively deep, freshwater pond surrounded by a white spruce forest (Yansa, 1998). Although the oldest lacustrine deposits in the Oro basin postdate those of the Andrews site by about 500 years, conditions were similar: Unit 1 in Oro Lake was deposited in a relatively deep (greater than 5 m), freshwater to slightly brackish lake.

Sedimentation in the offshore area of this newly developed basin was dominated by detrital inorganic material and both detrital and endogenic organic matter. The influx of most of the inorganic sediment was from freshly-exposed glacial deposits of the small watershed and basin slopes, although the unusually high calcite/dolomite ratio of Unit 1 indicates bio-induced CaCO₃ precipitation was also important. Even though the lake was deep, fresh, and dominated by clastics and organic sediment, the nearshore and peripheral mudflat areas of the basin were likely sites of evaporative concentration and carbonate mineral precipitation as evidenced by the occurrence of small amounts of aragonite, magnesite, protodolomite, and gypsum in Unit 1 in core OR3.

However, this early Holocene freshwater lake was short-lived and by about 9300 BP limnological conditions in the Oro basin changed dramatically. Alkaline, high salinity brines with high to very high Mg/Ca ratios dominated the lake throughout most of the remainder of the Holocene. Although the water was saline, lake levels remained high and relatively stable; at no time during the past 9300 years did the water drop sufficiently to subaerially expose the bottom sediments. Indeed, for much of the Holocene a stable, deep-water meromictic lake existed in the Oro basin.

During the two thousand year period between about 9300 and 7400 BP, offshore sedimentation in the basin was dominated by precipitation of subaqueous soluble salts from a saturated monimolimnion. Water salinities were likely about 30-40 ppt, with occasional excursions to greater than 70 ppt. An abrupt change to elevated salinities and alkalinities after the basal freshwater phase is also recorded in the ostracode stratigraphy of OR1 (Cywinska and Delorme, 1995). Closer to shore, endogenic and authigenic carbonates derived from the nearshore and mudflat carbonate "factory" intermixed and diluted the basinal salts, creating a sedimentary facies pattern similar to that which occurs in a number of other deep-water perennial

saline lakes in the region today (e.g., Valero-Garces and Kelts, 1995; Last, 1994; 1993; Sack and Last, 1994).

The occasional excursions to hypersaline conditions were relatively frequent about 8300 yr BP suggesting Oro Lake brine reached maximum salinity at this time. Likewise, Padden (1996) shows that maximum inferred $*O^{18}$ enrichment (i.e., maximum evaporative influence) in the lake waters also occurred at this time. The ~8300 BP salinity maximum in Oro Lake corresponds well with subaerial exposure and desiccation of the offshore bottom muds at Clearwater Lake, a small perennial lake on the Missouri Coteau about 200 km northwest of Oro (Last et al., 1998), and maximum drought conditions interpreted at the nearby Andrews site (Aitken et al., 1999; Yansa and Basinger, 1999).

The transition of Oro Lake from a freshwater, clastic-organic matter dominated sedimentary environment to a saline/hypersaline salt-precipitating basin was abrupt. Similar early Holocene transitions from fresh to saline and/or hydrologically open to closed, evaporitic conditions have been documented at numerous other sites in the region, including the Andrews site, Ingebright Lake, and Clearwater Lake (all in Saskatchewan), Lake Manitoba and Killarney Lake (both in Manitoba), Moore Lake (Alberta), and Pickerel Lake, Moon Lake, Medicine Lake, Devils Lake, and Coldwater Lake in United States (see discussions and compilations of recent work in Dean and Schwalb, 2000; Aitken et al., 1999; Shang and Last, 1999; Last et al., 1998; Laird et al., 1996; Valero-Garcés et al., 1997; Valero-Garcés and Kelts, 1995; Vance and Last, 1994). Not all of these fresh-to-saline transitions were as abrupt as that recorded at Oro, nor are they precisely synchronous over the region. This is probably due, in part, to limited chronological control (Vance, 1997), and, in part, to various local hydrological or topographic factors that may buffer a lake's response to an external signal, including such factors as position within the landscape, magnitude and source of groundwater discharge and lag time of this groundwater-driven signal, and the development of complex intrinsic sedimentary feedback mechanisms (see also discussions in Wilson and Smol, 1999; Remenda and Birks, 1999; Birks and Remenda, 1999; Webster et al., 1996; Valero-Garces and Kelts, 1995). Nonetheless, it is clear from the consistent regional response that this early Holocene change in the Canadian Plains was the result of a widespread decrease in available moisture under a warmer and/or drier climate, which was most likely associated with increased summer insolation.

Although Oro Lake has remained a saline alkaline system since 9300 BP, beginning about 7400 years ago deposition gradually shifted from mainly soluble sulfate salts to sparingly soluble carbonates mixed with fine clastics and only minor evaporites. It is tempting to view this mid-Holocene period of dominantly aragonite-laminated mud deposition in the Oro basin as reflecting a slight freshening of the brines, possibly associated with a more moderate climate, following the maximum salinity conditions at ~8300 BP. An increased effective precipitation component in the hydrologic budget of the basin could result in an undersaturated monimolimnion (with respect to gypsum) and increased aragonite production from the mixolimnion. Increased runoff might also account for the increase in proportion of fine-grained detrital components of Unit 3 and could lead to occasional destratification of the meromictic water column to create the poorly bedded and indistinctly banded zones that occur in Unit 3.

The interpreted climatic conditions in the northern Great Plains during this time are still enigmatic. The onset of a somewhat more positive hydrologic budget in Oro Lake about 7400 years ago corresponds well with several other lacustrine records from the Canadian Plains region: (i) the formation of a fresh to brackish semipermanent pond at the Andrews site (Aitken et al., 1999; Yansa, 1998); (ii) a return to a hydrologically open, non-evaporitic freshwater system in Clearwater Lake (Last et al., 1998); (iii) the occurrence of relatively humid conditions at Ingebright Lake, a hypersaline playa in southwestern Saskatchewan (Shang and Last, 1999); (iv) the development of a "permanent" (i.e., non-playa) lake in the Manitoba basin in the eastern Prairies (Risberg et al., 1999; Last et al., 1994; Curry, 1997); and (v) a shift from groundwaterdominated inflow to mainly surface influx in Harris Lake, southwestern Saskatchewan (Last and Sauchyn, 1993). Likewise, in Devils Lake, North Dakota, maximum salinity also occurred early in the Holocene (~8 kyr) and was followed by a 4500 year period of fluctuating but generally lower salinities (Haskell et al., 1996). Finally, the increase in clastic influx in Oro Lake at this time is coincident with a widespread northern hemisphere cooling event, which has been linked to a short-lived perturbation in the North Atlantic thermohaline circulation caused by the final catastrophic draining of Lake Agassiz and Lake Ojibway (Barber et al., 1999). However, within the constraints of our chronostratigraphy, the influence of this "8.2 k cal. year cooling event" in Oro Lake must remain tentative.

In contrast to a more positive hydrologic budget, an alternative explanation for the larger amounts of detrital clastic influx in Oro Lake between 7300 and 4000 BP is that this material could have been air-borne rather than transported by streams or sheetwash. Although indications of increased eolian (loess) activity are anomalously absent from the Canadian Plains region (Lemmen and Vance, 1999b), increases in eolian sediment during this time have been noted in Pickerel Lake, South Dakota (Dean and Schwalb, 2000), and Deep Lake and Elk Lake in Minnesota (Hu et al., 1999; Dean, 1997). In these lakes, the mid-Holocene increased eolian influx is interpreted to be a response to decreased available moisture (and, hence, decreased vegetation cover) combined with strengthening of westerly zonal winds. There is also abundant paleolimnological evidence from the northern Great Plains to support this mid-Holocene increased aridity as discussed in numerous overviews (e.g., Lemmen and Vance, 1999; Laird et al., 1996; Vance et al., 1996).

In addition to the examples cited above in the United States, Chappice Lake, a small hypersaline playa in southeastern Alberta, experienced significant fluctuations in water levels, from dry to shallow to deep, during 7.5-6.0 k yr (Vance et al., 1993;1992). Ceylon Lake, about 80 km southwest of Oro, changed from a deep, hydrologically open, freshwater lake to a saline playa about 7000 years ago (Last, 1990). Deep Lake, a small ephemeral basin near Regina, records maximum salinity and increases in xerophytic and saline-tolerant pollen taxa about 7.2-6.4 k BP (Vetter et al., 2000; Sauchyn and Porter, 1996).

Although an eolian source for the fine-grained clastics of Unit 3 in Oro Lake is plausible, nonetheless, it is somewhat more difficult to reconcile the *decreased* evaporite content of the unit if a relatively more arid climatic setting were in place. Similarly, higher aridity during the mid-Holocene is not readily compatible with the general trend toward lower *O¹⁸ brines (less

evaporative enrichment) and lower $*C^{13}$ values for cellulose in the lake after the early Holocene (Padden, 1996).

One final possible scenario to explain the carbonate-rich/gypsum-depleted muds of the mid-Holocene in Oro Lake is that increased aridity lead to lower water levels and eventual complete breakdown of the chemically stratified system. Mixing of the relatively dilute upper water mass with the saturated monimolimnion would result in a net salinity decrease in the newly holomitic water column and a shift from gypsum-dominated offshore sediments to aragonite-rich muds. In this case, presumably seasonal development of a thermally stratified water column was sufficient to prevent bioturbation and disruption of the aragonite laminae. Although somewhat shallower, the lake was still deep enough, or the basin sheltered enough, to prohibit wind generated wave mixing of the bottom sediments. A more arid mid-Holocene climate over a period of several millennia might also decrease the regional groundwater table sufficiently such that the basin no longer received influx from the sulfate-rich near surface and shallow groundwater (see also Teller, 1998).

About 4000 years ago sedimentation in Oro Lake again shifted toward higher sulfate salt precipitation and lower carbonate and siliciclastic deposition. Although the increase in evaporite content in Unit 4 seems incongruous with the general record of overall cooler and wetter conditions in the Great Plains after the mid-Holocene (cf. overviews in Lemmen and Vance, 1999b; Laird et al., 1996; Ritchie and Harrison, 1993), this probably occurred in response to renewed development of a chemically stratified water column in which gypsum was being derived from the saturated monimolimnion and aragonite was precipitating from the mixolimnion. In addition, less arid conditions gave rise to a relatively greater contribution of sulfate-rich groundwater. Similarly, the striking decrease in clay-sized material in the offshore sediments deposited after 4000 BP probably reflects a decrease in eolian influx to the basin. The lateral gradation from gypsum-rich sediments in core OR1 to mixed gypsum-aragonite in OR2 and dominantly aragonite in the OR3 indicates the peripheral mudflats and nearshore areas of the basin were likely sites of carbonate mineral precipitation, rather than areas of evaporitic sulfate formation as was the case during the mid-Holocene. Padden (1996) also interprets a continuing trend toward decreased aridity during the late Holocene from the stable oxygen and carbon records in OR1.

Although the physical and mineralogical records suggest a relatively complacent late Holocene history in the Oro basin, our chronology of the past 4000 years of deposition is only poorly constrained, and poor core recovery of the upper meter of section precludes a more detailed, high resolution exposition of the most recent history of the lake. Relatively constant proportions of soluble salt, endogenic carbonate minerals, and detrital components indicate the continued persistence of a relatively deep, stable, saline and chemically stratified water column. According to Cywinska and Delorme (1995), the ostracode record preserved in OR1 similarly indicates few environmental changes over the past 4-5k years. Although the Medieval Warm Period (~1000 BP) does not appear to be documented in the physical/mineralogical record of Oro, however, beginning about 600 years ago, the indistinct bedding suggests meromixis periodically broke down, perhaps due to increased aridity associated with the Little Ice Age. The development of a holomictic water column is coincident with an increased enrichment in $*O^{18}$ lake water (Padden, 1996) and an increase in soluble salts. Finally, beginning about 1700 AD episodes of hypersalinity became more frequent and coincided with a gradual trend toward a more Mg²⁺-rich brine. In addition to this increase in Mg-salt precipitation, in the early part of the 20th century the basin experienced a significant increase in detrital influx, probably associated with European land clearing and agriculture.

10.5.5 Take-home message from Oro Lake

There are few long paleoenvironmental records in the vast northern Great Plains of western Canada. Thus, with its 10,000 year long record of uninterrupted deepwater sedimentation, Oro Lake is one of the most important paleolimnological sites in the region. However, meromictic conditions, combined with saline to hypersaline brines and a groundwaterdominated hydrologic budget, complicate the climatic and hydrologic interpretations of the mineralogical and physical records. Early Holocene events in the Oro basin are clear and unambiguous: an early freshwater lake occupied the basin immediately after deglaciation. This quickly and abruptly gave way to a deep, saline-hypersaline meromictic lake by 9300 BP. Maximum salinity occurred about 8300 years ago, coinciding with other regional evidence of early Holocene maximum aridity. The mid-Holocene environmental conditions at Oro Lake are enigmatic. Although it is reasonable to attribute the decrease in soluble salts and increased carbonate and detrital sedimentation during the mid-Holocene to a more positive hydrologic budget, it is equally plausible that increased aridity in the region resulted in an a significant increase in eolian influx, an overall more dilute body of water because of the breakdown of meromixis, and a more carbonate-enriched/sulfate depleted chemical system through reorganization of the groundwater input to the basin. The sedimentary sequence deposited during the past 4000 years lacks strong evidence for significant fluctuations in the general environmental and limnological conditions (i.e., deep water, saline, meromixis, stable lake levels) although the past several hundred years have seen an increase in Mg^{2+} in the brine and greater frequency of a nonstratified water column.
10.6: WILLOW BUNCH LAKE

Objectives

The objectives of this overview stop are to: (i) introduce field trip participants to the realm of salt lake sedimentology, geochemistry, and paleolimnology in the northern Great Plains, and (ii) briefly examine the geolimnology and Holocene stratigraphy of one of the region's large, riverine saline lakes - Willow Bunch Lake.

Willow Bunch Lake

Willow Bunch Lake is a large (30 km²) but very shallow ($z_{mean} < 1m$) salt lake occupying a long, topographically-closed riverine basin. The Willow Bunch Lake - Lake of the Rivers -Twelve Mile Lake - Big Muddy Lake channel complex is a major glacial meltwater spillway system that was active about 12-10k yr BP in draining runoff from the glacial lakes at the retreating ice margin southward into the Missouri River (Parizek, 1964; Christiansen, 1979). Although the present-day drainage basin of Willow Bunch is large (>1000 km²), the hydrologic budget of the lake today appears to be dominated by groundwater influx and diffuse overland inflow rather than stream inflow. Typical of most of the shallow, playa basins in the region, the lake undergoes dramatic water level fluctuations on a seasonal as well as longer-term temporal basis, however, the basin has not completely dried during the period 1983 to present. Similarly, the brine concentration and ionic composition also vary greatly on a seasonal and spatial basis. Willow Bunch Lake water is saline (average salinity over the past decade is about 50 ppt), alkaline (ph = 9.8), and usually dominated by Na⁺ and SO₄⁻² (Cl⁻). The concentration of Ca²⁺ is anomalously low relative to the inflowing groundwater and surface streams. Seasonal variations in brine chemistry result from dilute inflow during spring, evaporative concentration during the ice free season, and precipitation of salts due to freeze-out concentration. Spatial variations are most likely caused by subaqueous spring discharge of Ca^{2+} and HCO_3^{-} -enriched groundwater.

Willow Bunch Vital Statistics (average 1983-1994)				
Surface Area (A)	32.9 km^2			
Drainage Basin Area	1128 km ²			
Maximum Length (L _{max})	34.2 km			
Maximum Width (W _{max})	1.2 km			
Maxiumum Depth (z_{max})	2.1 m			
Mean Depth (z _{mean})	0.4 m			
Relative Depth (z _r)	0.04			
Volume (V)	0.002 km^3			
Shoreline Length (L)	79.2 km			
Shoreline Development (D _v)	3.87			

Willow Bunch Lake Hydrochemistry					
	mg L-1	log molal			
Ca ²⁺	136.8	-2.446			
Mg ²⁺	592.8	-1.592			
Na ⁺	15,490	-0.150			
K^+	370	-2.003			
HCO ₃ -	3847.6	-1.179			
SO4 ²⁻	23,666	-0.587			
Cl	3415.4	-0.995			
TDS	47.8	3 ppt			
Ionic Strength	0.8	305			
pН	9.8				
Total Alkalinity	66.23 meq				
Carbonate Alk.	66.11	meq			

The modern sediments in the lake are a mixture of fine to coarse detrital clastics (mainly quartz, feldspars and clay minerals), and endogenic carbonate and sulfate minerals. The ratio of detrital to endogenic sediments shows a gradation from relatively high at the western end of the basin to low at the eastern end. The organic matter content is low and dominated by detrital rather than endogenic organics. The dominate endogenic carbonate mineral present in the modern sediment is aragonite, although both magnesian calcite (with 10-14 mol% MgCO₃) and protodolomite both occur in minor proportions. The small amount of protodolomite is unusual because it contains excess MgCO₃ rather than being Ca-enriched. The lake water is at all times of the year undersaturated with respect to gypsum and this evaporite mineral does not occur in the modern sediments despite its common occurrence in soils and drift surrounding the lake.

Even a casual examination of a large-scale topographic map or satellite image of the northern Great Plains shows that the region contains many lakes occupying riverine basins. Although the presence and geomorphology of these meltwater spillways have played a pivotal role in helping Quaternary scientists deduce the deglaciation of the region (e.g., Kehew & Teller, 1994a, b; Christiansen, 1979), the Holocene lacustrine sediments in the extant basins have been

largely ignored by paleolimnologists. Only Ceylon, Little Manitou, Bitter, Lydden, and Verlo lakes have been examined in detail.

The Holocene lacustrine stratigraphy from Willow Bunch Lake is known from just one 7 m long core taken at the eastern end of the basin. With only two ¹⁴C dates (on bulk organic matter and endogenic carbonate material), the chronostratigraphy is highly suspect. The lithostratigraphic units identified in this core consist of a basal coarse clastic (alluvial?) unit that is sharply overlain by calcareous lacustrine clays with abundant mollusc shells, and fine, irregularly-spaced lamination. Most of the laminae in the lower part of this unit are dominated by normal (low-Mg) calcite, suggesting a Mg/Ca ratio of less than 1 in the lake. The upper 50 cm of the unit contains laminae composed of magnesian calcite with 4-10 mol% MgCO₃ content, indicating a Mg/Ca of 2-5%. Grading upward, the carbonate content decreases whereas gypsum and other evaporites dominate the endogenic component component of the sediment. This change from carbonate-rich to sulfate-rich laminated sediment probably reflects a gradually increasing brine concentration. The occurrence of pedogenic horizons and microbial-laminated zones indicate the lake experience shallow water to completely conditions. Overlying the gypsum-rich laminated unit is a thin, structureless, black, highly reducing sulfide-rich mud which passes sharply up into well indurated salt. Although sediment recovery from this salt unit was poor, the detailed evaporite mineralogy indicates that the precipitating brine was initially high in Na⁺ and SO_4^{-2} but became increasingly Mg⁺²-rich. Finally, the upper 1.5 m of sediment consist of structureless, clavey silt and silty clay with relatively high endogenic aragonite contents.



10.7: INGEBRIGHT LAKE

Objectives

Time and weather conditions permitting, our jaunts into and around the Great Sand Hills area will give field trip participants an opportunity to visit two exceptional lacustrine basins. The Ingebright Lake complex (Ingebright Lake and North Ingebright Lake) is Canada's largest sodium sulfate deposit and contains the thickest sequence of Holocene lacustrine evaporites in North America. A few kilometres east of Ingebright is Freefight Lake, Canada's deepest saline lake and also the country's most saline permeant lacustrine water body. The objectives of this first stop overlooking the Na₂SO₄ plant at Ingebright Lake are to: (I) summarize the sodium sulfate minerals industry in the Great Plains, (ii) discuss for the formation of saline lacustrine giants like Ingebright, and (iii) summarize the Holocene geochemical evolution of North Ingebright Lake.



The Sodium Sulfate Minerals Industry of the Northern Great Plains

The northern Great Plains region has been an important source of commercial sodium sulfate for over 75 years. Some of the earliest industrial efforts in the Great Plains were centred on salt extraction from the alkaline sloughs and saline lakes of southern Saskatchewan. Total composite reserves of both sodium sulfate and magnesium sulfate for the region are among the largest in the world. Presently about 400,000 tonnes of sodium sulfate are produced per year from the lakes, with an annual value of the product normally exceeding \$20 million.

Commercial exploitation of the salts in these lakes began in 1918 with the extraction of MgSO₄, Na₂SO₄, and NaHCO₃ from Muskiki Lake near Saskatoon. In fact, prior to this many of the lakes were "staked" (formal mineral rights claim established) and drilled under the false

assumption that the white, powdery salts contained nitrate minerals which were useful in the early munitions industry. Production of anhydrous sodium sulfate (salt cake) from some 20 different lake basins in Saskatchewan and Alberta reached a peak in the early 1980's (Slezak and Last, 1985). Historically, the two largest uses of sodium sulfate have been in producing kraft paper and allied products, and in the manufacture of detergents. Although demand for salt cake has decreased significantly over the past decade, the lakes of the northern Great Plains still supply about 55% of North America's total demand.

The salts are extracted from the lakes using a variety of open pit and solution mining techniques. Here at Ingebright, a combination of dredging, "brining" (allowing the lake water to precipitate Na₂SO₄ minerals in evaporation ponds), and direct excavation. The extracted salts (referred to as "Glauber's salt") are dehydrated and concentrated to form relatively pure, finely crystalline thenardite (Na₂SO₄) which is shipped to markets in eastern Canada by rail.

Ingebright and North Ingebright Lakes

Ingebright Lake, a 290 hectare hypersaline playa, occupies the terminus of a relatively large, closed drainage basin on the western flanks of the Great Sand Hills region. Although small in area, the basin contains an extraordinary thickness of Holocene evaporites. Nearly 45 m of mainly sodium and magnesium sulfates overlie poorly sorted gravelly clay (till?). This salt sequence has been mined since 1967 and, unfortunately, there was no detailed mineralogy or sedimentology done on this unusual deposit before the stratigraphic record was disturbed. However, bulk chemical data presented by Cole (1926) clearly demonstrates that there are (were) major stratigraphic changes in the ionic composition of the salts in Ingebright. An even smaller hypersaline playa, North Ingebright Lake, occupies a narrow (0.5 km wide) riverine channel to the northeast of the main Ingebright basin. North Ingebright Lake also contains large thicknesses of evaporites but has not yet been mined and has been the site of detailed stratigraphic investigations as part of the ongoing Palliser Triangle Project.



Modern Sediment Facies of North Ingebright Lake

(Last, 1994).

Holocene Stratigraphy and Geochemical Evolution

The Holocene lacustrine sequences recovered from these two lakes consist mainly of well-indurated salt with only minor amounts of mud and organic debris. Indeed, the sections are remarkable in their lack of obvious bedding, colour variations, detrital material, and other visible sedimentary features. The mineral suite of the North Ingebright deposit consists mainly of hydrated Na, Ca, and Mg+Na sulfates, carbonates, chlorides. Based on the bulk mineral composition of these salts, 7 lithostratigraphic units have been identified. Closely spaced (2 cm) detailed evaporite and carbonate mineralogy was used to further subdivide these units into some 31 individual "compositional zones". The specific major and ancillary evaporite minerals (and mineral ratios) in these individual compositional zones form the basis of the chemical reconstruction of the precipitating brine. These detailed mineral assemblages were also used to back-calculate various thermodynamic activity parameters and, from these activities, to estimate relative humidity in the Ingebright basin as shown on the following figures.

The extraordinary thicknesses of relatively pure evaporites in the Ingebright and North Ingebright basins present some interesting dilemmas for sedimentologists, geochemists, and limnologists. Several strikingly different depositional scenarios have been put forward to account for these types of saline giants. The "shallow water, build-up" hypothesis is probably the most sedimentologically and geochemically reasonable explanation, although there are no well documented modern analogues in the Great Plains today. Similarly, the hydrodynamics of groundwater flow in and around such a vertically accreting playa system are difficult to imagine. Conversely, the "deep water, fill-up" hypothesis, originally proposed by Rueffel (1968), was, until recently, discounted because of the lack of any known modern deep water evaporite mineral formation. Nonetheless, the discovery of several modern lakes in the Great Plains (e.g. Freefight Lake, Deadmoose Lake) in which high rates of evaporite mineral precipitation and deposition are occurring has restored some scientific credibility to this hypothesis

Generalized Evolution of Brine Types at North Ingebright lake

Unit 7 Ca-Mg-CO₃ + Na-SO₄ + Mg-Na-SO₄

- 3 Ca-Mg-CO₃ + Na-SO₄ + Na-Mg-SO₄
- 2 Ca-Mg-CO₃ + (Ca-SO₄) + Na-SO₄ + Na-Mg-SO₄ + (Mg-Cl)
- 1 Na-SO, + Na-Mg-SO,

Unit 6 Ca-Mg-CO₃ + Ca-SO₄ + Na-SO₄

- 3 Ca-Mg-CO₃ + (Ca-SO₄) + Na-SO₄
- 2 Ca-Mg-CO₃ + Ca-SO₄ + Na-SO₄ + Na-Mg-SO₄
- 1 Ca-Mg-CO, + (Ca-SO,) + Na-SO,

Unit 5 Na-SO

- 3 Na-SO,
- 2 (Ca-SO₄) + Na-SO₄
- 1 Na-SO₄ + (K-Mg-Cl)

Unit 4 Ca-Mg-CO₃ + Ca-SO₄ + Na-SO₄

- 5 Ca-Mg-CO₃ + Ca-SO₄ + Na-SO₄
- 44 Ca-Mg-CO, + Ca-SO, + Na-SO,
- 3 Ca-Mg-CO₃ + Ca-SO₄ + Na-SO₄
- 2 Ca-Mg-CO, + Ca-SO, + Na-SO, + (K-Mg-SO,)
- 1 Ca-Mg-CO, + Ca-SO, + Na-SO, + (Mg-SO,)

Unit 3 Mg-CO₃ + Ca-SO₄ + Na-SO₄

- $Ca-Mg-CO_{4} + Ca-SO_{4} + Na-SO_{4} + Na-Mg-SO_{4} + (Mg-K-CI) \qquad 5$
 - $Mg-CO_{s} + Ca-SO_{4} + Na-SO_{4} + (K-Mg-SO_{4})$
 - Ca-Mg-CO, + Ca-SO, + Na-SO, + (Na-CO,) 3
 - Ca-Mg-CO, + Ca-SO, + Na-SO, + (K-Mg-SO,) 2
 - $Ca-Mg-CO_3 + Ca-SO_4 + Na-SO_4 + (K-CO_3) = 1$

Unit 2 Mg-CO₃ + Na-SO₄ + Mg-Na-SO₄

- $Ca-Mg-CO_3 + Ca-SO_4 + Na-SO_4 = 7$
- Mg-CO, + Ca-SO, + Na-SO, + Na-Mg-SO, 6
- $Ca-Mg-CO_{3} + Ca-SO_{4} + Na-SO_{4} + (Mg-SO_{4}) \qquad 5$
 - Ca-Mg-CO₃ + Na-SO₄ 4
 - Mg-CO, + Na-SO, 3
- $Ca-Mg-CO_{3} + Ca-SO_{4} + Na-SO_{4} + (Mg-SO_{4}) \qquad 2$
 - Na-SO, 1

Unit 1 Na-SO₄

- Mg-CO₃ + Ca-SO₄ + Na-SO₄ 5
 - Na-SO, + (Na-Cl) 4
 - Na-SO, 3
 - Ca-SO, + Na-SO, 2
 - Na-SO, 1



Interpreted Relative Humidity for N.Ingebright Lake Region

10.8: FREEFIGHT LAKE

Objectives

Having resolved once and for all the dilemma of deep versus shallow water lacustrine evaporite mineral formation, a short drive eastward into the Great Sand Hills will allow us to visit Canada's deepest salt lake, Freefight Lake. Note: the 12 km track into Freefight Lake is normally impassable during spring. Track conditions are strongly dependent on weather conditions and the amount of oilwell drilling. The objectives of this stop are to: (I) discuss deep water evaporite mineral formation; (ii) scrutinise (and sample) algal mat/microbialite sedimentary facies; (iii) examine penecontemporaneous dolomitization; and (iv) discuss late Holocene geochemical and sedimentological changes that have occurred in this lake.

The Modern Lake

Until the early 1980's Freefight Lake and surrounding drainage basin have been bypassed by all limnological and geolimnological researchers, presumably because of the remoteness of the location and poor accessibility. There is no reference to the lake in any scientific publication prior to that of Last & Slezak (1987), even though the basin is well known among local land owners and ranchers. During the 1960's and 70's it was a popular recreation site. However, a series of severe droughts in the area during the past decade brought lowered water levels to the lake and the high salt content decreased its recreational attractiveness.

Freefight Lake receives inflow from two ephemeral streams, numerous subaerial springs, diffuse subaqueous groundwater discharge, direct precipitation, and diffuse surface runoff. Although a detailed hydrologic budget is not yet known for the basin, during the period 1984-90, groundwater sources contributed about the 35% of the inflow, with direct precipitation and diffuse surface runoff making up most of the remaining inflow. The two streams contributed only about 3% of the total inflow. The basin is topographically closed and most likely also hydrologically closed. The inflowing groundwater is dilute (average: 1000 mg L⁻¹ TDS), alkaline (pH 8), and dominated by Mg²⁺ and Na⁺, with subequal proportions of Cl⁻, SO₄²⁻, and HCO₃⁻.

Freefight Lake is a meromictic, hypersaline lake with a distinctive morphology: a large expanse of seasonally flooded mudflats and sandflats surround a deep, flat-bottomed basin. The mixolimnion, with an average salinity of ~110 ppt, is dominated by Mg²⁺, Na⁺, and SO₄²⁺. A stable chemocline occurs at about 6 m depth separating a monimolimnion of ~200 ppt from the overlying water column. The chemical stability of this stratification is extreme (0.9 J cm⁻²) and is among the highest calculated for any meromictic lake. The chemocline is also very turbid due to dense populations of purple phototrophic bacteria.

Freefight Lake Vital Statistics				
Surface Area (A)	2.94 km^2			
Drainage Basin Area	55.2 km^2			
Maximum Length (L _{max})	2.95 km			
Maximum Width (W _{max})	1.25 km			
Maxiumum Depth (z _{max})	25.60 m			
Mean Depth (z _{mean})	19.5 m			
Relative Depth (z _r)	2.18			
Volume (V)	0.02 km^3			
Shoreline Length (L)	9.16 km			
Shoreline Development	1.66			
Volume Development (D _v)	3.8			

Freefight Lake Hydrochemistry					
(conc in mg L^{-1})	Mixolim	Monim.			
Ca ²⁺	89	395			
Mg ²⁺	13,279	15,192			
Na ⁺	20,930	48,531			
K^+	3366	3734			
HCO ₃ -	4471	15,360			
SO4 ²⁻	77,483	118,318			
Cl	8361	10,316			
TDS (ppt)	111	189			
Ionic Strength	1.788	2.873			
pH (pE)	8.4 (3.4)	7.9 (- 5.3)			
H ₂ S	0	959			

Geolimnology

Freefight Lake is a sedimentologist's wonderland. A wide range of physical, chemical, and biological processes operate to form six major modern sedimentary facies (colluvium, mud flat and sand flat, delta, algal flat, slope and debris apron, deep basin). Inorganic and biomediated chemical processes dominate in most of these facies. The lake water at all depths and at all times of the year is at or near to saturation with respect to gypsum. The mixolimnion is supersaturated with respect to many Ca, Mg, and Ca-Mg carbonates including calcite, aragonite, dolomite, huntite, hydromagnesite, and magnesite. Similarly the monimolimnion is also highly supersaturated with respect to many of these carbonates despite having a slightly lower pH than the overlying mixolimnion. During the course of a typical year, the surface brine shifts from being slightly undersaturated with respect to Na, Mg, and Na-Mg sulfates (mirabilite, thenardite, bloedite, epsomite) during summer to slightly supersaturated during winter, whereas the lower water mass is at or above saturation with respect to these highly soluble sulfates at all times. Finally, the monimolimnion is strongly supersaturated with respect to most metal sulfides and many clay minerals. Over 40 endogenic and authigenic minerals have been identified in the sediments of Freefight Lake (Slezak, 1989; Last, 1993); many of these have been reported from no other lacustrine or continental setting in the Great Plains.

Several of these facies are of particular interest because they are not commonly found in other lakes of the region. For example, the mudflat facies is the site of penecontemporaneous dolomizitation. The algal flat facies, with its living pustular microbial mat, appears to be unique among the salt lakes of the Great Plains. Modern sediment accumulation rates in the deep basin facies are remarkably high. Over the past decade, the average annual rate of sedimentation in the offshore area of the basin is approximately 30 kg m⁻², with a range from 10 to over 60 kg m⁻² yr⁻¹

The mid to late Holocene stratigraphy in the basin is known from over 40 metres of core taken from 25 locations. Although the mudflat and sandflat facies stratigraphies are difficult to interpret because of the large amount of post-depositional and penecontemporaneous mineral diagenesis, the laminated microbialite sediments of the near shore and shallow water areas provide a good record of water level fluctuations and mixolimnion hydrochemistry changes. Unfortunately, In the offshore deep basin facies, lack of suitable material for ¹⁴C dating is a serious problem hindering the interpretation of an otherwise outstanding late Holocene record of water chemistry changes.











10.8: CLEARWATER LAKE

Objectives

I donno? Wanna just talk about the early Holocene in this puppy? I don't have any idea where the late and middle Holocene is...

The Modern Lake and Recent Changes

I know my colleagues will find this hard to believe, but I have absolutely nothing of interest to say about either the water composition or the modern/recent sediments in this lake: the "modern" is all yours – any takers? It seems like this would be a prime basin for some groundwater work? Why IS this thing soooo darned fresh? A GSC report says water must be leaving the basin via groundwater routes just as fast as it comes in, but even then....

Clearwater Lake occupies a small groundwater-fed lake in southwestern Saskatchewan. Although topographically closed, the modern lake maintains a relatively low salinity (~1 ppt TDS), presumably due to the presence of an open hydrologic system in which the basin acts as both a discharge and recharge site for shallow groundwater.

ClearwaterLake Hydrochemistry								
concentrations in mg L ⁻¹	7/1938	11/1966	2/1967	6/1967	9/1967	8/1994	1/1995	
Ca ²⁺	8.9	4	7	11	8	5.6	11.6	
Mg ²⁺	136	126	158	115	133	163	211	
Na ⁺	84	68	76	54	63	87.6	122	
K^+	nd	22	25	19	21	27.8	2.9	
HCO ₃ -	541	579	733	566	537	685	847	
SO_4^{2-}	134	158	187	139	165	248	312	
Cl	20.5	24	29	19	23	32.5	40.9	
TDS (ppt)	0.7	0.8	0.9	0.6	0.7	0.9	1.2	
рН	nd	8.75	8.55	8.4	9.0	9.25	8.98	

Here is the hydrochemistry in table form; (Just one curious thing: look at the K change) Also a figure of the short core and long core changes.

Stratigraphy

A 7.7 m long core collected at a shallow water, near shore location provides insight into the early Holocene history of this lake. AMS ¹⁴C dates range from 9975 BP at the base to 7310 BP at 1.9 m depth. Five lithostratigraphic units can be identified. The basal meter of sediment is massive, relatively coarse grained, siliciclastic-rich sediment with low moisture and organic matter contents. Although quartz, feldspars, and clay minerals dominate this unit, the sediment also contains appreciable amounts of disordered, nonstoichiometric dolomite. This dolomite,

having up to 15 mol% excess calcium, is most likely authigenic in origin. Sharply overlying this nonbedded, basal clastic material is a 45 cm thick, faintly bedded, organic-rich gypsite. Both aragonite and Na₂SO₄ salts also occur in this thin evaporitic unit. Overlying this, from about 625 cm depth in the core to 400 cm depth (~9500-8900 BP), is a considerably finer grained, faintly laminated and indistinctly colour banded, aragonite-rich unit. The upper and lower contacts of this unit are gradational. Within these 2 m of calcareous sediment, the aragonite content increases gradually to about 5 m depth and then decreases further upward in the unit. Similarly, nonstoichiometric dolomite also increases upward to about 5 m, whereas both organic matter and gypsum contents show a gradual but sporadic decrease upward in the unit. The δ^{18} O and δ^{13} C of the aragonite both in this unit and in the underlying gypsite show a strong positive correlation and are high relative to the endogenic carbonates above and below, suggesting closed basin, evaporitic conditions. The meter of sediment overlying this aragonitic unit is unusual. It is a well bedded, siliciclastic unit composed almost entirely of non-sandy detrital quartz and feldspars with very low clay mineral contents. There is a very sharp contact at the top of this unit. The sediment at 303 to 310 cm depth in the core exhibits a distinctive pedogenic-like structure and has a considerably lower moisture content relative to immediately above 303 cm depth. This distinctive zone most likely represents a lowered water phase in the basin such that the bottom sediments at this location were exposed to subaerial desiccation and incipient soil formation. This low water event occurred at about 8400 BP. Immediately overlying the dry marker horizon at 3 m depth is a relatively coarse grained, faintly bedded, aragonite-rich unit. Gypsum contents decrease upward in this unit, from as much as 40% at the base of the unit to only sporadic occurrences above 150 cm depth indicating a gradual freshening of the lake water. Similarly, clay minerals show a gradual decrease upward with a complimentary increase in both guartz and feldspar contents, likely related to greater erosion and runoff from the watershed. The stable oxygen and carbon isotopes of the aragonite in this upper unit are negatively correlated. likewise suggesting a change toward more open basin conditions after 8400 BP.





CLEARWATER LAKE, CORE CWS2

10.9: ANTELOPE LAKE

Objectives

(actually, guys, believe it or not, but I don't have much to say at this stop!!! I just like to come here to eat the popcles and swim in the spring-fed pool; Here are some notes and illustrations; use as you like). The objectives of this brief stop are to: (I) summarize the complexity recent changes that have occurred in a 'simple' closed basin, perennial lake, and (ii) discuss evidence of longer-term variability as illustrated by the stratigraphic record.

The Modern Lake and Recent Changes

Antelope Lake, a relatively large, closed-basin hyposaline to saline lake on the eastern margin of the Great Sand Hills area, has, unlike many other basins in the northern Great Plains, experienced a dramatic decrease in lake level over the past two decades. High water levels during the 1960's and 70's prompted the construction of regional park facilities. During this time the lake was routinely stocked with fish and was a popular recreational fishing site. Since the mid-1970's levels have steadily decreased, with concomitant increase in salinity from less than 10 ppt to over 30 ppt. During the summer of 1994 the lake became chemically stratified. Presently the lake water is strongly supersaturated with respect to aragonite and protodolomite and slightly undersaturated with respect to gypsum.

A ²¹⁰Pb chronology was established for the upper meter of section in the offshore area of the basin by Turner (1994). These data, combined with the historical hydrochemical and hydrologic information and detailed sediment composition, emphasize the complex interrelationships that exist between water level, salinity, endogenic mineral saturation and precipitation in even a relatively simple saline lake. The deposition of aragonite throughout the past 100 years in Antelope Lake confirms that the brine has maintained a relatively high Mg/Ca ratio. The sporadic occurrence of a disordered species of dolomite (protodolomite) further indicates occasional excursions toward very high Mg/Ca and probably also very high carbonate alkalinities. The distribution of gypsum, a soluble evaporitic mineral, shows the influence of (i) generally elevated salinities, particularly during the periods 1920-1940 and after 1970, and (ii) lowered carbonate alkalinities and corresponding increased sulfate concentrations.

Antelope Lake Hydrochemistry								
	A	Ct	T	Gent	Augus	t, 1994	January	y, 1995
nin mg L ⁻¹	Aug. 1938	Sept. 1957	June 1971	Sept. 1985	surf	4 m	surf	4.75 m
Ca ²⁺	22	63	67	51	31	25.7	37.7	30.7
Mg ²⁺	1132	1276	642	1149	1470	2860	1970	2760
Na ⁺	2328	1232	1360	2543	2730	5350	4020	5600
K^+	nd	nd	123	220	247	443	242	334
HCO ₃ -	717	645	662	781	977	2020	1393	2065

SO4 ²⁻	801	4450	4840	8668	10700	22100	15200	21100
Cl	325	169	239	428	439	857	547	768
TDS (ppt)	12.4	7.3	8.4	15.1	16.4	33.9	24.6	33.9
рН	8.9	8.7	9.0	9.0	9.1	8.9	9.0	8.8

Stratigraphy

I now realize why I've put Antelope "aside" to do later - nothing makes too much sense in this puppy; how about we just sit on the shore and eat popules and drink beer at this stop?

The close proximity of Antelope Lake to the Great Sand Hills suggests that this basin holds considerable promise for the possibility of recording variations in aeolian activity. Indeed, the 6.25 meters of section recovered from the offshore area of the basin shows considerable fluctuations in various grain size parameters and in the proportions of fine grained siliciclastic components. Unfortunately, the paucity of lamination in the upper half of the section obscurs any high resolution paleointerpretations that might be made. The presence of both gypsum and aragonite combined with the absence of sedimentary structures throughout this upper part of the core suggests that the lake was a relatively shallow, nonstratified body of water that probably varied on a seasonal basis from a modestly saline (hyposaline?), bicarbonate-rich solution with Mg/Ca ratios of 2-10 to a somewhat more saline (TDS $> \sim 30$ ppt), sulfate-dominated lake. The sediments in the lower 3 m of core are much better laminated and have a much more irregular distribution of endogenic precipitates implying that lower-salinity conditions were more common. Particularly noteworthy in this lower half of the section is the occurrence of a nonbedded, 50 cm thick quartz-rich unit. This unit is also characterized by very low organic matter content, and low endogenic and clay mineral components and may represent an extended period of increased aeolian input to the basin. And if you believe this, I have some really good real estate near a sceinic swamp for sale.



ANTELOPE LAKE CORE S2



APPENDIX A BIOLOGICAL THINGIES IN THE LAKES (Compiled from Hammer, 1982, 1986)



Deadmoose Lake

phototrophic bacteria: *Thiocapsa roseopersicina* common phytoplankton: *Diatoma tenue, Nodularia spumigena, Aphanizomenon flos-aquae, Chaetoceros* Annual primary production: algal: 69 g C m⁻² yr ⁻¹ bacterial: 14.3 g C m⁻² yr ⁻¹ Macrophytes: *Scrirpus americanus, Eleocharis, Salicornia rubra*

Lenore Lake

common algae: *Cladophora, Enteromorpha, Microcystis* fish: walleye, pike

Little Manitou Lake

common phytoplankton: *Chaetoceros, Rhizoclonium* Annual primary production: 70 g C m⁻² yr⁻¹

Muskiki Lake common phytoplankton: *Dunaliella salina*

Patience Lake

dominant alga: Dunaliella

Quill Lakes

common algae: *Enteromorpha, Nodularia spumigena, Pediastrum, Cladophora* zooplankton: *Diaptomus, Cyclops, Daphnia pulex* fish: 9-spine stickleback, pike, sucker

Waldsea Lake

phototrophic bacteria: *Chlorobium* common phytoplankton: *Botryococcus braunii, Fragilaria* spp., *Sphaerocystis schroeteri, Stephanodiscus niagarae* Annual primary production: algal: 38 g C m⁻² yr ⁻¹ bacterial: 32 g C m⁻² yr ⁻¹ Macrophytes: *Potamogeton pectinatus, Ruppia* Zooplankton: *Diaptomus connexus, Hexarthra fennica, Brachionus plicatilis, Daphnia similis* Littoral fauna: Hemiptera; *Cenocorixa expleta, Thichocorixa verticalis interiores,* Diptera, *Cricotopus ornatus,* Coleoptera; *Hygrotus salinarious*

APPENDIX B. MINERALS IN QUATERNARY LACUSTRINE SEDIMENTS (from Last, 2001)

Mineral Name Composition		Occurrence ¹				
Carbonate Minerals						
Aragonite	CaCO ₃	D, E, A				
Artinite	Mg ₂ CO ₃ (OH) ₂ 3H ₂ O	E, A				
Ankerite	Ca(Fe,Mg)(CO ₃) ₂	E, A				
Benstonite	Ca7Ba6(CO3)13	Α				
Burbankite	Na ₂ (Ca,Sr,Ba,Ce) ₄ (CO ₃) ₅	Α				
Calcite	CaCO ₃	D, E, A				
Dawsonite	NaAl(CO ₃)(OH) ₂	А				
Dolomite	CaMg(CO ₃) ₂	D				
Eitelite	Na ₂ Mg(CO ₃) ₂	А				
Gaylussite	Na ₂ Ca(CO ₃) ₂ 3 5H ₂ O	E, A				
Hydromagnesite	Mg5(CO ₃) ₄ (OH) ₂ 3 4H ₂ O	E, A				
Huntite	CaMg ₃ (CO ₃) ₄	E, A				
Kutnohorite	Ca(Mn,Mg)(CO ₃) ₂	E, A				
Magnesite	MgCO ₃	E, A				
Magnesian Calcite	(Mg _x Ca _{1-x})CO ₃	Е				
Monohydrocalcite	CaCO ₃ WH ₂ O	Е				
Minrecordite	CaZn(CO3) ₂	E, A				
Nahcolite	NaHCO ₃	E, A				
Natron	Na ₂ CO ₃ ₩ 10H ₂ O	E, A				
Nesquehonite	Mg(HCO ₃)(CO ₃) ₄	E, A				
Pirssonite	Na ₂ Ca(CO ₃) ₂ 3 2H ₂ O	А				
Protodolomite	$(Mg_xCa_{1-x})(CO_3)_2$	E, A				
Rhodochrosite	MnCO ₃	А				
Scarbroite	Al ₂ (CO ₃) ₃ 3 13Al(OH) ₃	А				
Shortite	Na ₂ Ca ₂ (CO ₃) ₃	А				

Siderite	FeCO ₃	E, A
Strontianite	SrCO ₃	E, A
Thermonatrite	Na ₂ CO ₃ WH ₂ O	E, A
Trona	NaHCO ₃ 💥 Na ₂ CO ₃ 💥 2H ₂ O	E, A
Vaterite	CaCO ₃	E, A
Witherite	BaCO ₃	Α
Zemkorite	$Na_2Ca(CO_3)_2$	Е, А
<u> </u>	Phosphate Minerals	
Anapaite	Ca ₃ Fe(PO ₄) ₃ 3 4H ₂ O	А
Apatite	Ca ₂ (PO ₄) ₃ (OH,F)	D, A
Brushite	CaHPO ₄ 2 2H ₂ O	E
Fluorapatite	$Ca_{10}(PO_4)_6F_2$	A
Lipscombite	Fe ₃ (PO ₄) ₂ (OH) ₂	Α
Ludlamite	$(Fe,Mn,Mg)_3(PO_4)_2 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	Α
Lüneburgite	Mg ₃ (PO ₄) ₂ B ₂ O ₃ 3 8H ₂ O	E, A
Newberyite	MgHPO ₄	E, A
Phosphoferrite	(Mn,Fe) ₃ (PO ₄) ₂ 3 H ₂ O	А
Rockbridgeite	(Fe, Mn)Fe ₄ (PO ₄) ₃ (OH) ₅	E, A
Strengite	FePO ₄ 2 H ₂ O	E, A
Struvite	MgNH ₄ PO ₄ 3 6H ₂ O	E, A
Vivianite	Fe ₃ (PO ₄) ₂ 3 8H ₂ O	Α
	Sulfate Minerals	
Alunite	KAl ₃ (OH) ₆ (SO ₄) ₂	E
Anhydrite	CaSO ₄	D, E, A
Aphthitalite	$K_3Na(SO_4)_2$	А
Arcanite	(K,NH ₄) ₂ SO ₄	А

	Barite	BaSO ₄
Bassanite	$2CaSO_4$ ${\bigotimes}$ H ₂ O	Α
Bloedite	Na ₂ Mg(SO ₄) ₂ 3 H ₂ O	Е, А
Celestite	SrSO ₄	Α
Coquimbite	Fe(SO ₄) ₃ 3 9H ₂ O	Е, А
Despujolsite	Ca ₃ Mn(SO ₄) ₂ (OH) 3(H ₂ O)	Е, А
Epsomite	MgSO ₄ 3 7H ₂ O	Е
Eugsterite	Na ₂ Ca(SO ₄) ₃ 2 H ₂ O	Е, А
Glauberite	Na ₂ Ca(SO ₄) ₂	Е, А
Görgeyite	K ₂ Ca ₅ (SO ₄) ₆ WH ₂ O	Е, А
Gypsum	CaSO ₄ 2H ₂ O	D, E, A
Hexahydrite	MgSO ₄ ₩ 4H ₂ O	Е, А
Hydroglauberite	Na ₁₀ Ca ₃ (SO ₄) ₈ 3 6H ₂ O	Α
Jokokuite	MnSO ₄ 5H ₂ O	Е, А
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	Α
Kalistronitite	$K_2Sr(SO_4)_2$	Α
Kieserite	MgSO ₄ ₩ H ₂ O	Α
Krausite	Fe ₂ (SO ₄) ₃ 2 H ₂ O	Α
Langbeinite	2MgSO ₄ W K ₂ SO ₄	Α
Lecontite	NaKNH ₄ SO ₄ 2H ₂ O	Е, А
Leightonite	$K_2Ca_2Cu(SO_4)_4$ 2 H_2O	Α
Leonhardtite	MgSO ₄ ¾ 4H ₂ O	Е, А
Leonite	$MgK_2(SO_4)_2 4H_2O$	Е, А
Loeweite	Na ₁₂ Mg ₇ (SO ₄) ₁₃ 2 15H ₂ O	E, A
Mallardite	MnSO ₄ ₩ 7H ₂ O	E, A
Melanterite	FeSO ₄ ₩ 7H ₂ O	E, A
Mercallite	KHSO ₄	Α
Mirabilite	Na ₂ SO ₄ 3 10H ₂ O	E, A

Pentahydrite	MgSO ₄ 3 5H ₂ O	E, A
Picromerite	MgK ₂ (SO ₄) ₂ 36 H ₂ O	E, A
Polyhalite	$K_2Ca_2Mg(SO_4)_4$ 2H ₂ O	А
Potassium alum	KAl(SO ₄) ₂ 3 12H ₂ O	E, A
Quenstedite	FeSO ₄ 3 10H ₂ O	E, A
Sanderite	MgSO ₄ 2 H ₂ O	E, A
Siderotil	FeSO ₄ 3 4H ₂ O	А
Starkeyite	MgSO ₄ 3 4H ₂ O	E, A
Sulfur	S	Е
Syngenite	$K_2Ca(SO_4)_2 \bigotimes 2H_2O$	А
Szomolnokite	FeSO ₄ WH ₂ O	E, A
Thenardite	Na ₂ SO ₄	E, A
Vanthoffite	Na ₆ Mg(SO ₄) ₄	А
Wattevilleite	$Na_2Ca(SO_4)_2$ H_2O	А

Carbonate-Sulfate, Carbonate-Sulfate-Chioride, and Carbonate-Phosphate Minerals			
Ardealite	CaMgCO ₃ PO ₄	E, A	
Bonshtedite	Na ₃ Fe(PO ₄)(CO ₃)	Е, А	
Bradleyite	Na ₃ Mg(PO ₄)(CO ₃)	E, A	
Burkeite	Na ₄ (SO ₄)CO ₃	E, A	
Collophanite	$Ca_{10}(PO_4)_6CO_3$ H_2O	Α	
Galeite	Na ₂ SO ₄ 💥 Na(F,Cl)	Α	
Hanksite	KNa ₂₂ (CO ₃) ₂ (SO ₄) ₉ Cl	E, A	
Kainite	4MgSO ₄ 3 4KCl 3 5H ₂ O	Α	
Northupite	Na ₂ Mg(CO ₃) ₂ WaCl	Α	
Rapidcreekite	Ca ₂ (CO ₃)SO ₄ 3 H ₂ O	E, A	
Schairerite	Na ₂ SO ₄ With Na(F,Cl)	Α	
Sulfohalite	2Na ₂ SO ₄ 3 NaCl 3 4H ₂ O	Α	
Tychite	Na ₆ Mg ₂ SO ₄ (CO ₃)	E, A	

	Chloride and Iodate Minerals	
Antarcticite	CaCl ₂ 2 6H ₂ O	E, A
Bischofite	MgCl ₂ ‰ 6H ₂ O	E, A
Bruggenite	$Ca(IO_3)_2$ H_2O	E, A
Carnallite	KMgCl ₁₃ ‰ 6H ₂ O	Е, А
Douglasite	KFeCl ₄ 2H ₂ O	Α
Halite	NaCl	E, A
Hydrohalite	NaCl 🗱 2H ₂ O	Е
Lautarite	Ca(IO ₃) ₂	Е, А
Rinneite	K ₃ NaFeCl ₆	E, A
Sylvite	KCl	Α
Tachyhydrite	CaCl ₂ 2MgCl 2H ₂ O	Α
Teepleite	Na ₂ B(OH) ₄ Cl	А
	Nitrate and Borate Minerals	
Ameghinite	NaB ₃ O ₃ (OH) ₄	Α
Binorite	Ca ₂ B ₁₄ O ₂₃ 3 8H ₂ O	Е, А
Borax	$Na_2B_4O_7$ 310 H ₂ 0	Α
Carboborite	MgCa(CO ₃) ₂ 3 B(OH) ₄ 3 H ₂ O	Е, А
Colemanite	$Ca_2B_6O_{11}$ \lessapprox 5H ₂ O	E, A
Darapskite	Na ₃ SO ₄ NO ₃ W H ₂ O	E, A
Howlite	Ca ₂ SiB ₅ O ₉ (OH) 5	E, A
Humberstonite	K ₃ Na ₇ Mg ₂ (SO ₄) ₆ (NO ₃) ₂ 2 6H ₂ O	E, A
Hungchaoite	MgB4O5(OH)4 🗱 8H2O	E, A
Hydroboracite	$CaMgB_6O_{11}$ $\lessapprox 6H_2O$	E, A
Inderborite	CaMgB ₆ O ₁₁ WH ₂ O	А
Inderite	Mg ₂ B ₆ O ₁₀ 3 15H ₂ O	E, A
Inyoite	Ca ₂ B ₆ O ₆ (OH) ₁₀ 3 8H ₂ O	E, A

Kaliborite	HKMg ₂ B ₁₂ O ₁₆ (OH) ₁₀ 2 4H ₂ O	E, A
Kernite	$Na_2B_4O_7$ $Heighted Heighted Height$	Е, А
Kurnakovite	MgB ₆ O ₁₉ 3 15H ₂ O	Е, А
Macallisterite	Mg ₂ B ₆ O ₇ (OH) ₆ 3 9H ₂ O	Е, А
Meyerhofferite	Ca ₂ B ₆ O ₁₁ 3 7H ₂ O	Е, А
Niter	KNO ₃	Е, А
Nitrobarite	Ba(NO ₃) ₂	Е, А
Nobleite	CaB_6O_{10} H_2O	Е, А
Pinnoite	MgB ₂ O ₄ 3 H ₂ O	Е, А
Priceite	CaB ₁₀ O ₁₉ 3 7H ₂ O	E, A
Proberite	NaCaB₅O ₉ ₩ 5H ₂ O	E, A
Santite	KB5O6(OH)4 \$\$2H2O	А
Sborgite	NaB ₅ O ₆ (OH) ₄ 3 H ₂ O	А
Soda Niter	NaNO ₃	E, A
Tincalconite	$Na_2B_4O_7$ $\gtrsim 2H_2O$	Α
Ulexite	NaCaB ₅ O ₉ 3 8H ₂ O	E, A
Oxide,	Fluoride, and Chromate Minerals	
Anatase	TiO ₂	D, A
Birnessite	(Na,Ca)Mn ₇ O ₁₄ 3 H ₂ O	D, A
Boehmite	Alooh	D
Corundum	Al ₂ O ₃	D
Diaspore	Alooh	D
Dietzeite	Ca ₂ (IO ₃)2CrO ₄	E, A
Fluorite	CaF ₂	А
Geothite	FeOOH	D, E, A
Gibbsite	Al(OH) ₃	D
Hematite	Fe ₂ O ₃	D, A
Ilmenite	FeTiO ₃	D

Jacobsite	MnFe ₂ O ₄	D
Lepidocrocite	FeOOH	D, A
Lopezite	K ₂ Cr ₂ O ₇	Е, А
Psilomelane	$(Ba,K)(MnO_2)_{2.5}$ H_2O	Α
Maghemite	Fe ₃ O ₄	D
Magnetite	Fe ₃ O ₄	D
Pyrolusite	MnO ₂	Α
Rancieite	$(Ca,Mn)Mn_4O_9 $ $3H_2O$	Е
Rutile	TiO ₂	D
Tarapacaite	K ₂ CrO ₄	E, A
Todorokite	(Na,Ca,K,Ba,Mn) ₂ Mn ₅ O ₁₂ 3 H ₂ O	D, A
Ulvöspinel	TiFe ₂ O ₄	D
Ν	Non-Clay Silicate Minerals	
Adularia	KAlSi ₃ O ₈	А
Amphiboles	$(Na,Ca,K)_2$ (Mg,Fe,Ti,Al,Li, Mn) ₃ (Si,Al) ₈ O ₂₂ (OH,F) ₂ ²	D
Analcime	NaAlSi ₂ O ₆ 2 H ₂ O	Α
Cristobalite	SiO ₂	D
Clinoptolite	(Na,K,Ca) ₂ Al ₃ (Al,Si) ₂ Si ₁₂ O ₃₆ 2 12H ₂ O	А
Erionite	$(K_2Ca,Na_2)_2Al_4Si_{14}O_{36}$ $15H_2O^2$	А
Kanemite	NaHSi ₂ O ₄ (OH) ₂ 2 H ₂ O	Е
Kenyaite	Na ₂ Si ₂₂ O ₄₁ (OH) ₈ % 6H ₂ O	Е
K-Feldspars	KAlSi ₃ O ₈ ²	D, A
Magadiite	NaSi ₇ O ₁₃ (OH) ₃ 3 H ₂ O	Е
Makatite	Na ₂ Si ₄ O ₈ (OH) ₂ 2 4H ₂ O	Е
Micas	K(Mg,Fe,Al) ₃ AlSi ₃ O ₁₀ (OH) ²	D
Moganite	SiO ₂	А
Mordenite	$(Ca,Na_2,K_2)Al_2Si_{10}O_{24}$ \approx 7H ₂ O	А
Natrolite	Na ₂ Al ₂ Si ₂ O ₆ 2 H ₂ O	А

Olivenes	$(Mg,Fe)_2SiO_4^2$	D
Opal	SiO ₂ 3 nH ₂ O	D, E, A
Phillipsite	$KCa(Al_3Si_5O_{16})$ $\stackrel{\text{\tiny $\ensuremath{\&}}}{\longrightarrow}$ $6H_2O$	А
Plagioclase	(Na, Ca)Al (Al, Si)Si $_2O_8^2$	D
Pyroxenes	$(Ca,Mg,Fe)_2Si_2O_6^2$	D
Quartz	SiO ₂	D
Searlesite	NaBSi₂O ₆ ∰ H₂O	А
Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂ ‰ 6H ₂ O	Е
Thomsonite	NaCa ₂ Al ₅ Si ₅ O ₂₀ 2 6H ₂ O	А
	Layered Silicate Minerals	
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	D
Illite	$(K,Al,Mg,Fe)_2(AlSi)_4O_{10}(OH)_2 H_2O^2$	D
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	D, A
Mixed-layer Clays	Variable ²	D, E, A
Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH)$ $4H_2O$	D, A
Smectite	(Na,Ca) _{0.33} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ nH ₂ O ²	D, A
Vermiculite	(Mg,Fe,Al) ₃ (Al,Si) ₄ O ₁₀ (OH) ₂ 3 4H ₂ O	D, A
	Sulfides	
Griegite	Fe ₃ S ₄	А
Mackinawite	FeS	Е, А
Marcasite	FeS ₂	D, A
Pyrite	FeS ₂	D, E, A
Pyrrhotite	FeS	D, A
Sphalerite	ZnS	Е
Wurtzite	ZnS	A

¹D=detrital; E=endogenic; A=authigenic ²Formula represents a series or group of minerals

Italics indicate minerals are common in lake sediments.

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