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Iron phosphate sedimentation in a meromictic kettle lake: a Holocene record of geochemistry and paleoenvironment in Teapot Lake, Southern Ontario

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Iron phosphate sedimentation in a meromictic kettle lake: a Holocene record of geochemistry and paleoenvironment in Teapot Lake, Southern Ontario

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Abstract

High iron phosphate mineralization in sediments (>3 m with 15 to 20% vivianite) and the water column (up to 6 ppm PO_4 and 9 ppm Fe) of Teapot Lake, a meromictic kettle lake in Brampton, Ontario, was investigated to understand the origins of such remarkable phosphorus enrichment. The lake is surrounded by palimpsest topography composed of Halton Till and Holocene organic matter. Groundwater is the primary recharge source of Teapot Lake, contributing dissolved ferrous iron to the system. Phosphorus concentrations remain low in lake sediments deposited over the past 1335 years, therefore anthropogenic phosphorus contributions are negligible compared to natural accumulations over the Holocene. The source of phosphorus was concluded to be airborne, likely from waterfowl faeces entering the lake from the surface and is subsequently assimilated by algae in the mixolimnion. Phosphorus released from decomposing biomass below the redox boundary is then sequestered by iron as vivianite in the reduced sediments. Currently, the acidic monimolimnion prevents vivianite from precipitating from the lake water, however vivianite can form in the sediments when iron and phosphorus activities are high and the Eh remains above the sulfate/sulfide reduction zone.

Résumé

Les minéralisations de phosphate riches en fer dans les sédiments (>3 m avec 15-20% de vivianite) et dans la colonne d'eau (jusqu'à 6 ppm de PO_4 et 9 ppm de Fe) du lac Teapot, un lac kettle meromictique situé à Brampton en Ontario, ont été étudiées dans le but de déterminer l'origine de ces enrichissements exceptionnels en phosphate. La topographie entourant le lac est de type palimpseste, formée par les tills de Halton ainsi que de matières organiques Holocènes. Les eaux sous-terraines sont la source primaire de recharge du lac Teapot, contribuant ainsi à la dissolution de fer ferreux dans le system. Les concentrations en phosphore demeurent faibles dans les sédiments de lac déposés au cours des 1335 dernières années, ce qui implique que la contribution en phosphore anthropogène est négligeable en comparaison avec l'accumulation naturelle pendant la période Holocène. Il a été conclu que l'apport en phosphore s'est fait principalement par voie des airs, par l'intermédiaire des matières fécales des oiseaux aquatiques. Ces matières ont été incorporées au lac par la surface et subséquemment assimilées par les algues dans le mixolimnion. Le phosphore ainsi libéré par la décomposition de la biomasse située sous la limite d'oxydoréduction est saisi par le fer dans la vivianite par les sédiments réducteurs. Présentement, l'acidité du monimolimnion empêche la précipitation de la vivianite mais ce minéral peut se former dans les sédiments lorsque l'activité du fer et du phosphate est élevée et que le Eh est maintenu au dessus de la zone de réduction sulphate/sulphure.

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1 Introduction

Phosphorus is possibly the most widely studied element in lacustrine environments due to its pivotal role in stimulating primary productivity and microbial activity. Its naturally low abundance compared to other biologically essential nutrients lends to its statues as the "limiting" nutrient in surface waters and aquatic ecosystems. Humans have added significant amounts of phosphorus to water through input from untreated sewage, fertilizers and detergents. These activities have been curbed after eutrophication of natural waters proliferated to such a degree that mitigation policies and best practices have been established throughout Canada and North America (Vollenweider, 1968). Despite these efforts, some lakes continue to demonstrate critical phosphorus levels. This raises the question whether nutrient flux in lakes is solely due to human activities or whether naturally occurring phenomena are at play. Lake sediment records may be utilized to evince occurrence and disparities in phosphorus levels in addition to other trace metals prior to settlement in North America.

Teapot Lake is a meromictic kettle lake located adjacent to the Brampton Esker, and to the south of the Oak Ridges Moraine. This site is the focus of a comprehensive research program that will integrate micropaleontological-geochemical-sedimentological-chronological-cyclostratigraphic approaches to identify limnological/ climatic conditions over several time scales in eastern Canada through the late Holocene, the last 5000 years (CFCAS 2004 Proposal. Patterson, R. T. 2004). The objective of this present thesis is to reconstruct a paleoenvironmental record from the lake water and sediment profiles. Initially, this component of the research sought to extract potential paleoclimatic records from the stable isotopes of organic and carbonate phases. However, the dominant mineral phases, and

indeed the major component of the sediment in this lake was determined to be vivianite with the remaining sediments composed of organic matter. Of the 4.8 m sediment core extracted from the lake, over 3 m are dominated by horizons of vivianite mineralization. Thus, the research approach is oriented to understanding the unique geochemical dynamics of Teapot Lake water and sediment, and the paleoenvironmental implications.

1.1 Background

Kettle lakes within Southern Ontario hold records of environmental changes since the end of the Wisconsin Glaciation ~12,000 ka, and beginning of the Holocene ~10,000 years ago (hereafter referred to as 10,000 BP, as in years before present). These lakes are thought to have formed as the Laurentide Ice Sheet retreated, releasing blocks of ice that were subsequently buried by glacial outwash. A kettle lake is small depression (0.1 to 1.0 ha) formed by the slow melting of buried dead ice blocks that are permanently filled with water (Frielinghaus & Vahrson, 1998). Ice blocks are calved from the snout of a melting glacier, eventually becoming trapped by outwash aggrading and melting over hundreds of years (Florin & Wright, 1969; Eyles *et al.,* 2003).

Meromictic lakes are unique in that the depth to surface ratio is sufficient to prevent seasonal over turn, resulting in dense bottom water becoming isolated from surface modifications and seasonal dynamics. The anoxic and isolated monimolimnion of meromictic lakes allow sediments to remain relatively undisturbed (Larsen & MacDonald, 1993; Lowe *et al.,* 1997). Therefore, the sediments provide an excellent proxy record as permanently stratified bottom waters are commonly anoxic and benthic organisms that mix bottom sediments (bioturbation) are absent. Accordingly, sediments accumulating in meromictic lakes are typically laminated and in many cases record annual deposition,

allowing for high resolution paleoenvironmental reconstruction (O'Sullivan, 1983; Anderson *et al.*, 1985; Anderson & Dean, 1988). For example, Crawford Lake in Hamilton, Ontario has been extensively studied due to the undisturbed laminated sediments. Pollen assemblages, diatoms, stable oxygen isotopes of marl, etc., from Crawford Lake sediments have been used as proxies for reconstructing climatic and vegetative changes since the Laurentide Ice Sheet retreated from this region (Yu & Wright, 2001; Ekdahl *et al.,* 2004; Ekdahl *et al.,* 2007).

Fluctuations in the watershed and climate directly affect surface waters. Meromictic lakes that are presently unaffected by glaciers have well preserved laminated sediments due to dense, cold bottom waters and inherent lack of mixing induced by the high relative depth of water (O'Sullivan, 1983; Last & Schweyen, 1985; Larsen & MacDonald, 1993). Any reduction of lake levels due to climate or hydrological changes, to a critical point can subsequently terminate meromixis as well as the deposition of laminations (Larsen & MacDonald, 1993; Hammer, 1994; Kennedy, 1994). For example, decreased precipitation will reduce water levels and dissolved ions will become concentrated in the water, possibly leading to increased mineral precipitation (Williams *et al.,* 1998).

Lake sediments can affect eutrophication arising from external phosphorus loading because of their capacity to sequester or liberate phosphorus, depending on limnological conditions (Williams *et al.,* 1971). Vivianite, $Fe^{2+}{}_3(PO_4)_2{\cdot}8H_2O$, a hydrated iron phosphate, is the most stable phase of ferrous orthophosphate ($Fe_3(PO_4)_2$) in lacustrine sediments (Einsele, 1938; Mortimer, 1941; Nriagu, 1972; Nriagu & Dell, 1974). The formation of vivianite in anaerobic sediments relates to the phosphate concentration, while ferrous iron (Fe^{2+}) causes precipitation and removal of orthophosphates (Nriagu, 1972). A more detailed account of vivianite will be given in subsequent chapters.

The methodology for trace element analysis in lake sediments has been well established and several variations exist. However, each method does not necessarily apply ubiquitously to all types of sediments or soils and as such, preliminary analysis should be done to establish a suitable analytical methodology. Modifications were made to the benchmark methods as the intention of this research was to analyze multiple elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, Ti, Zn). Phosphorus is often sequentially analyzed to obtain the non-apatite inorganic phosphorus (NAIP), apatite and organic phosphorus fractions (Williams *et al.,* 1971; Engstrom & Wright, 1984). The digestion method used by this author was a single extraction that allowed a large number of elements to be dissolved from the sediments, therefore all values are the total concentration of a given element. Inferences on the type of specific elements such as phosphorus will be attempted by comparison with other indicators.

The interactions between elements and transportation mechanisms (atmosphere, organisms, surface waters, soils, bedrock, tills and sediments) are supplementary towards quantifying the geochemical behaviour of sediments and towards developing models to explain variations in depositional environments (Boyle, 2001). Therefore understanding these underlying factors can assist in identifying the environmental situation leading to precipitation, mineralization, diagenesis and mobilization.

1.2 Research topic

There are two distinct types of sediments deposited in Teapot Lake; high iron (Fe), phosphorus (P) and manganese (Mn) horizons with iron phosphate mineralization and sediments rich in organic carbon, nitrogen and elemental sulfur. The two types of sediment horizons are hypothesized to represent either distinct limnological conditions taking place at

the time of formation or that formation occurs in the sediments after deposition. The possibility of Teapot Lake sediments holding a climatic record shall be explored by identifying the unique factors involved in formation of iron phosphate minerals and determining the time period when the system switched to produce organic rich sediments.

The concentrations of iron and phosphorus in Teapot Lake waters and lake sediments are exceedingly high. This author proposes that phosphorus entering Teapot Lake is sequestered by vivianite in the lake sediments. The sources of Fe and P will be identifies by comparing the geochemistry of lake water and lake sediments with the geochemical signatures of available hydrological parameters. The consequences of vivianite formation are pivotal to understanding the mobility of phosphorus in the system, therefore, a model of iron and phosphorus cycling in the lake will be used to demonstrate the hypothesis of vivianite as a sink for phosphorus. It should be noted that the intention of this thesis is not to reconstruct lake productivity, however, because the %C and %N concentrations are opposite to the Fe, Mn and P concentrations, it is hypothesized that productivity increases as mineral formation ceases and vice versa.

2 Study Site

Teapot Lake is a small meromictic kettle lake located in the north-eastern corner of the Heart Lake Conservation Area. The Heart Lake Conservation Area is located in the north-eastern corner of Brampton, within Southern Ontario. It was acquired by the Toronto and Regional Conservation Authority (TRCA) in 1957, and is used for recreational activities including hiking, picnicking, camping, swimming and fishing (Etobicoke and Mimico Creek Watersheds Task Force and TRCA, 2002). Heart Lake is accessible by roads leading straight onto the beach area and is heavily used for recreational swimming, boating and fishing.

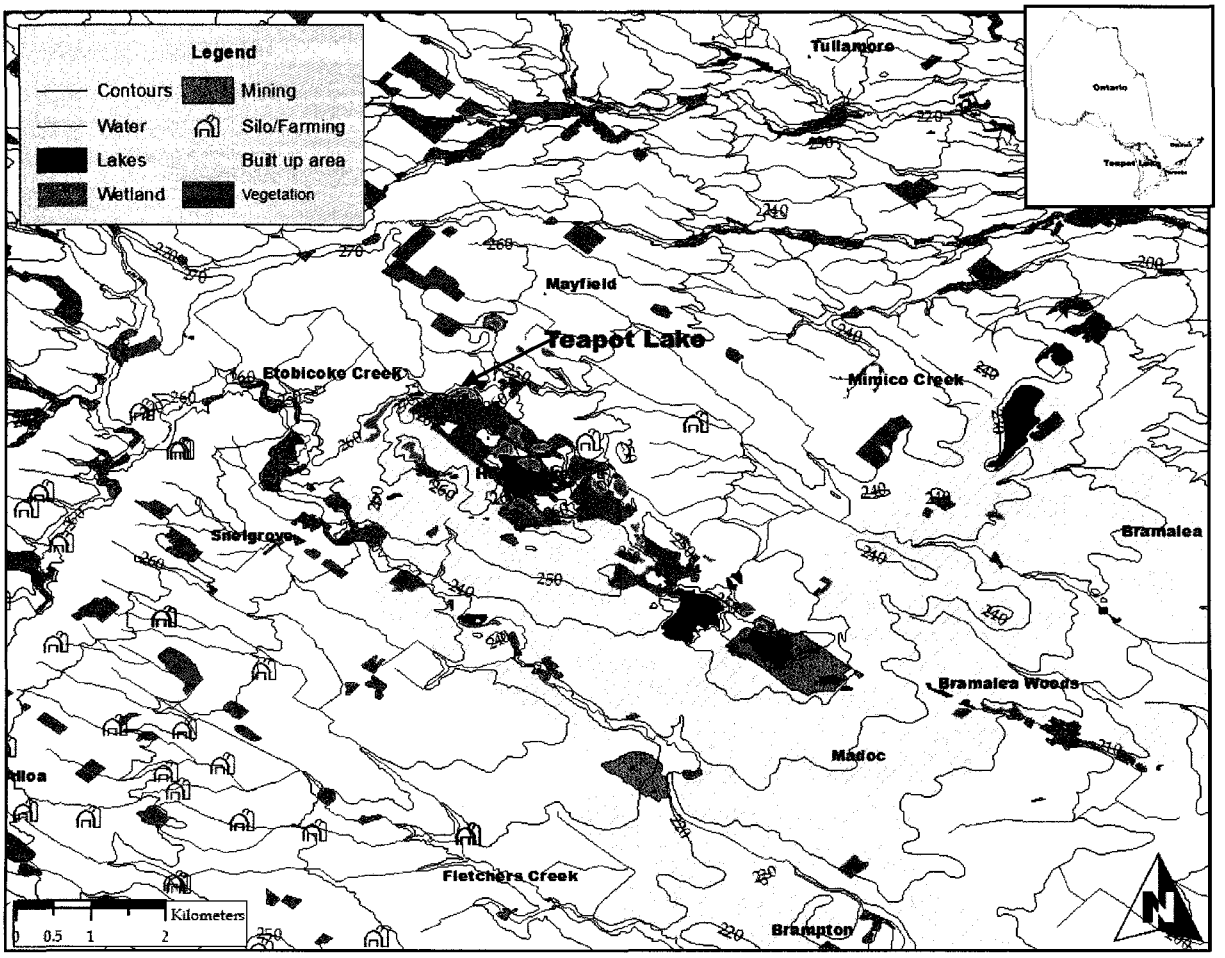


Figure 1. Regional map of Heart Lake Conservation Area, showing land usage and surface water.

2.1 Brampton History and Development

Chinguacousy and Gore townships were surveyed in 1818, and settlers arrived in 1825 where Queen and Main Streets intersect in modern Brampton. On January 1, 1853 Brampton received its charter and became an official village and rail arrived in 1856, bringing industry and greater population to settle the area (City of Brampton, 2007).

The town of Brampton has a population of 433,806. The greater area has seen large developments within the past few years, in 2004 Brampton awarded 9,500 residential building permits and had the second highest total construction dollars in Canada, $2.7 billion, $700 million of which was non-residential construction (City of Brampton, 2005). Brampton City council recently placed a cap of 5,500 units for residential development per annum, having approved 4,058 units for 2007 construction, and 12,300 submissions for development in Brampton's "green areas" have been received (Smith, 2007). This places significant pressure on the Heart Lake natural corridor, including destruction of natural wetlands, creation of waste water impound ponds in the north-western section (***Figure 2: F***), and illegal dumping of building waste and hazardous materials within the conservation area (***Figure 2: E***) due to high dumping fees. Adjacent to the Heart Lake Conservation Area is a designated industrial area and several aggregate quarries are operational within the general area of Heart Lake as well as on the Oak Ridges Moraine (City of Brampton, 1983). The quarries posse significant harm to the natural hydrology by altering the water table levels, impacting drainage and potential contamination of groundwater (City of Brampton, 1983).

2.2 Teapot Lake

Teapot Lake (43°45'N, 79°48'W) has a surface area of 0.5 Ha, maximum depth of 12.4 meters, a circumference of 288.7 meters, 87 meters across from east to west, 83.5 meters across from north to south, and is located within the Etobicoke Creek Watershed. Teapot Lake is one of several meromictic lakes in Southern Ontario. It is a kettle lake that originated during deglaciation by ice blocks calving at the snout of the receding Laurentide Ice Sheet. The lake itself is surrounded by dense shrubs, bushes and trees. Once ascended off the slope of the property, a path has been cleared but not maintained with brush covering the wooden planks. The ground in this lower area is soft and water saturated, with stagnant water pooling around the path towards the lake during spring. This suggests that the water table is close to or at lake level. Attempts to explore the shoreline were not possible on foot due to the dense vegetation and boggy grounds. The shoreline was surveyed in a small boat and no inlet or outlet sources of water were found. The shoreline vegetation consists of cattails, lily pads and tall grasses.

Teapot Lake has remained relatively pristine, as the Ontario Ministry of Natural Resources declared it an "Area of Natural or Scientific Interest". Teapot Lake is located on a large single home property, with a residential structure on top of a ridge, ~300 m from the lake on the northern corner of the property. The former superintendent of Heart Lake, Ron Dawe, fenced the Teapot Lake area and prohibited access to the lake as it was part of his private domain (Etobicoke and Mimico Creek Watersheds Task Force and TRCA, 2002). The Teapot Lake property is surrounded by agricultural lands from the north-east to the north-west, with the Heart Lake Conservation Area to the South East and 0.5 km forested buffer to the South West beyond which are residential communities.

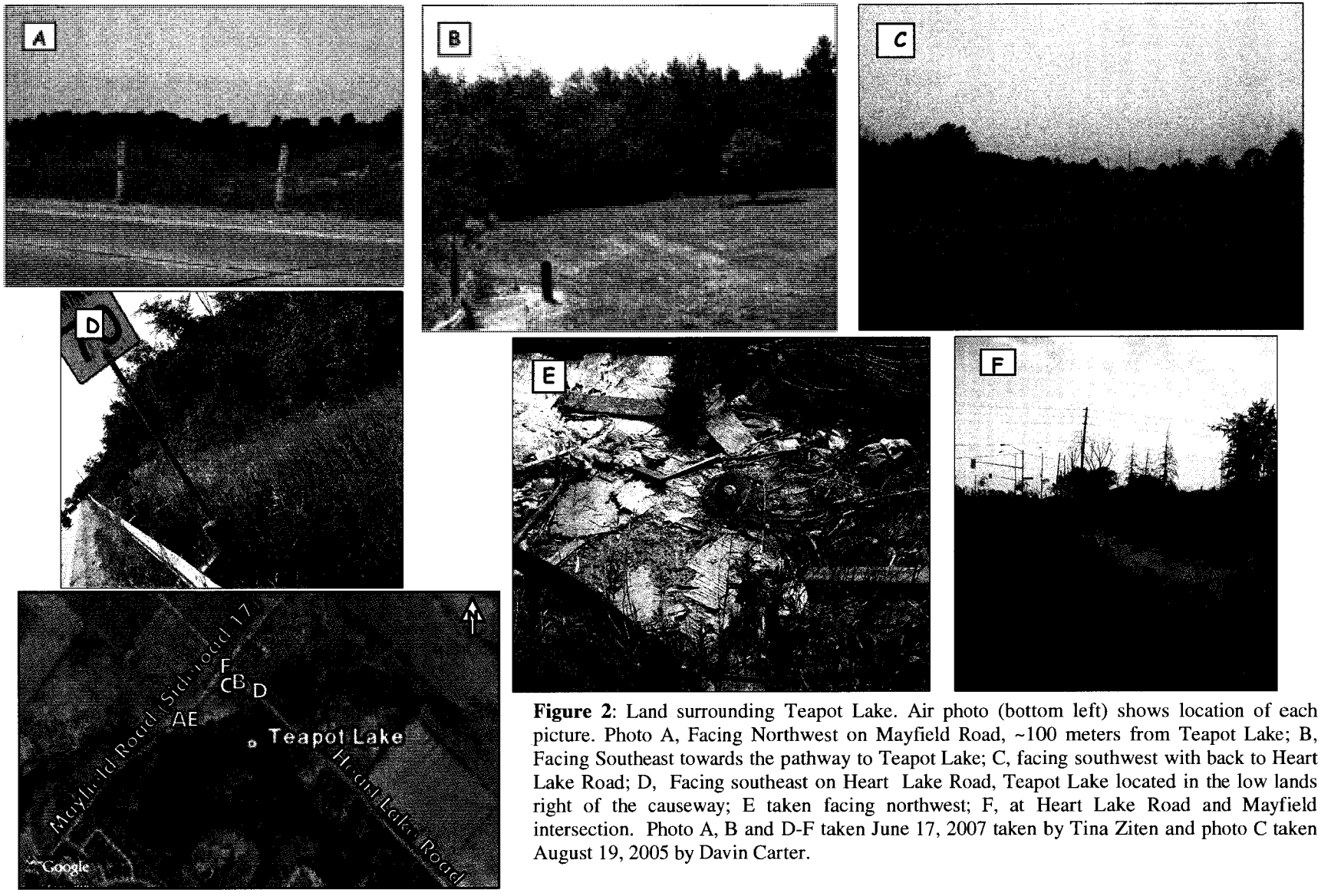


Figure 2: Land surrounding Teapot Lake. Air photo (bottom left) shows location of each picture. Photo A, Facing Northwest on Mayfield Road, ~100 meters from Teapot Lake; B, Facing Southeast towards the pathway to Teapot Lake; C, facing southwest with back to Heart Lake Road; D, Facing southeast on Heart Lake Road, Teapot Lake located in the low lands right of the causeway; E taken facing northwest; F, at Heart Lake Road and Mayfield intersection. Photo A, B and D-F taken June 17, 2007 taken by Tina Ziten and photo C taken August 19, 2005 by Davin Carter.

2.3 Bathymetry and Morphology

The shape and size of the Teapot Lake basin affects the physical, chemical and biological parameters of the water column. The Lake has a U-shaped basin with no inlet or outlet sources. Terraces observed from sonar images (***Figure 3***) occur between 2-4 meters on the eastern side of the lake and 8-10 meters through the whole lake, and may have resulted from slumping or reductions in lake water levels (***Figure 4***). Based on the sonar images, the deep lake sediments are evenly deposited and show no evidence of faulting.

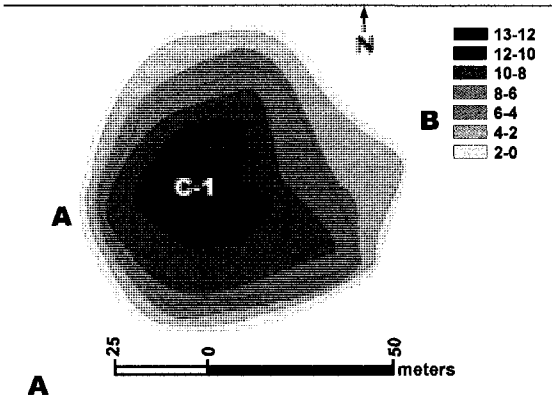
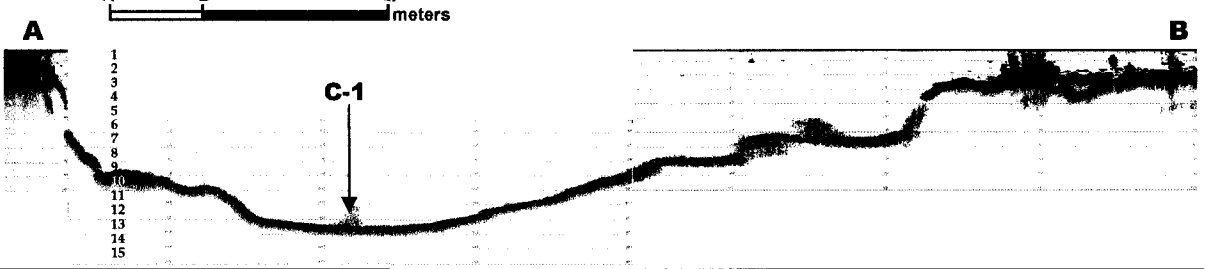


Figure 3 (left). Bathometry of Teapot Lake showing cross-section A-B for sonar image and C-1 indicates sample location of core 1.

Figure 4 (below). Sonar image of Teapot Lake showing basins morphology.



The littoral zone is small due to the steep basin. The steep basin also affects the depth of the photic zone, where light would not penetrate below the thermocline due to high turbidity (based on observation). The land gently slopes towards Teapot Lake and the area immediately surrounding the lake appears to be the lowest elevation. The low elevation and emergent vegetation on the shoreline verifies that the water table is very close to the surface.

2.4 Bedrock Geology

Teapot Lake is found at the southern most section of the "South Slope" physiographic region, while the rest of Heart Lake Conservation Area belongs in the Peel Plains region (Chapman & Putnam, 1984). The scarp to the east of Brampton below the Niagara escarpment was formed by the basal Silurian Whirlpool formation of sandstone and overlying Manitoulin Formation dolostones, which overly Queenston Formation red-shale (Hewitt, 1971). Peel Plains is an area of low relief caused by the changing levels of glacial Lake Peel that deposited sediments and till in the low-lying plains (Chapman & Putnam, 1984).

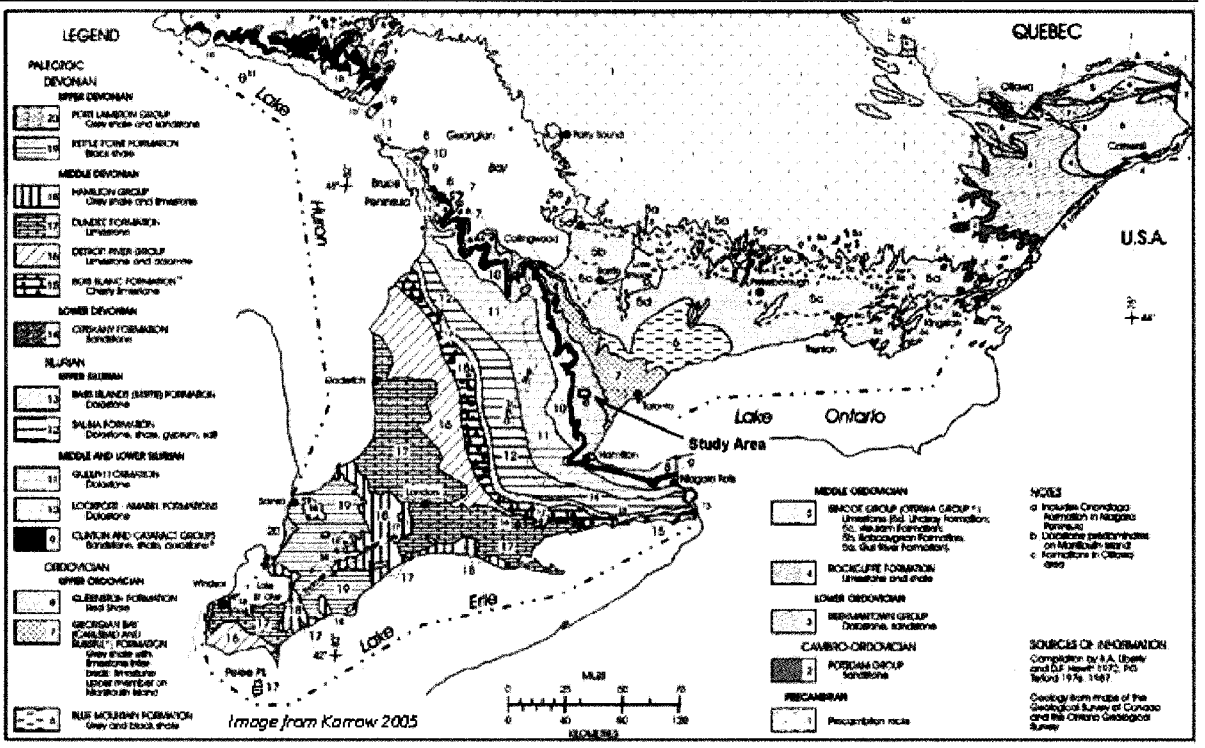


Figure 5. Bedrock Geology of Southern Ontario. From Karrow, 2005.

The bedrock geology of the Brampton region of Southern Ontario is composed of Paleozoic sedimentary bedrock, with Ordovician age shale and Silurian dolomites (***Figure 5***). Brampton lies on the youngest Ordovician bedrock, the Queenston Formation composed of red-sandy shale, with minor limestone (Liberty & Caley, 1969). The narrow and older

Meaford Formation of grey, blue and brownish shales with thin layers of limestone, calcareous sandstone and arenaceous shale, is slightly to the east. Beyond the Meaford is the Dundas Formation consisting of grey and blue shales, thin sandy beds and thin lenticular limestone beds. The Silurian Lockport formation lies to the west, which is composed of light grey dolomite with some brownish bituminous dolomite on top.

Red shale is associated with high iron oxide content that precipitated from water with dissolved iron and high amounts of oxygen (Chernicoff & Venkatakrishnan, 1995). Queenston shales are dominated by illite and chlorite clay (Guillet, 1967; Kwong *et al.*, 1985; Martini & Kwong, 1986), with CaO and MgO increasing from southeast to northwest (Sanford, 1961; Guillet 1967) related to a local increase in dolomitization (Brogly *et al.*, 1998). High concentrations of P_2O_3 were also found in the shales that are related to high organic content of initial materials (Brogly, 1990; Brogly *et al.*, 1998).

2.5 Quaternary Geology

The surficial geology of the region is best depicted in Sharpe *et al.*, (1997). Heart Lake Conservation Area and Teapot Lake are located on Halton Till Glacial Deposits, which is 1-15 meters in thickness consisting of clayey silts to silts, 1-2% stone content, occurring in till or lake plains often with interbedded fine sands, silts and clay (Sharpe *et al.*, 1997). The Brampton Esker runs parallel to Heart Lake road, ending at the southern end of Heart Lake (***Figure 6***).

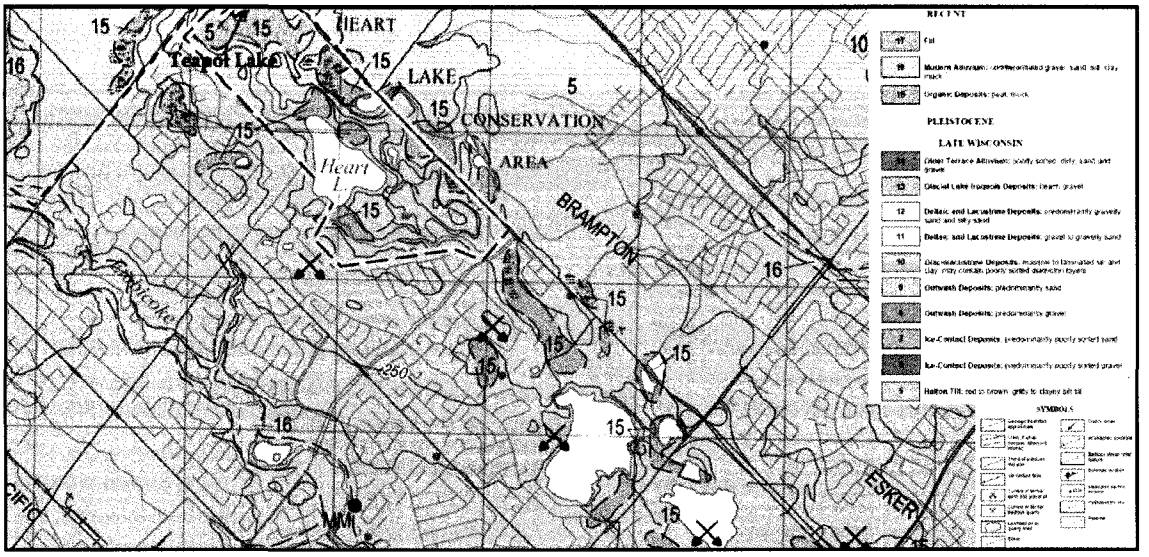


Figure 6. Quaternary Geology of Heart Lake Conservation Area. From Karrow & Easton, 2005.

Outwash terraces composed of coarse gravels north of Heart Lake Conservation Area in Caledon resulted from high-energy discharge during glacial retreat (Barnett *et al.,* 1998). This region likely experienced massive melting episodes, as demonstrated by the outwash and eskers located to the north and south, both of which would have carried a large amount of debris accumulated as the Laurentide Ice Sheet advanced and regressed.

The Brampton esker is an example of palimpsest topography (present surface formed from previous landforms), possibly deposited during the Newmarket ice retreat prior to the Halton ice advance (Karrow *et al.,* 1977; Karrow, 2005). The esker is composed of clasts ranging in size from clay to boulder gravel with unconsolidated sand and gravel (Saunderson & Jopling, 1980), produced by seasonal, diurnal, and storm meltwater discharge demonstrated in changes of sediment transport patterns (Church & Gilbert, 1975; Gustavson *et al.,* 1975). The esker trends northwest, is ~ 7 km long, 0.2 to 0.6 km wide, ~ 15 meters high, and has a till cap of 1 to 3 meters thick (Karrow, 2005). It has been suggested that the ice blocks which eventually produced the regional kettle lakes were covered by esker sediments during the Newmarket ice retreat, and the subsequent ice advance (Halton)

deposited a till cap of 1-3 meters (Karrow, 2005). Heart Lake and Teapot Lake are kettle lakes formed in the esker region. It should be noted that the maximum depth of both lakes surpasses that of the Halton Till cap and has a depth closer to the height of the esker.

2.6 Hydrology

The Heart Lake Conservation Area lakes are part of the Etobicoke and Mimico Creek Watersheds (***Figure 7***), both beginning in the Halton Till plains (Singer *et al.,* 2003). Etobicoke Creek begins northwest of Teapot Lake at 256 meters elevation, flowing through Brampton with an average gradient of 7 m/km over its 27 km course and drains into Lake Ontario (Karrow, 2005). Mimico Creek enters Brampton from the north at an elevation of 245 m with an average gradient of 8 m/km (Karrow, 2005). The Etobicoke Creek watershed has been significantly modified for flood prevention, land development and agricultural activities, which in the past three decades has led to a 25% increase in runoff (Etobicoke and Mimico Creek Watersheds Task Force & TRCA, 2002).

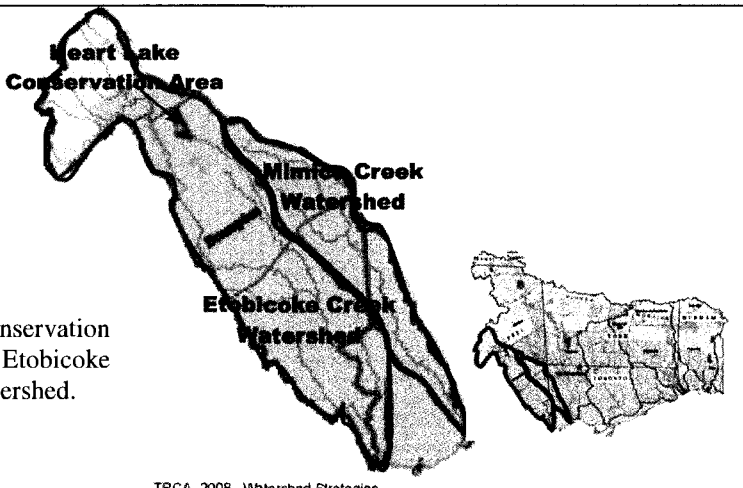


Figure 7. Toronto and Regional Conservation Authority jurisdiction with respect to Etobicoke Creek Watershed and Mimico Creek Watershed.

The Etobicoke Aquifer is a confined aquifer covered by Halton Till located within the headwaters of Etobicoke Creek, with a static water levels ranging from 1 to 15 meters depth (Singer *et al.,* 2003). The economic value of aggregate from the Brampton esker resulted in

extensive gravel extraction during the previous century, which degraded the eskers previous capacity for water filtration. The Brampton esker was identified as a major water table aquifer due to its granular composition (Saunderson & Jopling, 1980), however, land development after this publication likely altered the composition and in that the esker's capacity to act as a viable aquifer. The municipalities surrounding the study site (Cheltenham, Caledon East, Caledon Village, Palgrave, Inglewood and Alton) distribute groundwater from several pumping stations, and it is relevant to note that all pumping station use techniques to removed iron and manganese from groundwater for residential consumption (Region of Peel, 2006).

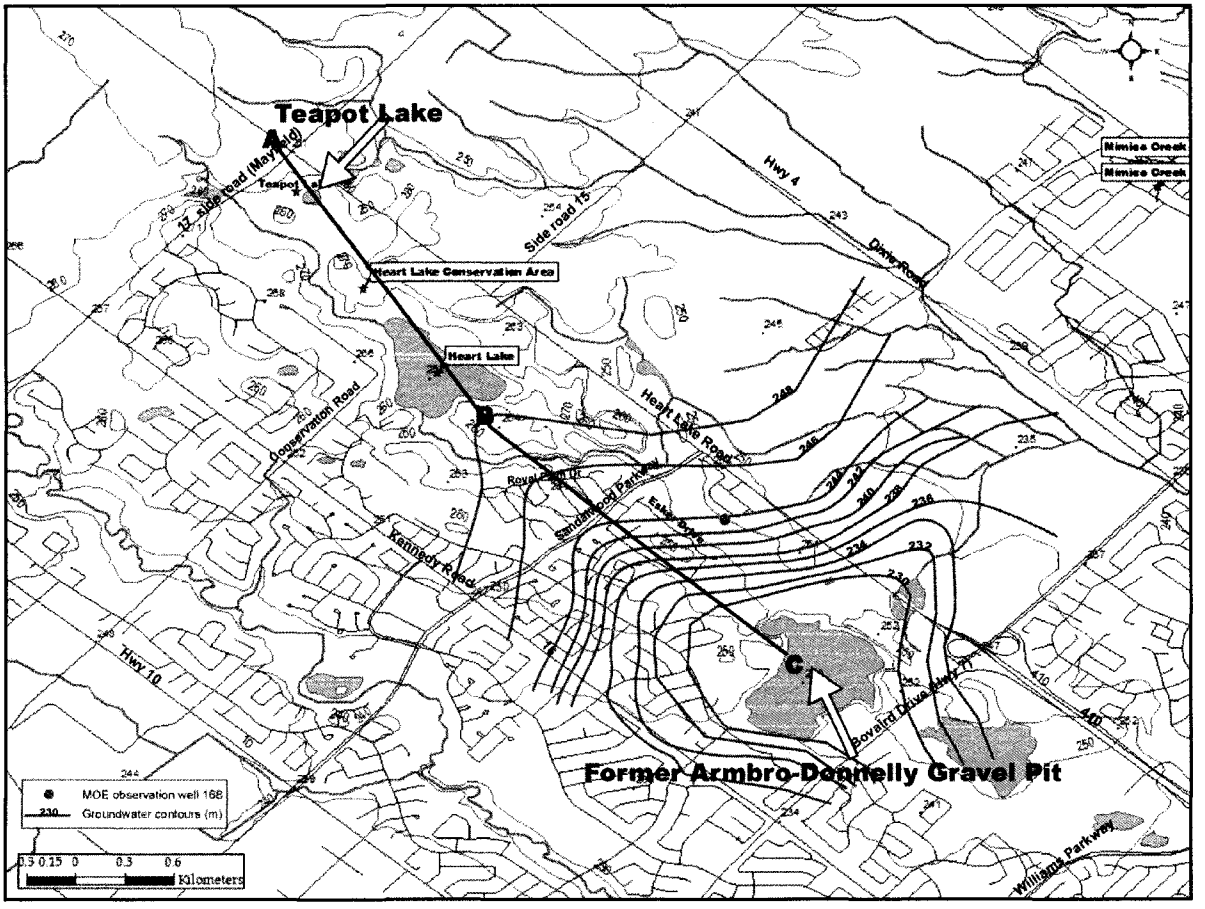


Figure 8. Groundwater contours on base map of surface water, elevation and location of Brampton Esker.

Studies commissioned by the Ontario Ministry of Environment (MOE) in 1983 evaluated the hydrogeology of the Brampton esker, including the south-eastern section of Heart Lake. The groundwater contours (***Figure 8 & 9***) were obtained from the Brampton Esker Hydrology Study (1983) and from Ontario Ministry of the Environment (MOE) observation well 168. No significant hydrological or limnological studies have looked at Teapot Lake or the surrounding drainage area. Therefore, the groundwater levels are inferred from the available data. It should be noted that these records are dated and are taken as a best approximate and not as quantitatively resolved values.

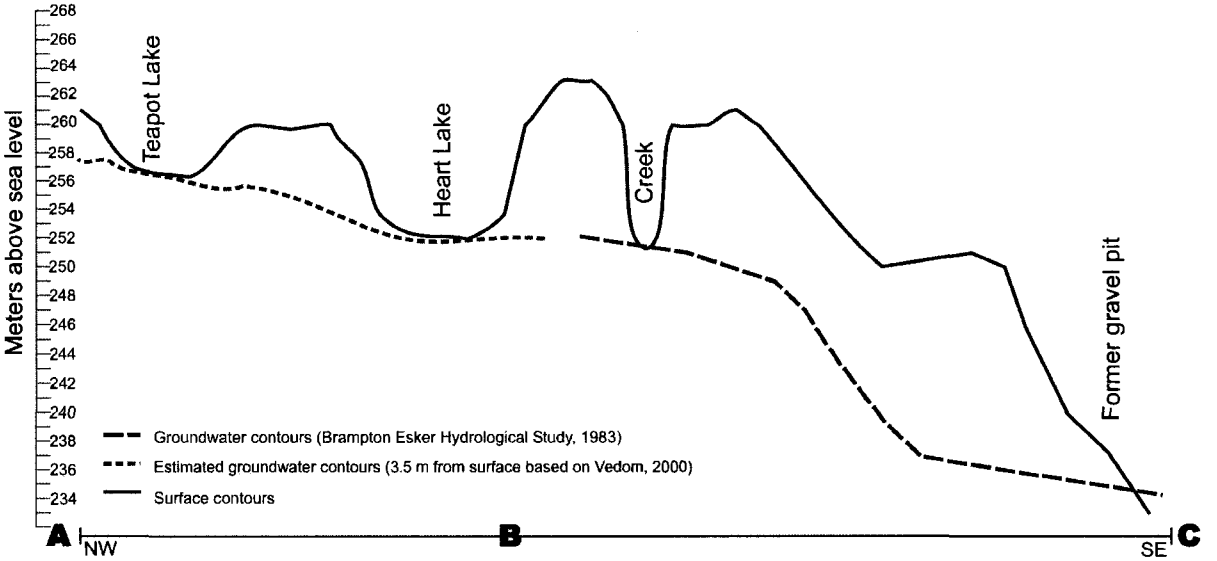


Figure 9. Plan view of topography and groundwater levels from base map in Figure 8. Scale is exaggerated.

It has been speculated that Teapot Lake is a perch lake. The above information can be used to identify the source of Teapot Lake waters. The lake does not have any visible in and out flow sources, so the water levels are likely maintained by groundwater and runoff, whereas Heart Lake has an outflow source at the south-western section (TRCA, 2007). The actual groundwater depth (hydrostatic level) is unknown, therefore is has been inferred as 3.5 meters depth as measured at Heart Lake (Vedom, 2000). It seems that Teapot Lake is not perched; rather it is at the water table depth (I D Clark 2007, pers. comm.) (***Figure 9***).

2.7 Climate

Southern Ontario is in a temperate climatic zone that presently experiences four seasons. Data from Brampton was not available, instead two stations that are representative of the region were selected; Orangeville (43° 55' N, 80° 5' W, 411.5 MASL) located ~34 km northwest of the Heart Lake Conservation Area and Teapot Lake; and Toronto's Lester B. Pearson International Airport (43° 40' N, 79° 37' W, 173.4 MASL) located ~8 km southeast from the Heart Lake Conservation Area and Teapot Lake. The temperature records show that Pearson is slightly warmer than Orangeville, likely due to the industrial setting causing something of an urban heat island effect whereas Orangeville is proximal to agriculture areas and has more green space. Orangeville received 99 mm more precipitation than Pearson, with the major differences occurring in late spring (May-June) and late summer (August-September). The warmest temperatures occur in July and the greatest amount of precipitation occurs in August. The coldest temperatures occurred from December to February and February had the least precipitation.

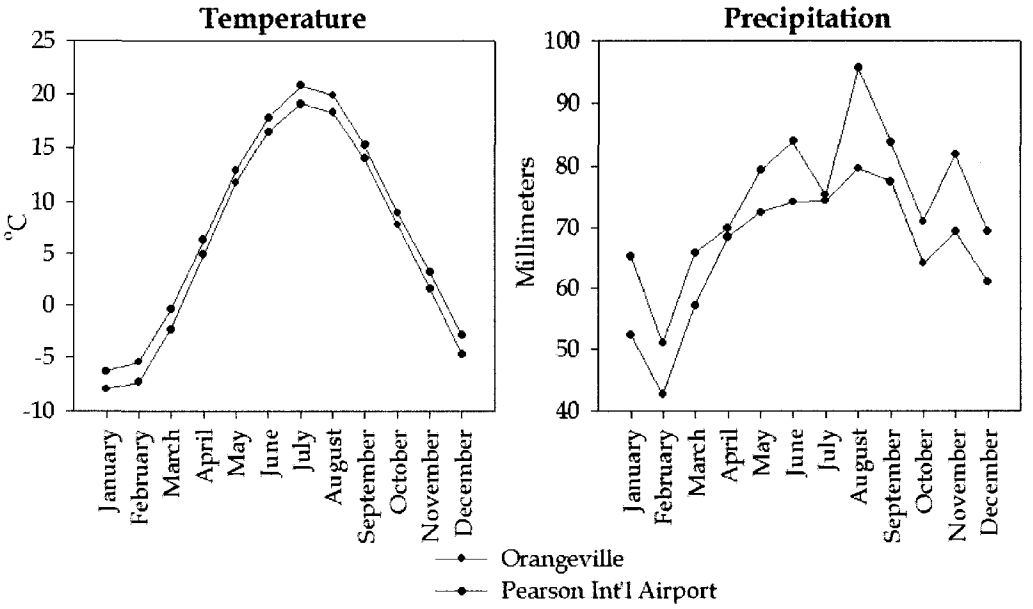


Figure 10. Climate normal data have been obtained from Environment Canada (2006) representing 1971 to 2000.

3 Methods

3.1 Field Work – Sediment Core Collection

Short and long lake sediment cores were collected *in-situ* from Teapot Lake in late August 2005. The core that was used in this thesis research was Core 1, taken from the middle and deepest point in the lake (***Figure 3 & 4***), collected with a modified livingstone corer. The sediment cores were taken from the consolidated sediments above Pleistocene clays. The core depths were measured using 1 meter rods, where rods were progressively added to collect deeper sediments. A dense plastic cap was secured to the bottom opening of the sediment filled plastic barrels while still submerged to prevent oxidation and loss of sediment. Once removed from the water, the top of the barrels were sealed for insulation with Styrofoam, capped and both ends were covered with plumbers tape to prevent leakage. Each section of the cores was measured with the depth and sample location documented.

3.2 Water Column Sampling: Properties

Teapot Lake water column was sampled on four occasions to obtain seasonal data. In August 2005, Teapot Lake and Heart Lake were sampled at one meter intervals. The water columns were sampled with a plastic Kemmerer bottle type sampler at the deepest basin of the lake and a HydroLab was also used to measure temperature, pH, Redox potential, conductivity and dissolved oxygen at each interval. A different water sampling unit was constructed for more accurate water sampling at intervals during spring, summer and fall 2006. A 15 meter PVC tube was attached to the HydroLab so reading would coincide with water samples. At the surface, a 60 ml syringe was joined to the PVC tubing using two smaller pieces of Tygon tubing for an airtight fit. The lake water column was sampled at one meter intervals and water was drained from the tube after each interval was sampled to prevent mixing.

3.2.1 Carbon and Trace metals

In summer 2005, samples collected for dissolved trace metals and dissolved carbon were immediately filtered upon removal from lake using a sterile 60 ml syringe and an Acrodisc® 25mm syringe filter with 0.45 μm Supor ® Membrane to reduce the biological component (algae and some larger bacteria). Samples collected for total inorganic carbon (TIC) and total organic carbon (TOC) were not filtered. Dissolved carbon samples were collected in 40 ml amber baked glass vials with silica gel septa liners inside open-top caps and every attempt was made to keep the water samples cool to prevent biological activity that would alter the carbon values. Trace metals samples were collected into 15 ml high-density polyethylene (HDPE) Nalgene bottles. All of the 2006 measurements, trace metals and anions were sampled at each interval, using a 0.8μm filter in a 25 mm Easy Pressure Syringe Filter Holder and collected into a 30 ml HDPE Nalgene bottle. It should be noted that the size of filtered changed from summer 2005 because the 0.45 μm was not available. It will be seen from the analytical results that the difference did not affect trace metals or carbon in the water samples.

A different method was attempted for spring 2006. Samples for methane, dissolved and total carbon were collected into 500 ml Nalgene bottles at each interval of the lake water column. Sodium Azide [NaN_3] was added to each bottle prior to sampling to eliminate biological activity and allow simple preservation. Due to the extremely toxic nature of NaN_3, ~1 mg was put into each of ten 500 ml Nalgene bottles under a fume hood prior to departure to prevent possible contamination of the lake environment. The 500 ml bottles were filled in the field without filtration. Samples for DIC and DOC were filtered in the Geochemistry Laboratory at University of Ottawa on April 17th, 2006 with 0.45μm cellulose microfiber filters into amber vials and TIC and TOC samples were poured into amber vials

without filtration. The trace metal values obtained were questionable and were excluded from interpretation in this thesis.

3.2.2 Methane

For summer 2005 water left in the vials after TIC/TOC analysis was used for methane analysis, however the results were dubious and were not included in interpretation. For spring 2006 samples for methane were poured without filtration from 500 litre Nalgene bottles that were spiked with NaN_3 into 70 ml Wheaton vials in the laboratory. Separate methane samples were collected in summer and fall 2006, where water was pumped into 70 ml Wheaton vials that were capped with butyl rubber stoppers and crimp-sealed with an aluminum to prevent gas from escaping the vial.

3.2.3 Groundwater

Groundwater geochemical data was provided by the Toronto and Regional Conservation Authority from their routine sampling procedure. Sampling took place intermittently from 2003 to 2006, with minor differences in analytical parameters and no physical water measurements were taken (pH, DO, Eh). Samples were analyzed either by the Ontario Ministry of the Environment Central Laboratory or by Entech. The well on the Teapot Lake property was sampled twice by the Toronto Conservation Authority solely for the purposes of this research project. The first samples were collected on May 1st, 2007 and analyzed by Entech and the second samples were collected in June 17th, 2007 and analyzed for trace metals and $\delta^{18}O$ at University of Ottawa using the same procedure as the lake water described in *Section 3.3.3.* and *3.3.4.*

3.3 Water analysis

3.3.1 Carbon

Analysis was performed at G.G. Hatch Isotope Laboratories (University of Ottawa) within 3 weeks of collection to prevent degassing and other potential alterations to the carbon content. Each sample "run" was accompanied by 4 standard solutions prepared in house, distilled water used for a wash in between runs; sodium phthalate KHP (-28‰); sucrose (-12‰); glucose (-5‰); TIC *heavy* (0‰) and TOC *light* (-25‰). An O.I. Analytical Model 1010 Wet Oxidation TOC Analyzer, with a 2 ppb error was used for TIC/ TOC and $\delta^{13}C$ analysis. The $\delta^{13}C$ of the inorganic/ organic carbon in the water were determined by analyzing the CO_2 gas produced on the O.I. Analytical TOC Analyzer by the reactions with phosphoric acid (DIC) and sodium persulphate (DOC) on a continuous flow FinniganMAT DeltaPlus mass spectrometer, with an analytical error of 0.2‰ (G.G. Hatch, 2001).

3.3.2 Methane

Analysis of dissolved methane was done from headspace made in each vial by flushing with helium as 2 to 4 mls of water was removed. The samples were left for 24 hours so methane would equilibrate in the headspace. Concentrations were measured with a gas chromatographer with an FID detector. A 99.9% pure methane standard was first analyzed in three different volumes, 100μl, 50μl and 25μl. Isotopes of CH_4 were measured on a Finnigan DeltaPlus XP with GC-C and PreCon peripherals. Samples with very high amounts of CO_2 were first introduced into the PreCon. Larger volumes of gas with low concentrations of CH_4 were "cleaned" using pre-con and direct injection, depending on the results of concentration.

3.3.3 $\delta^{18}O$ and δD

Water was removed from the vials collected for DIC after they were analyzed. Each vial was shaken to homogenize any condensed water, and then 20μl was transferred into 12 ml exetainers with a pipette. Samples for $\delta^{18}O$ were flushed and filled with helium for two minutes then left in a 25°C water bath for 24 hours to equilibrate. Hokko beads were added to samples for δD, which were then flushed and filled with a gas mixture of 2% hydrogen in helium for two minutes. All samples were run on a Finnigan MAT Delta plus XP + Gasbench IRMS. Ambiguous results from summer and fall 2006 raised questions about the impact of H_2S on the δD values. To verify whether the values were accurate, copper shots and activated carbon chips were added to each vial and left to react for a week. The results showed no significant differences.

3.3.4 *Trace metals*

From the HDPE bottles collected in summer 2005, 10 ml of water was removed with a pipette and added to 50 ml sterile centrifuge vial. The water was then diluted as 3 ml H_2O: 3 ml HNO_3 and repeated in another test tube diluted 100 times 1:9 (0.5 ml H_2O: 4.5 ml acid). Smaller volumes of sample and acid were prepared from the summer and fall 2006 samples. 10 ml was transferred from each sample into 15 ml sterile plastic centrifuge tubes using a pipette. Each sample was acidified to pH of <2 by adding 20 μl of ultra pure HNO_3 into the 10 ml of sample in the centrifuge tubes.

This method changed for spring 2006 based on whether the sample was spiked with NaN_3. The spiked spring 2006 samples were filtered in the laboratory with 0.45μm cellulose microfiber filters and 10 ml of water was added to a 15 ml sterile Fisher centrifuge vial and 5 mls of 60% nitric acid was added, and the same volumes of water and acid were taken from

the unspiked samples. A blank of NaN_3 was prepared to test the trace element concentration, although the exact volume of NaN_3 added to each of the spiked samples varied.

The solution was measured at the University of Ottawa's Earth Sciences Department on a Varian Vista-Pro Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a simultaneous solid-state detector (CCD).

3.3.5 Phosphorus

Waters left in the 10 ml Nalgene vials from trace metal analysis were brought to the Department of Biology at University of Ottawa. The waters were analyzed on a Lachat QuickChem FIA+ 8000 Series using an in line Total Phosphorus 10-115-01-3-A module.

3.3.6 Mineral Saturation

WATEQ4F (Wat4) is a free geochemical software developed by the U.S. Geological Survey that calculates major and trace element speciation and mineral saturation of lake waters, first created as WATEQ by Truesdell & Jones, (1974) and has been modified to WATEQ4F by Ball & Nordstrom, (1991). The speciation of elements and saturation of minerals in lake waters were determined using WAT4. The determining factors for vivianite, strengite and ferrihydrite saturation were tested by entering varied elemental concentrations, Eh, pH and temperature.

3.4 Lake Sediment

Isolating the desired proxy materials from bulk sediment typically requires chemical pre-treatment and homogenizing samples; therefore, materials being analyzed must be ground and sieved to obtain a homogeneous and representative measurement (Boyle, 2001). Total lake sediment digestion allows the measurement of lattice bound elements using oxidizing acids (Boyle, 2000). A total sediment digestion involves either aqua regia ($3HCl:HNO_3$) digestion followed by hydrofluoric acid (HF) digestion (Rantala & Loring, 1975) to dissolve

the matrix of silica-bound compounds; or digesting with a mixture of HF and perchloric acid ($HClO_4$) in an open vessel so HF and silica escape (Allen *et al.,* 1974; EPA, 1991). The perchloric and HF method require a special fume hood, silica cannot be analyzed from this type of digestion and above all using HF is onerous due to its corrosive and poisonous properties (EPA, 1994; MSDS, 1999). Trace elements in lake sediments can also be analyzed with XRF (x-ray fluorescence), but XRF requires 1 g of sample and has a lower detection limit than analyzing with ICP-MS/ ICP-OES (Nielson & Sanders, 1983; EPA, 1994). Aqua regia digestion procedure (ISO standard 11466) is commonly used to chemically separate trace metals and elements in soils, sediments and other materials recovered from the environment (Chen & Ma, 2001).

Partial sediment digestion using aqua-regia was employed as it provided cost-efficient and timely results. Additionally, several labour intensive steps were taken to avoid potential contamination of sediments during pre-treatment (M Wilk & N De Silva 2006, pers. comm.) and to this end, plastic tools were used as much as possible during sediment sampling.

3.4.1 Sediment Core Sampling

The lake sediment sampling and drying method was developed to ensure samples were not contaminated and were completely dry. Although freeze drying is the general protocol for drying sediments, a significant risk of contamination is involved due to the number of other research projects that use the freeze-dryer available for this research. The procedure described below provided reliable quality control as well as verified that sediments were completely dry by routinely weighing dried samples until the weight was constant.

1.) Sediment samples were taken from Core 1- Section 1 of Teapot Lake sediment cores, where sediment horizons with obvious mineralization were selected for preliminary testing. The entire length of the core (5 sections) was sampled at 10 cm intervals and

horizons of distinction (sharp contacts, obvious blue or white coloration) were sampled at higher resolution. Sample thickness ranged from 0.5 to 2 cm.

2.) Sediment samples were removed from the core and sealed in small zip-lock bags using plastic spoons. The sediment bags were kept in Tupperware containers lined with paper bags and refrigerated for less than 3 days prior to drying.

3.4.1.1 Material preparation

1.) Glass plates were used to dry samples. Plates were cleaned with methanol to remove markings and thoroughly rinsed with deionized water. Plates were then placed in a clean 1 L glass beaker and immersed in a 500 ml of 60% HNO_3 to 500 ml deionized water (DIW 17-18) solution for 2 hours. Acid/ water solution was drained and plates were thoroughly rinsed with DIW and oven dried for 20 minutes at 50°C.

3.4.1.2 Weights and Drying

1.) The plates were weighed then the wet sediment samples were placed on the plates using plastic spoons and weight on a Sartorius balance.

2.) Sediment samples were dried in a Lindberg Oven for 24 hours at 85°C, after which they were weighed on the plates and the initial plate weights were subtracted. Samples were returned to the oven for 24 hours at 50°C and weighed again to ensure complete dryness. Drying was repeated until the sediment weight remained constant.

3.) Samples were scraped from the glass plates using plastic spoons onto weight paper, sealed, labelled and stored at room temperature in a Tupperware wrapped in a brown hand towel to prevent light penetration.

3.4.2 Experimental Analytical Methodology #1

Preliminary experimentation with lake sediment digestion was performed in order to insure the ICP-OES could detect trace elements in Teapot Lake sediments. The Teflon beakers

used for digestion were stored in the geochemistry lab so background analysis was carried out on them to determine if new beakers were needed. Two sediment samples were analyzed in duplicates.

3.4.2.1 Cleaning

1.) Teflon beakers used in the initial experiment were thoroughly rinsed in DIW.

2.) A 300 ml HCl: 100 ml HNO_3 aqua-regia solution was prepared and each Teflon beaker was filled half full with the solution. The Teflon beakers were then left on a hot plate for 1 hour without heat to allow initial reaction to occur, then were heated to 100°C in a plastic encasement and left to react for 2 days. Additional aqua-regia solution was added when evaporation occurred.

3.) After 2 days, Teflon beakers were rinsed with DIW and submerged in 1500 ml HNO_3: 1500 ml H_2O in a 3000 ml beaker for 3 days at 100°C.

4.) The Teflon beakers were rinsed and submerged in DIW for 1 hour, then dried on a hot plate.

3.4.2.2 Digestion and Sample Homogenizing

1.) Samples were homogenized using a porcelain pestle and mortar was used to crush dried sediment and quartz grain were ground after each sample was crushed to prevent contamination. Crush sediments were then dry sieved through a 150μm sieve and caught in weight paper.

2.) Aqua-regia solution was prepared (3:1 HCl: HNO_3).

3.) 50 mg and 100 mg of dried sediment were weighed out from two samples, put into the clean Teflon beakers, and covered with cleaned small glass plates.

4.) One blank of aqua-regia was included to test the background of the Teflon beakers.

5.) 1 ml HNO_3: 3 ml HCl was added to each Teflon beaker using disposable plastic pipette tips. The samples were then left to react at room temperature for one day.

6.) After sitting for one day at room temperature, the beakers were heated to 150°C on a hot plate for 8 hours, aqua regia evaporation was observed and solution was added to each beaker as needed.

7.) Following the heating, the samples were left to react at room temperature for four days.

8.) 50 ml plastic centrifuge vials were weighed. The digested sample and residue on the sides of the beakers was removed with DIW, carefully poured into the vials and DIW was added until the digested sample was diluted to 20 ml of solution in the vials.

9.) The vials containing the samples were centrifuged for 5 minutes at 1500 rpms and the supernatant was analyzed on an ICP-OES in the University of Ottawa geochemistry lab.

3.4.2.3 Experimental Results

The results from the ICP-OES were positive in that elements of interest were present in measurable concentrations and methodological problems were identified and mitigated. Duplicates of each sample were run in 50 and 100 mg volumes to determine the best size for analysis. The 50 mg of sediment sample was determined to be the optimal size since more acid was needed in the larger sample, which did not change the concentrations (M Wilk & N De Silva 2006, pers. comm.).

The Teflon beakers used for digestion contributed contaminants despite cleaning efforts. The blank value of elements such as Ba, Cu, Ni and Zn approached the values of the digested samples (**Table 1**), confirming that using new vials that could be sealed was essential for accurate results.

Table 1: ICP-OES Experimental Results in ppm

Sample	*Blank*	1	1	5	5
Dry weight (mg)	-	46.3	100.5	50	101.5
Al	*0.08*	24.42	47.01	8.09	17.08
Ba	*0.52*	1.19	1.81	1.27	2.24
Ca	*0.1*	8.32	14.45	15.94	27.43
Cu	*0.12*	0.18	0.26	0.15	0.2
Fe	*0.21*	214.4	354.7	128.1	331
K	*0*	4.84	8.7	1.09	2.61
Mg	*0.21*	4.9	8.92	2.03	3.51
Mn	*0*	0.91	1.63	3.17	5.65
Na	*0.06*	0.52	0.76	0.29	0.46
Ni	*0.02*	0.07	0.12	0.07	0.11
P	*0.03*	61.87	103.9	33.56	112.7
S	*0.15*	15.91	26.61	10.3	18.1
Si	*0.03*	2.68	5.04	0.08	0.98
Sr	*0*	0.05	0.09	0.07	0.13
Zn	*0.03*	0.21	0.34	0.42	0.69

The issue of sample homogeneity was not considered in the initial experimental design and the results suggest that sediments within a sample are heterogeneous. The 50 mg sample should have twice the elemental concentration as the 100 mg sample, but this was not the case for all elements.

Several problems were identified using standard grinding and sieving methods for dry sediments. Pestle and mortars commonly used to grind dried samples before analysis are composed of porcelain (Al and SiO_2), with quartz grains used to clean the pestle and mortar between samples. The potential of contamination from the pestle, mortar and quartz grains, as well as the time required to process a large number of samples was deemed unsuitable. An alternative method was developed, where dried sediments were placed between two pieces of weight paper and ground with the base of a beaker. Additionally, the potential contamination from sieving (homogenizing) the sediments with a standard steel or brass sieve was avoided by using a very small sieve designed by Dr. Nimal De Silva (N De Silva

2006, pers. comm.). The sieve itself was composed of glass and plastic, using 500μm nylon sieve sheets that were cut into 20 mm circles and inserted into the sieving device.

3.4.3 Modified Preparation and Materials Methodology

1.) The same sample collection, drying and plate cleaning methods were used.

2.) One 12 by 12 inch sheet of nylon 500μm mesh was cut up into 15 mm diameter circles to fit into the sieving devise. The edges were melted to fit snugly. The mesh filters were thoroughly rinsed with DIW, soaked in 5:1 H_2O HNO_3 for an hour and a half, then rinsed again with DIW and dried in between two KimWipes.

3.) After each use the device was sprayed with Dust Off and wiped through with a KimWipe and the sieves were soaked in 1% HNO_3, rinsed with DIW and dried.

4.) Dried sediment samples were placed between two pieces of weight paper, the sides folded, and a glass beaker was rolled over the sample to powderize the sediments without contamination. The ground sediment was then passed through the sieve and the <500μm fraction was caught in a 1 ml sterile plastic vial and sealed. The remaining >500μm fraction of the sediment was placed in weight paper, folded, labelled and stored for organic geochemical analysis.

5.) Eleven 50 ml Teflon vials were purchased. The vials and caps were labelled from 1 to 10, and one vial and lid were not labelled to be used for the blank. They were soaked for one day in 1:1 HNO_3 to DIW water in a clean 1000 ml beaker, rinsed and soaked in DIW for two days, then rinsed again and dried on a hot plate. This procedure was repeated after each batch of sediments was digested.

3.4.4 Experimental Analytical Methodology #2

1.) Nine large sediment samples (>0.7 g) were selected to test the background on the new vials, in case they needed to be reanalyzed and for duplication.

2.) Each Teflon vial was weighed with the caps on and less than 0.5 mls of DIW was put into the vial with a plastic 3 cc syringe and weighed. The samples were weighed on weight paper then placed into the vials. The blank vial was weighed, and DIW was added and weighed.

3.) HNO_3 and HCl were added to the samples separately. The two acids (HNO_3 and HCl) were poured into separate 50 ml centrifuge vials. A plastic pipette was used to add 1 ml of HNO_3 to each sample and the lids were closed immediately after. Then 3 mls of HCl was added to each vial, the lids were firmly closed and the vials were placed on a hot plate at 150°C for two days and then the samples were left without heat for another two days. The blank was treated the same as the samples.

4.) The samples were poured into 15 ml sterile plastic centrifuge vials, weight and diluted with DIW to 10 mls and weighed again. Samples were then centrifuged at 1500 rpm for 5 minutes.

5.) From the diluted sample, 1 ml was drawn with a mechanical pipette into a 15 ml plastic centrifuge vial and diluted to 10 mls with HNO_3. Samples were then centrifuged at 1500 rpm for 5 minutes.

6.) Teflon vials were thoroughly rinsed with DIW, any residue was scraped off the and they were left to soak in a 1200 ml beaker with 400 mls HNO_3 and 500 mls H_2O for two days.

3.4.5 Resolved Analytical Methodology

The results obtained from Methodology 2 were good and this method was repeated for the remaining samples, with slight modifications as outlined below.

1.) 50 mg of dried sediment weighed, sieved and added to clean Teflon vials.

2.) 0.5 ml HNO_3 and 1.5 ml HCl was added to sediment.

3.) One blank vial containing aqua-regia was included in each batch of sediments. The blank vial changed for each batch to observe randomness and identify any potential contamination of the vials through the course of analysis.

4.) The samples were digested for 24 hours at room temperature and then samples were heated for 9-12 hours at 150°C.

5.) The samples were left to react at room temperature for 17-24 hours.

6.) Digested sediments samples were poured into 50 ml centrifuge vials, weighed, then diluted to 20 mls with DIW and weighed. The vials were centrifuged for 5 minutes at 2400 rpms, and then 10 mls of solution was transferred into 15 ml centrifuge vials using a pipette and were left in a glass cabinet until all samples were digested (2 months to digest 71 samples).

3.4.6 ICP-OES

A Varian Vista-Pro Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a simultaneous solid-state detector (CCD) was used to measured elemental concentration in ppm, from the digested solution, which were normalized to dry sediment weight in mg/kg:

Eq.1. $Cs\ (mg/kg) = C * V * D / W$

Where Cs is sample concentration (dry-weight basis), C is concentration in extract (mg/L), V is volume of extract (L, 100 ml = 0.1 L), W is dry weight of sample aliquot extracted (kg, 1g=0.001 kg), D is dilution factor. The analytical methods, blanks, precision and errors have been carefully scrutinized to confirm that the measured values are authentic.

3.4.7 XRD

A number of samples that represented different materials observed in the sediments were analyzed with X-Ray diffraction. Additionally, sediments were analyzed before digestion

and after to determine what minerals were initially present and which minerals remained after digestion. As expected, the sediments contained vivianite before digestion and mainly quartz minerals remained after digestion. A slight hump appeared in the XRD patterns that are assumed to clay minerals. Based on the XRD results, it can be assumed that the residual materials left in the centrifuge vials represent the silica component of the lake sediments. The method of preparations is as follows:

1.) The pH of the solution in the 50 ml centrifuge vials was measured at ≤ 0. The solution was carefully removed with a pipette to avoid disturbing the sediments and 20 mls of DIW was added to each vial.

2.) The vials were then centrifuged for 5 minutes at 2000 rpm. This step was repeated 3 times until the pH was nearly neutral (6-7).

3.) About 5 mls of solution was added to each vial and pH was determined to be neutral. Each vial was covered with a KimWipe and sealed with an elastic band to allow water to evaporate while preventing material from escaping.

4.) The vials were frozen for three days at -80°C and then freeze dried for two days.

3.5 Lake Sediment Organic Geochemistry

The remaining dried sediment from inorganic geochemical analysis were used to measure %C, %N, $\delta^{13}C$ and $\delta^{15}N$ isotopes of organic matter in the lake sediments. Although the sediments seemed to be 99% void of carbonate as determined by adding a drop of HCl to <10 mg of wet sediment with no visible reaction occurring and no reaction observed under a microscope, sediments were acidified to guarantee only organic matter was being analyzed.

1.) The powderized sediments were placed in small plastic vials ranging in size. Acid fumigation was used to remove carbonate by adding HCl into each vial and leaving them in a desiccator for 24 hours (Harris *et al.,* 2001).

2.) Vials were capped with a KimWipe and elastic bands, frozen for 1 hour at 80°C then placed in a freeze drier for three days.

3.) Once dried, eight samples that best characterize the range of sediment materials were selected to determine optimal sample weight for carbon and nitrogen isotopes and concentrations of carbon and nitrogen.

4.) A microbalance was used to weigh out 2 mg from each of the samples, with four standards and four blanks, for concentrations.

5.) Once the optimal weight of sample for analysis was established, all samples were weighed and analyzed at the G.G. Hatch Stable Isotopes Laboratory, University of Ottawa.

The isotopic composition of organic carbon and nitrogen was determined by the analysis of CO_2 and N_2, produced by combustion on a CE 1110 Elemental Analyser followed by gas chromatograph separation and on-line analysis by continuous-flow with a DeltaPlus Advantage isotope ratio mass spectrometer coupled with a ConFlo III (G.G. Hatch Stable Isotope Laboratory, 2006).

4 Results: Geochemistry of the Water Column

Teapot Lake fits the definition of a meromictic lake in that the waters are high in dissolved solids, the basin is steep, and the lower water column is stratified and perennially unmixed (Hutchinson, 1937). There are two parts of the water column structure; mixolimnion, the upper water stratum that is mixed; and the monimolimnion, the deeper portion of the water column that is permanently isolated from the surface and does not mix with the upper stratum (Hutchinson, 1957; Wetzel, 2001).

4.1 Physical Water Measurements

The chemocline is analogous with the redox transition boundary (redox boundary), situated at the interface between the two stratums and the thermocline remains at 2.5 meters annually. The redox boundary and oxycline occur at 4-5 meters (***Figure 11***). The mixolimnion, the least dense waters in the lake where temperature fluctuates with respect to regional surface climate (Mook, 2001), occurs from the surface waters to ~4 meters depth annually. The mixolimnion is warm, neutral to mildly acidic, oxidizing environment with sufficient dissolved oxygen (DO). A substantial shift in chemistry occurs at the redox boundary (~4 meters) and continues down to the monimolimnion (5-12.3 meters) where the DO, pH, redox potential (Eh) and temperature all drop abruptly and the conductivity increases substantially.

Temperature is a fundamental measurement that demonstrates the positioning of the thermocline, and seasonal shifts in the mixolimnion due to mixing, inflows and general surface temperatures. The temperature profile of Teapot Lake (***Figure 11:A***) is related to the morphometry of the lake and the surface area. Temperature in the mixolimnion shows strong seasonal changes while temperatures in the monimolimnion are nearly constant.

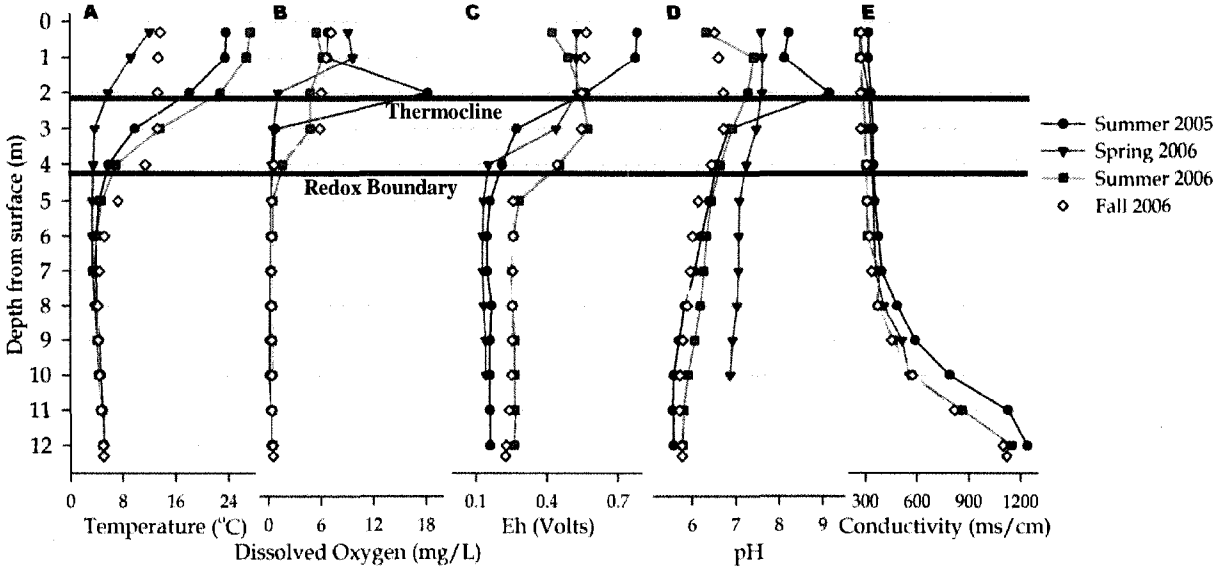


Figure 11. Physical water properties showing seasonal values of Teapot Lake water column. The Eh in figure C are values corrected with Ag/AgCl as outlined in **Eq.2**.

The mixolimnion is <20°C during the summer; spring temperatures are the coolest with little variation due to input of snowmelt and colder surface temperatures; and fall temperatures are uniformly cooler due to mixing over the previous two seasons, fewer hours of direct sunlight and colder surface temperatures. The monimolimnion temperatures do not fluctuate between seasons, as the waters are dense, do not mix with surface waters, sunlight cannot penetrate and is isolated from surface modifications.

Oxygen supply and demand are important factors influencing geochemical reactions in Teapot Lake. The dissolved oxygen profile in Teapot Lake (***Figure 11:B***) indicates a clinograde present during all seasons, resulting in biological oxygen consumption at the mixolimnion, below which the DO values decrease dramatically. The mixolimnion has an average seasonal DO range of 6.6 to 4.2 mg/L, with summer 2005 having an anomalously high concentration of 18.2 mg/L at 2 meters. Spring 2006 had high DO in the upper two meters then dropped to < 0.57 mg/L, which is the least available DO and is likely related to rapid commencement of photosynthesis above the thermocline following spring thaw. The lake remains nearly anoxic (≤0.44 mg/L DO) in the monimolimnion. The dissolved oxygen

sensors on the Hydrolab probe may be impeded by the low redox potential and the detection limit will be considered <1 mg/L (F Pick 2007, pers. comm.). Dissolved oxygen below 3 meters depth will be considered 0 mg/L for geochemical calculations in subsequent sections.

The redox potential of Teapot Lake waters were measured using an Ag-AgCl platinum redox probe attached to the Hydrolab. The raw values (E_{raw}) were corrected to Eh using known $E_{Ag/AgCl}$ values for specific water temperatures with the following equation:

Eq.2. $Eh = E_{raw} + E_{Ag/AgCl}$

The corrected Eh values were used for interpretation. The mixolimnion is seasonally oxidizing and the monimolimnion remains reducing (***Figure 11:C***), with the redox transition boundary occurring at 4 meters depth. The mixolimnion is seasonally oxidizing with an average value of 0.48 V, although the extent of oxidation varies between seasons. The Eh abruptly moves towards reducing conditions in the monimolimnion with an average Eh of 0.2 V. The summer 2005 Eh values show the greatest variation and summer 2006 values had the least variation through the water column. The most oxidizing values in the mixolimnion (0.77 V) were measured in summer 2005 and most reducing values in the monimolimnion (0.13 V) occurred in spring 2006. The average mixolimnion values are highest in fall 2006.

The pH decreases with depth, with the mixolimnion pH ranging from slightly basic to neutral and below the thermocline, water becomes increasingly acidic (***Figure 11:D***). The pH does vary between seasons, where the summer 2005 water column has greatest change in pH from 9.16 to 5.6, spring 2006 remained neutral throughout the water column ranging from 7.6 to 6.8 and the water column in summer and fall 2006 was acidic and showed little variation. The monimolimnion is generally the most acidic due to higher concentration of organic matter of which 50% occurs as organic acids (Wetzel, 2001a). The higher pH in the upper water column relates to mixing with free CO_2 and the buffering capacity of the water.

Electrical conductivity is a measurement of the amount of dissolved ions in water and is controlled by bedrock, watershed size, wastewater, urban runoff and evaporation. The conductivity of Teapot Lake increases with depth (***Figure 11:E***), remaining low from 1 to 7 meters. Below 10 meters it increases significantly, where value are 4 times greater than the surface values, which is consistent with stratification in the monimolimnion and the build-up of dissolved ions at the greatest depths.

4.2 Stable Isotopes of water: $\delta^{18}O$ and δD

Oxygen has eight protons and eight to ten neutrons. It has three stable isotopes (^{16}O, ^{17}O and ^{18}O) depending on the number of neutrons present. Hydrogen has two stable isotopes, protium (^{1}H) which is the most abundant with one proton and deuterium (^{2}H or δD), which has one proton and one neutron. Reactions involving temperature, precipitation, biological processes and distance traveled from the ocean govern the isotope ratio of an oxygen atom and the isotopic ratio also depends on the material being analyzed.

Oxygen isotope fractionation of lake water is largely controlled by evaporation, while local precipitation, groundwater and surface run-off modify the isotopic signal. As surface waters are heated by the sun, evaporation will preferentially remove the lighter isotopes ($^{1}H_2{}^{16}O$) from the surface waters into water vapour, causing the residual surface waters to become enriched in the heavier isotopes $^{2}H_2{}^{18}O$. Therefore, warmer surface temperatures induce more evaporation that results in $\delta^{18}O$ values of the water to become more positive and approach 0‰.

The relationship between lake water and local meteoric water can be observed from $\delta^{18}O$ and δD, where a strong linear relationship exists between $\delta^{18}O$ and δD in precipitation ($\delta^{2}H = 8\ \delta^{18}O + 10$ ‰ VSMOW) that is represented by the global meteoric water line

(GMWL) with a slope of 8 (Craig, 1961; Rozanski *et al.,* 1993). The slope and deuterium intercept of local metric water line (LMWL) differs from the GMWL due to regional climate and geography (Clark & Fritz, 1997). This relationship is the result of isotopic fractionation, where a vapour carrying air mass "rains-out" as it mores from the initial source, depleting the isotopic composition of the residual water vapour (Dansgaard, 1954). As a cloud moves from its vapour source along a trajectory inland the precipitation formed from vapour will become progressively depleted in the heavier isotope (Dansgaard, 1954). Therefore, the meteoric water line will always show similar results in a region, with local meteoric variation having a slight impact on the linearity of the $\delta^{18}O/\delta^{2}H$ relationship.

4.2.1 $\delta^{18}O$ and δD in the water column

The isotopic signature of local precipitation is valuable in determining the source of water for Teapot Lake. Egbert station was used as it was closest to Teapot Lake, lying south west of Lake Simcoe and approximately 53 km north of Teapot Lake (***Figure 12:A***).

The seasonal $\delta^{18}O$ and δD of Teapot Lake show evaporative enrichment compared to the Local Meteoric Water Line (LMWL), the Egbert Station precipitation and to Teapot well, which represents regional groundwater (***Figure 12:A***). The slope of the LMWL is 7.92, and the slope of Teapot Lake waters ranges from -3 to 4, implying that precipitation entering Teapot Lake is modified by evaporation. The small difference of 0.3‰ between $\delta^{18}O$ of groundwater and precipitation indicates that local groundwater is very close to local precipitation.

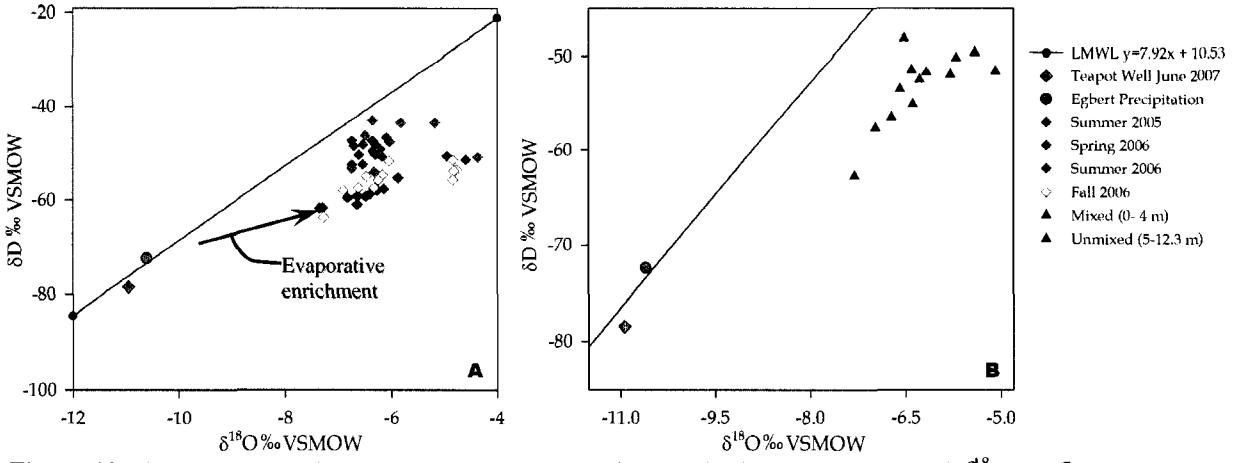


Figure 12. **A**: Local meteoric water line (Edwards & Fritz, 1986) plotted with seasonal $\delta^{18}O$ vs. δD for Teapot Lake water and Ebert Station precipitation. **B**: Same as **A** with seasonal average values for the mixolimnion (Mixed) and the monimolimnion (Unmixed). The stable isotope value for Egbert represents amount weighed mean annual isotopic values of precipitation from October 1998 - September 2002 (Birks *et al.*, 2004).

Considering the open system of surface water compared to groundwater, the lake water enrichment is likely a combine result of evaporation, run-off and mixing between sources of precipitation and groundwater flows. The average seasonal values for the unmixed monimolimnion (***Figure 12:B***) are closer to the groundwater and precipitation values as the bottom waters are unaffected by atmospheric influence, which modify the upper, well-mixed portion of the lake.

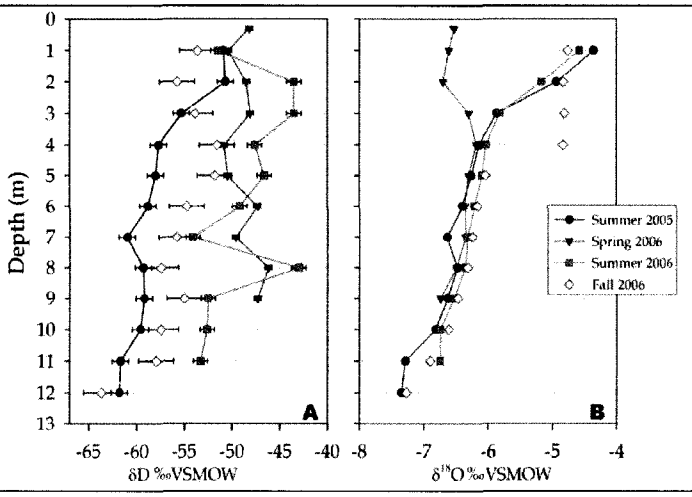


Figure 13. Teapot Lake δD and $\delta^{18}O$ seasonal profiles.

The deuterium values do not behave as predictably the $\delta^{18}O$ in ***Figure 13:A***. The waters were initially analyzed without pre-treatment and reanalyzed after adding activated carbon

and copper to remove H_2S, however the treated and untreated waters had the same δD values. The seasonal variations in the δD profiles cannot be explained at this point.

The seasonal $\delta^{18}O$ water column profile (***Figure 13:B***) confirms that Teapot Lake is seasonally stratified. The monimolimnion is isolated from interactions with the upper water column and the mixolimnion was modified by surface temperatures. The mixolimnion (0-4 meters depth) is mixed and shows variation between seasons, where the summer values are enriched in the upper few meters compared to spring and fall. The $\delta^{18}O$ values in the mixolimnion differ during each season by as much as 1.5‰. The $\delta^{18}O$ water column profile shows the mixolimnion in the spring is the most ^{18}O-depleted, which is expected as snow melt would contribute isotopically heavy runoff, combined with cooler air temperatures. The summer $\delta^{18}O$ profiles show substantial enrichment in the upper 2 meters, and then slope towards depletion to four meters where the values are similar to spring. The mixolimnion is well mixed in the fall compared to the other seasons and the nearly uniform enrichment results from of evaporative loss of the lighter ^{16}O isotope over the summer leaving the residual waters with a higher $\delta^{18}O$. The difference in $\delta^{18}O$ of the upper water column from spring to fall illustrates the effect of evaporation on Teapot lake waters, where the spring waters reflecting snow melt are modified by evaporation over the summer and by fall the waters have evaporated, producing a ~2.5‰ enrichment.

Below 5 meters $\delta^{18}O$ is nearly uniform during all seasons, varying by <0.31‰ and a standard deviation less than the analytical error of 0.15‰. This is due to the combined effect of the thermocline and pycnocline; the layer in the lake water column where the water density changes dramatically with depth where the temperature rapidly decreases. The average $\delta^{18}O$ in the bottom 2 meters of the monimolimnion is -7.1‰, which is closer to the

$\delta^{18}O$ of groundwater. This confirms that the monimolimnion is isolated from atmospheric influences; that the lake does not turn over; and essentially that Teapot Lake is a permanently stratified meromictic lake.

4.3 Geochemistry of the water column

As discussed in the introduction, the Teapot Lake sediments are dominated by iron phosphate mineralization, which is periodically replaced by organic sediments. Here, the major geochemical controls on such sedimentation are examined for the water column, including the geochemistry of P, Fe and Mn in the water column, and carbon cycling in the water column. The conductivity (***Figure 11:E***) represents the total dissolved solids and indicates that the ionic concentration increases dramatically with depth. The chemistry of the monimolimnion is conductive for reduction of redox sensitive elements (Mn, Fe and S) and decomposition of organic matter, which mobilizes ions and produces a distinct geochemical system therein.

4.3.1 Phosphorus, Iron, Manganese and Sulfur - Background

Phosphorus is considered a limiting nutrient in lakes as it binds carbon in living organic matter. In freshwater, generally 90% of phosphorus is organic and 10% is inorganic phosphorus. The inorganic phosphorus is mainly orthophosphate [PO_4^{3-}] also known as soluble reactive phosphorus (SRP) (Wetzel, 2001b). Orthophosphate occurs as $H_2PO_4^-$ under acidic conditions and as HPO_4^{2-} under alkaline conditions (Busman *et al.,* 1998), and is readily available to aquatic organisms (Stevenson & Cole, 1986; Wetzel, 2001b). High phosphorus content in lacustrine systems instigates increased primary productivity and algal blooms (Schindler, 1971). The heightened primary productivity removes dissolved oxygen

when it settles in the monimolimnion, inhibiting survival of higher aquatic organisms (Pitois *et al.,* 2000).

Phosphorus in lake sediments has been described and divided into three types; apatite phosphorus; non-apatite inorganic phosphorus (NAIP); and organic phosphorus (Williams *et al,* 1976; Williams *et al.,* 1980). The most significant to this research is the NAIP, which comprises all non-apatite orthophosphate ions, non orthophosphates such as pyrophosphate and polyphosphate usually present in low concentrations, and soluble orthophosphates ions in sediment porewater. NAIP as soluble orthophosphate is available to algal growth while apatite P is not utilized by algae (Williams *et al.,* 1980).

The length of time P-bound particles remain in the photic zone is critical from algal utilization, which is affected by the sinking rate between different particle sizes and shapes, water turbidity and resuspension of sediments (Lam & Jaquet, 1976; Williams *et al.,* 1980). Short term phosphorus release from lake sediments is linked to anoxia at the water- sediment interface, while long term trends in retention are likely coupled with the redox conditions at greater depth in the sediments, therefore variation in sedimentary phosphorus and lake water concentration of phosphorus cannot be invariably linked (Katsev *et al.,* 2006).

The behaviour and speciation of iron in lacustrine environments influences biologically significant elements (Tessier & Campbell, 1988) and formation of iron oxides affects the accumulation of trace metals in lake sediments (Jenne, 1968; Veronesi *et al.,* 2002). Ferrous iron, Fe^{2+}, is the reduced, moderately soluble species of iron and ferric Fe^{3+} is the oxidized form of iron that is highly insoluble, and precipitates in the pH range of natural waters by hydrolysis (Tipping *et al.,* 1981; Mayes & Jarrell, 2000). The redox condition of water governs the speciation of iron, where Fe^{2+} will oxidize to Fe^{3+} in an oxidizing environment, and Fe^{3+} will be reduced to Fe^{2+} in a reducing environment.

According to the model proposed by Mortimer (1941), phosphorus flux occurring at the water-sediment interface is mainly controlled by ferric iron. Iron speciation is known to control the mobility of phosphorus in aquatic systems (Nriagu, 1972; Mortimer, 1941, 1942). The large surface area of iron oxyhydroxides provide binding sites for trace metals and organic molecules, efficiently absorbing phosphorus and sequestering it at the water-sediment interface (Rosenberry *et al.,* 2003). When bottom waters remain permanently oxic, ferric hydroxide forms and due to the strong binding capacity will trap phosphorus (Mortimer, 1941; 1971). Ferric iron oxyhydroxide has the capacity to co-precipitate and/ or absorb phosphate under oxic conditions and near neutral pH (Einsele, 1936; Mortimer, 1941; 1971).

Ferrous iron and phosphate accumulate simultaneously in the anoxic hypolimnion/ monimolimnion during stagnation when no oxygen is present. When the lake turns over and O_2 is reintroduced, Fe^{2+} is oxidized to Fe^{3+} resulting in ferric oxyhydroxide to co-precipitate with phosphate (Einsele, 1936; Tessnow, 1974; Gunnars *et al.,* 2002). This suggests that phosphorus can form soluble complexes with iron under both reducing and oxidizing conditions, so long as iron is present in large concentrations and the Eh remains at a level where sulfate reduction does not occur.

Iron and manganese behave similarly in lake sediments and water. The abundance of Fe and Mn in lake sediments is determined by contribution from the catchment and conditions within the lake (Engstrom & Wright, 1984). The formation of Fe and Mn hydroxides in the water column is controlled by the ionic makeup of waters, pH, Eh, light penetration, and microbial activity (Engstrom & Wright, 1984). Fe and Mn accumulate in reducing sediments become mobilized in the interstitial fluids, eventually migrating towards an oxidizing zones if one exists at the water-sediment interface, with the upper most

sediments showing high concentrations that are unrelated to past limnological changes (Kemp *et al.,* 1976; Sasseville & Norton, 1975; Carignan & Flett, 1981). Fluctuations of Fe and Mn supply from the watershed will dictate the concentration in sediments and must be considered when interpreting the sediment core chemo-profiles (Engstom & Wright, 1984).

Manganese has three oxidation states, Mn^{2+}, Mn^{3+} and Mn^{4+}, where Mn^{2+} accounts for 90% of the total Mn in solution in anoxic waters with pH between 6 and 8 (Turner *et al.,* 1981), and can replace Fe^{2+} in the crystal lattice of rock-forming minerals (Davison, 1993). The oxidation rate of Mn^{2+} is slower than that of Fe^{2+} to Fe^{3+}, while MnOH is readily reduced to Mn^{2+} compared to reduction of ferric to ferrous iron, so Mn is quickly released into solution (Davison, 1993). Particulate Mn directly above the reduction zone is considered reactive as it is easily reduced, whereas reactive Mn does not occur below the reduction zone (De Vitre *et al.,* 1988). This is relevant to sedimentation as mobilized Mn^{2+} and a small fraction of Mn contained within minerals will be incorporated into sediments. Prolonged anoxia in seasonally or permanently stratified lakes generates a maximum Mn^{2+} solubility that develops at the redox boundary, which is the point source of Mn in the water column and Mn will subsequently diffuse towards surface waters or away from the source to the sediments (Kjensmo, 1967; Mayer *et al.,* 1982; Stauffer, 1986; De Vitre *et al.,* 1988; Davison, 1993).

Sources of sulfur (S) in natural waters include rock weathering, fertilizer, and atmospheric precipitation, which accounts for the greatest contribution at present (Wetzel, 2001c). Sulfate [SO_4^{2-}] is the principal form of dissolved sulfur in natural waters under oxic conditions. Sulfate becomes reduced to sulfide [H_2S] when the Eh deceases below 1 volt and Fe^{2+} reacts with H_2S to form insoluble FeS at the water-sediment interface (Doyle, 1968).

Acid produced by atmospheric S deposition absorbs to soil particles, where 90% of total S in soils is bound to organic matter (Houle & Carignan, 1995). Snowmelt, heavy precipitation and flooding will flush soluble SO_4^{2-} from the organics and upper soil horizons (Steele & Buttle, 1994), and it will enter surface water as seston. Organic S then accumulates in the sediments, accounting for up to 70% of total S because the seston does not mineralize (David & Mitchelle, 1985). Small amounts of sulfur are released from organic S compounds (flora) by microbial decay and in peat-forming plants (Dellwig *et al.*, 2001).

4.3.2 Saturation of Iron Phosphate minerals – Vivianite and Strengite

Vivianite will precipitate and remain stable when ferrous iron and phosphate activities are high, low sulfide activity, under moderately reducing conditions and neutral to weakly alkaline pH (Nriagu, 1972; Nriagu & Dell, 1974; Emerson & Widmer, 1978; Postma, 1981). Nriagu (1972) determined that formation of vivianite would occur and control the HPO_4^{2-} concentration of the hypolimnion if the redox state remains above the sulfate/ sulfide reduction limits. The solubility of vivianite governs the geochemical migration or immobilization of phosphorus in solution (Einsele, 1938; Mortimer, 1941). The formation of vivianite significantly controls phosphate concentration in anoxic sedimentary environments where Fe^{2+} removed orthophosphate from solution (Nriagu, 1972). Shifts in redox potential towards sulfate reduction will remove Fe^{2+} in porewaters to precipitate FeS, lowering the Fe^{2+} concentration and higher PO_4^{3-} concentration will be needed to exceed the solubility product of vivianite (Gächer & Müller, 2003). Sulfate reduction is then associated with the dissolution of vivianite because the excess PO_4^{3-} remaining in the sediment porewaters enhances the phosphate diffusion out of the sediments (Gächter & Müller, 2003).

Anoxic sediments will diagenetically reduce buried "ferric phosphate" allowing the mobilized Fe^{2+} and PO_4^{3-} ions in sediment pore-waters to diffuse upwards to the water-

sediment interface, downward into deeper sediments or in both directions according to the concentration gradient (Gächer & Müller, 2003). This results in a zone where the solubility product of ferrous phosphate could be exceeded resulting in precipitation of vivianite (Tessenow, 1974; Emerson & Widmer, 1978; Manning *et al.,* 1999).

Rosenqvist (1970) reported the chemical parameters of interstitial water in vivianite bearing lake sediment horizons of Eh -0.39 Volts and pH of 7.4 and non-vivianite horizons had values of Eh -0.3 to -0.42 V and pH 7.7 to 8.5. Nriagu (1972) reported Eh values of -0.2 to -0.4 and activity (*a*) of HPO_4^{2-} ranging between 1 and 0.00001, suggesting that iron phosphate minerals would not form in sulfide-generating anoxic conditions without anomalously high phosphorus concentrations.

Conversely, strengite [$Fe^{3+}(PO_4)\cdot 2(H_2O)$] forms under oxidizing conditions at a higher $aHPO_4^{2-}$ range (0.1 to 0.001) and at a lower pH than vivianite. High ferrous ion activity is required to stabilize vivianite and a lower pH to allow Fe^{2+} concentrations greater than 10^{-5} mols/L and a stoichiometric solubility of hydroxyl apatite of more than $10^{-4.5}$ mol/L (Rosenquist, 1970).

Strengite, is a ferric phosphate mineral that is often found in soils (Sposito, 1989), and is a source of phosphorus for plants (Tiessen, 1995). Strengite solubility in soils is linked to pH and redox potential, where lower pH and Eh result in increased amounts of dissolved iron and phosphate (Patrick *et al.,* 1973). The reduction of strengite and production of H_2PO^{4-} and Fe^{2+} was described by Patrick *et al.,* (1973) in the following equation:

Eq.3. $FePO_4\cdot 2H_2O + H^+ + e^- \leftrightarrow Fe^{2+} + H_2PO^{4-} + 2H_2O$

The Fe^{2+} and PO_4^{3-} rendered are thought to remain in amorphous phases and vivianite will not precipitate due to its extreme insolubility (Patrick *et al.,* 1971).

4.3.3 *Iron and Phosphorus in Local Groundwater*

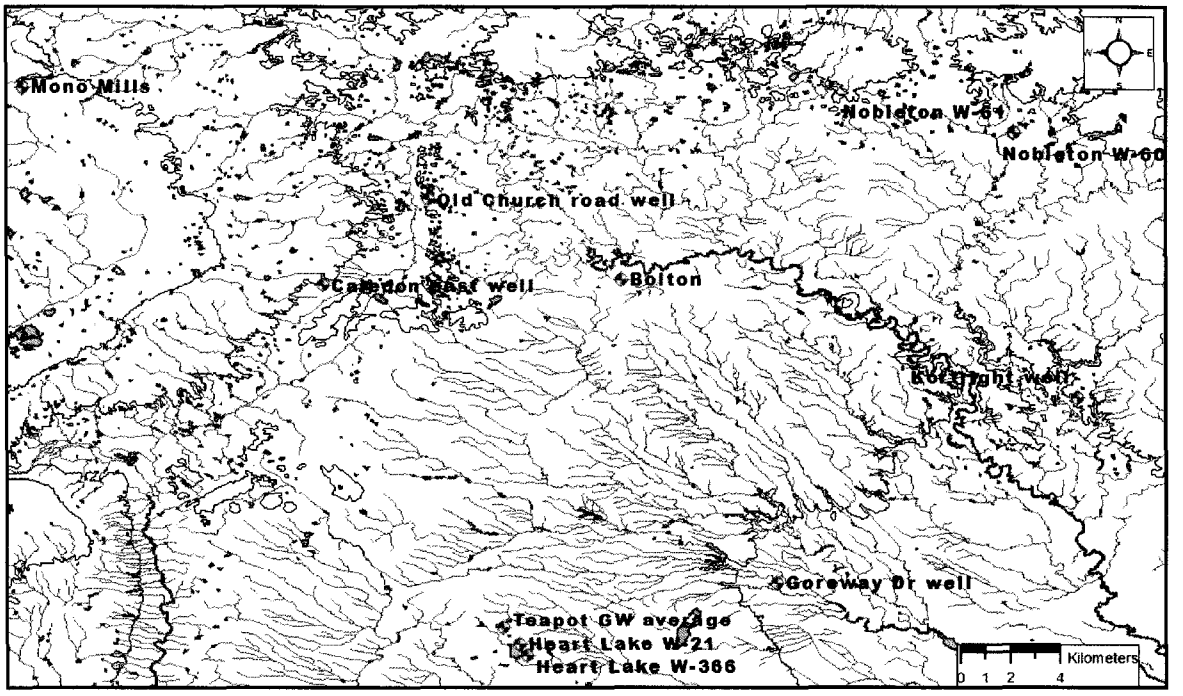


Figure 14. Regional Map showing well/ groundwater sampling stations.

The phosphorus and iron represent average values from three years of data from stations north of Teapot Lake and in the Heart Lake Conservation Area (***Figure 14***). The total phosphorus (TP) is high in the northern section of the region, and groundwater in the immediate vicinity of Teapot Lake has TP concentrations ranging from 0.019 to 0.039. The iron in groundwater is likely ferrous as the solubility of ferric is 0.0064 mg/L ($Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$ and $K=10^{-2.19}$) and groundwater from all stations had Fe concentrations $\geq$ 0.0137 mg/L (***Figure 15***). The highest Fe of all wells was measured from Heart Lake well 21, which is slightly closer to Teapot Lake than Heart Lake well-366. The groundwater from stations north-west of Teapot Lake also had high iron and the well on the Teapot Lake property has an appreciable Fe concentration. These results confirm that Fe is traveling through the watershed and that the concentrations vary spatially.

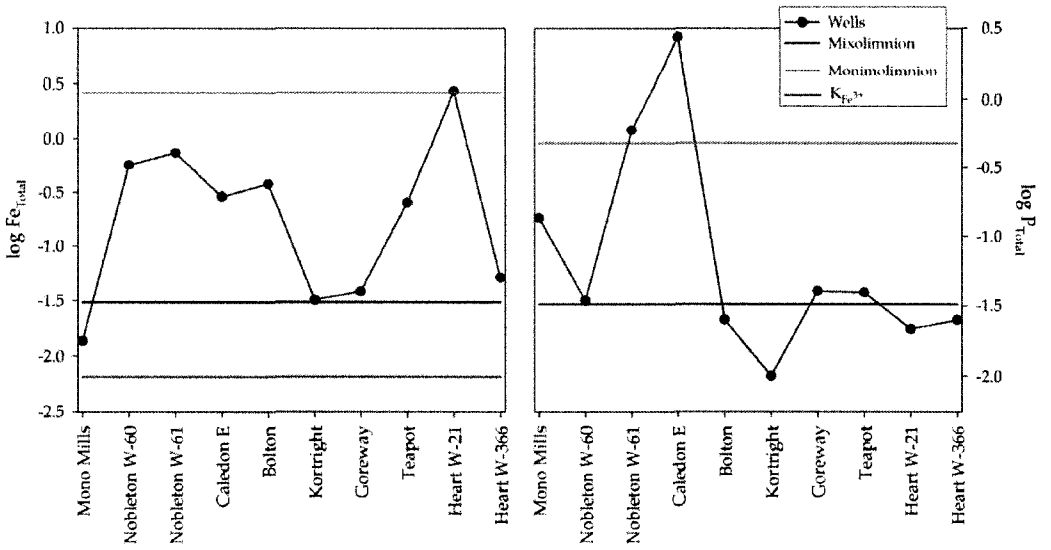


Figure 15. Total phosphorus and iron of Teapot Lake mixolimnion and monimolimnion, and wells representing regional groundwater.

The average mixolimnion Fe/P value is nearly the same as the Kortright well, close to the Heart Lake well-366 value and has a similar P value to the Teapot well (***Figure 15***). Teapot Lake monimolimnion has higher P and Fe concentrations than nearly all the wells, except for Heart Lake well-21 that has a similar iron value. This confirms that there is high iron in the groundwaters and that phosphorus is present in groundwaters, but in areas removed from Teapot Lake. Although the well data represent average values over a number of years, the geochemistry is similar and is likely a source of dissolved elements into the lake waters, except for P.

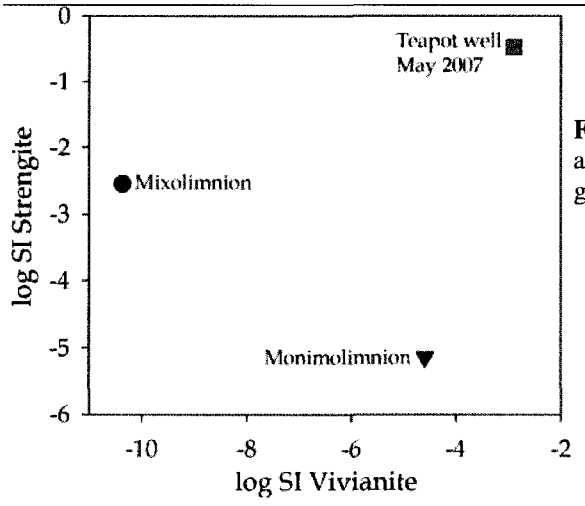


Figure 16. Comparison of the saturation index of vivianite and strengite from Teapot Lake water and regional groundwater.

Teapot Lake monimolimnion is close to the Teapot well groundwater SI of vivianite and further from strengite saturation compared to the Teapot well (***Figure 16***). The mixolimnion strengite SI is closer to Teapot well than the monimolimnion and is the most undersaturated with respect to vivianite due to contact with O_2 and low Fe.

4.3.4 Phosphorus, Iron, Manganese and Sulfur in Teapot Lake Water

Rigler (1964) reported phosphorus concentration in Teapot and Heart Lake from waters taken in the center of the lakes sampled at 0.5 meters depth. Phosphorus distribution was 5% inorganic, 29.6% soluble organic and 65.2% seston in Teapot Lake, which was greater than sestons phosphorus in Heart Lake. Therefore, it can be assumed that phosphorus in Teapot Lake water is primarily organic.

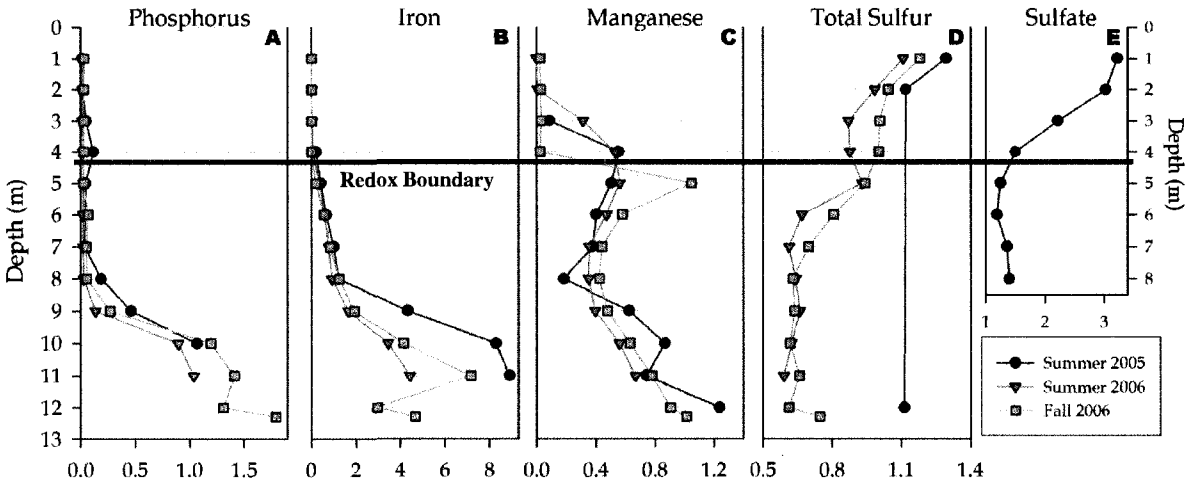


Figure 17. Seasonal water column profile of redox sensitive elements. All values in ppm.

The phosphorus concentration in Teapot Lake water column varies moderately between seasons and varies substantially with water depth (***Figure 17:A***). Phosphorus in the mixolimnion has an average seasonal value of 0.032 mg/L, the upper monimolimnion (5 to 9 meters) has an average of 0.103 mg/L and P concentration in the lower monimolimnion (10 to 12.3 meters) increases to reach the highest values at the greatest depths, with an average of 1.25 mg/L. Fall 2006 had the highest value at 12.3 meters depth and the highest overall

concentrations of P in the lower monimolimnion. Summer 2005 had the highest concentrations in the mixolimnion and upper monimolimnion; however this is likely due to the waters being unfiltered (see Phosphorus Results in Appendix).

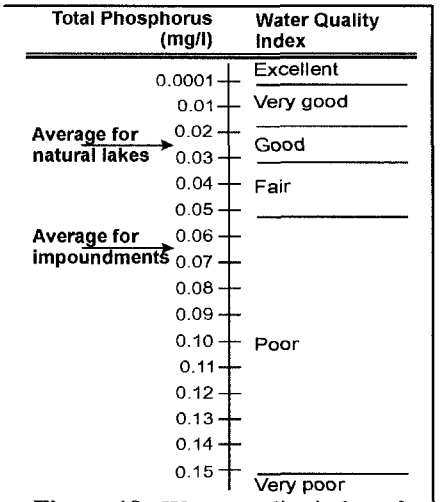


Figure 18. Water quality index of phosphorus, from Lillie *et al.*, 1983.

Overall, the dissolved and total phosphorus values in the mixolimnion are within the average natural lake range (***Figure 18***). Values below 9 meters are within the poor to very poor range typically of impounds. Clearly, Teapot Lake waters have elevated P concentrations that may or may not be naturally occurring. This will be further discussed in Chapter 6.

Iron is absent in the upper few meters during summer, and when present is in low concentrations in the mixolimnion, which is expected as ferric oxyhydroxides have low solubility under oxidizing conditions (Clark, 2005; I D Clark 2007, pers. comm.). An anomalously high measurement at 12 meters in summer 2005 of 24.6 ppm Fe is considered either a sampling or an instrumental error. It can be assumed that ferrous iron is the dominate species throughout the water column during summer 2005 and below 4 meters in summer and fall 2006 as iron concentrations are $\geq$0.1 mg/L (Clark, 2005). This is further demonstrated from Wat4 calculations where, although ferric iron occurs throughout the water column, its average seasonal concentration is 3.59 x 10^{-14} moles, which is an artefact of Wat4 calculation that will be discussed in the subsequent section.

Iron is present in low concentrations in the mixolimnion and in higher concentrations in the monimolimnion seasonally (***Figure 17:B***). From the surface to 7 meters iron concentrations are <1 ppm, followed by a rapid increase at 10 meters to reach maximum

values between 11 and 12 meters. It seems that iron is entering the lake at 10 meters from the groundwater. Furthermore, the iron is a redox sensitive element and may diffuse upwards to the oxycline, above which it is oxidized to Fe^{3+}. The iron concentration at 11 meters during summer 2005 and fall 2006 are both > 7 ppm, while the value from summer 2006 reach a maximum of 4.4 ppm at 11 meters. By far, summer 2005 has the highest concentrations of iron on whole.

The redox boundary at 4 meters generates a reducing environment and the absence of O_2 prevents oxides from forming in the lower water column, allowing the reduced more soluble metal species to dominate the monimolimnion of Teapot Lake (Mortimer, 1941). Normally iron in a water column profile is erratic and is affected by resuspension, mixing, pH, and oxidation state (Leppard *et al.,* 1988; Hamilton *et al.,* 1996). Due to the size of Teapot Lake, it is unlikely that mixing and resuspension are affect iron, and therefore pH would have the greatest impact.

Manganese concentration is seasonally bimodal in the water column, increasing at the redox boundary then slightly declining below the boundary and increasing again at 9 meters to the deepest point of the monimolimnion (***Figure 17:C***). Summer 2006 shows an increase from 3 to 5 meters; the concentration in summer 2005 increases abruptly at 4 meters and Mn concentration during fall 2006 is <0.05 ppm from 0 to 4 meters and at 5 meters the highest concentration measured in the water column occurs. Mn increases progressively into the lower monimolimnion with concentrations remaining high below 9 meters during each season.

Total sulfur (TS) is generally more concentrated in the mixolimnion than in the monimolimnion. Summer 2005 had the highest values measured at 1, 2 and 12 meters with no TS present between 4 and 11 meters (***Figure 17:D***). Summer and fall 2006 showed high

TS in the mixolimnion and concentrations dropped ≤0.7 ppm below the redox boundary. Total sulfur increased slightly in fall 2006 at 12.3 meters, although the value was less than the mixolimnion values. Sulfate (SO_4^{2-}) was analyzed from the summer 2005 lake samples and was detected within the upper 8 meters of the water column with concentration decreasing to ≤1.5 ppm below the redox boundary (***Figure 17:E***). Additionally, its was noted during field work that water samples retrieved below 10 meters depth produced an H_2S odour, suggesting that sulfate reduction occurs in the lower monimolimnion. This is verified by the decrease in total sulfur below the redox transition boundary during each season.

4.3.5 Wat4 Test Results

Ferrihydrite [$Fe_5O_3(OH)_9$] is uniformly oversaturation regardless of phosphorus concentration and becomes undersaturated in the absences of iron and under reducing to slightly oxidizing Eh (***Figure 19***).

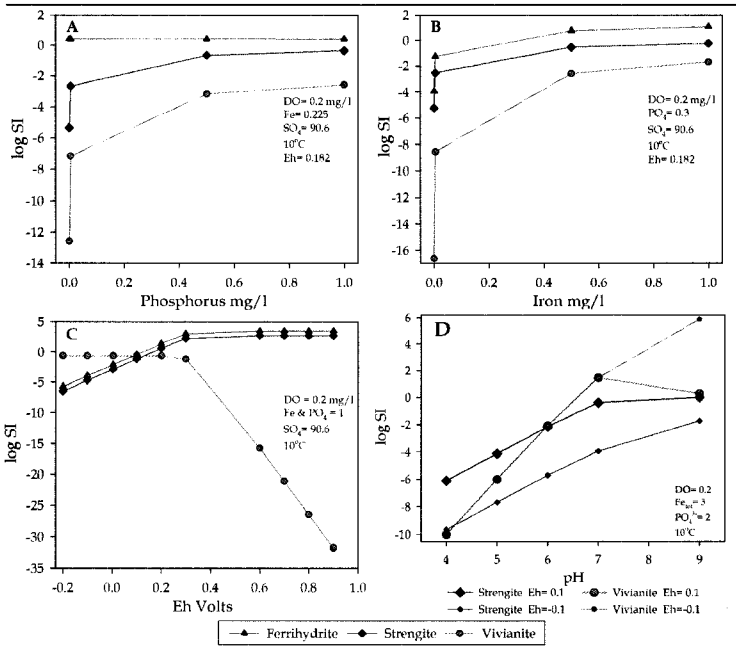


Figure 19. Wat4 result using different phosphorus, iron, Eh, and pH values to test the model calculation method for ferrihydrite, strengite, and vivianite saturation.

The stability of strengite varied with all the parameters, with marked changes occurring with the onset of oxidizing conditions (***Figure 19:C***). Strengite was undersaturated in acidic and reducing conditions, and approached saturation at pH 9 and Eh 0.1 V. The Eh significantly

effected the stability of vivianite (***Figure 19:C***), where Eh above 0.2 V resulted in a linear decline in vivianite saturation until the SI reached ≤ -28 at 0.9 V. Vivianite was supersaturated with pH >6.5 and under slightly reducing to slightly oxidizing Eh (***Figure 19:D***). Therefore, vivianite becomes saturated at neutral to slightly alkaline pH and reducing conditions. These results indicate that pH in combination with Eh control the mineral saturation of vivianite and strengite using the Wat4 modelled saturation index.

4.3.6 Saturation of Fe phosphate minerals in Teapot Lake water

The Wat4 modeled saturation index of strengite and vivianite produced questionable results for the water column. Although no O_2 would exists below 4 / 5 meters depth, ferric phosphate was saturated and ferrous phosphate was undersaturated. This is primarily due to the Redox Potential (Eh), where the raw value was corrected with $Fe(OH)_3/Fe^{2+}$ for calculating the saturation index:

Eq.4. $Eh_{Fe}= 0.059\ pe$ and $pe = \log K\ (aFe(OH)_3/aFe^{2+}) + 3pH$

Although the Eh_{Fe} values were >0 Volts where reducing values would be expected.

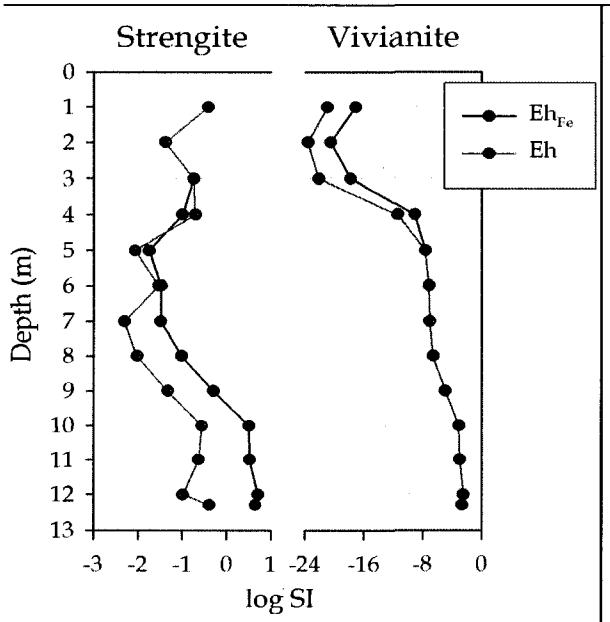


Figure 20. Seasonal average saturation index for vivianite and strengite

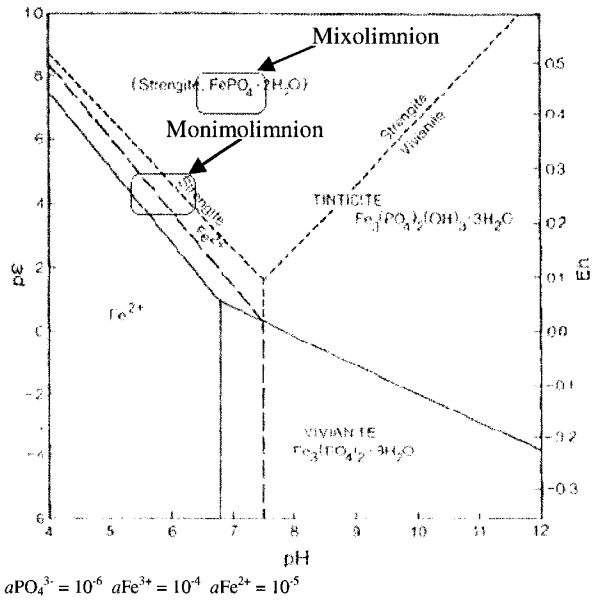


Figure 21. Stability of Iron Phosphates, Image from Nriagu & Dell (1974)

The two redox values (Eh_{Fe} & Eh) show strengite to be saturated in the bottom waters over vivianite, as Eh and Eh_{Fe} are >0.2 V throughout the water column and vivianite stability requires Eh of < 0 Volts (***Figure 20***). Vivianite is extremely undersaturated in the upper four meters and approaches saturation below this point where Fe and P concentrations increase, DO is assumed to be 0 and the pH becomes increasingly acidic. Strengite is close to saturation in the upper water column where oxidizing conditions allow Fe^{3+} to dominate over Fe^{2+} and below 4 meters strengite saturation decrease then at 10 meters the saturation increase and the Eh_{Fe} shows strengite is saturated in the lower monimolimnion. The pH may be limiting vivianite stability as the bottom waters have an average pH of 5.6 and as demonstrate in ***Figure 21*** where vivianite is stable from pH 7.5 to 12.

4.4 Carbon

Freshwater carbon is measured as dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). The behaviour of DIC and DOC in a lacustrine system can be used to determine levels of primary productivity, rates of respiration, bacterial activity, concentrations of available oxygen and factors limiting these processes.

The distribution of DIC species in lacustrine environments is a function of pH and atmospheric CO_2 exchanging with surface water (Clark & Fritz, 1997; Wetzel, 2001a). Lakes are open systems where atmospheric $CO_{2(g)}$ dissolves and is constantly exchanging with surface water to form aqueous $CO_{2(aq)}$, which is then hydrated to form carbonic acid (Mook, 1980). Carbonic acid (H_2CO_3) decreases the pH of water as H^+ ions are removed from solution, changing the distribution towards bicarbonate (HCO_3^-) and as pH becomes alkaline carbonate (CO_3^{2-}) becomes the dominate DIC species (Clark & Fritz, 1997). The

hydration of CO_2 forms carbonic acid, the dissociation of carbonic acid forms bicarbonate and dissociation of carbonic acid forms carbonate as demonstrated in **Eq.5**.

Eq.5. $CO_{2(g)} + H_2O \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

The species of DIC present in lake water governs the boundary where aquatic organisms can survive, where acidity will decreases CO_2 availability that is required for photosynthesis (Titus & Andorfer, 1996; Pagano & Titus, 2004). As the pH decreases below neutral and dissolved oxygen declines, aerobic biological activity ceases and anaerobic mediated reactions (methanogenesis) ensue (Clark & Fritz, 1997).

Dissolved organic carbon (DOC) generally comprises allochthonous materials from precipitation, derivatives of bacterial metabolization from soils (humic acid and fulvic acid), and in Quaternary aged sediments the dissolution of peat and marine sediments into groundwater are another sources of allochthonous organic carbon (Mook, 1980; Clark & Fritz, 1997). Autochthonous organic matter occurs within the lake, such as dead aquatic organisms (biomass), and photosynthates such as carbohydrates and amino acids (Clark & Fritz, 1997). In surface waters, DOC is generated from biological productivity under aerobic and anaerobic conditions. Aerobic photosynthesis fixes CO_2 from the DIC pool and converts it into biomass [**Eq.6**], and respiration in anaerobic conditions decomposes the biomass, reintroducing the CO_2 into the system [**Eq.7**].

Eq.6. $CO_2 + H_2O \rightarrow O_2 + CH_2O$ **Eq.7.** $CH_2O + O_2 \rightarrow H_2O + CO_2$

The concentration of DOC can significantly influence the biological productivity in a lake by limiting or permitting light penetration (Jones & Arvola, 1984); increasing acidity and can acts as a nutrient source (Mierle & Ingram, 1991). The health of a lake ecosystem can be assessed using the DOC, where high DOC levels result in depletion of DO, thereby limiting biodiversity (Robards *et al.,* 1994).

4.4.1 Stable Isotope $\delta^{13}C$

The $\delta^{13}C$ of DIC is govern by oxidation and respiration of organic matter in the water column; interactions of CO_2 in photosynthesis; exchanges between atmospheric CO_2 and water; effervesces of CO_2 from water; detrital organic and inorganic carbon influx; seasonality of lake turnover and the $\delta^{13}C$ of dissolved carbonate rocks (Fritz & Fontes, 1980; Clark & Fritz, 1997). The chemistry of lake water and inflow sources affects the reactions that produce measurable $\delta^{13}C$. Continental atmospheric $^{13}C_{CO2}$ is typically more negative than coastal areas as a result of mixing between biospheric CO_2, decaying plant matter and from fossil fuel combustion (Keeling, 1958; Mook *et al.*, 1983).

The amount of dissolved oxygen governs the metabolic activity of microorganisms and in that will affect $\delta^{13}C$. Photosynthesis will preferentially remove the lighter ^{12}C isotope from $\delta^{13}C_{CO2/DIC}$ leaving water enriched in the residual $\delta^{13}C$ (Hodell & Schelske, 1998). Aquatic organisms consume CO_2 from the DIC pool during photosynthesis and convert it into carbohydrate. The photosynthetic fraction from $\delta^{13}C_{DIC}$ to $\delta^{13}C_{DOC}$ reflects the incorporation of lighter carbon isotopes, resulting in $\delta^{13}C_{DOC}$ becoming substantially depleted compared to the initial $\delta^{13}C_{DIC}$ (Bade *et al.,* 2006). Algal organic matter will consume more ^{12}C when dissolved CO_2 is abundant and consume less when CO_2 is low (Fogel & Cifuentes, 1993). Therefore, the degree of $\delta^{13}C_{DIC}$-enriched and $\delta^{13}C_{DOC}$-depletion demonstrates the levels carbon cycling in the lake and the levels of productivity. The isotopes of methane behave similarly to $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$. As with photosynthesis, bacteria preferentially remove the lighter ^{12}C from the already depleted organic carbon ($\delta^{13}C_{DOC}$), producing highly depleted $\delta^{13}C_{CH4}$ (Clark & Fritz, 1997; Mook, 2001). The $\delta^{13}C_{CH4}$ and

$\delta^{13}C_{CO2}$ produced from oxidation of methane have distinctly different values from primary CH_4.

4.4.2 Methane

Methane in lacustrine carbon cycle occurs through intermediate and end-member reactions as organic matter is decomposed. In the water column, anaerobic bacteria convert organic materials (carbohydrates, proteins and lipids) that accumulate as dead aquatic organisms sink and are converted into fatty acids by hydrolysis and fermentation (Deyl, 1961; McCarty, 1964; Nedwell, 1984). Acetate produced during fermentation is converted to CO_2 and CH_4 (***Figure 22***). Microorganisms convert organic matter into sugars, volatile fatty acids, H_2 and CO_2, and the products are converted to acetic acids and finally converted to CH_4 and CO_2 (***Figure 22***).

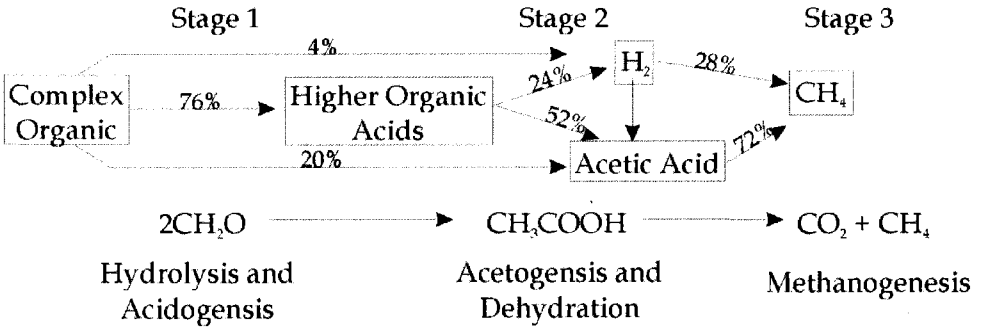


Figure 22. Methanogenesis from McCarty, 1982

Organic molecules are represented as CH_2O (Klass, 1984; Clark & Fritz, 1997). The basic requirements for growth of methanogenic bacteria include the normal nutrients needed for cellular growth, neutral pH (6.4-7.4), a reducing agent and a source of nitrogen, as well as large supply of CO_2 as a source of carbon, based on studies of pure methanogenesis (Klass, 1984). Methane oxidation observed in the water column is restricted to the thermocline during summer stratification of naturally eutrophic lakes (Patt *et al.,* 1974). In lacustrine environments, methanogenic bacteria utilize organic mater as an energy source in waters

void of O_2. Due to the low energy of CH_4, it is often the end product of the carbon cycle in lake waters. Methane can be oxidized into CO_2 when O_2 is present and therefore plays an important role as both an intermediate and end product in the carbon cycle (Rudd *et al.*, 1974).

4.4.3 Dissolved Carbon in Teapot Lake Water

Dissolved inorganic carbon (DIC) is seasonally low in the mixolimnion and upper monimolimnion, and climbs dramatically to maximum values in the lower monimolimnion (*Figure 23* and see Appendix for values).

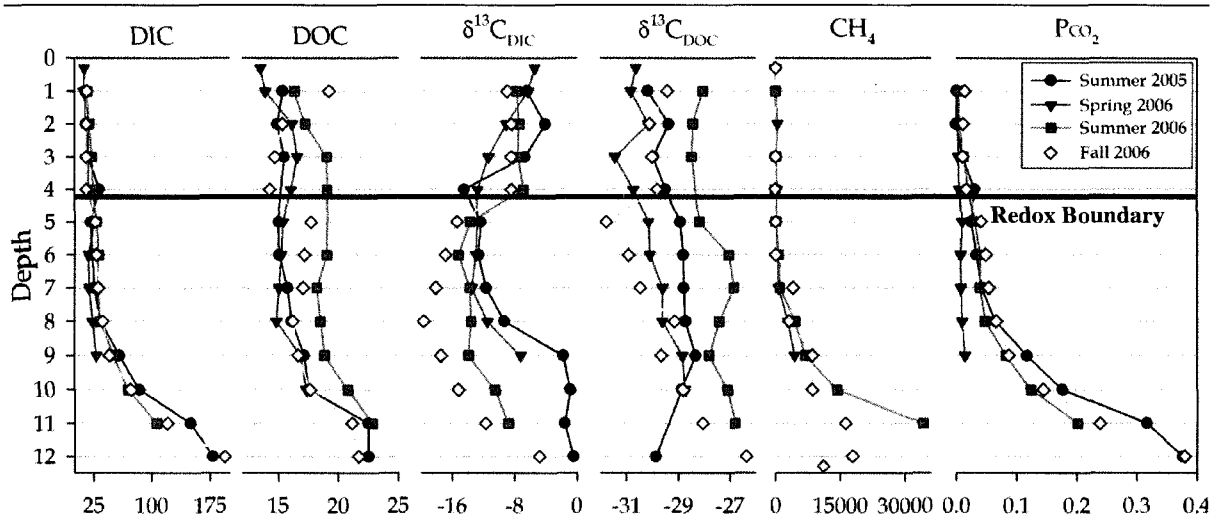


Figure 23. Dissolved Carbon Concentrations and Stable Isotopes in Lake Water. Concentration of DIC, DOC and CH_4 in ppm, and stable isotopes in ‰.

The dissolved organic carbon (DOC) profile is more erratic throughout the water column and seasonally. The mixolimnion has a seasonal range of 13.5-19.3 ppmC, with summer 2006 having the highest values and fall 2006 has the highest value at 1 meter depth. The concentration remains low in the upper monimolimnion during summer 2005 and spring 2006, and increase slightly during summer and fall 2006. The lower monimolimnion has the highest concentrations for all seasons, with an average range of 15.6-22 ppmC. Summer 2006 has the highest average values and the highest concentration total for all the seasons,

while spring 2006 has the lowest. Methane concentrations are similar to the DIC, low in the mixolimnion then rapidly increasing towards the lower monimolimnion.

The $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ vary between seasons and throughout the water column. The $\delta^{13}C_{DIC}$ shows a general trend of enrichment in the mixolimnion, depletion in the upper monimolimnion and moves towards enrichment in the lower monimolimnion. During 2006, seasonal changes are clearly demonstrated from spring, summer and fall show the seasonal changes through the year. The mixolimnion is generally close to atmospheric values (-7.38 to -8.50‰) with summer 2006 being most enriched due to increased biological activity. The monimolimnion becomes progressively depleted from spring to fall, and below 9 meters the $\delta^{13}C_{DIC}$ shift towards enrichment. Fall shows the most variability and spring shows the least variability during 2006. Summer 2005 has the greatest overall variability, but this is likely due to the delay in analysis after sampling that caused anomalous enrichment below 9 meters. The $\delta^{13}C_{DOC}$ varies significantly between each seasonal and within the water column.

The $\delta^{13}C_{CH4}$ fluctuates between seasons and through the water column (***Figure 24***). Spring has the most depleted values, occurring in the upper monimolimnion that become enriched into the lower monimolimnion and methane was not detected in the mixolimnion. The summer 2006 mixolimnion has more enriched $\delta^{13}C_{CH4}$ values, where methane was detected at 1 and 4 meters. The monimolimnion remained ~-50‰, with depletion occurring from 8 to 11 meters. Methane was not detected until 3 meters in fall, where the mixolimnion had the most enriched values of all seasons. The monimolimnion becomes increasingly depleted from 7 meters, where the $\delta^{13}C_{CH4}$ values were enriched compared to spring and summer.

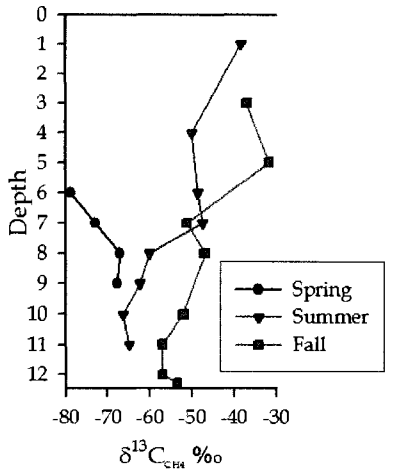


Figure 24. 2006 Water column $\delta^{13}C_{CH4}$

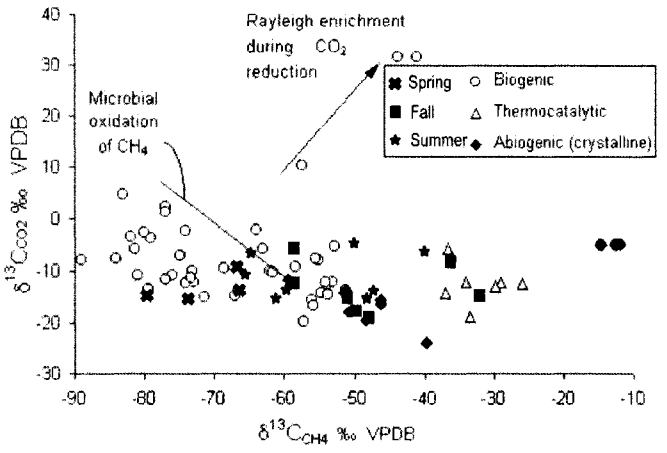


Figure 25: 2006 Water column $\delta^{13}C_{DIC}$ vs. $\delta^{13}C_{CH4}$

The process of methane formation is determined using $\delta^{13}C_{CO2(DIC)}$ vs. $\delta^{13}C_{CH4}$ (***Figure 25***). During all seasons, the values clustered towards microbial oxidation of CH_4. The spring values group closest to the biogenic values, while the summer values are more scattered, clustering between biogenic and abiogenic values. The fall values cluster around the abiogenic and thermocatalytic values. It seems most likely that biogenic methane production occurring in the spring is then oxidized during summer and fall where $\delta^{13}C_{CH4}$ becomes increasingly enriched.

4.5 Summary of Water Column Geochemistry

The steep slopes of Teapot Lake basin and small surface area prevent wind mixing, leaving the monimolimnion relatively undisturbed. The bottom waters below ~7 meters range from 3.4 to 5°C seasonally, preventing vertical mixing of the dense waters with the less dense mixolimnion waters, verifying that Teapot Lake is in fact a meromictic lake and permanently stratified. On whole, Teapot Lake is neutral to acidic. The mixolimnion is neutral and below the thermocline the waters become increasingly acidic. The acidity in the monimolimnion may arise from oxidation of organic matter and the increase in P_{CO2} (***Figure 23***).

Surface waters are enriched in $\delta^{18}O$ and δD, which is often observed in regions where evaporation causes a higher net loss of vapour and subsequent removal of lighter isotopes (Craig & Gordon, 1965). The meteoric water line shown in black (***Figure 12:A***), demonstrates that the waters in Teapot Lake are more enriched in the heavier isotopes. The surface water of Teapot Lake (1 meter depth) has an average seasonal value of -4.36‰, which is enriched by 2.04‰ compared to the IAEA precipitation data. This offset is a factor of isotopic fractionation caused by evaporation, so lake water and precipitation will seldom have the same $\delta^{18}O$ value. The $\delta^{18}O$ values decrease simultaneously with temperature at the thermocline and remain depleted at greater depths. The role of seasonality governs the timing of lake stratification, where sharp thermal and chemical stratifications are observed in the summer months. The $\delta^{18}O_{lake\ water}$ illustrates water column stratification where bottom waters are ^{18}O depleted, so it can be assumed that bottom waters have a longer residence time resulting from the lack of mixing. The bathometry of Teapot Lake certainly has a part in the $\delta^{18}O$ water column record, as the size and depth induce greater evaporation. Furthermore, the $\delta^{18}O$ of the bottom waters are closer to the $\delta^{18}O$ of groundwater.

Overall, groundwater and precipitation feed Teapot Lake ions, but below the thermocline, the bathymetry and morphology limit the impact of surface temperatures and mixing. Based on the geochemical and stable isotope data from groundwater, precipitation and lake water, it seems reasonable to assume that the primary source of water to Teapot Lake is groundwater, which has the most prominent signal in the monimolimnion while surface run-off and precipitation largely control the geochemistry of the mixolimnion. There are no visible inflow or outflow sources and the lake does not appear to be connected to any of the local creeks and rivers. The phosphorus concentration in the lake water is

significantly higher than the groundwater, implying that P is derived from another source that is entering the lake directly. The phosphorus in the upper water column accumulates in living biomass, where the water temperatures are warm and ample sunlight for photosynthesis.

The dissolved carbon and phosphorus values in the lake are positively correlated, suggesting that the majority of P in the lake is organic. As biomass decays in the monimolimnion, the P would be released and would build up in the lower water column. The groundwater sampled near Teapot Lake may contribute phosphorus; although the values from the Heart Lake and Teapot wells (0.037 and 0.041 mg/l) are equal to or less than the P in the upper 3 meters of Teapot Lake. Two other potential sources of P are waterfowl faeces and flux from the lake sediments, which will be discussed in Chapter 6.

It is clear that Teapot Lake is a redox-controlled system. The transitional boundary between oxic and anoxic waters at the chemocline will host a number of redox transformations where immobile elements become soluble and move along hydraulic pathways (Davison, 1993). The concentrations of reducible elements (Fe, Mn, SO_4, CH_4) show marked response at the redox transition boundary. Manganese is very sensitive to changes in redox as illustrated in ***Figure 17:C*** where its concentrations jump as the water column moves from oxidizing to reducing. Iron reacts conservatively compared to Mn, as it is reduced from Fe^{3+} to Fe^{2+} around the redox boundary and it is most concentration in the bottom 3 meters of Teapot Lake. The presence of sulfate in the upper water column and absences at depths suggests that sulfate reduction is occurring below the redox boundary. Finally, methane concentrations in the lower most lake waters suggest that bacteria are metabolizing organic carbon. Based on the reactivity of electron acceptors, the lower

monimolimnion probably reaches negative Eh values, despite the oxidizing values obtained from the corrected Eh and calculated Eh_{Fe}.

The Eh range of the Teapot Lake waters are sufficient to for vivianite saturation, but the pH is the limiting factor for its stability. This is verified by the two Eh calculations, where the difference in saturation index of the upper water column is the result of Eh values, while the SI is constant below 5 meters where pH values become increasingly acidic. The effects of pH on vivianite and strengite are observed in ***Figure 20*** and ***Figure 21***, where vivianite was saturated at the expense of strengite being undersaturated, under both reducing (Eh= -0.1) and oxidizing (Eh= 0.1) condition as long as pH remained above 7. Therefore, pH is controlling mineral saturation in Teapot Lake and the Eh is a secondary factor, not only for iron phosphate, but for saturation of carbonate minerals. Calcite saturation is inhibited due to the low pH, which allows dissolved carbon species $H_2CO_3^{2-}$ to dominate. The acidity and near reducing conditions would hinder apatite stability, allowing Fe to suppress Ca in phosphate mineral formation.

Intense photosynthetic activity in the mixolimnion produces oxygen and removes dissolved inorganic carbon along with other nutrients to produce organic matter (Culver & Brunskill 1969; Takahashi *et al.,* 1970; Sorokin & Donato 1975; Lawrence *et al.,* 1978). The $\delta^{13}C_{DOC}$ depletion in the mixolimnion during spring is linked to the low P_{CO_2} and enriched $\delta^{13}C_{DIC}$ as aquatic organisms uptake CO_2 from inorganic carbon, which is close to atmospheric $\delta^{13}C$ values, to synthesis organic compounds (Galimov, 1974; Deines, 1980). This is also apparent as CH_4 concentrations below the mixolimnion increase substantially with the P_{CO2}, demonstrating that biomass accumulated in the mixolimnion dies, sinks and decomposes in the lower monimolimnion. The conversion of biomass into to organic acids

is implied by the increase of DOC, and the by-products of CH_4 and CO_2 increase as methanogenesis persists in the bottom waters and at the water sediment interface (McCarty, 1964).

Dense waters below the thermocline prevent dissolved CO_2 from mix with surface water. This trapping effect was observed during field sampling, where waters sampled below ~7 meters depth effervesce when exposed to atmospheric pressure. The abundance of organic carbon at greater depths and the depleted $\delta^{13}C_{DOC}$ suggest that aerobic biological reactions cease and anaerobic methanogenesis commences (Clark & Fritz, 1997; Bullen & Kendall, 1998).

5 Results: Lake Sediment Bulk Geochemistry

The sediment geochemistry was determined following the method outlined in Chapter 3: *Section 3.4.5.* The blank values for each element except for Na was at least 100 times less than the concentration of samples, therefore the ICP-OES data is reliable. Duplicated samples varied by <10% and in most cases <5%, therefore the instrumental precision is satisfactory. In order to best identify significant horizons and elements, the geochemistry will be categorized into groups of elements. The first group is the redox sensitive group includes Fe, Mn and P. The second group is the clay forming/ less mobile elements Al, Cu, K, Mg and Ti. The third group will be the other elements that are dissimilar to all other, Zn, Ca, Ba, Sr and Na. The final group is the organic component elements, including %C, %N and Sulfur, and the stable isotopes of organic matter $\delta^{13}C$ and $\delta^{15}N$.

Table 2: Descriptive Statistics of Sediment Geochemistry
Values are total elemental concentrations in mg/kg

mg/kg	N	Sum	Mean	Std. Dev	Min	Max
Fe	70	5340864	76298	48869	12276	180741
P	70	1503035	21472	18794	559	74669
Ca	70	429803	6140	1565	1683	10211
S	70	413638	5909	2062	2881	11052
Al	70	329786	4711	2721	692	13789
Mn	70	118070	1687	1091	258	4709
Mg	70	118030	1686	1177	218	4310
K	70	50867	727	448	177	1893
Ba	70	18578	265	124	82.8	510
Na	70	8068	115	175	17.4	892
Zn	70	6625	94.6	26.0	54.4	178
Ti	70	5227	74.7	36.4	14.5	149
Cu	70	2051	29.3	13.25	4.17	55.0
Sr	70	1813	25.9	5.76	10.04	45.9

Table 3: Lake Sediment Geochemistry Correlations

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Sr	Ti	Zn	%N	%C
Al	-	-0.48	0.32	0.54	-0.34	0.83	0.85	-0.37	0.30	-0.49	0.18	-0.18	0.93	0.02	-0.07	-0.12
Ba	-	-	0.07	-0.32	0.04	-0.34	-0.71	0.05	0.10	0.12	0.12	0.55	-0.58	0.56	0.50	0.51
Ca	-	-	-	0.55	-0.38	0.20	0.35	-0.33	0.09	-0.53	0.28	0.65	0.35	0.30	0.37	0.36
Cu	-	-	-	-	-0.78	0.19	0.61	-0.76	0.22	-0.84	0.49	-0.03	0.56	0.11	0.47	0.46
Fe	-	-	-	-	-	0.02	-0.36	0.89	-0.34	0.93	-0.46	0.09	-0.30	-0.27	-0.63	-0.63
K	-	-	-	-	-	-	0.58	-0.05	0.24	-0.16	0.05	-0.02	0.80	0.00	-0.16	-0.21
Mg	-	-	-	-	-	-	-	-0.36	0.06	-0.49	0.06	-0.21	0.90	-0.22	-0.25	-0.26
Mn	-	-	-	-	-	-	-	-	-0.34	0.85	-0.40	0.09	-0.33	-0.29	-0.67	-0.66
Na	-	-	-	-	-	-	-	-	-	-0.31	0.44	-0.10	0.21	0.40	0.39	0.35
P	-	-	-	-	-	-	-	-	-	-	-0.52	0.01	-0.48	-0.24	-0.59	-0.57
S	-	-	-	-	-	-	-	-	-	-	-	0.05	0.16	0.33	0.55	0.48
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-0.14	0.32	0.23	0.25
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.07	-0.14	-0.18
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.57	0.55
%N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.97
%C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

5.1 Chronology

The upper sediment core was dated with ^{210}Pb, with the oldest measured age of 1848±24.89 AD was obtained from ~17 cm depth. The age of data points below 17 cm were estimated assuming a constant sedimentation rate of 1 cm= 19 years (C Black 2007, pers. comm.). The ages since 1000 AD will be reported as *Anno Domino* (AD) and ages determined from the constant sedimentation rate will be reported as years before present (BP) for any age before 1000 AD.

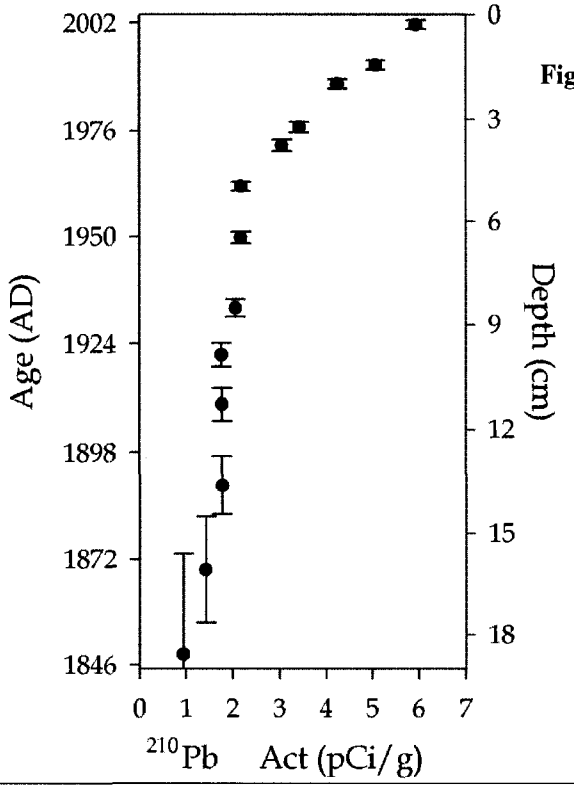


Figure 26. ^{210}Pb dates for Teapot Lake sediment core.

Although the ages of the sediments are not resolved, the sedimentation rate ages provide an estimate that can be used for comparison with other paleolimnological records. Human disturbance in the region was observed in Crawford Lake sediments between 1268-1486 AD (740-522 BP) (Ekdahl *et al.,* 2004), which will represent the commencement of regional settlement.

5.2 Vivianite and Lake Sediment Mineralogy

Vivianite has been found inside fossil marine shells or attached to fossil animal/ human bones (Robles *et al.,* 2002; McGowan & Prangnell, 2006) and in as concretions in Quaternary aged lacustrine sediments with high organic content (Einsele, 1938; Rosenqvist, 1970; Stamatakis & Koukouzas, 2001; Fagel *et al.,* 2005). In lake sediments, vivianite will form as amorphous masses; microcrystalline precipitates; or a radiation of monoclinic crystals (Read, 1970). Vivianite can precipitates from pore fluids in anaerobic sediments with high PO_4^{3-} and Fe^{2+} concentrations that are void of carbonates (Knyazeva, 1954; Nriagu, 1972; Nriagu & Dell, 1974; Mizandrontsev, 1975), and is stable when iron concentrations exceed sulfide formation (Murphy *et al.,* 2001). Porewaters can be supersaturated with respect to vivianite without precipitation and so the formation and stability of vivianite in lake sediments is yet to be fully understood (Boers & de Bles, 1991).

Vivianite concretions recovered from Åsrum Lake, Norway, formed under lacustrine conditions, and were absent in lagoonal and marine sediments. The author designed a model that estimates the time required for vivianite to precipitate from interstitial waters at 2000 years (Rosenqvist, 1970). Vivianite in Swiss lake sediments occurred with P and Fe rich grains, suggesting authigenic formation in the sediments from interstitial waters and that vivianite acts as a sink for P in these sediments (Emerson & Widmer, 1978). Upper Miocene lacustrine basin sediments with vivianite deposits in Greece were suggested to form as ferrous ions were released from decaying biomass in the lake bottom, and diatom cells, plant debris and fecal pellets were identified as the source of PO_4^{3-} ions (Stamatakis & Koukouzas, 2001). Several publications have addressed authigenic vivianite formation in Lake Baikal sediments (Deike *et al.,* 1997; Fagel *et al.,* 2005; Sapota *et al.,* 2006). The formation processes of vivianite in Lake Baikal sediment cores revealed that secondary alteration to

amorphous santabarbaraite ($Fe^{3+}_3[(OH)_3(PO_4)_2]\cdot 5H_2O$) changed the geochemical signature of vivianite by a decline in Mn (Fagel *et al.,* 2005). More importantly, it was determined that vivianite formation in the sediments was mainly controlled by porewater chemistry and sedimentation rates, was concluded that vivianite was unsuitable for a lacustrine paleoproductivity proxy record (Fagel *et al.,* 2005). This study documented high porewater PO_4^{3-} and Fe concentrations up to 9.4 and 5.4 mg/L and suggested the source of P and Fe in the porewaters arose from sediments degassing methane that subsequently killed fish, and released P from the decaying biomass in the sediments (Granin & Granina, 2002; Fagel *et al.,* 2005).

Climatic inferences were proposed for the formation of vivianite in hemipelagic facies in Lake Baikal and it's predominate in Pliocene and Quaternary aged strata associates its formation with cold and dry climate that favours ferrous authigenic mineral formation (Sapota *et al.,* 2006). Eutrophication of Lake Biwa, Japan, has been associated with the dissolution of vivianite in sulfide-enriched sediments, producing porewater P of >3 mg/L (Murphy *et al.,* 2001). Although each of these studies attempts to resolve the condition of vivianite formation, there seems to be consensus that the dissolution of vivianite may result in eutrophication, there is little to no acknowledgment of sources of iron and phosphorus.

5.2.1 X-Ray Diffraction and Mineralogy Results

Vivianite was clearly identified in several sediment samples, even with clay interference that has hindered its identification in other studies (Hupfer *et al.,* 1998; Sapota *et al.,* 2006). Samples taken from Teapot Core 2 were the attempt to isolate what was thought to be calcite, which subsequent to sampling turned blue and has been confirmed as vivianite.

Table 4: Details of Sediment Mineralogy

ID	Method	Core	Section	Depth (m)
1	SEM	2	1	0.86
2	XRD	2	2	1.35
3	XRD	1	2	1.77
4	SEM	2	4	3.24
5	XRD	2	4	3.36

Sample 1 and 4 were analyzed by Cherylee Black at Carleton University, who indentified pyrite framboids. Detailed accounts of SEM work will not be described here as they will be the focus of her PhD thesis. However, the occurrence of pyrite in the sediments is relevant to understanding the changes in Teapot Lake geochemical systems. Sample 2 is composed of vivianite and siderite, with minimal interference suggesting that clay minerals are not present in significant quantities. Sample 3 shows abundant vivianite peaks as well as quartz peaks. Significant background interference demonstrated in the arching signal is assumed to be caused by clay minerals (R Hartree 2005, pers. comm.). The mineralogical composition of residual sediment material after digestion was tested on sample 3. The results show vivianite is absent and quartz is the most abundant mineral. This verified the effectiveness of the aqua-regia digestion in removing all mineral matrix and elements from the sediments leaving only silicates. Sample 5 has the highest amplitude vivianite peaks and no other mineral peaks appear.

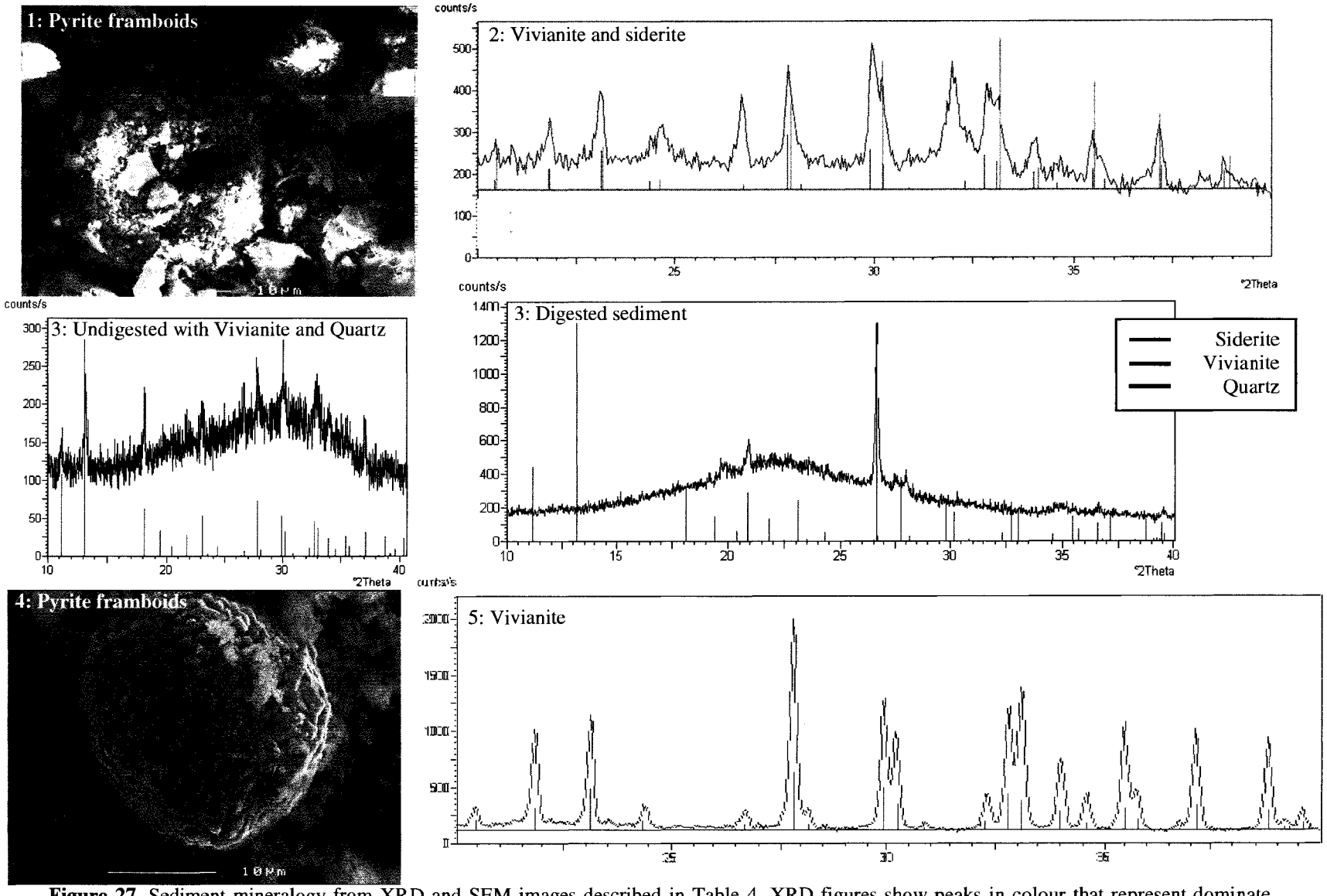


Figure 27. Sediment mineralogy from XRD and SEM images described in Table 4. XRD figures show peaks in colour that represent dominate mineral. Sample 3 undigested sediments are a mixture of vivianite and quartz, digested is quartz. SEM images provided by Cherylee Black.

5.3 Redox Sensitive Sediment Geochemistry

Iron and phosphorus have the highest over all concentration in the lake sediments compared to all the elements analyzed (**Table 2**) and Fe, Mn and P are highly correlated (***Figure 28: A C D)***, while showing weak or negative correlations with all other elements (**Table 3**). A linear dependence is obviously occurring between Fe, P, and Mn demonstrated by parallel increases and decreases in concentrations (***Figure 30***).

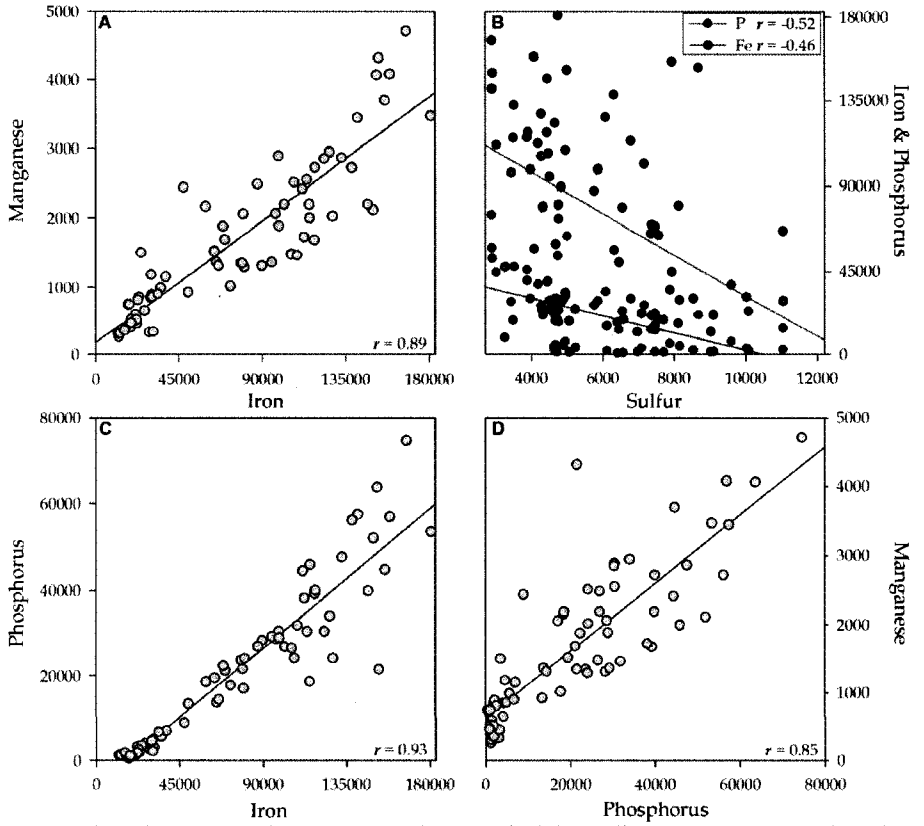


Figure 28. Correlations between redox sensitive elements in lake sediments. Concentrations in mg/kg dry wt.

The co-dependence of Fe, P, and Mn can be interpreted as the elements originating from a similar source; that the chemistry of the sediments is conducive to retain them; that Fe, Mn and P bearing minerals form under specific conditions in the water column; and/ or that the dissolved P will be drawn to sediment horizons with higher concentration of elements is can form complexes with (Fe, Mn). Negative correlation between S and P signifies that one

element will be enriched when the other's concentration declines (***Figure 28:B***). This may be occurring in pyrite bearing horizons, where residual Fe is high and pyrite was identified (***Figure 29***), or in organic rich horizons, as S showed the strongest correlations with %C and %N (r= 0.55 and 0.48 respectively). The weaker negative correlation of S with Fe and greater scatter of samples furthers the above suggestion that organic sulfur is dominating these sediment horizons.

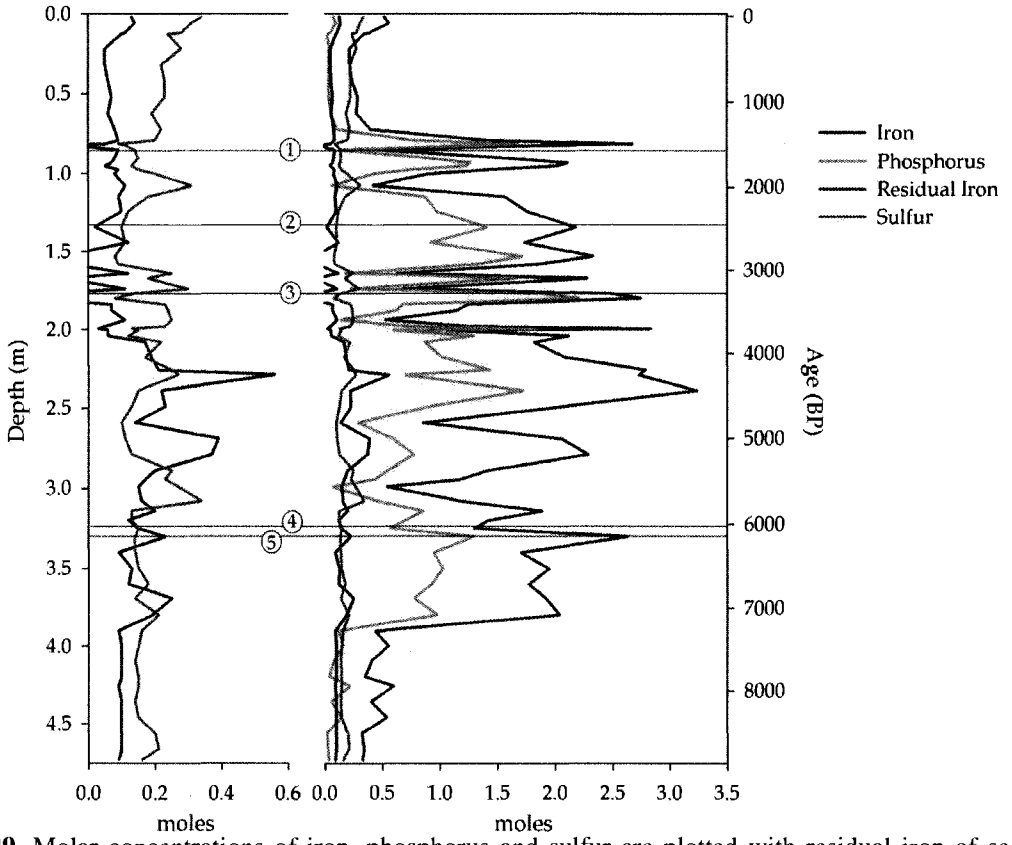


Figure 29. Molar concentrations of iron, phosphorus and sulfur are plotted with residual iron of sediments. Residual iron represents the amount of iron left in the sediments after vivianite has been former, calculated as m residual iron= (mFe/3)- (mP/2)

The sediment horizons with lower P molar concentration correspond to higher S molar concentration, the residual iron peaks correspond to peaks in Fe and P, and residual iron peaks occur with diminished P and amplified S (***Figure 29***). This is clearly exemplified at 2000 BP where P concentration drops substantially, S concentration increases sharply and

residual iron is present. It seems reasonable to assume that sulphate reduction occurred and precipitated with ferrous iron to form pyrite in the low phosphorus horizons. The horizons that best represent vivianite formation are 1500 BP, 2400 BP, 2800 BP, 3100 BP, 3300 BP, 3700 BP and 4400 BP, where Fe and P concentrations are superlative, residual iron does not occur or is present in <0.05 moles and S concentrations are appreciably low.

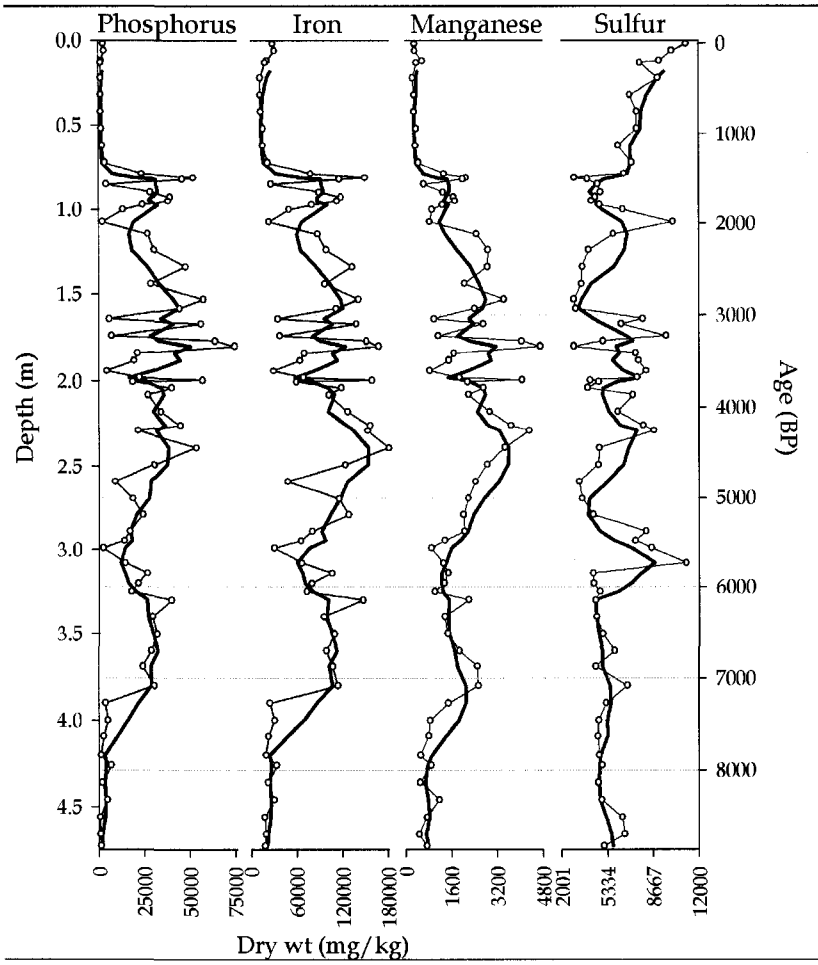


Figure 30. Redox sensitive elements in sediment geochemical profile with depth and age. Concentrations in mg/kg dry wt, solid line represent 4-period running mean, line and circle represents measured values.

The redox group elements (Fe, P, Mn) are present in low concentrations in the upper most and lower most portions of the sediment core (**Table 5** and ***Figure 30***). The concentrations increase substantially at 0.8 meters, with the highest concentrations of Fe, P, and Mn occurring where vivianite mineralization was identified from XRD and/ or visually observed (***Figure 27: 2, 3, 4***). Fe, Mn and P have the highest concentrations after human settlement in

the region (based on Ekdahl *et al.,* 2004), with peaks beginning ~1378 to 1392 BP, 2380 BP, 2741-2836 BP, 4945 to 5135 BP, 5800 BP, 6104 BP, and 6845 to 7054 BP. The highest concentrations in the sediment core occurred between 3197 to 3254 BP and 3710 to 4565 BP. Redox elements concentration declined substantially following peak periods, with the lowest concentrations occurring from 1183 to 1949 AD, 1012 BP, 7814 BP, and 8498 to 8821 BP. The S values vary from the other redox elements. In some cases the highest S concentrations occurred when Fe, P and Mn were at the lowest concentrations, for example sulfur concentrations were greatest over the last century (1753 to 2001.5 AD). S enrichment also occurs in 1867.5 BP, 3140 BP, 3520 BP, 4185 BP, and between 5515 to 5686 BP. Low S concentrations occurred between 1378.5 to 1392 BP, between 2380 to 2836 BP, 3254 BP, 3710 BP, and between 4755 to 4945 BP. Mn values are appreciably lower than Fe and P, and considering Mn is not a constituent of vivianite, it may have replaced some iron, as it is unlikely that vivianite was pure.

Table 5: Value ranges for Sediment Sections

	Depth (m)			
	0-0.78	0.79-2.49	2.5-3.8	3.9-4.75
Fe	12276- 31144	23450- 180741	30409- 146775	17621- 33575
Mn	258- 1348	651- 4709	892- 2552	469- 1501
P	1069- 23631	1971-74669	2183- 39860	559- 6754

The relationship between iron and manganese in lake sediments can indicate changes in lake chemistry and/or changes in catchment contribution of these elements by comparing the Fe/Mn ratio with Fe concentration (Mackereth, 1966). When eroded materials are the predominate source of Fe and Mn to the lake, the ratio resemble that of the bedrock, while deviation from the bedrock Fe/Mn ratio could result from redox mobilization and transport (Mackereth, 1966). Mn mobilized readily when redox conditions change in the lake compared to Fe, thus the Fe/Mn ratio would increase independently of Fe.

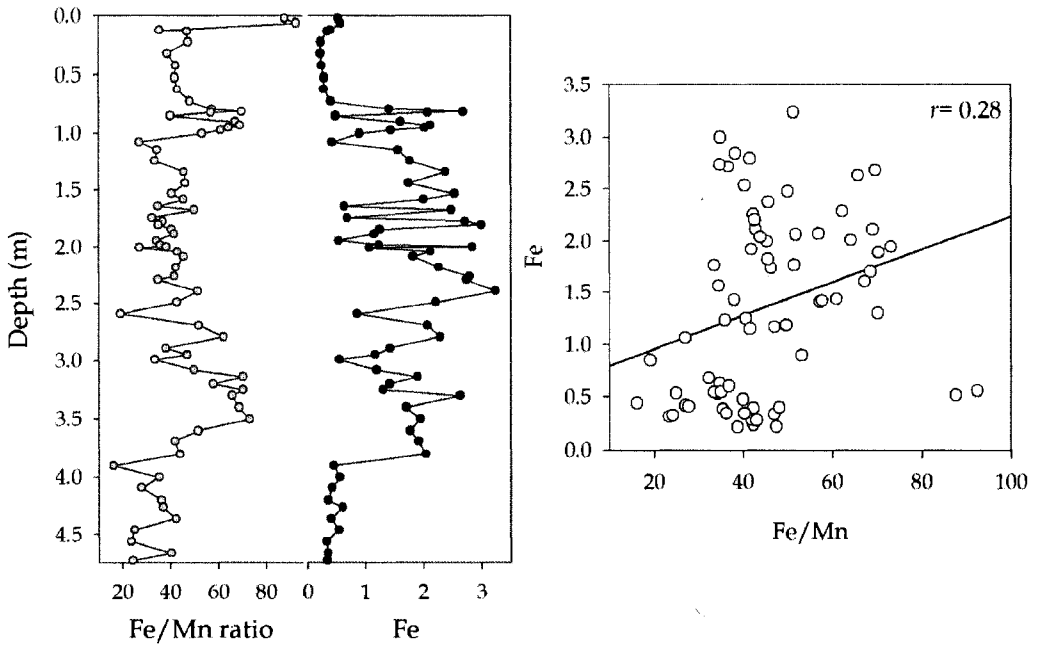


Figure 31. Molar Fe/Mn ratio vs. Fe concentration of sediments to elucidate whether the Fe and Mn concentrations co-vary based on watershed contributions of by redox fluctuations in Teapot Lake.

Teapot Lake Fe/Mn ratio peaks do not correspond well with peaks in iron concentrations, suggesting their concentrations in the sediment core were controlled by the redox conditions in lake waters during deposition (***Figure 31***). It is likely that these elements are derived from a similar source; however, their behaviour would be modified by lake chemistry. Based on this, the sediment record of Fe and Mn has potential use for reconstructing historical redox changes in Teapot Lake.

5.4 Allochthonous/ Clay Component

This group represents the allochthonous component of the sediments that were likely derived from weathered or eroded bedrock that was transported by wind or runoff into Teapot Lake, possibly when there was less vegetative cover in the drainage basin. These elements show good correlations amongst each other were likely derived from the same source and are often found in clay minerals. Cu does not correlated as well with all of these elements, but is included in this group as it is the best fit. The highest concentrations of Al, K, Mg, and Ti

occurred ~ 1930 AD, and again ~ 6000 BP (***Figure 32***). The lowest values occurred after 1930 AD until ~1250 BP and between 2600 to 3200 BP. Cu concentrations were highest between ~1753-1500 AD and 5325 to 5510 BP, while the lowest values occurred at 1450 BP and 3400 BP. All of the elements concentrations were lowest at 1.77 meters, or 3197 BP, which is the horizon with the highest Fe, P, Mn and vivianite concretions.

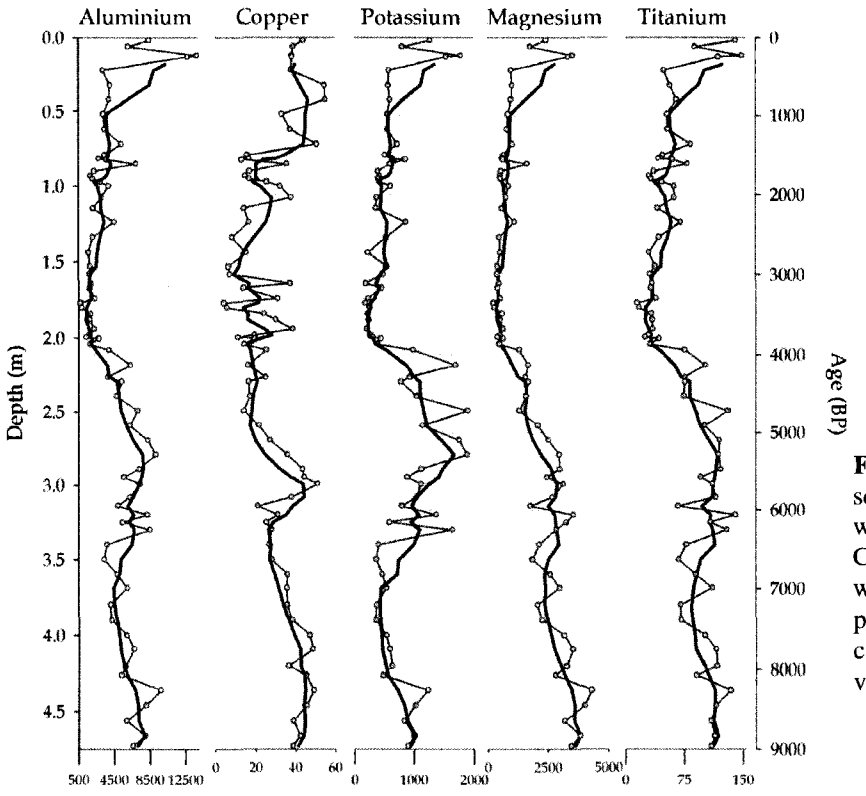
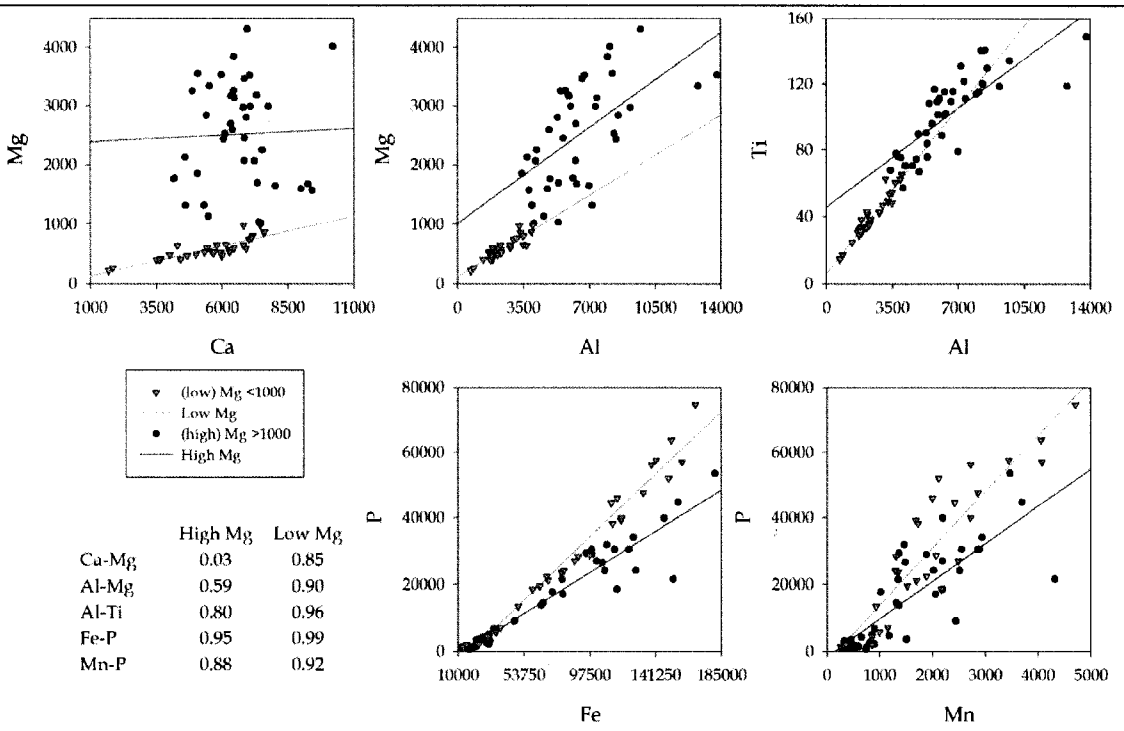


Figure 32. Clay elements in sediment geochemical profile with depth and age. Concentrations in mg/kg dry wt, solid line represent 4-period running mean, line and circle represents measured values.

The most interesting result is the relationship between Mg and Ca, where Mg values below 1000 mg/kg correlated strongly with Ca and Mg values >1000 mg/kg correlated very poorly. The relationships between other elements displays a similar change, where relevant elements become strongly correlated in the low Mg horizons and the correlations are reduced in the high Mg horizons between these same elements (***Figure 33***). The lowest Mg concentrations coincide with the lower Al and Ti concentrations, whereas the Fe, Mn and P values vary. This may indicate different sources of these elements, such that the clay elements and redox

elements have been transported and accumulated under different conditions. The low Mg sediments coincide with the vivianite bearing sediments, which may be indicative of dissolved ions being transported from weathered bedrock, tills or elsewhere in the watershed into Teapot Lake.



	High Mg	Low Mg
Ca-Mg	0.03	0.85
Al-Mg	0.59	0.90
Al-Ti	0.80	0.96
Fe-P	0.95	0.99
Mn-P	0.88	0.92

Figure 33. Correlations between low and high magnesium horizons and elements of interest. High Mg = >1000, Low Mg = <1000.

5.5 Other Elements

This group is poorly correlated with all other elements and show some weak correlations within the group. Ba, Zn, Sr and Na correlated with each, and Ca has the strongest correlation with Sr (***Figure 34***). Ca is the most relevant element towards this research as it forms apatite. It is negatively correlated with P (r= -0.53) and with Fe (r= -0.38), and the Ca/Fe ratio ranges from 0.848 to 0.015 indicating that the pH of porewaters is lower than 7.5 as demonstrated by Rosenqvist (1970). This also verifies that Ca is not affecting P, as apatite

stability requires a higher pH. The Na concentration is highest in the upper core likely due to road salt.

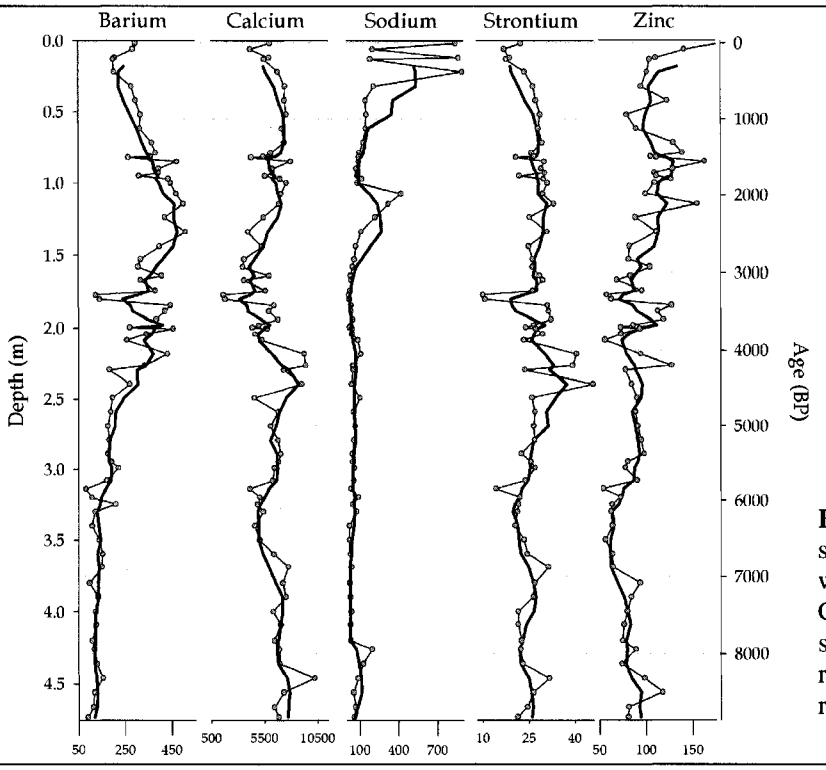


Figure 34. Other elements in sediment geochemical profile with depth and age. Concentrations in mg/kg dry wt, solid line represent 4-period running mean, line and circle represents measured values.

5.6 Organic Geochemistry

Organic matter in lakes can be authigenic, plants and aquatic vertebrates in the lake, or allogenic, leaves and soil materials from the shore area or transported into the lake by flooding, seasonal drainage patterns and groundwater. The organic materials derived from each source can be categorized by non-vascular plants as the authigenic component, rich in cellulose and have little carbon (i.e. phytoplankton and macrophytes in lakes,); and the allogenic component as vascular plants that are mainly terrestrial that such as grasses, shrubs and leaves and with fibrous tissue and correspondingly higher carbon contents than the former (Meyers & Lallier-Vergès, 1999; Meyers & Teranes, 2001). Human effluents can add to the organic matter of a lake and the increase of nutrient loading can limit natural processes and have implication on the diversity of aquatic organisms.

The C/N ratio is often used to indicate whether the source of OM in lake sediments is from terrestrial plants or aquatic organisms (Meyers & Teranes, 2001). Organic matter produced in different environments will have a distinctive C/N value and can be used to trace the origin, for example, whether from marine or terrestrial source, or from algae or C_3 plants (Herfort *et al.,* 2006). Lower C/N values (4-12) are values typical of phytoplankton and aquatic plants, values below 20 typically indicate a mix of terrestrial and aquatic materials, and vascular land plants (cellulose rich and protein poor) have C/N ratios of 20 or greater (Meyers & Lallier-Vergès, 1999; Wolfe *et al.,* 2001). The availability of nitrogen should be considered when interpreting of the C/N values as limited nitrogen can result in N-limited algae producing excess C/N values from normal phytoplankton organic materials (Healey & Hendzel, 1980). Additionally, %C and %N can be used to identify periods of increased biological activity by comparison with the presence of minerals in lake sediments. The %C has been used as an indicator of historical lake level (Jellison *et al.,* 1996), and is a factor in calculating sedimentation rates (Hodell & Schelske, 1998).

The stable isotopes $\delta^{13}C_{OM}$ and $\delta^{15}N_{OM}$ can be used to indentify sources of organic matter related to changes in the hydrological regime of a watershed, changes in primary productivity and climatic changes resulting in fluctuating lake levels (Meyers & Lallier-Vergès, 1999). Depleted $\delta^{13}C_{OM}$ may represent lower limnetic nutrient concentrations, while more enriched $\delta^{13}C_{OM}$ has been associated with higher nutrient content and/ or anthropogenic impact (Brenner *et al.,* 1999). Denitrification preferentially removes the lighter ^{14}N isotope, leaving the residual enriched in ^{15}N. Microorganisms dissolve nitrates in anoxic water and sediments, releasing $^{14}N_2$ and the remaining nitrates are enriched in ^{15}N (Cline & Kaplan, 1975). Microorganism denitrification can be used to observe recycling of heavier nitrogen

from the sediments. Shifts to lower $\delta^{15}N_{OM}$ values have been associated with eutrophication, where more nitrogen fixing cyanobacteria contribute depleted ^{15}N to the organic matter (Brenner *et al.,* 1999).

5.6.1 Organic Geochemistry Results

Plotting the C/N verse $\delta^{13}C_{OM}$ of sediment organic matter shows that Teapot Lake values are closest to lacustrine algae (***Figure 35***), and are similar to lake surface sediment values reported from around the world (Meyers & Lallier-Vergès, 1999). The C/N ratio of Teapot Lake sediments ranges from 9.7 to 13.2 (***Figure 35***), confirming that the lake sediment organic material is predominantly aquatic in origin.

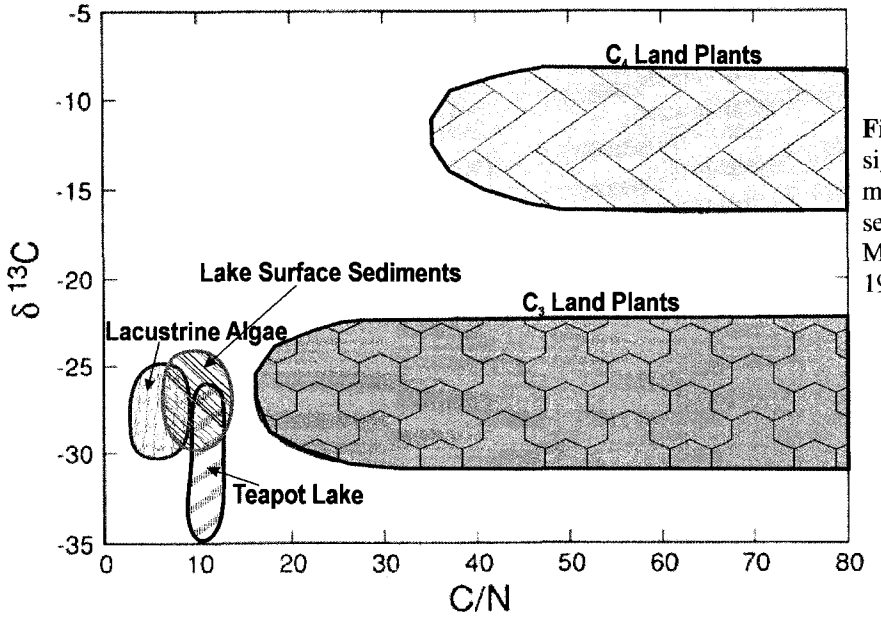


Figure 35. The C/N vs. $\delta^{13}C$ signature values of different materials contained in sediments. Modified from Meyers & Lallier-Vergès, 1999

The 11 lowest values of %C and %N in the sediment core, 8 occur when the vivianite/ redox related elements have the highest concentrations, at 2741 BP, 3007 BP, 3197 to 3254 BP, 3624.5 BP, 4185 to 4375 and 6107 BP. The other low values occur at 6009 BP and from 6674 to 6845 BP. The highest organic concentrations occurred from 1753 to 1373 AD, then

from 1012 to 1335 BP, 1449 BP, 1876.5 BP, 2950 BP and 3140 BP. The high OM values also correspond to the highest sulfur values and the lowest redox elements values.

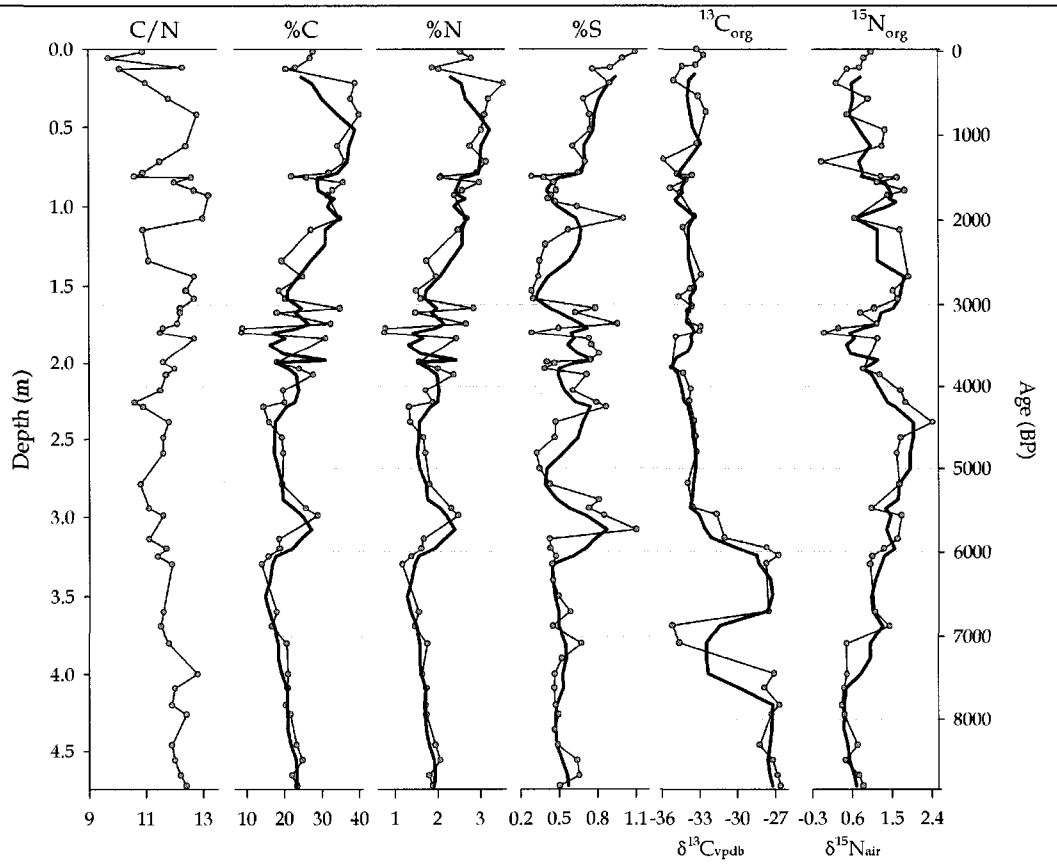


Figure 36. Organic Components of Teapot Lake Sediments. Concentrations in percent (%), and stable isotopes in permil (‰). Solid line represent 4-period running mean, line and circle represent measured values.

The stable isotopes of organic matter show different trends and correlate poorly (r= -0.28), however both $\delta^{13}C_{OM}$ and $\delta^{15}N_{OM}$ values were depleted in 1753 AD and 1202 BP. The $\delta^{13}C_{OM}$ was most depleted during 1378.5 BP, 1544 BP, 2836 BP, 3710 BP and 6845 BP, while the most enrich values occurred during 6009 BP, 6674 BP, 7434 to 7928 BP, and 8498 to 8821 BP. The $\delta^{15}N_{OM}$ was depleted from 3197 to 3254 BP, 7605 to 7928 BP, and at 8498 BP, and was enriched from 1544 BP, 2013.3 BP, 2570 BP, 3976 to 4565 BP, and 5515 BP.

The organic %Carbon (%C) and %Nitrogen (%N) correlated best together (R=0.97), and their concentration in the sediments represent, aquatic biomass production. Increased

aquatic productivity would heighten the amount of organic biomass within the lake and increased amounts of biomass would decay and sink into the sediments. This likely occurred in sediment horizons with high %C and %N (***Figure 36***).

Sulfur does not correlate perfectly with %C, suggesting that both organic and inorganic sulfur exist in the sediments. It can be assumed that organic sulfur is present in the sediments horizons where S concentration is similar the %C and %N and that inorganic sulfur dominates the horizons where its concentration departs from the %C and %N values.

6 Discussion

It is clear that Teapot Lake has an unusually high concentration of phosphorus in the lake water, particularly in the monimolimnion, and in the lake sediments deposited before human settlement. As discussed in the literature, there are several potential internal and external sources and transport mechanisms that shall be reviewed sequentially vis-à-vis data collected and physical landscape attributes. This chapter will look at the dynamics of iron and phosphorus in Teapot Lake sediments and conjecture the sources, why iron phosphate mineralization occurs in particular horizons, whether a limnological switch marked by inorganic and organic sediments occurred in Teapot Lake and identify the potential factors related to the system reversals.

The sediment horizons can be grouped into two categories based on visual observation and geochemical attributes. The first group, the inorganic sediments, are highly enriched in iron and phosphorus, have high manganese concentration and iron-phosphate minerals present. The second group, the organic sediments, are sulfur rich and have high organic carbon and nitrogen content. Each type of deposit would be produced and deposited under specific environmental and limnological conditions at the time of formation. Paleolimnological inferences can be made by identifying the unique factors involved in formation and determining the time period when the system switched from producing inorganic to organic sediments.

6.1 Sources of Iron and Phosphorus in Lake Sediments

Source of phosphorus in temperate lacustrine systems first depends on the mineralogical composition of bedrock and overburden and the land use practiced in the overall drainage basin. Phosphorus can enter an aquatic system through precipitation, dust in air, transported

with groundwater (soil particles sorbs phosphorus) and inputs from shore through surface runoff.

The most significant source of natural phosphorus is sedimentary phosphate deposits of phosphorite. Mechanical erosion and weathering of phosphate bearing minerals such as apatite [$Ca_5(PO_4)_3OH$], and related minerals (octocalciumphosphate, hydroxyapatite, fluorapatite, chlorapatite), as well as dissolution of iron phosphate minerals (strengite, vivianite, and variscite) will release lattice bound PO_4^{3-} into solution depending on the pH, Eh, DO. Earth materials transported by glacial advances and retreats deposits tills, moraines, eskers, etc., which develop into soils and act as a source of phosphorus as water percolates through these materials, thereby accumulating dissolved phosphorus complexes.

Phosphorus can be cycled within the lake by internal loading, sediment flux and biological availability. Lake sediments can be a source of phosphorus depending on the redox chemistry, dissolved oxygen concentration, existence of phosphate binding elements (Al, Ca, Fe) at the water-sediment interface, the level of sediment compaction and the general composition of sediments. Biological pathways of phosphorus regeneration are zooplankton and fish excretion. Lake sediments and particulate matter in lake water can also act as a source of phosphorus, where decaying and settled organic matter contribute to the total P (Malmaeus & Rydin, 2006).

Anthropogenic sources of phosphorus include untreated sewage, fertilizer, and detergent. The agricultural industry commonly adds phosphorus to soils in the form of inorganic phosphate or as organic phosphorus derived from confined animal-feeding operations manure (Smith *et al.,* 1998; Pope *et al.,* 2002). Long-term addition of phosphorus to soils has resulted in a build-up and the additional phosphorus is more likely to be transported by run-off than absorbed by plants (Sharply *et al.,* 1999). Studies conducted on

phosphorus in acidic soils concluded that inositol hexaphosphate, the main form of phosphorus stored in plant tissues, has a higher sorption capacity than inorganic phosphorus and even lowers the sorption of inorganic P due to the different number of PO_4^{3-} ester groups in organic molecules (Anderson *et al.,* 1974; Frossard *et al.,* 1989).

The red shale bedrock would contribute significant amounts of iron to the system and little to no phosphorus. Leaching of eroded materials in the Halton Till deposits may also contribute to the high iron horizons in Teapot Lake sediments. The bedrock is nearly barren of fossils (Karrow, 2005), however the Halton Tills that cover the region has limestone component and invertebrate remains and weathering of these materials would contribute inorganic phosphorus (P Gammon 2007, pers. comm.). The organic matter and swamp surrounding Teapot Lake may be a source of P, where precipitation percolates and leaches excess P from soils, which then enters the lake. Organic deposits of peat, muck, swamps and bogs are found in the Heart Lake Conservation Area and kettle lakes are found in close proximity to these deposits (***Figure 6***, Chapter 2). Phosphorus may be released from the organic deposits or from the sediment organics, migrating towards the iron rich sediments and eventually leading to mineral formation. However, local groundwater collected from the Teapot Lake and Heart Lake properties had lower concentration of P (0.019 to 0.039 mg/L), furthering the supposition that P is entering the lake directly rather than from an external source.

Groundwater measured from the Teapot Lake well has iron concentrations higher than ferric solubility, (0.24- 0.27 mg/L) therefore the majority of iron is ferrous iron as found in the lake water. The municipal wells located north of Brampton and Teapot Lake (Cheltenham, Caledon, Palgrave, Inglewood) have documented high iron and manganese in wells. The region on Peel, including Brampton, and northern cities mentioned above, sit on

Queenston red shales (Liberty & Caley, 1969), and the surficial deposits surrounding Teapot Lake are organic deposits of peat and "muck" (Karrow, 1991). Both would contribute large amounts of iron into the system, although the concentrations vary depending on depth of the water table, proximity to treatment facility and the season. The lower elevation of Teapot Lake with respect to the surrounding area would amplify the influence of groundwater, as the lake water is probably at the same level as the water table, particular during spring.

Biological productivity can be a significant factor contributing to internal phosphorus cycling. Plankton quickly remove inorganic phosphate from solution in the mixolimnion, which was observed by the loss of radioactive tracer ($^{32}PO_4$) from solution (Coffin *et al.*, 1949). Phosphate is then transferred as phosphorus into the monimolimnion as organisms die and decompose, releasing soluble inorganic phosphate (Hutchinson & Bowen, 1950; Whittaker, 1953; Rigler, 1956). Consequently as phosphorus becomes available in the photic zone (upper water column where light penetration allows photosynthesis), P will be removed during photosynthetic production of biomass and O_2 is consumed as biomass dies, sinks and decays (Stumm & Baccini, 1978).

Eq.8. $$106CO_2 + 16NO_3^- \quad HPO_4^{2-} + 122H_2O + 18H^+ \underset{R}{\overset{P}{\rightleftharpoons}} C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

Where P is photosynthesis and R is respiration.

This is due to endogenic cycling, where phosphorus assimilated during photosynthesis is released within a few days as biomass decays (Schwedt, 1996).

Nriagu, (1983) determined that the incongruent dissolution of fish bone was accompanied by secondary vivianite formation in sediments. Vivianite has been associated with archaeological studies, where it replaces apatite in human remains (Johanson, 1976; McGowan & Prangnell, 2006), with the sources of iron varying from underlying gneiss

bedrock, tools, coffins, etc (Pabst & Hofer, 1998). The phototrophic zone in Teapot Lake is limited to the upper 4 meters and the small surface area of the lake would not sustain a large population of higher aquatic organisms, therefore fish bones could not be a significant source of phosphorus.

The issue of lake sediments acting as a source or a sink for P has been discussed by many authors. The P in lake sediments has been used as a proxy of paleoproductivity; however P is more so linked to Fe than productivity in Teapot Lake. An increase in productively would result in high %C and %N values in sediments, and if P were related to these increases, its concentrations would inherently increase with the OM. Phosphorus concentrations are lower in the %C and %N rich horizons and is negatively correlated with both (r= -0.57 %C & r= -0.59 %N), demonstrating that it cannot used as an indicator of past productivity. Because P correlates highly with Fe, it is obvious that Fe is acting in concert with P in the sediment.

Phosphorus may be entering the lake from run-off carrying organic particles from the boggy surroundings during periods of high precipitation and snowmelt. The phosphorus would be consumed in the mixolimnion and/or sorbed onto Fe^{3+} molecules forming ferric phosphate compounds. As biomass dies and sinks the P is released, or as ferric precipitates gain mass they may sink and dissociate as ferric iron is reduced to ferrous below the redox transition boundary. However, bank erosion would be minimized by the dense vegetation and reeds on the shoreline, impeding erosion and retaining sediments within the littoral zone (Petticrew & Kalff, 1992).

6.2 Birds and Phosphorus

Another significant source of phosphorus is waterfowl excrement. Guano is the most notable source of phosphate derived from bat and marine bird faeces. The phosphate is mobilized as rainwater leaches it from faeces and is transported into porous bedrock where it reacts with silicates or carbonates to form aluminum, calcium or iron phosphate minerals (McLane, 1995).

A Canada Goose can consume up to four pounds of grass and defecate about three pounds of faeces per day, which can lead to nutrient loading, with reported values of 76% C, 4.4% N and 1.3% P in faeces (New Hampshire Department of Environmental Services, 2004). Goose faeces can act as a fertilizer, where phosphorus improves nitrogen acquisition and retention in plants (Güsewell *et al.,* 2003). Manny *et al* (1994) developed a nutrient load-response model to determine whether waterfowl degraded water quality in lakes and reservoirs. Their study determined that the highest monthly nutrient loading occurred in November and lowest in May, with an annual average of 76% of 4462 kg C, 280 kg N and 88 kg P of nutrients added by waterfowl to Wintergreen Lake. Of total nutrient loading, birds contributed 69% of all C, 27% of all N, and 70% of all P entering the lake. Bazely and Jefferies (1985) carried out experiments using plots of tidal flats where goose droppings were observed for seasonal relationships to nitrogen and biomass. The results demonstrated that increases in snow geese faeces enhanced above-ground biomass accumulation during the summer and the soluble nitrogen content of the faeces declined significantly from 31% after 2 hours and 62% after 30 hours that is associated with rapid water loss. They also found that nitrogen values ranged largely among individual droppings (1.60 to 4.14%). Though faeces can enhance plant growth, nitrogen is quickly removed by plants so little would be left to travel through the watershed (Bazely & Jefferies, 1985). The C/N ratio of surface sediments

was greater than 15 (Jefferies, unpublished) and nitrogen to phosphorus ratio in duck faeces was reported as 3.3:1 by atoms (Ryther & Dunstan, 1971).

Bird faeces seems the most likely source of phosphorus to the system. More than half of the total P loading occurs during migration (Portnoy & Soukup, 1990; Manny *et al.*, 1994), therefore, sharp increases in P may be linked to migration and thus identify how significant the impact of waterfowl is on Teapot Lake. The diet of waterfowl is particularly important in considering their impact on nutrient loading. Canadian geese presently in the Teapot Lake area likely graze in farmers fields, thus they would be consuming biomass lower in P than ducks feeding on fish (D Lean 2007, pers. comm.) and the nutrient addition would be proportional to the nutrient content of their food (Kear, 1963). It is important to note that the vivianite rich horizons were deposited far before agriculture activity took place in the region.

The presence of water foul on Teapot Lake has been observed during field sampling. During spring and fall 2006 water column sampling Canadian Geese were perched on the dock and fled to the open waters where they remained while water sampling was carried out. Another attempt to observe the number of waterfowl on Teapot Lake was made in early summer 2007 over a 3-hour period. No waterfowl were seen on this occasion, as it was not during their migratory period, or they may have been deterred by the temperature (30°C) if the area around Teapot Lake is used for roosting.

Faeces occurrence and quantity can be used to estimate the degree of water foul usage of the lake. During spring 2006 (April 13, 2006) a significant amount of droppings were observed on the floating dock; less faeces was observed during summer 2006 (August 2006); faeces was present in a dried out form during fall 2006 (October 14, 2007) and a small amount was observed on the floating dock and the shore dock on June 17, 2007. Based on these

observations, it can be assumed that the lake has higher waterfowl usages during periods of migration (spring and fall) and that warmer weather deters usage of the lake.

6.3 Iron Phosphate Formation from Lake Water to Sediments

The concept of coupled iron and phosphorus cycling suggests that under oxic conditions and neutral pH Fe^{3+}-oxyhydroxides can co-precipitate and/or sorb PO_4^{3-}, while the onset of anoxic leads to reductive dissolution of Fe^{3+} (Einsele, 1936a). Reduction of Fe^{3+} to soluble Fe^{2+} during lake stratification and meromixis will release Fe^{3+}-bound PO_4^{3-}, which can be marked by an increase in total iron concentrations below the redox boundary. This is occurring in Teapot Lake, where is absent or is near detection limits and it reaches the highest concentrations in the monimolimnion, with P concentration escalating into the monimolimnion. Iron phosphate minerals nearly reach saturation in the water column as strengite, ferric phosphate, and vivianite, ferrous phosphate. Both minerals are undersaturated because vivianite is unstable at the low pH of the monimolimnion where it is most likely to form; and strengite requires oxidizing conditions and iron that do not occur together in Teapot Lake. The kinetic processes of vivianite formation were not found to be limited to diffusion of iron and phosphorus as crystal growth rate of vivianite is slow, precipitating from 1-20 days from pore fluids (Emerson & Widmer, 1978), implying that under ideal geochemical conditions, vivianite could form within the upper sediments, but does not due to pH.

Based on the water column geochemistry and the lake sediment record, the input of P and Fe are incongruent at present, but may not have been in the past. Iron is likely derived from bedrock and transported by groundwater into the lake, while phosphorus concentration is presently very low in groundwater that is entering the lake.

This author propose that iron in Teapot Lake acts as a phosphorus trap, where ferrous iron ion transported by groundwater enter the lake, and sorb PO_4^{3-} ions released from decomposition of faecal matter, and decay of biomass settling from the upper water column of the lake. Modern lake water and recent lake sediments indicate that less PO_4^{3-} is available for vivianite formation and that less iron is being carried through the system than in the past. Thus, the present limnological conditions in Teapot Lake limit the stability of vivianite formation at the water-sediment interface and upper sediments. Looking at ***Figure 37***, it is apparent that the upper sediments representing present day to ~1370 BP and the lower sediments representing ~7500 to 8900 BP have low Fe and P and higher values of in the organic component. The current environmental conditions during these periods could have been similar; at present aquatic productivity is moderately high in the mixolimnion and the surrounding landscape is covered by marsh type vegetation.

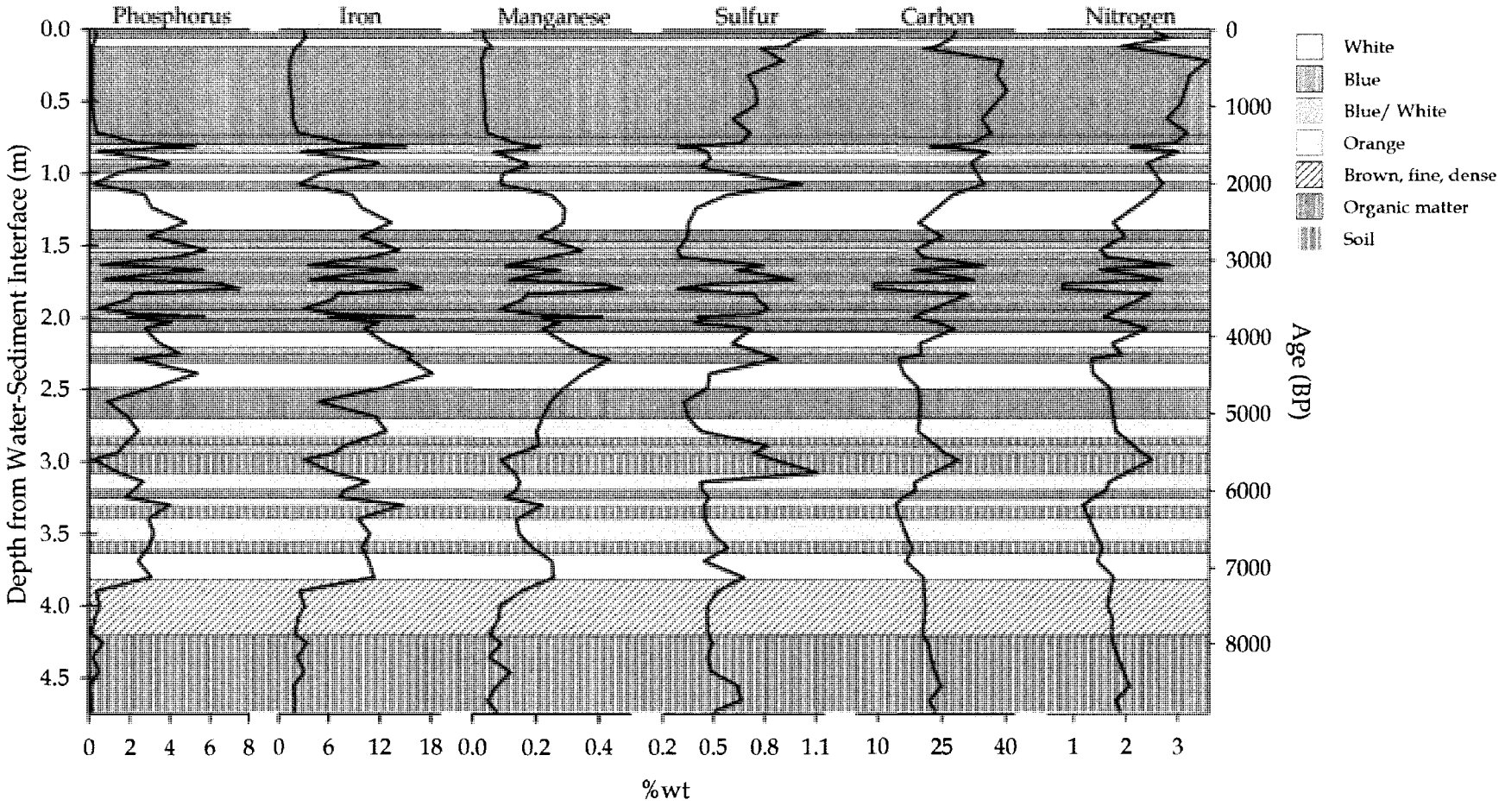


Figure 37. Sediment horizons and geochemistry of interest.

6.4 Post-Glacial Lake Sediment Record

Subsequent to the retreat of the Laurentide Ice Sheet, exposed land/ bedrock surfaces would have been more susceptible to weathering and erosion that would stimulate transport of iron oxides. The retreating ice sheet would release the sediment load held within the ice as it melted, producing till blanks, moraines, kettle holes and eskers. The Brampton esker was deposited before the last ice advance (Halton), possibly during the last ice retreat (Newmarket) and since Teapot Lake is deeper than the Halton Till cap (2-5 meters), is has been proposed that ice blocks that resulted in kettle lakes were enclosed in the esker sediment during stagnation and ablation (Harrison & Saunderson, 1977; Karrow, 2005). Over time, water percolating through these deposits would have transported dissolved ions in groundwater.

A postglacial climate record for Brampton was described by Edwards and Fritz (1986) inferred from stable isotopes of wood cellulose. They identified four climatic zones, ~12,500 to 8500 BP was cold and very dry; 7400 to 6000 BP was warm and dry; 6000 to 3000 BP was warm, very moist and had mean annual temperatures of ~10°C; and 3500 to present is cool and moist.

Figure 37 illustrates the sediment type and the geochemistry, where the blue, white and beige horizons are presumed to be mineralized sediments and the other horizons are primarily organic matter. Fe, Mn and P all increase within the mineral horizons and decrease in the organic horizons. From ~2500 to 7000 BP, the majority of Fe, P and Mn increases occurred, and iron phosphate minerals are present in the sediments. Hypsithermal conditions from 3000 to 7400 BP fostered warmer temperatures than present (Wright, 1976; Harrison & Metcalfe, 1985; Edwards & Fritz, 1986), which corresponds to an abrupt increase in Fe, P

and Mn concentrations and mineralization in the sediments begins to appear (***Figure 37***). As the climate moved from glacial to post-glacial, warmer conditions would enhance the reactions between till and groundwater, which may be observed by increased ion concentrations in the lake sediments. This is also replicated in the allochthonous/clay elements (***Figure 32***), where their concentrations increased from 4000 to 7000 BP. Reducing conditions in the catchment soils would increase mobility and solutional transport of Fe and Mn into the lake through groundwater (Pennington *et al.*, 1972). The warmer conditions would also encourage longer residence times of migratory birds on the lake, initiating nutrient, specifically P, addition to the system through faeces. These conditions would presumably lead to vivianite mineralization in the upper sediments.

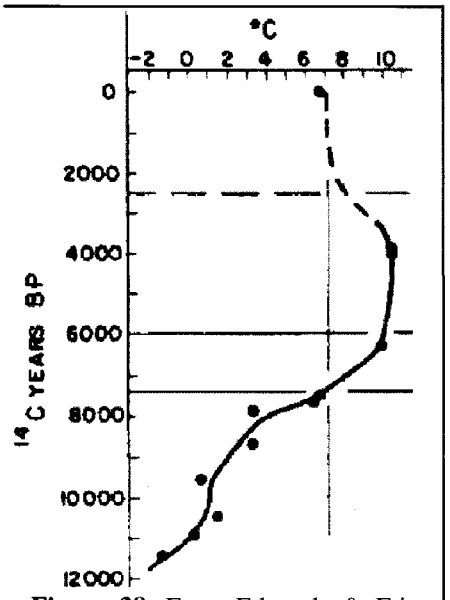


Figure 38. From Edwards & Fritz (1986). Temperature reconstruction for Brampton based on $\delta^{18}O$ from wood cellulose.

The system changed towards higher organic contents in the sediments around 1500 BP, where %C, %N and S concentrations begin to increase and the Fe, Mn and P suddenly plunge. A shift towards cooler climate (**Figure 38**) and longer winters would limit the flux of subsurface waters (Digerfeldt, 1972) and potentially cut of Teapot Lake from receiving dissolved ions from groundwater. Climatic stability during this period is implied as the organic and redox components show less fluctuation compared to earlier periods.

Changes in the hydrological system may have occur at some point and can be observed from air photos, where paleo-riverbeds may have connected Teapot Lake to a larger river system (***Figure 39***). Surface water flow-through before 1500 BP would assist in explaining the

massive increase in Fe and P concentrations, the onset of iron phosphate mineralization and the higher degree of fluctuations of elemental concentrations in the sediments. Oscillations in climate leading to periodic drought would affect surface water; lowering lake levels and allowing dissolved ions to precipitate from solution as they became more concentrated. However, the sedimentological record in Teapot Lake disagrees with the idea of past through flow because no clastic materials were found in the sediments (T Patterson 2008, pers. comm.).

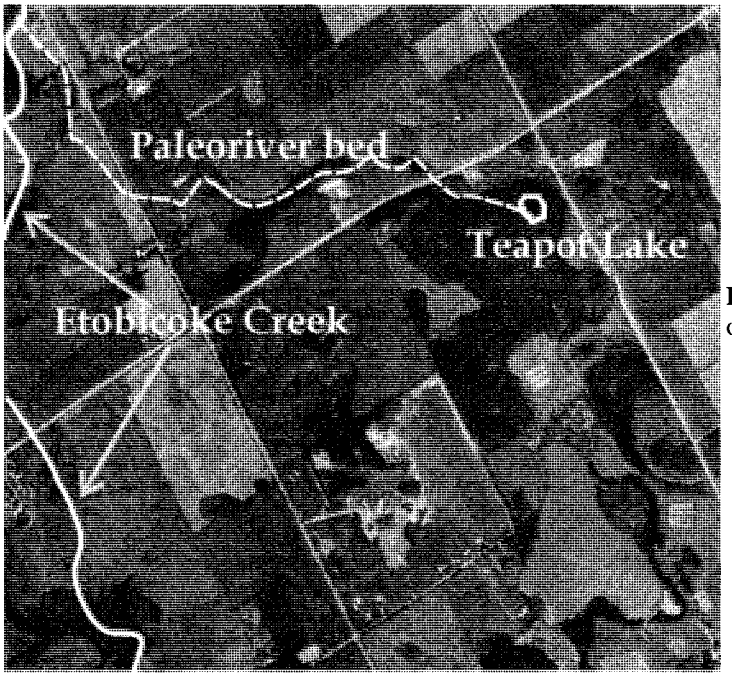


Figure 39. Air photo and interpretation of old riverbed

A pollen record from Crawford Lake found well-preserved Canada Geese faecal pellets in sediments from 1331 and 1520 AD, while P concentrations in Teapot Lake remained low during these periods (McAndrews & Turton, 2007). The Crawford Lake sediment cores show intact faeces that are surrounding by seemingly undisturbed laminations, which are unlike the Teapot Lake sediments. If faeces were the source of P in Teapot Lake, it would have accumulated away from the lake and the dissolved nutrients would have been subsequently transported through the lake and deposited into the lake sediments.

Conversely, faeces deposited directly into the lake may have decomposed at a faster rate or was completed replaced by vivianite.

Fe and Mn become mobile once reduced in the upper sediments, and have been found to diffuse from lower sediments towards the water-sediment interface to precipitate in oxidized surface sediments (Engstrom & Wright, 1984; Carignan & Flett, 1981). The Fe and Mn do not conform to this type of redox drive diffusion, as reducing conditions dominate the monimolimnion, allowing these elements to remain mobile. The Fe and Mn in the sediments advocate against redox diffusion as well, where concentrations become substantive beginning ~ 1500 BP or 0.8 meters from the sediment-water interface. Sulfur concentration reaches its highest value within the upper sediment core where the other redox sensitive elements are in very low concentration relative to the rest of the core. Pyrite formation in at this depth illustrates strongly reducing sediments, yet the Fe and Mn do not appear to be diffusing towards this section of the sediments. Moreover, the previous chapter demonstrated the relationship between Fe and Mn in the sediments is linked to redox rather than fluctuations in watershed contributions, but the watershed must be affecting the redox relationship since Fe and Mn do not respond to the redox conditions in the upper sediments.

7 Conclusion

Teapot Lake demonstrates a classic state of meromixis. The permanently stratified water column allows mixing and atmospheric exchange in the upper four meters, best exemplified by the evaporative enrichment of $\delta^{18}O$ in the mixolimnion compared to regional precipitation. The aqueous geochemistry in the monimolimnion below the thermocline and at the redox transition boundary differs substantially from the mixolimnion, with low DO, increase concentrations of Fe, P, Mn, DIC and CH_4, as well as depleted $\delta^{18}O$ reflecting groundwater values.

It has been established that the redox potential and concentration of dissolved oxygen controls the speciation of iron in lake waters and that Fe^{3+} absorbs PO_4^{3-} under oxidizing conditions, while under anoxic conditions Fe^{3+} is reduced to Fe^{2+}. Subsequently, phosphate is dissolved and released into the water column. As mentioned in previous sections, dissolved oxygen is likely absent below 5 meters and iron is likely present at Fe^{2+}. Based on Wat4 calculations, strengite is supersaturated in the lower water column although Fe^{3+} should not be present due to lack of O_2. Vivianite is extremely undersaturated above the redox boundary due to oxidizing conditions and below 5 meters vivianite rapidly approaches saturation, although it saturation is not reached. The pH controls the saturation of vivianite and strengite in the water column, while Eh influences the saturation to a lesser degree.

The geochemistry of inorganic phosphorus is interesting in that iron is likely controlling its migration from the lake water column into the lake sediments. Vivianite is close to saturation and strengite is least saturated near the water-sediment interface. The acidic pH prevents vivianite from reaching saturation and strengite cannot precipitate because O_2 was input into Wat4 as 0 when <0.5 mg/L Do was measured so Fe^{3+} does not

occur. Phosphorus and iron are negatively correlated with pH (seasonal average P r= -0.60 and Fe r= -0.73), furthering the presumption that pH is a significant factor in controlling the formation of iron phosphates in the lake water.

Iron and manganese originating from reduction of hematite in the Queenston Formation shales are transported by groundwater into Teapot Lake, which settle into the sediments. Phosphorus enters at the surface of the lake from faeces and is fixed by biomass in the mixolimnion. Decomposition of organic matter releases phosphorus into the monimolimnion and will diffuse towards the Fe rich sediment horizons to form vivianite, thus trapping the P in Teapot Lake sediments. The Fe/Mn peaks occurring in the upper core (0.81-1.34 meters depth/ ~1600-2600 BP) correspond to Fe and P peaks, furthering the hypothesis that sediment phosphorus concentrations are controlled by iron as well as manganese in the sediments. The fluctuating P values in the sediments demonstrate that the trapping mechanism was discontinuous over the Holocene.

Phosphorus entering the system was exceedingly high in the past, with ≥2.4% P beginning ~1335 BP, suggesting that anthropogenic sources of P are negligible compared to natural sources. Although the actual source of P cannot be quantitatively identified in this thesis, water foul faeces is likely the largest source of nutrients entering the system as the contribution would have varied with residence time and migratory patterns. Fossilized organic remains and apatite fragments in the Halton Till blanket within the Teapot Lake region may have contributed additional P through dissolution and groundwater transport.

This thesis has observed the behaviour of phosphorus and its interactions with iron and organic matter in lake water and lake sediments. There is evidence that the mineralization of iron phosphate in Teapot Lake sediments responds to changes in climate, as formation occurred during the warmer hypothermal and ended ~1500 BP. However, it is

difficult to resolve this relationship given the scope of this thesis. Further research on the $\delta^{18}O$ of PO_4^{3-} in the vivianite rich sediments, on the paleohydrology of the region and consistent groundwater monitoring would greatly assist in resolving these unknowns. Additionally, greater emphasis on the chemistry of water foul faeces and monitoring would assist in identifying sources of phosphorus.

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Appendix

Temperature Profile

Depth (m)	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.1	23.70	12.06	27.38	13.72
1	23.53	9.23	26.79	13.39
2	18.12	5.81	22.79	13.32
3	9.85	3.77	13.65	13.28
4	5.90	3.54	7.02	11.44
5	4.41	3.40	4.78	7.33
6	3.98	3.39	4.05	5.24
7	3.96	3.43	2.53	4.5
8	4.17	3.72	3.94	4.29
9	4.42	4.17	4.15	4.32
10	4.71	4.35	4.4	4.5
11	5.00		4.73	4.77
12	5.12		4.97	5.02
12.3				5.06
Average	*8.99*	*5.17*	*10.09*	*7.87*

Dissolved Oxygen (mg/L) Profile

Depth (m)	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.1	6.82	9.11	5.5	7.2
1	6.80	9.67	6.25	6.7
2	18.20	1.15	4.8	6.09
3	0.82	0.57	4.82	5.91
4	0.62	0.40	1.67	0.67
5	0.46	0.32	0.56	0.47
6	0.34	0.31	0.51	0.47
7	0.27	0.30	0	0.41
8	0.23	0.30	0.46	0.42
9	0.21	0.39	0.48	0.44
10	0.20	0.52	0.44	0.46
11	0.35		0.44	0.47
12	0.33		0.47	0.5
12.3				0.53
Average	*2.74*	*2.09*	*2.03*	*2.20*

Redox and Eh (Volts) Seasonal Water Column Profile

	Redox				Eh			
Depth (m)	Summer 2005	Spring 2006	Summer 2006	Fall 2006	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.1	0.578	0.316	0.223	0.360	0.782	0.527	0.423	0.569
1	0.570	0.313	0.289	0.351	0.774	0.526	0.491	0.562
2	0.358	0.313	0.344	0.339	0.566	0.529	0.548	0.550
3	0.060	0.222	0.365	0.338	0.273	0.440	0.576	0.549
4	-0.004	-0.064	0.240	0.233	0.212	0.154	0.455	0.446
5	-0.054	-0.085	0.069	0.045	0.162	0.133	0.285	0.260
6	-0.069	-0.087	0.045	0.044	0.149	0.131	0.261	0.260
7	-0.068	-0.088	0.036	0.043	0.150	0.130	0.254	0.259
8	-0.048	-0.082	0.039	0.040	0.168	0.136	0.257	0.256
9	-0.055	-0.074	0.051	0.039	0.161	0.142	0.267	0.255
10	-0.055	-0.073	0.051	0.037	0.161	0.143	0.267	0.253
11	-0.055		0.052	0.027	0.161		0.268	0.243
12	-0.057		0.046	0.012	0.160		0.262	0.228
12.3				0.009				0.225
Average	*0.085*	*0.056*	*0.142*	*0.137*	*0.298*	*0.272*	*0.355*	*0.351*

Teapot Lake water *pe* and Eh_{Fe}

$pe = \log K\ (a\mathrm{Fe(OH)_3}/a\mathrm{Fe^{2+}}) + 3\mathrm{pH}$ | $Eh_{Fe} = 0.059\ pe$

Depth (m)	Summer 2005	Summer 2006	Fall 2006	Depth (m)	Summer 2005	Summer 2006	Fall 2006
1			8.32	1			0.491
2		8.48	8.13	2		0.501	0.480
3		8.22	8.10	3		0.485	0.478
4	3.79	5.53	6.45	4	0.224	0.326	0.380
5	3.95	3.88	5.02	5	0.233	0.229	0.296
6	4.27	3.99	4.94	6	0.252	0.235	0.291
7	4.57	4.04	4.92	7	0.269	0.238	0.290
8	5.17	4.20	4.96	8	0.305	0.248	0.293
9	5.04	4.34	5.08	9	0.297	0.256	0.300
10	5.09	4.47	4.96	10	0.300	0.264	0.293
11	5.15	4.70	4.76	11	0.304	0.277	0.281
12	4.69		5.03	12	0.277		0.297
12.3			4.78	12.3			0.282

pH Profile

Depth (m)	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.1	8.23	7.60	6.33	6.53
1	8.13	7.63	7.43	6.62
2	9.16	7.62	7.3	6.73
3	6.85	7.49	6.93	6.74
4	6.57	7.26	6.66	6.46
5	6.41	7.10	6.45	6.16
6	6.22	7.08	6.34	6.02
7	6.07	7.07	6.28	5.97
8	5.84	7.04	6.2	5.9
9	5.70	6.94	6.07	5.8
10	5.59	6.88	5.92	5.73
11	5.56		5.81	5.72
12	5.57		5.78	5.76
12.3				5.77
Average	*6.61*	*7.25*	*6.42*	*6.14*

Conductivity Seasonal Profile

Depth (m)	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.1	320	279	266	277
1	319	282	269	276
2	334	322	290	276
3	348	35	300	276
4	348	340	306	311
5	358	348	310	313
6	378	353	313	325
7	399	362	381	339
8	488	410	375	374
9	592	516	464	456
10	793	557	570	577
11	1132		865	819
12	1239		1150	1100
12.3				1121
Average	*542*	*346*	*451*	*489*

Teapot Well and Local Precipitation $\delta^{18}O$ and δD

	δD‰	$\delta^{18}O$‰
Egbert Precipitation	-72.4	-10.6
Teapot Well	-78.5	-10.9

Station	Latitude	Longitude	MASL
Egbert	44.23	-79.77	224

Teapot Lake Seasonal $\delta^{18}O$ and δD

$\delta^{18}O_{H2O}$	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.5		-6.53		
1	-4.36	-6.61	-4.58	-4.76
2	-4.94	-6.70	-5.17	-4.83
3	-5.87	-6.30	-5.82	-4.81
4	-6.14	-6.18	-6.03	-4.83
5	-6.26	-6.30	-6.09	-6.04
6	-6.40	-6.36	-6.21	-6.16
7	-6.64	-6.35	-6.32	-6.25
8	-6.48	-6.49	-6.35	-6.32
9	-6.63	-6.74	-6.53	-6.47
10	-6.82		-6.74	-6.61
11	-7.29		-6.74	-6.90
12	-7.35			-7.27

δD_{H2O}	Summer 2005	Spring 2006	Summer 2006	Fall 2006
0.5		-48.20		
1	-50.90	-50.40	-51.50	-53.64
2	-50.70	-48.50	-43.50	-55.75
3	-55.30	-48.10	-43.50	-53.86
4	-57.70	-50.80	-47.60	-51.56
5	-58.00	-50.45	-46.60	-51.81
6	-58.80	-47.30	-49.15	-54.72
7	-61.00	-49.60	-54.10	-55.82
8	-59.30	-46.20	-43.00	-57.44
9	-59.20	-47.30	-52.50	-55.01
10	-59.60		-52.60	-57.45
11	-61.70		-53.30	-57.95
12	-61.80			-63.70

Wat4 Test Results

Phosphorus	Ferrihydrite	Strengite	Vivianite
0	0.42		
0.00001	0.42	-5.35	-12.56
0.005	0.42	-2.65	-7.16
0.5	0.42	-0.65	-3.17
1	0.42	-0.35	-2.57

Iron	Ferrihydrite	Strengite	Vivianite
0			
0.00001	-3.93	-5.22	-16.66
0.005	-1.23	-2.52	-8.56
0.5	0.77	-0.53	-2.57
1	1.07	-0.23	-1.68

Redox	Ferrihydrite	Strengite	Vivianite
-0.2	-5.73	-6.51	-0.64
-0.1	-3.95	-4.73	-0.64
0.005	-2.09	-2.86	-0.64
0.1	-0.39	-1.17	-0.64
0.2	1.38	0.61	-0.65
0.3	2.99	2.22	-1.16
0.6	3.46	2.70	-15.75
0.7	3.46	2.70	-21.09
0.8	3.46	2.70	-26.43
0.9	3.46	2.70	-31.76

pH	Strengite	Vivianite
	Eh -0.1 V	
4	-9.67	-10.01
5	-7.67	-6.02
6	-5.71	-2.08
7	-3.94	1.45
9	-1.70	5.87
	Eh 0.1 V	
4	-6.11	-10.01
5	-4.12	-6.02
6	-2.15	-2.08
7	-0.38	1.45
9	0.01	0.28

TRCA Well Geochemistry

Station	samples	Dates	Watershed	Lat	Long	Well depth ft	Fe	SO_4	pH	DO mg/L	Redox V	PO_4	TP
Mono Mills	5	2004-2006	Humber	-79.97	43.95	-	0.014	3.94	7.65			0.007	0.136
Nobleton W-60	3	2003-2006	Humber	-79.61	43.93	60.5	0.562	26.03	7.87			0.011	0.034
Nobleton W-61	4	2003-2006	Humber	-79.61	43.93	192.6	0.735	0.22	7.84			0.410	0.596
Old Church	4	2004	Humber	-79.83	43.91	-	20.02		5.89			0.371	2.293
Caledon East	5	2003-2005	Humber	-79.87	43.87	-	0.287	19.03	7.94			0.013	2.717
Bolton	4	2004	Humber	-79.76	43.88	-	0.376		7.98			0.014	0.025
Kortright	3	2003-2004	Humber	-79.59	43.83	36.0	0.032	45.80	7.73			0.013	0.010
Goreway	5	2004-2006	Humber	-79.70	43.77	-	0.038	12.78	7.91			0.011	0.040
Teapot	5	2007	Etobicoke	-79.80	43.75	-	0.252	57.63	7.24	6.7	0.182		0.039
Heart W-21	4	2004-2005	Etobicoke	-79.79	43.74	26.1	2.739		8.09				0.019
Heart W-366	5	2003-2004	Etobicoke	-79.79	43.74	-	0.052	26.50	7.32				0.025

Fe, SO_4, PO_4 and Total P (TP) in ppm

Teapot Lake Phosphorus

	Summer 2005	Summer 2006	Fall 2006
1	0.0141	0.0212	0.0339
2	0.0188*	0.0147	0.0290
3	0.0500	0.0154	0.0291
4	0.1170	0.0200	0.0251
5	0.0461	0.0239	0.0261
6		0.0210	0.0715
7	0.0369	0.0208	0.0505
8	0.1885	0.0286	0.0541
9	0.4620	0.1366	0.2693
10	1.0679	0.8960	1.1960
11		1.0393	1.4099
12			1.3117
12.3			1.7918

Lake Average	0.319
Mixolimnion	0.032
Upper monimolimnion	0.103
Lower monimolimnion	1.245

Values are in mg/l. All summer 2005 values are total phosphorus, with one exception indicated (*) as dissolved phosphorus. Summer and fall 2006 values are dissolved phosphorus.

Teapot Lake Trace Metals

values in ppm

	Depth	Ba	Ca	Fe	K	Mg	Mn	Na	TS	SO4	Si
Summer 2005	1		29		3.0	5.2		31	1.30	3.22	1.0
	2		29		3.0	4.9		30	1.12	3.06	1.1
	3		29		3.0	5.0	0.09	31	<1.0	2.33	1.7
	4		29	0.21	3.2	5.0	0.56	32	<1.0	1.56	1.9
	5		30	0.42	3.4	5.2	0.51	33	<1.0	1.29	2.0
	6		30	0.67	3.3	5.1	0.40	33	<1.0	1.08	2.0
	7		31	1.00	3.5	5.3	0.38	35	<1.0	1.51	2.7
	8		32	1.22	3.8	5.5	0.19	35	<1.0	1.46	4.9
	9		34	4.34	4.4	5.7	0.63	33	<1.0		9.4
	10		38	8.30	7.0	6.7	0.87	24	<1.0		19.2
	11		36	8.91	4.7	5.9	0.74	31	<1.0		12.2
	12		43	24.60	7.9	7.4	1.24	20	1.12		21.1
Spring 2006	0.1	0.187	22	0.03	2.2	3.7	0.05		1.23		1.6
	1	0.201	19	0.03	2.0	3.4	0.07		1.96		2.0
	2	0.280	23	0.34	2.6	4.0	0.25		1.36		3.9
	3	0.016	28	0.28	2.7	4.9	0.31		1.21		1.9
	4	0.274	24	0.29	2.7	4.3	0.27		1.50		3.6
	5	0.015	29	0.43	2.8	5.0	0.30		1.03		2.1
	6	0.194	23	0.37	2.3	4.0	0.25		2.22		3.0
	7	0.014	28	0.53	2.7	4.7	0.30		0.85		2.2
	8	0.018	30	1.11	2.9	4.9	0.39		0.99		3.5

	9	0.015	30	0.50	2.8	5.0	0.31		0.92	2.2
Summer 2006	1	0.010	25		2.4	4.7		27	1.11	0.6
	2	0.012	27	0.01	2.6	4.9	0.01	28	0.99	1.1
	3	0.016	29	0.03	2.8	5.1	0.31	29	0.87	1.8
	4	0.018	29	0.07	2.9	5.1	0.53	29	0.88	2.1
	5	0.018	30	0.36	3.0	5.2	0.56	30	0.93	2.2
	6	0.017	30	0.58	3.0	5.2	0.47	30	0.67	2.2
	7	0.016	30	0.78	3.0	5.3	0.36	30	0.61	2.4
	8	0.018	31	0.93	3.1	5.3	0.35	31	0.64	2.9
	9	0.023	32	1.66	3.4	5.4	0.40	32	0.66	4.7
	10	0.036	33	3.44	4.0	5.6	0.56	32	0.62	7.8
	11	0.041	34	4.44	4.5	5.7	0.67	30	0.59	11.4
Fall 2006	1	0.011	24	0.02	2.6	4.5	0.02	34	1.18	1.3
	2	0.012	26	0.01	2.6	4.8	0.03	28	1.04	1.1
	3	0.011	26	0.01	2.6	4.8	0.03	28	1.01	1.2
	4	0.011	26	0.01	2.6	4.8	0.03	27	1.00	1.1
	5	0.023	31	0.18	3.2	5.2	1.05	29	0.95	2.5
	6	0.019	31	0.58	3.0	5.3	0.58	29	0.81	2.6
	7	0.018	31	0.84	3.1	5.4	0.44	30	0.70	2.9
	8	0.019	31	1.25	3.2	5.4	0.42	30	0.63	3.4
	9	0.024	32	1.91	3.5	5.4	0.48	31	0.64	5.0
	10	0.038	33	4.14	3.9	5.6	0.63	31	0.62	8.6
	11	0.058	35	7.17	4.6	5.9	0.78	28	0.66	12.8
	12	0.014	36	2.95	6.3	6.5	0.91	22	0.61	18.0
	12.3	0.032	37	4.68	7.3	7.0	1.01	19	0.75	20.5

Saturation Index from Wat4 using Eh and Eh_{Fe}

	Summer 2005				Summer 2006				Fall 2006			
	Vivianite		Strengite		Vivianite		Strengite		Vivianite		Strengite	
Depth	Eh_{Fe}	Eh	Eh_{Fe}	Eh	Eh_{Fe}	Eh	Eh_{Fe}	Eh	Eh_{Fe}	Eh	Eh_{Fe}	Eh
1									-17.2	-20.9	-0.41	-0.41
2					-23.6	-26.0	-2.12	-2.12	-17.4	-21.1	-0.65	-0.65
3					-18.3	-23.1	-0.83	-0.83	-17.4	-21.1	-0.65	-0.65
4					-9.0	-13.4	-0.72	0.11	-12.1	-14.8	-0.81	-0.55
5	-6.2	-6.2	-1.46	-1.67	-7.2	-7.2	-2.03	-1.01	-9.0	-9.0	-1.52	-2.18
6	-6.6	-6.6	-1.71	-3.00	-7.1	-7.1	-1.97	-1.50	-7.2	-7.2	-0.98	-1.55
7	-6.9	-6.9	-1.39	-3.56	-6.9	-6.9	-1.95	-1.66	-7.2	-7.2	-1.10	-1.67
8	-6.1	-6.1	-0.39	-2.88	-6.7	-6.7	-1.67	-1.50	-6.9	-6.9	-1.00	-1.67
9	-4.3	-4.3	0.13	-2.34	-5.1	-5.1	-0.83	-0.64	-5.3	-5.3	-0.19	-1.00
10	-2.7	-2.7	0.84	-1.68	-3.1	-3.1	0.16	0.21	-3.3	-3.3	0.52	-0.20
11	-3.2	-3.2	0.62	-1.97	-3.1	-3.1	0.36	0.19	-2.5	-2.5	0.58	-0.10
12	-1.3	-1.3	0.86	-1.26					-3.6	-3.6	0.55	-0.70
12.3									-2.6	-2.6	0.65	-0.39

Lake Sediment Bulk Geochemistry

	Ppm	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Sr	Ti	Zn
Detection Limit #1		*0.007*	*0.000*	*0.011*	*0.001*	*0.007*	*0.016*	*0.001*	*0.001*	*0.009*	*0.030*	*0.030*	*0.000*	*0.001*	*0.042*
6/26/2006	**Blank 2**	**0.007**	**0.001**	**0.010**	**0.000**	**0.075**	**0.005**	**0.003**	**0.000**	**0.013**	**0.017**	**0.083**	**0.000**	**0.000**	**0.014**
6/26/2006	14	16.2	1.2	19.1	0.0595	514	3.8	2.8	8.9	0.420	204	17	0.1	0.3	0.5
6/26/2006	24	9.7	2.3	18.2	0.0380	604	2.4	2.2	13.0	0.509	217	16	0.1	0.2	0.5
6/26/2006	26	8.0	1.4	15.8	0.0290	611	2.3	1.8	14.9	0.258	249	13	0.1	0.2	0.4
6/26/2006	27	8.2	1.4	15.9	0.0335	509	2.2	1.8	11.0	0.207	202	14	0.1	0.1	0.5
6/26/2006	29	7.8	1.4	16.3	0.0630	622	2.0	1.8	12.2	0.173	252	28	0.1	0.1	0.3
6/26/2006	31	3.1	0.6	7.5	0.0185	672	0.8	1.0	18.0	0.077	283	22	0.0	0.1	0.3
6/26/2006	31-dup	3.9	0.7	9.3	0.0245	799	1.1	1.2	22.8	0.114	352	28	0.1	0.1	0.3
6/26/2006	32	3.9	0.6	8.3	0.0260	760	1.1	1.2	21.4	0.095	339	13	0.0	0.1	0.3
6/26/2006	41	28.5	1.9	41.7	0.0735	570	7.6	7.5	13.3	0.487	154	27	0.2	0.5	0.4
6/26/2006	45	32.0	0.9	20.6	0.0635	553	8.5	5.9	12.8	0.453	136	21	0.1	0.6	0.4
Detection Limit #2		*0.003*	*0.000*	*0.005*	*0.003*	*0.003*	*0.029*	*0.001*	*0.000*	*0.015*	*0.020*	*0.032*	*0.000*	*0.000*	*0.022*
7/4/2006	**Blank 3**	**0.005**	**0.001**	**0.100**	**0.000**	**0.117**	**0.000**	**0.004**	**0.002**	**0.052**	**0.077**	**0.000**	**0.000**	**0.001**	**0.015**
7/4/2006	4	18.1	1.2	20.8	0.0930	69	1.6	4.3	1.7	0.240	11	12	0.1	0.2	0.4
7/4/2006	5	8.6	1.3	20.3	0.0750	232	1.2	2.1	3.7	0.341	70	14	0.1	0.1	0.4
7/4/2006	6	23.4	0.8	16.8	0.1220	81	3.5	6.8	0.9	2.336	7	31	0.1	0.4	0.5
7/4/2006	7	35.5	0.5	15.4	0.0990	55	4.6	9.1	1.5	2.226	4	23	0.0	0.4	0.3
7/4/2006	8	8.7	0.5	18.3	0.1020	33	1.5	2.6	0.7	2.395	3	24	0.1	0.1	0.3
7/4/2006	9	13.1	0.9	24.2	0.1770	40	1.8	3.3	1.0	0.676	4	23	0.1	0.2	0.3
7/4/2006	10	11.4	0.8	21.4	0.1580	38	1.7	2.8	0.9	0.417	3	21	0.1	0.2	0.4
7/4/2006	11	9.1	0.9	20.6	0.0910	43	1.5	2.3	1.0	0.415	4	20	0.1	0.1	0.2
7/4/2006	2	36.7	0.6	15.8	0.1100	54	4.4	9.6	1.1	0.523	3	22	0.1	0.3	0.3
7/4/2006	3	7.5	1.0	14.5	0.0450	401	1.7	1.6	5.7	0.262	139	8	0.1	0.1	0.3

7/8/2006	**Blank 4**	**0.007**	**0.002**	**0.065**	**0.000**	**0.213**	**0.000**	**0.006**	**0.005**	**0.017**	**0.069**	**0.000**	**0.000**	**0.000**	**0.008**
7/8/2006	12	7.1	0.6	14.7	0.0770	32	1.1	1.6	0.7	0.301	4	13	0.1	0.1	0.2
7/8/2006	40	10.4	0.7	14.0	0.0670	268	2.6	3.4	5.8	0.223	71	19	0.1	0.2	0.1
7/8/2006	42	10.7	0.9	26.6	0.0710	441	2.6	4.4	10.4	0.129	126	22	0.1	0.2	0.4
7/8/2006	44	13.3	0.8	25.1	0.0480	504	2.9	4.4	9.7	0.106	149	13	0.1	0.2	0.2
7/8/2006	48	28.5	0.6	21.2	0.1120	397	5.9	9.2	6.3	0.176	75	13	0.1	0.4	0.3
7/8/2006	49	22.3	0.5	21.6	0.1330	243	3.4	9.1	6.3	0.130	52	25	0.1	0.4	0.3
7/8/2006	50	24.7	0.7	21.6	0.1710	102	3.7	10.5	3.0	0.194	7	29	0.1	0.4	0.3
7/8/2006	51	15.5	0.4	15.6	0.0940	164	2.6	6.6	3.2	0.137	36	27	0.1	0.3	0.2
7/8/2006	52	13.6	0.5	16.7	0.1080	158	2.2	6.0	3.3	0.115	33	18	0.1	0.2	0.2
7/8/2006	43	13.9	0.5	19.1	0.0430	396	2.0	4.4	11.2	0.129	56	23	0.1	0.2	0.2
7/16/2006	**Blank 5**	**0.008**	**0.001**	**0.289**	**0.000**	**0.169**	**0.000**	**0.005**	**0.005**	**0.017**	**0.024**	**0.000**	**0.000**	**0.000**	**0.000**
7/16/2006	13	13.6	0.9	18.8	0.1290	56	1.8	2.6	1.2	0.322	8	18	0.1	0.2	0.3
7/16/2006	15	4.8	1.0	16.4	0.0390	309	1.1	1.4	4.4	0.230	103	12	0.1	0.1	0.3
7/16/2006	16	5.8	1.0	16.2	0.0440	230	1.0	1.4	3.4	0.187	73	12	0.1	0.1	0.3
7/16/2006	17	9.3	1.0	16.5	0.0430	211	1.4	1.7	3.6	0.256	63	18	0.1	0.1	0.4
7/16/2006	18	7.1	1.0	18.8	0.0570	377	1.4	1.8	5.8	0.282	128	14	0.1	0.1	0.4
7/16/2006	19	9.8	1.1	19.0	0.0810	125	1.5	2.2	2.3	0.205	33	16	0.1	0.2	0.3
7/16/2006	21	7.9	1.2	17.9	0.0960	59	0.9	1.9	2.2	1.063	5	25	0.1	0.2	0.3
7/16/2006	22	5.3	1.2	16.8	0.0350	212	0.9	1.4	6.0	0.780	65	14	0.1	0.1	0.4
7/16/2006	23	13.0	1.2	15.6	0.0480	281	2.5	3.2	8.2	0.626	87	11	0.1	0.2	0.3
7/16/2006	23-dup	13.1	1.0	13.4	0.0400	245	2.9	3.0	7.2	0.545	76	10	0.1	0.2	0.2
7/23/2006	**Blank 6**	**0.003**	**0.001**	**0.031**	**0.000**	**0.077**	**0.000**	**0.001**	**0.002**	**0.000**	**0.023**	**0.000**	**0.000**	**0.000**	**0.000**
7/23/2006	20	16.2	0.8	11.1	0.1030	82	2.1	4.7	0.9	0.525	8	27	0.0	0.2	0.4
7/23/2006	25	4.9	1.2	15.9	0.0460	289	0.7	1.6	6.1	0.211	85	10	0.1	0.1	0.2
7/23/2006	28	4.5	1.0	14.4	0.0900	85	0.4	1.1	2.4	0.076	14	19	0.1	0.1	0.2
7/23/2006	30	5.5	0.9	13.5	0.0740	90	0.5	1.2	2.7	0.066	17	23	0.1	0.1	0.2

7/23/2006	33	4.6	1.1	16.0	0.0600	172	0.5	1.5	4.2	0.089	52	18	0.1	0.1	0.3
7/23/2006	34	4.6	1.1	15.3	0.0780	165	0.6	1.3	3.9	0.083	50	20	0.1	0.1	0.3
7/23/2006	35	6.6	1.1	19.9	0.1130	86	0.6	1.9	2.5	0.127	13	24	0.1	0.1	0.3
7/23/2006	36	4.4	1.0	12.7	0.0490	174	0.7	1.2	4.8	0.083	57	19	0.1	0.1	0.2
7/26/2006	**Blank 7**	**0.007**	**0.000**	**0.035**	**0.000**	**0.133**	**0.007**	**0.002**	**0.003**	**0.000**	**0.035**	**0.000**	**0.000**	**0.001**	**0.000**
7/26/2006	37	7.8	1.3	16.2	0.0550	166	1.2	1.8	6.0	0.111	52	13	0.1	0.1	0.3
7/26/2006	38	3.3	0.6	10.6	0.0270	381	0.7	1.0	9.8	0.052	137	10	0.1	0.1	0.2
7/26/2006	39	4.8	0.9	12.4	0.0380	316	1.0	1.2	7.2	0.107	107	10	0.1	0.1	0.2
7/26/2006	46	14.7	0.4	16.1	0.0510	112	2.7	4.9	5.7	0.124	21	8	0.1	0.2	0.2
7/26/2006	47	24.9	0.5	18.3	0.0820	345	5.3	7.6	6.6	0.191	56	10	0.1	0.4	0.3
7/26/2006	53	12.7	0.2	10.8	0.0550	274	2.1	4.6	3.8	0.086	69	11	0.0	0.2	0.1
7/26/2006	54	24.5	0.3	15.1	0.0930	235	4.1	10.6	4.0	0.265	64	13	0.1	0.4	0.2
7/26/2006	55	21.9	0.3	13.9	0.0720	377	4.2	7.3	5.6	0.187	102	11	0.1	0.3	0.2
8/9/2006	56	9.4	0.3	11.7	0.0680	241	1.0	5.4	3.5	0.047	74	11	0.1	0.2	0.2
8/9/2006	57	8.8	0.4	13.1	0.0730	282	0.9	4.8	3.8	0.052	83	13	0.1	0.2	0.1
8/9/2006	58	13.6	0.4	17.9	0.1010	277	1.3	7.3	5.3	0.072	81	16	0.1	0.3	0.2
8/9/2006	59	16.6	0.4	21.4	0.0990	296	1.5	8.3	7.0	0.094	67	12	0.1	0.3	0.2
8/9/2006	60	10.3	0.2	17.9	0.0890	281	0.9	5.1	6.3	0.054	75	17	0.1	0.2	0.2
8/9/2006	61	10.1	0.3	18.1	0.0920	59	0.9	5.4	3.6	0.066	9	13	0.1	0.2	0.2
8/9/2006	62	16.1	0.3	17.2	0.1280	83	1.4	8.6	2.3	0.093	14	13	0.1	0.3	0.2
8/9/2006	63	18.0	0.3	18.8	0.1300	61	1.6	9.4	2.2	0.075	7	12	0.1	0.3	0.2
8/9/2006	64	16.6	0.3	18.7	0.1060	56	1.8	9.4	1.5	0.087	3	14	0.1	0.3	0.2
8/9/2006	65	14.6	0.6	13.0	0.0680	194	1.5	8.7	2.7	0.111	47	13	0.1	0.3	0.2
8/9/2006	66	15.4	0.3	20.0	0.1310	97	1.4	8.1	2.6	0.564	20	14	0.1	0.3	0.3
8/13/2006	**Blank 8**	**0.010**	**0.001**	**0.052**	**0.000**	**0.069**	**0.000**	**0.008**	**0.002**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
8/13/2006	67	24.3	0.3	17.4	0.1230	55	3.1	10.8	1.3	0.316	4	12	0.1	0.3	0.2

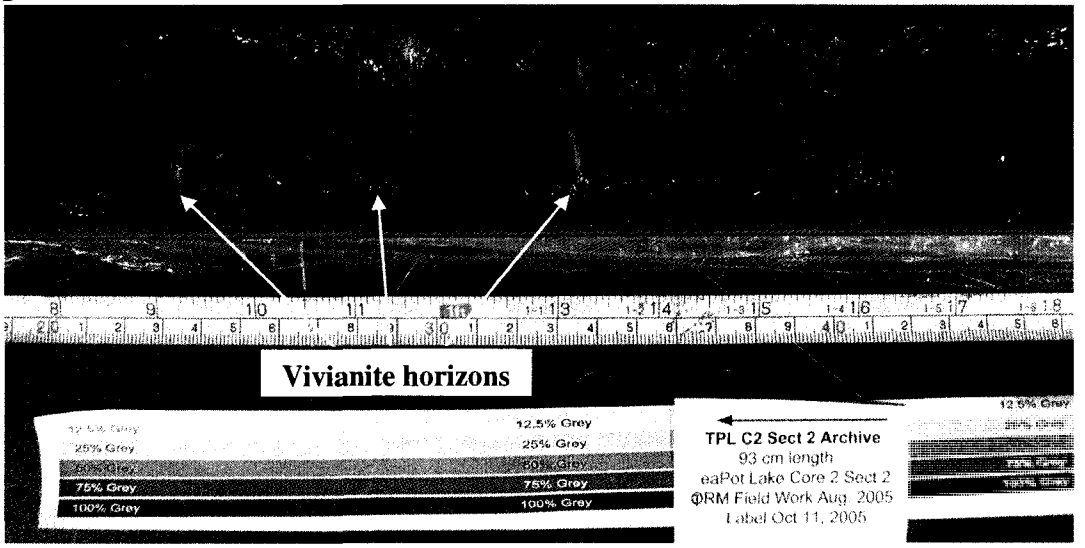
8/13/2006	68	21.7	0.4	27.4	0.1220	80	2.7	10.8	3.2	0.227	12	13	0.1	0.3	0.3
8/13/2006	69	14.7	0.3	18.3	0.0970	44	2.1	7.9	1.8	0.123	1	16	0.1	0.3	0.3
8/13/2006	70	20.0	0.3	16.2	0.1070	48	2.5	9.7	1.2	0.166	2	17	0.1	0.3	0.2
8/13/2006	71	17.3	0.2	17.9	0.1010	48	2.3	9.0	1.9	0.143	3	13	0.1	0.3	0.2
8/13/2006	71-dup	19.0	0.2	18.8	0.1060	51	2.7	9.7	2.0	0.172	3	14	0.1	0.3	0.2
8/13/2006	VIV	1.4	0.3	32.6	0.0160	173	0.1	2.6	1.2	0.074	12	49	0.1	0.7	0.1

Lake Sediment Organic Geochemistry

Depth (m)	%C	%N	C/N	$\delta^{13}C_{vpdb}$	$\delta^{15}N_{air}$
0.02	27.9	2.55	11	-33.12	1.04
0.06	27.16	2.81	10	-32.58	0.88
0.12	23.25	1.89	12	-33.22	0.78
0.129	20.65	2.04	10	-34.32	0.50
0.22	39.01	3.56	11	-34.99	0.25
0.32	37.83	3.21	12	-33.02	0.97
0.42	40.09	3.12	13	-32.42	0.50
0.52		3.04			1.35
0.62	34.36	2.77	12	-33.14	1.28
0.72	36.36	3.15	12	-35.81	-0.09
0.79	32.03	2.94	11		
0.813	22.13	2.09	11	-34.72	1.26
0.82	26.1	2.07	13	-33.52	1.62
0.85	35.8	2.99	12	-34.06	1.17
0.9	32.95	2.59	13	-35.30	1.79
0.93	31.67	2.4	13	-34.53	1.40
1.075	34.84	2.69	13	-33.36	0.66
1.147	27.24	2.49	11	-34.29	1.68
1.34	19.5	1.75	11		
1.44	24.96	1.97	13	-32.83	1.87
1.53	18.75	1.51	12	-33.72	1.52
1.58	20.46	1.61	13	-34.67	1.63
1.64	34.88	2.85	12	-33.58	1.10
1.67	18.18	1.49	12	-33.87	0.79
1.74	32.44	2.67	12	-33.90	1.16
1.77	9.06	0.78	12	-32.87	0.29
1.8	8.76	0.76	12	-32.97	-0.03
1.84	31.05	2.44	13	-34.88	1.17
1.995	18.2	1.57	12		
2.04	24.04	2.01	12	-35.21	0.85
2.081	27.73	2.38	12	-34.31	1.22
2.18	19.79	1.72	12	-33.68	1.69
2.26	20.11	1.89	11	-33.81	1.80
2.29	14.52	1.33	11		
2.39	15.99	1.36	12	-33.42	2.41
2.49	19.43	1.67	12	-33.31	1.69
2.59	19.82	1.71	12	-33.22	1.60
2.79	19.48	1.81	11	-33.95	1.66
2.945	25.74	2.32	11	-33.54	1.03
2.99	28.83	2.48	12	-31.64	1.71
3.14	18.59	1.67	11	-31.03	1.62

3.2	18.81	1.61	12	-27.68	1.31
3.25	15.8	1.38	11	-26.75	1.04
3.3	13.98	1.17	12	-27.71	0.99
3.6	17.92	1.55	12	-27.54	1.10
3.69	16.65	1.45	11	-35.22	1.43
3.8	20.7	1.76	12	-34.62	0.47
4	21	1.64	13	-27.07	0.48
4.09	20.93	1.74	12	-27.85	0.41
4.2	20.42	1.72	12	-26.66	0.36
4.26	21.61	1.74	12	-27.28	0.42
4.46	23.25	1.95	12	-28.22	0.72
4.56	24.81	2.06	12	-27.20	0.44
4.66	22.03	1.8	12	-26.81	0.75
4.73	23.39	1.88	12	-26.57	0.85

Teapot Lake Sediment Core 2, Section 2



Teapot Lake Sediment Core 3, Section 3