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**RABBITKETTLE HOTSPRINGS, NAHANNI NATIONAL PARK
RESERVE, N.W.T.:
A Hydrogeological Study**

by

Angela L. Gulley, Hon. BSc.

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science**

**Ottawa-Carleton Geoscience Centre
and the
Department of Earth Sciences
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A Hydrogeological Study
submitted by Angela L. Gulley, Hon. BSc.
in partial fulfillment of the requirements
for the degree of Master of Science

Thesis Supervisor

Chairman, Department of
Earth Sciences

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ABSTRACT

Rabbitkettle Hotsprings, at the north end of Nahanni National Park Reserve, Northwest Territories, are in the southern part of the Mackenzie Mountain Fold Belt. Calcium-carbonate-saturated waters discharge from four springs at the site; three of them are actively building two spectacular travertine-terrace structures.

The spring waters were investigated in terms of their chemistries and environmental isotopes. This information, in conjunction with field observations, geomorphology and a general understanding of the local geology, was used to provide an understanding of the subsurface flow system.

The spring water is of meteoric origin, entering into exposed carbonate bedrock along the mountain spur to the southeast of the hotsprings. The water descends to a depth of a little over 1 kilometre, reaching temperatures between 60° and 69°C as the result of conductive heating by an above average geothermal gradient. Carbon dioxide in the spring water from biological activity in the recharge zone and from a deep rooted metamorphic source dissolves carbonate from the aquifer. Upon discharge, degassing of carbon dioxide results in the precipitation of calcium carbonate in the form of travertine. Discharge is controlled by artesian pressures, localized by an underlying fault.

Chemical and isotopic compositions of both old and modern travertine deposited at the site have provided information about the environment of deposition. Rates of deposition were determined from the precipitation of travertine onto glass slides, the loss of calcium from solution and from carbon-14 dating of entrapped wood fragments. Because the region has numerous other travertine-precipitating springs, their chemistries, isotopic compositions and

prevailing hydraulic conditions were contrasted to Rabbitkettle's to determine why they lack the spectacular terrace development.

Rates of travertine precipitation are controlled by the rate of diffusion of carbon dioxide, which is dominantly a function of turbulence; however, discharge rates, vegetation and temperature play secondary roles. Travertine deposition has been ongoing at the site for nearly 10,000 years. Based upon travertine precipitation rates, the youngest of the two mounds is estimated to be about 7,000 years old.

Natural forms of degradation such as frost damage, river damage and animal traffic have had a considerable impact on the structures at the site. With an increase in tourism, humans have also had an impact. However, recent park policies to control visitation have been successful in minimizing damage. As a result of this study, a detailed monitoring program to observe and anticipate *all* forms of degradation has been designed.

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Many people provided their assistance during the course of this research. First, I thank my supervisor Dr. Frederick A. Michel for giving me the opportunity to do research in a beautiful and unique study area. I also thank him for his guidance and constructive criticism during the course of this research. I would like to express my thanks to all Nahanni National Park staff for providing extensive logistical support during the duration of this project, and for their hospitality during our stays in Fort Simpson. I express my appreciation to all the wardens and volunteer wardens who were stationed with us at Rabbitkettle Lake for their co-operation and companionship.

I thank Jim Banner of the National Hydrology Research Institute, Environment Canada, Saskatoon, for the use of time-lapse cameras, for his concise explanation of their setup procedure, and for looking after the unloading and processing of film. I acknowledge the Department of Indian Affairs and Northern Development for the loan of a Level and Rod for surveying. I express my appreciation to the technical staff at the Ottawa University Isotope Lab for teaching me how to process my samples in the lab.

Thanks are extended to the pilots of Simpson Air, Wolverine Air and Blackstone Aviation who flew us in and out of the park; transported our supplies, food and much anticipated mail while in the field; as well as for flying over the mounds so that they could be photographed.

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List of Duties Performed by the Author

Field Work Involved:

- sampling of spring waters and spring gases for the determination of chemistry and isotopes were performed on a regular basis, along with in-field chemical measurements.
- periodic sampling and chemistry of other local waters
- in-field determination of travertine sedimentation rates
- discharge measurements of all springs
- detailed mapping and elevation survey of mounds
- detailed delineation of mound conditions (permafrost, flow areas, etc...)
- investigation of local geomorphology and geology
- exploration and location of other travertine deposits in the area
- setting up and dismantling time-lapse camera equipment
- collection of travertine samples and datable material
- emplacement of erosion points and reference points (metal platelets)
- photography of the mounds, high traffic zones and local areas; detailed and aerial.

Lab Work Involved:

- carbon-13 and oxygen-18 analysis of travertine
- carbon-13 analysis of gas samples
- gas chromatograph analysis
- deuterium analysis of spring water and other local waters
- oxygen analysis of spring water and other local waters
- prepared samples for X-ray diffraction
- prepared samples for ^{14}C analysis

CHAPTER 1 - INTRODUCTION

1.1 Background

Rabbitkettle Hotsprings are located near the northwestern boundary of Nahanni National Park Reserve, Northwest Territories (Figure 1). Three springs precipitate calcium carbonate in travertine terraces which form two separate mound structures (Plate II). They represent one of the largest known and most spectacular hotspring structures in Canada, and consequently are becoming increasingly popular with tourists. They are unique in that few other known structures of this kind have developed such extensive terraces in a harsh northern climate. Because the fragile surfaces of the mounds are easily damaged by tourist traffic, Parks Canada has designated the site as one of seven special preservation areas within the park. This means that the area receives special protection because it contains a unique, rare, fragile or endangered feature. As a result, the hotsprings now have controlled visitation. The more than 300 annual visitors to the springs are accompanied by a park warden, are restricted to designated trails and may only walk on the north mound barefoot. These measures are to limit the degradative effects of tourist traffic while still allowing access to the mounds.

In 1984, a monitoring program, in addition to controlled visitation, was put into effect. It was based on biannual photograph comparison of a control strip. The photographs were visually assessed from year to year to interpret damage from both natural and human influences. In 1989, this program was abandoned since it failed to adequately detect adverse impacts. New methodologies for the continued preservation of the mounds are considered necessary by Parks Canada,

Figure 1.
Location map of Rabbitkettle Hot Springs.
Inset shows location of Nahanni National Park Reserve.

and has resulted in the commissioning of this project. These methodologies can only come from a comprehensive and quantitative study of the mounds and their associated spring waters.

1.2 Previous Studies

Rabbitkettle Hotsprings have been included as part of numerous large-scale groundwater studies, yet a detailed database for the area is limited. To date, no thorough inspection of the spring waters has been undertaken. In 1964, Atchison included Rabbitkettle as part of a Bachelor's Thesis that looked at a number of spring deposits in the Flat River area. Gabrielse *et al.* (1965), for whom Atchison was a summer assistant, mapped the geology of the Flat River, Glacier Lake and Wrigley Lake areas and provided a short descriptive reference to the hotsprings. In 1973, van Everdingen studied the chemistries of thermal and mineral springs of South Nahanni National Park including Rabbitkettle. A similar but broader study of thermal springs within the Yukon, N.W.T. and B.C. included Rabbitkettle and was prepared by Crandall and Sadlier-Brown (1978).

The springs were also mentioned in a geomorphological study of the Park by Ford (1974). Marsh and Scotter (1976) completed a vegetation report for Parks Canada and included recommendations for the preservation of the Rabbitkettle area. Cody and Brigham (1972) documented the plants collected directly on top of the mounds. The most detailed report to date was a geographical study produced for Parks Canada by Brown and Wright (1979). This report provided a detailed description of the physical aspects of the mounds as well as an assessment of human impacts and recommendations. The most recent reference to the springs was by Hamilton (1990) as part of a geochemical study of spring waters in the

South Nahanni River area conducted in 1986 and 1987. Bowman (1990) also included Rabbitkettle travertine as part of a Bachelor's Thesis on travertine isotope composition.

1.3 Objectives and Scope

This study was commissioned by Parks Canada to increase the existing database about the Rabbitkettle mounds and their associated hotsprings. The springs are located at UTM coordinates Easting 595,500 and Northing 6,868,800, and are located in the northwest portion of NTS map sheet 95E/14. Four springs were sampled during the summers of 1991 and 1992; these included three main mound-associated hotsprings and a smaller, cooler spring nearby.

The three main objectives of this study were:

1. To develop an understanding of the hydrogeological and geological parameters controlling the existence of the hotsprings and their travertine mound structures.
2. To document past, present and future (potential) sources of degradation to the travertine mounds.
3. To develop a new monitoring program for Parks Canada, designed from the quantitative insight provided by this research, to help in the continued understanding and preservation of the travertine mounds. This program is outlined as an appendix to the thesis.

Given the above objectives, the following elements will be covered:

- i. The geologic and hydrogeologic setting of the springs.
- ii. The origin and flow history of the spring waters, based on geology, geochemistry and isotopes.

- iii. The origin, development and age of the mounds through an understanding of the chemical and physical controls on travertine precipitation, rates of travertine precipitation, hydraulics and the geomorphological development of the site.
- iv. The degradation of the mounds with reference to both natural and human impacts and recommendations to anticipate and minimize damage in the future.

CHAPTER 2 - GEOLOGIC SETTING

2.1 Regional Geology

Rabbitkettle Hotsprings are located within the southern Mackenzie Mountain Fold Belt. This belt is characterized by northerly- and northwesterly-trending folds that are locally interrupted by numerous westerly dipping faults. The regional stratigraphy, as simplified by Hall *et al.* (1988), can be separated into platformal-carbonate and basinal-clastic sequences.

The Mackenzie Mountains, which lie to the northeast of the South Nahanni River valley, consist predominantly of thick platformal sequences with minor basinal formations that range in age from Helikian to Late Devonian (Gabrielse *et al.*, 1965). The region southwest of the South Nahanni River valley consists mainly of basinal sequences, ranging from Hadrynian to possibly Mississippian in age (Gabrielse *et al.*, 1965).

Thick Cambrian to Middle Ordovician platformal sequences, such as the Sunblood, Rabbitkettle and Broken Skull Formations, have the greatest exposure in the entire belt and locally form tight southeasterly-plunging folds. The Road River Formation, which is predominantly shale, has the greatest exposure of the basinal units.

The strata southwest of the South Nahanni River have been intruded by a broad northwesterly-trending belt of Cretaceous¹ quartz monzonite-to-granodiorite batholiths. These are the youngest rocks exposed in the area and form the jagged peaks of the Ragged Range.

¹ Samples from this region were dated at 110 million years by K-Ar techniques (Leech *et al.*, 1963; Galbriese, 1967)

Figure 2.
Simplified regional geology map showing the location of Rabbitkettle Hotspots and other travertine-precipitating springs.

Two major faults exist in the area shown in Figure 2. The southeasterly-trending, steeply dipping Broken Skull Fault follows the valley of the South Nahanni River and is considered to extend beyond and beneath Rabbitkettle Hotsprings (Hall *et al.*, 1988). An unmapped fault located to the south of the hotsprings is believed to extend down the valley of the Flat River. Evidence for this latter fault includes major gouge zones and a lineament visible on LANDSAT imagery (Hamilton *et al.*, 1991). Faults in this region are related to Mesozoic compressional deformation (Hall *et al.*, 1988).

2.2 Local Stratigraphy

The hotsprings are located near the junction of the South Nahanni and Rabbitkettle Rivers. Thick sequences of carbonates from the Rabbitkettle and the Sunblood Formations outcrop along the Rabbitkettle River to the west of the hotsprings, where they form tight southeasterly-plunging folds (Figure 3).

The Rabbitkettle Formation is Middle to Upper Cambrian in age and is composed of relatively uniform sequences of interbedded limestones, silty limestones and calcareous siltstones up to 1,200 metres thick (Gabrielse *et al.*, 1965, 1973). The lower member of this formation consists predominantly of siltstones and silty limestone, characterized by distinctive wavy banding of the silty layers within the limestone. The upper member consists of light grey, weathered, dark fissile argillaceous limestone and calcareous shale. It is the upper member that is exposed along the Rabbitkettle River, where it is between 90 and 300 metres thick (Gabrielse *et al.*, 1973).

The Sunblood Formation unconformably (angular unconformity) overlies the Rabbitkettle Formation and is of Ordovician and/or Cambrian age. In addition

to the Rabbitkettle valley, it also crops out near Hole-in-the Wall valley to the southeast of the hot springs. The lower member is composed of grey, slaty argillaceous limestones and buff calcareous slate up to 100 metres thick (Gabrielse *et al.*, 1965, 1973). The upper member is about 80 metres thick and includes well-banded light grey and dark grey weathered cryptograined limestones that are locally fossiliferous, are locally interbedded with dolostone and locally exhibit buff, pink and wine-coloured mottling (Gabrielse *et al.*, 1973).

The Road River Formation is the most extensive bedrock unit in the vicinity of the hot springs. Of Ordovician, Silurian and Lower Devonian age, the formation stratigraphically and unconformably caps the underlying carbonates. It consists predominantly of black to dark grey, thinly bedded, calcareous and non-calcareous shales and may contain thin beds of black cryptograined and argillaceous limestone, grey and black chert, calcareous siltstone and black cherty dolostone (Gabrielse *et al.*, 1965, 1973). Basal beds outcropping to the southwest of Rabbitkettle Lake are composed of black, pyritic, slightly calcareous siltstones and shales. These beds are overlain by thinly bedded argillaceous, black cryptograined limestones (Gabrielse *et al.*, 1965, 1973). The unit is best exposed in Hole-in-the Wall valley, overlying the Cretaceous quartz monzonite intrusions, where it has been uplifted and slightly hornfelsed by them. At this location its limestone member weathers to a pale rusty-red colour.

Pleistocene and Holocene unconsolidated glacial and fluvial deposits overlie bedrock within the valleys. The mounds at Rabbitkettle Hot Springs are positioned upon stratigraphically complex unconsolidated deposits within the Rabbitkettle River valley. The area to the north of the Rabbitkettle River along the South Nahanni River valley appears to be predominantly glaciofluvial in origin.

Figure 3. Local geology of the study area.

exhibiting kame and kettle deposits, left behind from northwesterly-retreating Cordilleran glaciers between 140,000 and 180,000 years ago. Silt and gravel deposits occur in the uplands at Rabbitkettle Lake, and are believed to be remnants of deltaic deposits associated with Glacier Lake Nahanni (Ford 1974, 1976). Ford (1976) believes these deposits are 145,000 years old, however; they may be as young as the Early Wisconsinan (90,000 to 40,000 years). The most recent glacial advance within Hole-in-the-Wall valley was during the Late Wisconsinan period, 10,000 to 12,000 years ago, but is not believed to have reached as far as the hot springs (Ford, 1974, 1976).

In the study area, the most northerly travertine mound structure sits upon the older glaciofluvial deposits where they have been exposed by postglacial down-cutting of the Rabbitkettle River (Figure 4). These deposits in the vicinity of the springs contain pebble- and cobble-sized water-rounded clasts intermixed with silt in a fining-upward sequence (Ford, 1974). Immediately adjacent to and below the most northerly mound, the deposits have been cemented by travertine to form a conglomerate. The more southerly mound sits upon glacial till deposits, which are Wisconsinian or older, that have been incised by past migration of Hole-in-the-Wall Creek. This incision into the local till is believed to be associated with either a Late-Wisconsinan glacial meltwater channel or postglacial fluvial down-cutting (Brown and Wright, 1979), which puts the age of the incision at less than approximately 10,000 years. The till generally has a silty matrix with larger clasts ranging from pebbles to boulders. Overlying all deposits at the site are fluvially transported water-rounded boulders that originated from the surrounding till deposits and were mobilized by Hole-in-the-Wall Creek. The site is littered with

boulders of travertine-cemented pebble conglomerates, travertine debris of varying sizes and calcium carbonate-rich soils.

Figure 4. Geomorphological setting of the mounds. Inset shows enlargement of mound area and identifies spring locations.

CHAPTER 3 HYDROGEOLOGIC SETTING

3.1 Hydrogeologic Controls:

The broad belt of intrusive rocks to the west and southwest of Rabbitkettle Hotsprings form the highest upland areas in the region. Jagged peaks up to 3,100 metres in elevation, with local relief as great as 2,000 metres, are the result of valley and alpine glaciation within an extremely resistant terrane. Thus, they have acquired the name "Ragged Range". Fresh alpine glaciation suggests that this region was influenced by repeated glaciation within the latest Wisconsin glacial period (Ford, 1976). The highest upland areas of the Ragged Range today remain covered by glacier fields. The South Nahanni River and its tributaries drain these glacier fields.

The folded carbonate and clastic units form rounded peaks extending to elevations of 3,000 metres. Abundant carbonate rock in the areas to the east and northeast of Rabbitkettle Hotsprings have developed karstic groundwater systems (Hamilton, 1990). All carbonate units in the region provide excellent potential for deep groundwater movement, especially where they are stratigraphically capped by less permeable shale units.

The region is cross-cut by deep U-shaped valleys infilled with thick unconsolidated glacial and postglacial deposits. Alluvial fans, coarse-grained talus debris and remnant till occur along mountain slopes. Topographically low areas consist of glacial sediments and fluvial deposits. This unconsolidated valley fill may offer potential for shallow groundwater circulation. However, being within the zone of discontinuous permafrost, groundwater flow is often inhibited, in

particular at higher elevations, as the prevalence of "frozen" ground restricts recharge and promotes surface flow.

The Rabbitkettle Hotsprings are located near the junction of the South Nahanni River and the Rabbitkettle River and at the southern extension of the Broken Skull Fault. Throughout the South Nahanni valley, there are numerous fault-associated springs, some of which are precipitating travertine (Hamilton, 1990) but none as extensively as at Rabbitkettle. The Flat River valley also contains many travertine-precipitating springs, most of which have high partial pressures of carbon dioxide (Hamilton *et al.*, 1991). All the travertine-precipitating springs in the region are associated with carbonate terrane.

3.2 Hydrochemical Controls

The most important factors controlling the chemical and physical properties of groundwater are: the rock types they have encountered, the sequence in which the waters encountered them, the presence of mineralization, subsurface temperature and the length of time the waters have resided in the subsurface. The resulting measurable properties of groundwater include pH, alkalinity, Eh, conductivity, groundwater chemistry, isotope composition and temperature.

The temperature is important in deciphering the chemistry of groundwater, because most minerals have increased solubilities at higher temperatures. Carbonate minerals are an exception, because their solubility is dependent not only on temperature but also on the concentration of carbon dioxide in solution. The solubility of carbon dioxide (like most gases) is reduced with increasing temperature, and therefore, so are carbonate-mineral solubilities.

"Thermal" groundwaters have been defined traditionally as being 5°C above the mean annual ambient air temperature (MAAT) (White, 1957). At Rabbitkettle, the MAAT is -8°C (Burns, 1973). By this definition, all waters in the region would be considered "thermal." Hamilton (1990) devised a classification based on the mean temperatures of groundwaters in the region, such that all spring waters greater than 7°C are regarded as "thermal," and all those greater than 20°C as "hot." Thus, all four springs at Rabbitkettle would be considered "thermal," and the three main springs would be considered "hot."

In Canada, most thermal springs are in the west, predominantly within the Cordilleran region, which is young, tectonically active and often associated with high geothermal gradients (Souther and Halstead, 1968). The high topographic relief of the region permits deep water circulation, and high precipitation supplies ample recharge. In general, thermal springs are associated with faults in ancient sedimentary terrane or with fractures in Mesozoic and Cenozoic crystalline rocks (Souther and Halstead, 1968).

In the Ragged Range, the quartz monzonite- to granodiorite-intrusive bodies are known to have high internal geothermal gradients, because most springs spatially associated with them are thermal (Hamilton *et al.*, 1988). Spring temperatures as high as 65°C have been observed emanating directly from the intrusive bodies. Rabbitkettle Hot Springs are spatially associated with these intrusions and are believed to be thermal because of this association.

3.3 Description of the Springs

On the south side of the Rabbitkettle River, approximately 2 kilometres upstream from its confluence with the South Nahanni River, a large travertine

(tufa) mound can be seen towering to a height of 27.3 metres over the riverbank (July 21, 1991 flow height). The mound itself is sitting on a terrace nearly 8.8 metres above the riverbank, so the mound is actually 18.5 metres thick. The mound is somewhat circular in shape, with a diameter of approximately 69 metres at the top and 79 metres at its base. The volume of travertine composing this structure is estimated at 81,000 cubic metres. On its crown, calcium carbonate-saturated spring waters discharge at a temperature of 21°C from a vent (spring 001) that is roughly 6 to 7 metres in diameter (Plate XV). The vent reaches a maximum depth of 15.85 metres. The edges of the vent are raised a couple of centimetres above the water level. Water exits the vent by incising channels through the rim and into the surface of the mound. At present, these channels exit the vent at three locations, all flowing toward the west. Waters within the channels are depositing substantial quantities of a hydrous iron oxide, colouring the channels red (Plate IX). Where the channels overflow, fresh white travertine is precipitated within shallow pools. The channels end where the slope of the mound steepens (between 15 and 20 metres from the vent). At this point the calcium carbonate-saturated water cascades down the western slope, forming intricate terrace structures due to the rapid deposition of travertine. On the northwestern edge of the mound, the water cascades over a falls that was created by local collapse due to undercutting of the mound by a former meander of the Rabbitkettle River (Plate XIII). The ground below the falls is littered with fragments and boulders of travertine which are overgrown with vegetation or covered with fresh precipitate.

The mound has been described as looking like a "giant layer cake," which has built up from successive layering of travertine in the form of terraces. These

terraces are composed of rimstone dam and pool structures with dams that can be metres high along the edges of the mound. Superimposed onto these larger structures are miniature basins or riffles only centimetres deep. On the steep outer edges of the deepest rimstone dams, stalactitic flowstone structures are present.

To the south of this mound, located on a terrace more than 10 metres higher, is another large mound. This mound covers an estimated area of 11,900 square metres. The south mound is actively discharging calcium carbonate-saturated water at 20°C from two vents. At the far south end of this mound, spring 003 discharges toward the south and is flooding the adjacent forest (Plate XVII). The spring vent is approximately 7.2 metres long, has an average width of 3.0 metres and is 1.3 metres deep at its deepest point. At the north end of the south mound, spring 002 discharges toward the east from a roughly circular 2.5-by-3.1-metre vent, which has a maximum depth of 1.85 metres (Plate XVI). Both vents are actively carving narrow channels into the adjacent travertine and precipitating hydrous iron oxide. Where the channels overflow or disappear away from the vents, travertine is being precipitated in the form of riffles and shallow pools.

An extinct vent occupies the centre of the south mound, located between the other vents but closer to the west side. The only evidence of its past existence is a raised mound of fragmented travertine and numerous wet spots along the surface with some associated iron-staining. Standing on top of this area, one can hear the gurgling of upwelling water just below the surface.

A fourth spring (004) is located to the east of the north mound and discharges cooler waters (10° to 12°C during the summer) from a 5-centimetre diameter opening 6.3 metres (July 21, 1991) above Rabbitkettle River (Plate

XVIII). This small spring is precipitating travertine over an area of approximately 10 square metres, down the river-cut bank and into the Rabbitkettle River.

The hotsprings support abundant and varied biota. Algae of several species are plentiful in and around the spring vents and may aid in the deposition of the travertine. Other forms of vegetation associated with the mounds are documented in reports by Cody and Brigham (1972); Marsh and Scotter (1976); and Brown and Wright (1979). Vegetation, as seen later, may also play a minor role in the development of these mound structures. The south mound is heavily vegetated along its perimeter where the forest has begun to overtake older deposits; overgrowth is concentrated toward the south end of this mound near spring 003. However, spring waters discharging toward the south from this vent are drowning trees, much the same as the original spring deposits would have done. The north mound, and the main part of the south mound associated with spring 002, remain relatively free of vegetation. However, both mounds exhibit evidence of their earlier encroachment upon the forest. For instance, small conduits with bark-like imprints were observed at the base of the north mound roughly within the first 2.5 metres above the contact with the underlying deposits; also within this zone are small fragments of travertinized wood. Both vents on the south mound contain entrapped wood fragments which fell into the vents during build-up. Entrapped wood and travertinized wood were also found within the flow areas.

3.4 Data Collected and Methodology

During two summer field seasons -- 10 weeks in total were spent at Rabbitkettle, 8 weeks during the summer of 1991 and 2 weeks in 1992 -- numerous samples were collected. On a weekly basis, the four springs were

sampled for complete chemistry and in-field measurements of temperature, conductivity, pH, Eh, titrated alkalinity and titrated carbon dioxide. Major and trace ion chemistry samples were filtered (45 μm pore diameter filter paper) and collected in two 250 ml Nalgene bottles, one of which had 10 ml of concentrated nitric acid added to keep cations and metals in solution. All major ions were analyzed, including Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} , as well as silica and trace elements. Cations and silica were analyzed by Induced Coupled Plasma (ICP). Anions were analyzed by an Ion Chromatograph Analyzer. Analyses were conducted by Bondar Clegg Limited of Ottawa.

Gas samples were collected from the three main hotspring vents into 100 ml glass bottles and sealed with vacuum grease. It was not possible to collect gas samples from the fourth cooler spring. The samples were processed and analyzed for the carbon-13 isotope content of the carbon dioxide with an analytical precision of ± 0.1 per mille. Analyses were performed at the Stable Isotope Laboratory, Ottawa-Carleton Geoscience Centre. A number of these samples were also analyzed by gas chromatograph to identify complete gas composition.

Water samples for the determination of deuterium, oxygen-18 and tritium isotope contents were collected from the springs on a weekly basis in 60-ml Nalgene bottles. Additional samples from local rivers, lakes, glaciers and rainwaters were taken sporadically over the summer for comparison with the spring waters. Oxygen-18 contents were determined by equilibration of the water with carbon dioxide. Deuterium contents were determined by zinc reduction to hydrogen gas. Analytical precisions are ± 0.1 per mille and ± 1.0 per mille (SMOW), respectively. These analyses were performed using the facilities at the Ottawa-Carleton Geoscience Centre. Tritium concentrations, expressed as T.U.

(tritium units), have an analytical precision of ± 8 T.U. Tritium analyses were performed by direct counting at the Environmental Isotope Laboratory.

Department of Earth Sciences, University of Waterloo.

Samples for the analysis of carbon-14, dissolved inorganic carbon (DIC) and SO_4^{2-} were precipitated in eight-litre bottles. Barium carbonate and barium sulphate precipitate were extracted from the spring-water samples by adding NaOH pellets, to raise the pH of the solution followed by the addition of BaCl_2 . After the precipitate had settled, it was decanted into smaller containers. Analyses were performed at the University of Waterloo.

Entrapped organic samples were dated by carbon-14 methods at the University of Waterloo. Carbon-14 content was determined by liquid scintillation counting on benzene produced from the sample and expressed as pmC (percent modern carbon where 100 pmC is defined as 95 percent of the National Bureau of Standards (NBS) oxalic acid standard and corresponds to wood grown in 1850 in a pollution-free environment). These analyses were performed at the University of Waterloo. Samples too small to be analyzed at the University of Waterloo laboratory were sent to the University of Toronto for AMS dating at the Isotrace Laboratory.

At one-month *and* two-week intervals over the summer, glass slides were laid out along the flow paths of the three main springs. Travertine precipitate was collected on the slides during this time and used to determine present sedimentation rates. Some were run for X-ray diffraction to verify the composition of the travertine. Travertine samples were also analyzed for carbon-13 contents. The travertine was converted to CO_2 gas by reaction with H_3PO_4 , and results are reported in the $\delta^{13}\text{C}$ notation and refer to the PDB standard with a

reproducibility of ± 0.1 per mille. Analyses were performed using the facilities of the Ottawa-Carleton Geoscience Centre.

Discharge rates from the four springs were measured twice during the summer of 1991; once in early July and once in early August. Discharge was measured once in late June during the 1992 visit. Detailed mapping of mound surfaces was carried out at a scale of 1:500 in 1991, and vent elevations were measured using a surveying level.

In August 1991, four time-lapse cameras were set up in the field to monitor seasonal variations of spring-water discharge and frost effects. These cameras took three frames per day and continued taking pictures over the winter but were not operating when they were dismantled in late June 1992. By counting the number of frames taken, it is estimated that the cameras were working well into January and possibly February.

CHAPTER 4 ORIGIN AND FLOW HISTORY OF THE SPRING WATER

4.1 Chemistry of the Spring Waters

The north spring (001) has been sampled by numerous researchers over the years, the earliest being in 1963. In comparing results between authors, we see in Figure 5 and Appendix 1 that, in general, the overall chemistries remain fairly consistent over the long term. Temperature measurements vary by less than 1°C; conductivities and Eh appear relatively constant and pH (where measured in the field) varies only between 6.40 and 6.85. Most ion concentrations show minor to essentially no fluctuation. However, some of the major ions do change. Sodium, which appeared constant for the most part, began showing variability in the last few years. Magnesium, also constant for the most part, dipped to nearly half its usual value during the winter of 1992. Calcium varies within a range of 100 ppm, and bicarbonate varies by more than 600 ppm. Much of this historical variation can be attributed to error caused by the use of different analytical and sample preparation techniques. For instance, calcium concentrations will vary if samples are not acidified immediately upon collection; therefore, lower concentrations may represent loss due to precipitation of calcium carbonate prior to analysis. Bicarbonate concentrations will also vary depending on whether they were determined from titrations in the field or if they were measured in the laboratory. Again, laboratory values will be lower due to the diffusion of carbon dioxide from solution as well as possible precipitation of calcium carbonate. Chemical variations observed in samples taken in 1991 and 1992 are considered to be real, because analytical and sample preparation techniques were identical. The chemical reasons for such variation will be discussed in detail later. However, it is

Figure 5. Chemistry of Rabbitkettle Hotsprings from 1963 to 1992 (All samples from spring 001).

important first to understand why the spring waters have their existing chemistry and how the chemistry can be used to decipher the subsurface flow history.

The chemistries of all four springs were measured weekly during the summer of 1991 and over two weeks in the summer of 1992. Comparing the geochemical data (Appendix 1) of the 3 main mound-associated springs shows that their chemistries are essentially the same (Figure 6), which means that all three springs issue from the same groundwater reservoir and have undergone the same subsurface flow history. The chemistry of spring 004 differs from the main springs in terms of all carbonate-related chemistry, yet, the remaining chemistry indicates that it originated from the same subsurface system. This spring will be discussed separately at the end of this section.

Figure 6 reveals that the chemistries of the three main springs remained relatively constant over the summer of 1991; the waters are moderately mineralized with conductivities between 1089 and 1170 $\mu\text{S}/\text{cm}$; temperatures are constant between 20° and 21.5°C; and pH is between 6.44 and 6.64. Ion concentrations are also notably consistent, all of which suggest a system that is in a state of equilibrium. A change in this state of equilibrium as the water discharges from the spring vents results in the deposition of calcium carbonate.

Any spring system that is precipitating calcium carbonate has acquired a partial pressure of carbon dioxide higher than atmospheric values of $10^{-3.5}$ atmospheres. When carbon dioxide dissolves in groundwater, it produces a very aggressive acidic solution according to the reaction:

This solution is able to dissolve large quantities of carbonate along its flow path according to the reaction:

Figure 6a. Physical Parameters, Rabbitkettle Hotsprings (1991).

Figure 6b. Major Ion Chemistry, Rabbitkettle Hotsprings (1991).

Figure 6c. Minor Ion Chemistry, Rabbitkettle Hotsprings (1991).

Figure 6d. Carbon Dioxide, Rabbitkettle Hotsprings (1991).

When the water reaches the atmosphere, carbon dioxide escapes, forcing the above reactions to proceed left which results in the precipitation of CaCO_3 . However, calcium carbonate does not precipitate instantaneously. Instead, the solution becomes progressively supersaturated (see section 5.1) as a result of the rapid loss of carbon dioxide as it tries to equilibrate with the atmosphere.

Not surprisingly then, all the springs degas carbon dioxide from the vent bottoms upon discharge. Degassing is more pronounced in spring 003, followed by 002 and 001, which may simply be a function of the increasing depths of these vents. Calculated values of carbon dioxide, based upon geochemical data, represent the equilibrium concentration of carbon dioxide that had to have been in solution prior to discharge. In 1991 the pCO_2 concentrations ranged from $10^{-7.8}$ to $10^{-6.3}$ atmospheres, which explains their slightly acidic pH levels and high bicarbonate concentrations.

The analytical results for the major components of each spring are presented in Appendix 1 and Figure 6. More than 90 percent of the total dissolved solids are accounted for by calcium (Ca^{2+}) and bicarbonate (HCO_3^-), which suggests that the most active process within the subsurface is the dissolution of carbonate by carbon dioxide. According to equation 2, the molar ratio of Ca^{2+} to HCO_3^- is 1:2 in the final solution. Calcium concentrations of the three springs ranged from 135 to 198 ppm during the summer of 1991, and 238 to 249 ppm in the summer of 1992. Bicarbonate concentrations, on-the-other-hand, ranged from 739 to 808 ppm in 1991 and from 909 to 958 ppm in 1992. Thus, the springs show an excess of bicarbonate. However, if all the magnesium present in solution

is assumed to be from the dissolution of magnesium-rich carbonate or dolomite ($\text{CaMg}(\text{CO}_3)_2(\text{s})$), all the bicarbonate in solution can be accounted for.

Between the summers of 1991 and 1992, there was a significant increase in bicarbonate and calcium concentrations and a negligible increase in magnesium of 3 to 4 ppm. These increases occurred in conjunction with higher equilibrium carbon dioxide concentrations, as 1992 values rose to values between $10^{-5.5}$ and $10^{-5.0}$ atmospheres. Therefore, a probable explanation for the increases is the greater dissolution of carbonate as a result of increased inputs of carbon dioxide within the subsurface. The effect on magnesium is considerably smaller than the effect on calcium because magnesium-rich carbonate or dolomite is much less soluble than calcium carbonate. The sources of the carbon dioxide will be discussed in detail in section 4.4 i.

The spring waters were sampled during the winters of 1992 and 1993. It was observed that the physical parameters changed very little from summer to winter (Figure 5). The temperatures of the three springs ranged between 18.1° and 20.5°C and pH was slightly higher, between 6.75 and 6.97. Most of ion concentrations remained unchanged except for magnesium, calcium and bicarbonate. Magnesium concentrations dropped by more than one-half, from a summer average of 41 ppm to a winter average of 18 ppm. Calcium and bicarbonate concentrations dipped to 167 ppm and 673 ppm, respectively. Since the samples were not acidified in the field, some of the loss reflects the precipitation of calcium carbonate and the loss of carbon dioxide during the transporting of the sample between Rabbitkettle and Ottawa. These processes were confirmed by lower laboratory pH values of 7.22 to 7.28. However, magnesium is less likely to be lost from solution in this manner. If it were

assumed that some of the decline in calcium and bicarbonate concentrations was real, which is possible given the slightly higher field pHs, then declines in *all* these parameters can be directly related to lower concentrations of carbon dioxide within the spring water. A significant decrease in carbon dioxide would cause more change in magnesium concentrations because it is the least soluble and most sensitive. However, the reason for such a fluctuation in carbon dioxide is uncertain.

Sulphate concentrations in the spring water fall between 29.5 and 34.6 ppm. Isotope data for the sulphur within the sulphate show an abundance of ^{34}S , between +3.73 and +4.83 ‰(CDT). These enriched values are indicative of a sulphide origin. Therefore, the source of the sulphate is likely from the oxidation of pyrite (FeS_2) which is common to the local formations.

Some of the sodium, potassium and chloride present in the spring waters may be the result of entrapped seawater within interbedded shales, which are quite common within the local stratigraphy. The presence of these ions is not due to the dissolution of evaporite deposits, because concentrations are much too low, and there are *no* evaporites within the local strata. Sodium and potassium in solution also result from cation-exchange processes. Na:Cl (and K:Cl) ratios average approximately 4 (to 6), indicating an excess of Na^+ (and K^+). The cation-exchange reaction that applies when a solution comes into contact with a shale or clay unit is:

{calcium (or divalent ions) are preferentially held in ion exchange for sodium (or monovalent ions)}. Any fluctuation in this ratio is predominantly due to variations in sodium. Increased cation exchange may explain the increased concentrations of

sodium, particularly in recent years, signifying more extensive contact with shales in the subsurface as water dissolves through more and more of the stratigraphic sequence.

The most significant trace-metal concentrations are those of strontium and barium. Strontium-ion concentrations range from 589 to 701 ppb, and barium-ion concentrations range from 172 to 188 ppb. High strontium-to-calcium ratios of 1:300 indicate that the limestones encountered by the water are most likely fossiliferous. Fossiliferous limestones are rich in strontium, whereas the average limestone has a Sr:Ca ratio of 1:1000 (Reeder *et al.*, 1972; Hem, 1989). Barium, too, likely originates from the carbonate rocks.

Measurable iron concentrations at the springs are low, ranging from 0.02 to 0.7 ppm. Yet substantial amorphous iron hydroxide ($\text{Fe}(\text{OH})_3$) is precipitating on the mound surfaces close to the vents. Water containing 1-10 mg/L of iron as ferrous iron (Fe^{2+}) appears clear when drawn from a spring, but will subsequently precipitate an amorphous iron hydroxide (Hem, 1989). At Rabbitkettle, the appearance of iron precipitate upon discharge suggests that the original concentration of ferrous iron in solution must be in the order of 1-10 mg/L. Dissolved oxygen activity in a typical soil atmosphere at ordinary air temperatures is approximately $10^{-3.5}$ moles/litre (Hem, 1989). This amount of oxygen reacting with pyrite in the recharge zone will produce a final solution that should contain about 5 mg/L ferrous iron and 17 mg/L sulphate (Hem, 1989). If there is no replenishing of oxygen to the system--that is, if the system is closed--these should be the final values. Given Rabbitkettle sulphate concentrations, the initial iron concentrations should be closer to 10 mg/L prior to discharge. Higher iron concentrations like these can occur from lower recharge temperatures and from

oxygen being transported faster than water into the unsaturated zone at the point of recharge. This can happen if water is able to percolate slowly into an aerated recharge zone. As will be discussed later, Rabbitkettle water is likely recharged through fractures and conduits where rocks are exposed to the atmosphere.

While filtering the water samples from the three main springs, it was noted that the greatest amount of amorphous iron precipitate occurred on the filters for spring 001, a faint discoloration occurred at 002 and trace to none occurred on the filter paper for 003. Yet, all the springs deposit the precipitate within their channels. This is the result of a noticeable difference in Eh between spring 001 and the other main springs. Eh values for spring 001 were consistently higher, averaging around 323 millivolts (mV). Spring 002 averaged 271 mV, and 003 averaged 267 mV. A higher Eh indicates a more oxygenated environment and, therefore, any iron present in solution will be in its oxidized state (Fe^{3+}). This ion is very insoluble and therefore tends to form hydroxides at the Eh and pH values of these springs. The lowest Eh values, and the least iron-hydroxide ($\text{Fe}(\text{OH})_3$) filtrate, were measured from the most southerly spring (003).

Pyrite is oxidized in the recharge and subsurface zones by the reaction:

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (4).$$

Calculated Eh values, based upon the above reaction, thermodynamic data, the activities of sulphate (assuming that all the sulphate is from sulphide), ferrous-iron concentrations and pH of the spring waters reveal an equilibrium value of 280 mV. This value is close to those measured at the springs. Thus, the oxidation of pyrite likely controls the Eh of the subsurface reservoir.

As the waters reach the surface vents and flow over into the channels, the Eh increases due to oxygenation by the atmosphere. The north spring has the

highest Eh because its large vent sits high above the treetops and is exposed to winds that help aerate the water. The Eh of this spring is controlled by the oxidation of ferrous iron according to these reactions:

The south mound is surrounded by forest. Smaller pools and greater isolation from winds result in less aeration of the vent waters, and therefore lower Eh values. Spring 003 is the most enclosed and has the lowest Eh. Lower Eh measurements from the south-mound vents may be enhanced by the decomposition of algae, wood and other organic debris accumulated within these vents as a result of their close association with the forest. It is only after the waters exit the vents that they become oxygenated; then the Eh is controlled by reactions 5 and 6. These transitions are represented in Figure 7, modified from Hem (1989).

The nearby cooler spring (004) is derived from the same groundwater system as the three main springs, because all ion concentrations are the same, except for calcium and bicarbonate which are consistently lower, ranging from 132 to 186 ppm, and 600 to 765 ppm, respectively (as for the major springs, the highest values were recorded in 1992). The lower concentrations of these ions are in conjunction with higher pHs, averaging 7.31, and lower conductivities, ranging from 790 to 850 $\mu\text{S}/\text{cm}$, and can be explained by the precipitation of calcium carbonate from solution prior to discharge. This is confirmed by the fact that the water in spring 004 is supersaturated with respect to calcium carbonate, in comparison to the other spring waters which are near or at saturation.

Figure 7.
Stability field for iron in solution (from Hem, 1989). Shown are the average Eh and pH measurements for the four Rabbitkettle springs.

The temperature of spring 004 is lower and subject to fluctuation in contrast to the constant temperatures of the main springs. During the summers of 1991 and 1992 the temperature changed from 10° to 12.5°C. The gradual increase in temperature appears to be related to the onset of summer, and therefore was likely the result of warming ground temperatures. During the winter of 1993 the temperature of this spring was only 1.5°C. It appears that unlike the main springs, this spring is not isolated from surface influences.

Spring 004 has an average Eh of 268 mV, which is similar to the values of the southernmost springs. Given the average Eh and higher pH for this spring, according to Figure 7, any iron precipitate will have long since precipitated out of solution, explaining why there is no iron-precipitate around this spring vent. Brown and Wright (1979) believed this spring to be the result of the re-emergence of water from spring 002 as a result of infiltration back into the travertine. If this were the case, waters which are more oxygenated than spring 002 would be expected to emerge from spring 004. This is not happening.

Since the chemistry of spring 004 suggests that its waters are originally part of the main subsurface system, the water emerging here has likely been diverted by a "leak" from the main conduit system. The "leak" is in the near-surface, where water temperatures are influenced by cooler ground temperatures, imposed by local permafrost in the sediment. However, the temperature of the water warms as the ground temperature gradient warms during the summer. Both iron and calcium carbonate precipitate within the subsurface, prior to discharging.

Overall, the chemistries of *all* the spring waters are remarkably consistent in the long and short term, particularly with respect to conservative ions such as chloride and fluoride. This suggests that the system is not experiencing any

mixing with other subsurface waters. Constant year-round temperatures also suggest that there has been no significant input of water from a different thermal reservoir. Mixing with shallow subsurface waters, such as those present in the active layer, would result in substantial seasonal fluctuation in water temperature as well as ion content. Proportional mixing of deeper subsurface waters is also not possible. First, as will be pointed out later in the study (section 4.6), discharge is known to fluctuate at the springs, yet the chemical parameters remain relatively constant. Second, tritium concentrations (discussed in section 4.3) reveal a lack of fluctuation both during the summer and seasonally. Any fluctuation in chemistry that does occur can *generally* be related to changes in carbon dioxide.

Subsurface mixing of gases is occurring. The gas bubbling out of the spring water was analyzed and was shown to contain 61 to 64 percent $\text{CO}_{2(g)}$ and 36 to 39 percent $\text{N}_{2(g)}$. The presence of $\text{N}_{2(g)}$ indicates a strong meteoric component. The high portion of $\text{CO}_{2(g)}$ will be discussed in section 4.4i and shown to originate from the subsurface mixing of both meteoric and a deep $\text{CO}_{2(g)}$ source.

4.2 Aquifer System

As determined from the spring water chemistry, the aquifer supplying water to the hot springs is dominantly composed of carbonate. The only carbonate units in the vicinity of the springs are the Rabbitkettle and the Sunblood Formations (Figure 3). The limited exposure of the Rabbitkettle Formation in contrast to the Sunblood Formation makes the latter a more likely aquifer. There is also significant chemical evidence to support this. High Ca-HCO_3 concentrations and low Mg/Ca ratios indicate that mainly limestone was encountered along the flow path, with minor contact with magnesium-rich carbonate or dolomite. High Sr/Ca

ratios indicate that the limestone is fossiliferous. Cation-exchange processes and thus contact with shales are indicated by an unbalanced Na/Cl ratio. The upper member of the Sunblood Formation, as exposed in this area, consists of grey, slaty argillaceous and fossiliferous limestone. Iron and sulphate concentrations in the spring water are the result of the oxidation of pyrite. Pyrite is associated with the upper member of the Sunblood Formation, as well as being found within the overlying shale unit (Road River Formation).

The Sunblood Formation carbonates crop out to the west, east and south of Rabbitkettle Hotsprings, where they are surrounded and overlain by the Road River Formation. This shale provides a stratigraphic cap for a confined aquifer system. To determine which of these three areas is the most probable zone of recharge, a complete understanding of the recharge environment and flow history of the water is required.

4.3 Recharge and Groundwater Residence

Isotopes of oxygen, hydrogen and carbon provide useful tools for identifying characteristics of the zone of recharge. The isotopic compositions of oxygen and deuterium in the spring water will closely reflect the average annual temperature of the recharge environment; tritium can be used to determine the residence time of the water from recharge to discharge; and carbon isotopes will contain a record of the original carbon source, as well as information about the recharge waters.

Craig (1961) defined a global meteoric relationship between oxygen and deuterium in precipitation where:

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \text{‰} \quad (7).$$

which is known as the Global Meteoric Water Line (GMWL). ^{18}O and ^2H are expressed in per mille (‰) SMOW (Standard Mean Ocean Water). The GMWL is based on the temperature dependence of these isotopes as a result of fractionation processes. Precipitation occurring at cooler temperatures, generally consistent with increasing altitude and latitude, is more depleted in the heavy isotopes. Local variations, due to the origin of precipitation, isolated evaporation effects and seasonal effects, can alter this line, reflecting the local climate.

From the collection of rainwater, snow and local river waters in the Rabbitkettle area, a Local Water Line (LWL) was established (Figure 8). The equation of this line is:

$$\delta^2\text{H} = 7.0\delta^{18}\text{O} - 14.9 \quad (R = 0.99) \quad (8).$$

The two shallow lakes in the area fall on an evaporation line. All spring waters fall on or near this local water line, indicating that the aquifer waters must have recharged under similar climatic conditions as exist today. These data also indicate that, despite the waters being thermal, they have not undergone enrichment in ^{18}O from exchange with reservoir rocks at elevated temperatures (see section 4.4 ii).

The meteoric relationship between the spring water and local waters can also be used to trace the origin of the groundwaters. The fact that isotope fractionation is temperature dependent and thus altitude dependent (Dansgaard, 1964) can be useful in interpreting the recharge elevation of the spring water. Gat (1980) documented the effect of altitude on $\delta^{18}\text{O}$ values of precipitation. Commonly observed isotopic gradients have $\delta^{18}\text{O}$ values between -0.15 and -0.50 ‰ (SMOW) per 100-metre rise in elevation (Gat, 1980). The recharge elevation for the springs at Rabbitkettle was roughly calculated from ^{18}O data for fresh

snow taken at 2,000 metres a.s.l. within the Ragged Range glacier fields and for summer rains taken at 620 metres a.s.l. at Rabbitkettle Lake. An elevation change in $\delta^{18}\text{O}$ of -0.37‰ per 100-metre rise was determined. Based upon the $\delta^{18}\text{O}$ values of the spring waters (which average -22.8 per mille), a simple calculation places the recharge zone at an elevation of approximately 1,000 metres a.s.l.

Tritium, which is a radioactive isotope of hydrogen and has a short half-life of 12.43 years, was injected into the atmosphere during the 1950s and 1960s by nuclear bomb testing. Any waters with appreciable tritium must have been recharged since this time. Tritium in the spring waters varies from 24 ± 8 to 35 ± 8 T.U. in the 1991/92 analyses, and was 34 ± 8 T.U. in 1986 (Hamilton, 1990); these numbers suggest that the waters were recharged within the last 10 to 25 years. The range is based upon tritium contents of precipitation collected in Whitehorse during the mid-1980s (personal communication, F.A. Michel, 1992), and extrapolated tritium levels in precipitation in the Central Mackenzie Valley between 1961 and 1975 (Michel, 1977). Tritium in the spring waters accurately reflect the age of the recharge waters because there has been no mixing with other subsurface waters. Modern tritiated rainwaters have not contaminated the large vent pools, as local rains contain lower concentrations of tritium, in the range of 12 ± 8 to 21 ± 8 T.U.

Carbon isotopes are useful in interpreting the environment in which the waters have recharged, by providing information about the original source of carbon. The most common sources of inorganic carbon in groundwater are atmospheric and plant carbon dioxide dissolved in the water during recharge, and carbon introduced due to the dissolution of carbonate rocks along the flow path.

Sources of carbon dioxide can be determined based upon the $\delta^{13}\text{C}$ values for both carbon dioxide ($\text{CO}_2(\text{gas})$) and dissolved inorganic carbon (DIC) present within the discharging spring. The isotopic composition of carbon in solution at the spring vents closely represents the $^{13}\text{C}/^{12}\text{C}$ ratio of the spring system before the waters reach the surface (Turi, 1986). The carbon-13 of the DIC, measured at the three main springs, ranges from -2.3 to -1.4 ‰(PDB). The carbon-13 of the DIC in the cooler spring is +0.29 ‰(PDB). These values appear to reflect carbon derived principally from the dissolution of carbonate, as the local carbonate rocks contain carbon-13 in the range of -2.8 to +0.7 ‰ (Hamilton, 1990). This suggests that the dissolution of limestone is occurring under closed-system conditions. In a closed system, water encounters and begins dissolving carbonate after becoming isolated from the atmosphere. The carbon in solution then shifts towards the isotopic composition of the surrounding carbonate rocks.

However, most studies of groundwaters in limestone aquifers have measured partial pressures of carbon dioxide that are almost always above atmospheric. This suggests that dissolution in carbonate terrane takes place predominantly under open-system conditions (Freeze and Cherry, 1979; Drever, 1988; Langmuir, 1971). Rabbitkettle spring waters are no exception, exhibiting high partial pressures of carbon dioxide (see section 4.1) which suggest that closed-system conditions do *not* dominate.

Under open-system conditions, the water acquires carbon dioxide prior to entering the saturated zone, and begins dissolving most of its carbonate before entering the flow system. Thus, there is a continual supply of carbon dioxide for the dissolution of carbonate, and complete equilibrium is established between the input- CO_2 and the DIC. The composition of the final DIC in terms of carbon-13

will be determined by the initial input- CO_2 , the relative proportions of DIC and most importantly, by the fractionation between $\text{CO}_{2(\text{gas})}$ and DIC; not by the dissolution of limestone.

The contribution of carbon dioxide to the subsurface groundwater system from the recharge "soil" environment originates from the decomposition of organic material. Since the rate of biochemical activity is temperature-dependent, the greatest concentrations of carbon dioxide in this zone are produced during the summer months (Trainer and Heath, 1976). Areas with shorter growing seasons, particularly high along mountain slopes, have lower overall carbon dioxide concentrations (Rightmire, 1978; Trainer and Heath, 1976).

Table 1. Carbon dioxide contributions

	pCO_2 (atm) range	$\delta^{13}\text{CO}_2$ (‰ PDB)
Atmospheric	$10^{-3.5}$	-7 to -10
Biogenic	$10^{-1.0}$ to $10^{-3.0}$	-15 to -23
Rabbitkettle	$10^{-5.0}$ to $10^{-7.8}$	-8.05 to -8.55

At Rabbitkettle, biological activity and recharge into the aquifer is suppressed during the long frozen winters. Therefore, most replenishment to the aquifer is presumed to occur during spring melting and by frequent rains during the summer. Contributions of carbon dioxide from the melting of snow during the spring would have isotopic values and partial pressures of carbon dioxide consistent with an atmospheric contribution. Carbon dioxide from the atmosphere has $\delta^{13}\text{C}$ values in the range of -7 to -10 ‰ (PDB) and partial pressures of $10^{-3.5}$ atmospheres. As the summer progresses, even high mountain slopes will contain an active recharge zone with some sort of biological activity. Higher levels of biogenic activity consistent with the decomposition of plant life ranging from

lichens to trees (Fritz, et al., 1978), would contribute carbon dioxide with $\delta^{13}\text{C}$ values between -15 and -23 ‰ PDB (Deines, 1980; Rightmire and Handshaw, 1973; Pearson and Handshaw, 1970). Generally, partial pressures of carbon dioxide from the decomposition of organics fall in the range of $10^{-1.0}$ to $10^{-3.0}$ atmospheres (Freeze and Cherry, 1979). However, at higher altitudes, the volume of carbon dioxide produced is likely to be at the lower end of this range as a result of cooler temperatures.

Since Rabbitkettle spring waters are composed of a mixture of both melting snow and summer rain, the resultant contributions of carbon dioxide should have $\delta^{13}\text{C}_{(\text{CO}_2)}$ values and partial pressures representative of both. However, the actual $\delta^{13}\text{C}_{(\text{CO}_2)}$ values of the gas being released from the spring vents are between -8.05 and -8.55 ‰, which initially suggests that carbon dioxide is being contributed only from an atmospheric source or during snowmelt, which we know is not the case. Also, partial pressures of carbon dioxide are much greater than expected for either an atmospheric or a biogenic source, as values fall in the range of $10^{-.50}$ to $10^{-.78}$ atmospheres. To enrich the $\delta^{13}\text{C}_{(\text{CO}_2)}$ enough to fall in the range seen in the spring water, some dissolution of the limestone must have taken place under partially closed-system conditions. This would also explain the enriched $\delta^{13}\text{C}_{\text{DIC}}$ values that occur in the spring waters. Since the process of dissolving carbonate decreases the partial pressure of carbon dioxide in solution, carbon dioxide *must* be coming from an additional source besides the recharge zone. The significance of this will be discussed in section 4.4 i.

This region is subject to discontinuous permafrost that becomes more continuous at higher elevations. Therefore, high-altitude recharge is likely inhibited by permanently frozen soils. Where high-altitude recharge does occur, it

likely infiltrates directly into permeable rocks in areas with little or no soil cover. The occurrence of detectable dissolved oxygen contents of 0.2 mg/L (van Everdingen, 1973) in the Rabbitkettle spring waters, suggests that waters have likely percolated into an aerated recharge zone (Freeze and Cherry, 1979). Iron and sulphate concentrations, discussed in section 4.1, also indicate such recharge conditions. Finally, open-system dissolution implies that carbonate mineralization occurs within the unsaturated zone. In this region it is likely the exposure of the Sunblood Formation to the atmosphere, with infiltration directly into fractures and dissolution cracks.

Of the three possible recharge areas mentioned earlier, the waters are believed to have originated along the mountain spur to the southeast of the hotsprings (Plate I), where the Sunblood Formation is exposed at and above the tree line (Figure 9). This mountain spur is considered to be the most likely site of recharge because it is the nearest exposure of permeable carbonate rocks in the area. The neighbouring shales and monzonites are impermeable, and the spring-water chemistry shows no evidence of these units. The $\delta^{18}\text{O}$ versus elevation change suggests that recharge takes place at roughly 1,000 metres a.s.l., which falls in the middle of this exposure. The area is also considered to be the most likely site of recharge because the alignment of this mountain spur and the hotsprings suggests a structural relationship between the two. The average hydraulic conductivity of the aquifer and fault based on the mean residence time and average distance to this exposure was determined to be in the range of 10^{-4} centimetres/second. This coincides with an average hydraulic conductivity for limestone of 10^{-4} to 10^{-7} centimetres/second (Freeze and Cherry, 1979). The distal outcrops of the Sunblood Formation across the South Nahanni River and to

Figure 9.
Local geology and topography showing the mountain spur where recharge is taking place. Line SE to NW is shown in cross-section in Figure 10 and is at a low angle to the fault.

Figure 10.
Cross-section from recharge to discharge.
Location of line SE to NW is shown in Figure 9.

the west along the Rabbitkettle River are too far away and have many opportunities to discharge into rivers prior to reaching the hotspring site.

The outcrop of the Sunblood Formation along the mountain spur forms part of the limb of a gentle syncline. At 1,000 to 1,100 metres a.s.l., along the mountain spur, a deep crevasse exists within the Sunblood Formation exposure. This crevasse is believed to be a catchment area for precipitation. Recharge is from direct runoff that enters the subsurface through dissolution channels, fractures and bedding planes. Most of the recharge occurs during spring snow melt and frequent summer rainfalls. During the long frozen winters, input into the aquifer is suppressed.

4.4 Subsurface Flow

i. Sources of Carbon Dioxide

Neither of the earlier mentioned closed- or open-system models can account for either the volume of CO₂ released at the discharge vents or the enriched carbon values, which suggests that there must be an additional source of carbon dioxide. Throughout most of the world, high-pCO₂ springs are generally associated with young orogenic belts and seismically-active areas. The carbon dioxide originates from either mantle sources or from the metamorphic decarbonation of limestones (Irwin and Barnes, 1980; Hamilton *et al.*, 1991). Volcanogenic and metamorphic sources can produce pCO₂ values much greater than 10⁻¹ atmospheres (Clark *et al.*, 1982).

The carbon dioxide being released from the spring waters at Rabbitkettle exhibit $\delta^{13}\text{C}$ values between -8.05 and -8.55 ‰, which are lower than the calculated equilibrium values of -6.40 to -7.40 ‰ ($\delta^{13}\text{C}_{(\text{CO}_2)}$) estimated from the

$\delta^{13}\text{C}_{\text{DIC}}$ data using the mass balance equation in Appendix 8). The slight depletion of ^{13}C in the gas samples over expected equilibrium values may be the result of the rapid degassing at the vents, resulting in the preferential loss of isotopically lighter CO_2 . Volcanogenic or mantle-derived CO_2 have $\delta^{13}\text{C}$ values between -8 to -4 ‰ (Irwin and Barnes, 1980). Although these values are in the same range as the carbon dioxide signatures for the Rabbitkettle springs, a volcanic source is unlikely, as all the high- pCO_2 springs in the region are associated only with carbonate rocks. A more reasonable source for the excess carbon dioxide would be the thermal metamorphism of carbonates.

In France, recent volcanic activity and associated contact metamorphism of carbonates produce fault-associated high- pCO_2 springs (Blavoux *et al.*, 1982). Similar systems occur in British Columbia, with high-partial-pressures of carbon dioxide from mantle sources and the decarbonation of carbonate rocks (Clark *et al.*, 1982, 1988). Also in Canada, high- pCO_2 discharges occur along the seismically active St. Lawrence valley (Barnes *et al.*, 1978, 1984).

Hamilton (1990) described a series of travertine-precipitating springs located along the Flat River valley to the south of Rabbitkettle, that have high partial pressures of carbon dioxide. This valley is fault-controlled and has been known to be seismically-active, although no major activity has been noted since 1961 (Hamilton *et al.*, 1991). Hamilton (1990) concluded that the high- pCO_2 values were the result of the decarbonation of limestones in close association with the quartz monzonite intrusions. Bowman (1990) and Timlin (1991) came to the same conclusion for springs along the Flat River valley. The Rabbitkettle springs have lower volumes of CO_2 than the Flat River springs, but may be more distal with respect to a similar system. In the Flat River valley, CO_2 -rich fluids are

believed to migrate up from depth through an open fault and mix with shallow meteoric waters (Hamilton, 1990). The absence of a thermal interaction between the spring water and rock, which would result in a shift in the spring water away from the Local Water Line, suggests that a separate CO₂-rich phase is travelling up the fault from depth (Hamilton, 1990). Rabbitkettle waters also show no such water/rock interaction and are believed to be controlled by a similar process. The underlying Broken Skull Fault, which creates a pipeline for the aquifer water to reach the surface (see section 4.5), also provides a path for deep-seated metamorphic CO₂ to migrate into the groundwater system prior to discharge. Considerable seismic activity has been noted along the Broken Skull Fault.

However, this system is not entirely the same as along the Flat River. The Flat River springs have higher partial pressures of carbon dioxide and the $\delta^{13}\text{C}$ values of the CO_{2(g)} and DIC are more enriched (Appendix 4). The thermal decomposition of limestone at depth produces CO₂ with $\delta^{13}\text{C}$ values similar to, or a few per mille greater than, the carbonates which are being altered (Shieh and Taylor, 1969). The final carbon dioxide produced at the springs should be in the range of the carbon-13 composition of the local carbonate formations (-2.8 to +0.7 ‰ PDB), or be slightly more negative to take into account the fractionation of ¹³C from metamorphism as well as the gradual depletion of the initial carbonate as metamorphism progresses.

The Flat River springs contain pCO₂ derived almost entirely from the decarbonation of limestones. Rabbitkettle spring waters contain CO₂ gas that is *not* derived solely from the decarbonation of marine carbonates, because the final gas is less enriched in ¹³C than the local rocks. As determined in Section 4.4, it is also *not* derived solely from biogenic soil CO₂. The actual $\delta^{13}\text{C}$ of the CO_{2(gas)}

indicates isotopic mixing between both sources. Since two sources are involved, a model needs to be derived which will estimate the relative proportions of each carbon source in the overall system.

The model should determine the proportion of carbon dioxide contributed from the soil-environment and from a metamorphic source. It will take into account the resultant dissolved inorganic carbon and the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values contributed by each source. Therefore, the model will need to predict in advance what these values will be at calcium carbonate saturation in a soil- pCO_2 environment. It will also need to predict the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values contributed from the metamorphic source.

First, we will consider the conditions when only soil- pCO_2 is contributing to the carbon dioxide pool. Theoretical values for a soil environment discussed in the previous section are summarized in Table 2. Both estimated isotope values and pCO_2 contributions are in agreement with other springs in the Nahanni region (data for these springs are from Hamilton, 1990; Hamilton *et al.*, 1991). From this region, carbonate-rich spring waters believed to have an input of only soil-generated CO_2 exhibit partial pressures of carbon dioxide between $10^{-1.5}$ to $10^{-2.5}$ atmospheres. These springs also produce $\delta^{13}\text{C}_{\text{CO}_2}$ values of -16 to -18 ‰ (PDB) and DIC values of -7 to -10 ‰ (PDB). In all cases carbonate is assumed to be dissolved *predominantly* under open-system conditions.

In order to estimate the contribution of soil- CO_2 to the Rabbitkettle system we must also assume *predominantly* open-system dissolution of carbonate. This assumption is not unreasonable, as it is known that the waters are heated in the subsurface (section 4.4 ii). Since the waters recharge at temperatures not far above 0°C , and carbonate minerals have the greatest solubility at low temperatures, the

system will soon become saturated with respect to calcium carbonate. Based upon estimates of the maximum subsurface temperatures (section 4.4 ii), calcium carbonate will reach two to three times its saturation point. It is unlikely that calcium carbonate will precipitate because of increased pressure at depth and the fact that calcium carbonate generally does not precipitate until reaching five to ten times its saturation (Stumm and Morgan, 1981; Lorah and Herman, 1988). The water cools as it rises to the surface, never reaching temperatures as low as those of the recharge zone. Therefore, opportunity for closed-system dissolution is limited.

Table 2. Carbon dioxide parameters defining the model

	pCO ₂ (atm)	δ ¹³ CO ₂ (‰ PDB)	δ ¹³ DIC (‰ PDB)
<u>Theoretical Values</u>			
Closed-system	<<10 ⁻¹	-7 to -10	-2.8 to +0.7
Open-system	10 ^{-1.0} to 10 ^{-3.0}	-15 to -23	-5 to -13 ²
Open-partially closed system (q = .8)	<10 ⁻¹		-4.2 to -10.6
<u>Regional Values</u>			
Local biogenic pCO ₂	10 ^{-1.5} to 10 ^{-2.5}	-16 to -18	-7 to -10
Decarbonation of local carbonate rocks	10 ^{-0.6} to 10 ^{+0.6}	-4.9 to +0.7	-0.5 to +2.5
<u>Rabbitkettle Values</u>	10 ^{-7.8} to 10 ^{-5.0}	-6.4 to -7.4 (equilibrium)	-2.3 to -1.4

Metamorphic CO₂ due to the decarbonation of limestone mixes with the saturated groundwater, decreasing the pH and enabling more carbonate to be dissolved, thus adding to the DIC pool in the range of the original rocks. The contribution of carbon dioxide from this source can also be estimated. However, the estimated values will represent both the carbon dioxide source and the

²ε_{HCO₃-CO₂} of approximately 10 per mille based on the fractionation equation 1000lnα = (9.483 × 10³/T) - 23.89 (Mook, 1974); where T = 280.15°K, the average groundwater temperature of the region (Hamilton, 1990).

dissolution of carbonate under closed-system conditions as these components can not be distinguished. The extremely high $p\text{CO}_2$ values exhibited by the Flat River springs indicate that essentially 99 percent of the CO_2 is from the decarbonation of carbonates. The ^{13}C composition of the CO_2 (-4.9 to +1.6 ‰, Hamilton, 1990; Hamilton *et al.*, 1991) therefore represents the isotopic values for a metamorphic CO_2 contribution in this region. Similarly, the $\delta^{13}\text{C}_{\text{DIC}}$ contributions for these springs (-0.5 to +2.5 ‰) are also representative of this source.

The following equation, the basis for this model, represents the isotopic equilibrium conditions for any solution of given molalities of dissolved inorganic carbon at neutral pH values:

$$\delta^{13}\text{C} \cdot m_{\text{DIC}} = [m_{\text{H}_2\text{CO}_3} \cdot (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3} \cdot (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{HCO}_3-\text{CO}_2})] \quad (9).$$

Where: m = molality, ϵ = enrichment = $1000 \ln \alpha$, (α = fractionation factor). The per mille difference between $\text{CO}_{2(\text{g})}$ and DIC is related to the $\delta^{13}\text{C}$ of the gas under equilibrium conditions. The model takes this equation farther by assuming that the isotopic composition and molarity of the total dissolved carbon in solution at the springs is equal to the sum of the soil and metamorphic components by the revised equation:

$$\delta^{13}\text{C}_{\text{DIC(f)}} \cdot m_{\text{DIC(f)}} = [m_{\text{H}_2\text{CO}_3(\text{s})} \cdot (\delta^{13}\text{C}_{\text{CO}_2(\text{s})} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3(\text{s})} \cdot (\delta^{13}\text{C}_{\text{CO}_2(\text{s})} + \epsilon_{\text{HCO}_3-\text{CO}_2})] + [m_{\text{H}_2\text{CO}_3(\text{m})} \cdot (\delta^{13}\text{C}_{\text{CO}_2(\text{m})} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3(\text{m})} \cdot (\delta^{13}\text{C}_{\text{CO}_2(\text{m})} + \epsilon_{\text{HCO}_3-\text{CO}_2})] \quad (10).$$

which can be simplified to:

$$\delta^{13}\text{C}_{\text{DIC(f)}} \cdot m_{\text{DIC(f)}} = [m_{\text{DIC(s)}} \cdot \delta^{13}\text{C}_{\text{DIC(s)}}] + [m_{\text{DIC(m)}} \cdot \delta^{13}\text{C}_{\text{DIC(m)}}] \quad (11).$$

The final concentrations of carbon dioxide and $\delta^{13}\text{C}$ values for Rabbitkettle spring waters will fall between the local soil-input and the metamorphic estimates. From solubility calculations, based on an estimated temperature of recharge of 7°C (average groundwater temperature, Hamilton, 1990), it was determined that for an average soil- pCO_2 of $10^{-1.9}$ atmospheres, the concentrations of bicarbonate at saturation would be 216 ppm. The data presented in Table 2 were used as the parameters in the above equations. Numerous iterations were performed to determine the possible variations within these parameters which would give the same DIC concentrations and isotopic values as seen in the Rabbitkettle spring waters. Based upon the model shown in Appendix 8, the CO_2 in the spring waters represents a mix of roughly 64 to 86 % metamorphic-derived CO_2 .

ii. Geothermal Controls

Because groundwater gradually cools as it migrates to the surface through contact with cooler material, the maximum temperature reached by the water tends to be higher than the measured temperature at the surface. Low surface temperatures either reflect this cooling, or indicate a lack of depth penetration in the subsurface. At Rabbitkettle, the constant warm spring-water temperatures are indicative of a deep circulating flow system. A shallow flow system, in a permafrost region, would cease to discharge in winter because of a frozen active layer; the Rabbitkettle springs discharge all year-round.

The fact that Rabbitkettle waters are thermal and the relationship with the local meteoric water line shows no geothermal shift (Figure 8) suggests that the waters have not reached temperatures in the subsurface in excess of 100°C (Truesdell and Hulston, 1980). Beyond this temperature, oxygen-18 values from

the local rocks, which range from +18.8 to +22.6 ‰(SMOW), would enrich the final isotopic content of the spring water. Since deuterium is not a common component of rock-forming minerals, there would be no equivalent shift away from the meteoric water line with respect to deuterium.

Further evidence that subsurface temperatures have not exceeded 100°C is provided by the low concentrations of silica and chloride, elements characteristic of higher-temperature systems. In addition, the low solubility of calcite at temperatures above 100°C rules out the deposition of travertine in the vent area for higher-temperature systems (White, 1970; Ellis and Mahon, 1977).

In establishing that the Rabbitkettle spring waters are of relatively low temperature, some common geothermometers were applied to the data in order to determine the maximum possible reservoir temperature. However, most of the standard geothermometers were found to be inadequate. The main reason is that the majority of chemical geothermometers are based upon dissolution within crystalline rock systems, and on the temperature-dependent equilibrium reactions controlling the dissolution of feldspars and other silicate minerals. Nonadiabatic cooling in the upflow zone (Fournier and Truesdell, 1973), and an influx of carbon dioxide from depth (section 4.4 i) also hinders the usefulness of these geothermometers. Lower temperature systems are sensitive to changes in the partial pressure of carbon dioxide because of the higher solubility of calcium carbonate. Common isotope geothermometers also proved to be ineffective because longer reaction times were needed to reach equilibrium conditions.

The silica geothermometer proved to be the only useful geothermometer for this low-temperature system, because it is not affected by conductive cooling with the surrounding wallrock over short time spans or by the influx of carbon dioxide

(dissolution of carbonate). With enough available silica in the source rocks to saturate the solution, this geothermometer works for the temperature range of 0° to 250°C. All polymorphs of silica have solubilities that increase over this temperature range. Quartz has the lowest solubility; chalcedony and cristobalite are more soluble and amorphous silica is the most soluble. For most natural waters, the solubility of quartz controls the concentration of silica in solution at temperatures greater than about 100° to 150°C (Fournier, 1970). Waters that have not exceeded temperatures of 90° to 100°C, such as Rabbitkettle, will have equilibrated with chalcedony (Fournier, 1981) rather than quartz.

To determine the silica-geothermometer temperatures of these springs, it is more appropriate to utilize the chalcedony rather than the quartz geothermometer, because chalcedony dominates the system. The silica-geothermometer temperature with respect to chalcedony can be calculated from the equation:

$$t^{\circ}\text{C} = 1032 / (4.69 - \log[\text{SiO}_2]) - 273.15 \text{ (Fournier, 1981)} \quad (12).$$

using silica concentrations in ppm. Table 3 includes silica concentrations from past and current studies at Rabbitkettle, and calculated reservoir temperatures.

Despite the variability in silica concentrations, the springs are always saturated with respect to quartz and undersaturated with respect to amorphous silica. However, the saturated conditions of chalcedony and the estimated subsurface temperatures differ. The variation of silica concentrations is not the result of speciation as all the silica in solution is reactive or in the form $\text{H}_4\text{SiO}_{4(\text{aq})}$. It is not due to precipitation of silica from solution as the samples exhibiting low silica concentrations are undersaturated with respect to chalcedony; loss through precipitation would result in supersaturated conditions. With the absence of subsurface mixing, the variation is not due to dilution with cooler

subsurface waters. Therefore, the fluctuation in silica concentrations is more apt to be the result of the "accessibility" of silica from the source rock.

Table 3. Silica geothermometer applied to spring 001

Date (Reference)	Silica concentration (ppm)	Chalcedony Saturation	Chalcedony Geothermometer Temperature (°C)
July 1963 (Gabrielse <i>et.al.</i> , 1963)	15	undersaturated	20.5
June 1973 (van Everdingen, 1973)	13	undersaturated	15.4
August 1976 (Crandall, 1976)	40	saturated	61.1
Summer 1986 (Hamilton, 1990)	16	undersaturated	22.9
Summer 1990 (Hamilton, 1990)	5.6	undersaturated	-11.3
June 1991	6.0	undersaturated	-9.3
March 1992	47.23	saturated	69
June 1992	7.2	undersaturated	-3.9

"Accessibility" is not, in this case, synonymous with "availability" as chalcedony can originate from chert within the Road River Formation or possibly from radiolaria within fossiliferous components of the Sunblood Formation. It refers to the water's ability to dissolve silica from these sources. At low temperatures, groundwaters need longer reaction times to equilibrate with the surrounding rock. If equilibrium is not reached, insufficient silica will be dissolved and result in estimates of subsurface temperatures that are too low. At Rabbitkettle, discharge is known to fluctuate (see section 4.6) and may provide the explanation for the deviation in silica concentrations. Low silica and

undersaturated conditions can be associated with higher discharge volumes and shorter contact times with the rocks in the subsurface, conditions common to the spring and summer. High silica concentrations can be associated with low flow rates and longer contact times with the rocks in the subsurface, conditions common during the winter. The anomalously high summer concentration in 1976 may reflect below-average rainfall and low aquifer flow rates at this time. Subsurface temperature estimates can be calculated from chalcedony-saturated water; at Rabbitkettle subsurface temperatures are calculated to be between 60° and 69°C.

iii. Groundwater Circulation

Although the flow system feeding Rabbitkettle Hotsprings is deep, it cannot be excessively deep because of the low geothermometer estimates, moderate Eh measurements (not anaerobic) and the presence of tritium, which all indicate that the waters have not travelled extensively within the subsurface. Thus, to reach temperatures of 60°C to 69°C, the spring waters must be subject to a higher-than-normal geothermal gradient.

This higher-than-normal geothermal gradient is imposed by the neighbouring quartz monzonite intrusions; high conductive heat flow within the intrusions is known to exist because most springs spatially associated with them are thermal (Hamilton *et al.*, 1988). The actual heat flow of the Ragged Range plutons is unknown due to a lack of study in the region. However, the Cantung mine in Tungsten reports mine waters of 16°C occurring in an adit only a few hundred metres below the surface of a mountain (Hamilton, 1990). The age of the intrusions (110 m.y.) excludes them as a source of heat (latent heat of crystallization), and there is no evidence of more recent magmatic activity in the

area. A probable source of heat is radioactive decay within the quartz monzonites; this is a conclusion also reached by Hamilton *et al.* (1991). The radioactive decay of uranium, thorium and potassium is responsible for more than 98 percent of heat generated in most terrestrial rocks (Turcotte and Schubert, 1982); granitic rocks have the highest concentrations of these elements. Although this idea needs further investigation, it could result in the metamorphism of nearby carbonates at relatively shallow depths, explaining both the apparent heat flow and the $\text{CO}_2(\text{gas})$ emissions where carbonates and intrusions are localized.

Average worldwide-regional heat flows have been estimated at 60 mW/m^2 (Forster and Smith, 1989). In general, the radioactive decay of isotopes is responsible for 80 percent of surface heat flow, whereas the remaining 20 percent is from the cooling of the earth (Turcotte and Schubert, 1982). Higher-than-normal heat flow is often associated with tectonically- or seismically-active regions or from areas with strong radioactivity (Turcotte and Schubert, 1982). In particular, high heat flow from radioactivity is common to regions of great crustal thickness, as such areas have a greater amount of radioactive heat per column of unit area (Majorowicz *et al.*, 1988). This region of study has both seismicity and radioactivity.

In the interior of the Cordillera the average heat flow is 82.2 mW/m^2 (Jessop *et al.*, 1984). To the east, toward the Mackenzie Valley, heat flow has been calculated at 130 to 140 mW/m^2 (Majorowicz *et al.*, 1988). The average heat production of neighbouring granitic to granodioritic plutons located 100 to 150 kilometres to the northwest of Rabbitkettle is $7.69 \mu\text{W/m}^3$ (personal communication, Trevor Lewis, 1993), which translates to an estimated heat flow of 127 mW/m^2 . Due to the proximity of these plutons and the similar

compositions, it is within reason to extrapolate these high heat flow values to the Rabbitkettle area.

Rybach (1981) derived an equation for the determination of heat flow based on the silica-geothermometer temperature of thermal spring waters. The equation is:

$$H = 1.49 \text{ mW/m}^2 * T(\text{silica}) - 13.2^\circ\text{C} \text{ (Rybach, 1981)} \quad (13).$$

and was used in this study on spring waters from within the intrusions of the Nahanni region. Quartz controls the solubility of silica in granitic terrane at temperatures greater than 90°C (Fournier, 1981). Therefore, the quartz-geothermometer³ was used on hot spring waters local to the Ragged Range intrusions, based upon silica concentrations from Hamilton (1990). The average silica temperature estimate for these hot springs was determined to be 103°C . Therefore, from equation 13, calculated heat flow within these intrusions is estimated at 140 mW/m^2 . Based on *all* the above heat flow estimates, the geothermal gradient for this region is estimated to be between 50° to 60°C per kilometre. Rabbitkettle spring waters, therefore, may have circulated to depths of little more than 1 kilometre.

The occurrence of metamorphic carbon dioxide and the spatial association of hot springs with the intrusive bodies suggest that subsurface temperatures have reached at least 180° to 300°C , which is the temperature of reaction for impure carbonate (Muffler and White, 1968, 1969). Therefore, the depth for the production of carbon dioxide would be roughly 3 to 5 kilometres (Hamilton, 1990; Hamilton *et al.*, 1991).

³ The equation for the quartz-geothermometer is: $t^\circ\text{C} = 1309 / (5.19 - \log \text{SiO}_2) - 273.15$ (Fournier, 1981). Silica concentrations used in the equation are from Hamilton (1990).

The above scenario does not explain how the spring water temperatures can remain essentially at 20°C when the water is being heated at depth, and discharge within the springs has been known to fluctuate by as much as 50 percent (see section 4.6). With a constant heat-flow source, changes in the advective disturbance (forced convection) as a result of changing discharge should result in fluctuating-discharge temperatures. Since this is not happening, the heat flux transferred by the passing water must be inconsequential with respect to the heat flux generated by the intrusive rock mass. Therefore, the thermal conditions of the system must be dominated by conductive rather than advective heat transfer.

To support the above assumption, the specific discharge (or darcian velocity, q) within the Rabbitkettle system was calculated to be a maximum of approximately 10^{-8} metres/second. This value is considered to be a maximum for the aquifer because it was derived for the entire flow system, including more rapid groundwater flow within the fault. Based on studies within horizontal sedimentary basins, Cermak (1989) noted that where darcian velocities are less than 10^{-8} metres/second, the groundwater imparts no advective distortion on the conductive heat flux.

The theory of a conduction dominated thermal system at Rabbitkettle can also be established by calculating a peclet number, which is actually a ratio of convective to conductive heat flux within an aquifer. Assuming an open system, the peclet number, Pe^* , can be calculated from the following equation:

$$Pe^* = \rho_f c_f * q_H * D^2 / \lambda * L \quad (14)$$

(van der Kamp and Bachu, 1989); where: $\rho_f c_f$ is the density and heat capacity of the water; q_H is the horizontal specific discharge (which we will assume equal to the maximum value of q); $\lambda = 2.5 \text{ Wm}^{-1}\text{K}^{-1}$, the average thermal conductivity of

the aquifer; $L = 4500$ m, the average horizontal distance to the recharge area; and D , is the aquifer thickness. The estimated thickness of the Sunblood Formation in the Rabbitkettle area is a maximum of 180 metres (Gabrielse *et al.*, 1965, 1973). From this, the peclet number is calculated to be $Pe^* = 0.12$, which suggests a dominantly conductive thermal system. Similarly, even if water was being contributed to the system by the underlying Rabbitkettle Formation with a thickness of 90 to 300 metres in the Rabbitkettle area (Gabrielse *et al.*, 1965, 1973), the maximum calculated peclet number would be 0.85; still suggesting a dominantly conductive aquifer system.

The fault zone is significantly more permeable than the surrounding rock mass, and advection is able to play a greater role here. Warmer isotherms are pulled toward the surface, resulting in the warm surface temperatures of the springs. Nevertheless, the spring water flux to heat flux ratio is still small enough to maintain constant spring water temperatures within 1°C. Therefore, a conduction-dominated system is able to explain the constant discharge temperatures of the hotsprings.

4.5 Hydraulics

Within the Cordillera, groundwater flow systems tend to recharge at higher elevations on mountain slopes, and discharge along valley floors or lower mountain slopes (van Everdingen, 1972; Michel, 1986). The spring waters discharging at Rabbitkettle are interpreted to recharge high along the mountain spur between 3 and 6 kilometres to the southeast of the hotsprings (Figure 9). Elevation differences provide the topographic drive for groundwater movement; flow is maintained by continual replenishment by precipitation and the hydrostatic

weight of the water extending down-dip from the recharge area under pressure in a confined aquifer.

The water flows through the aquifer in a northwesterly direction, following the hinge of a gently plunging syncline, until it intersects the fault underlying the hotsprings. This fault, an extension of the Broken Skull Fault, has been mapped along the Broken Skull River where it meets the South Nahanni River valley. Evidence for this fault includes the change in geology across the South Nahanni River and a line of travertine-precipitating springs along the South Nahanni River valley (Hamilton, 1990). A fault-controlled system at Rabbitkettle is suggested by the linearity of the mountain spur and its alignment with the springs. In addition, a 20-metre long exposure of old travertine was discovered along the fault line at the top of the west ridge at Hole-in-the-Wall Creek (Figures 4 and 9), above where the creek intersects the mountain spur. The spring which deposited this travertine was no doubt once part of the same fault-controlled system. Finally, the presence of excess carbon dioxide which has been generated at depth suggests that the hotsprings are fault-controlled.

The aquifer intersects this fault at depth, and the water is forced to flow upwards through the bedrock towards the surface. It then encounters an unknown thickness of unconsolidated Quaternary deposits. At one time, Hole-in-the-Wall Creek intersected the mountain spur near the hotsprings. At this time, the creek removed a substantial thickness of glacial material, evidenced by the "cut" in the local till to the west of the south mound. The removal of much of this overburden provided an easier passage for the groundwater to reach the surface from the underlying bedrock.

More importantly, it created potential for the development of taliks in the otherwise frozen ground. Taliks, which are thermal holes in the permafrost, were easily maintained within the glacial deposits long after the disappearance of the creek due to the high temperature of the spring waters flowing through them. The presence of taliks provides the best explanation for channelling flow through the unconsolidated sediment from the underlying bedrock fault. The geomorphological development around the hotsprings provided perfect conditions for talik development. Periglacial conditions associated with permafrost which were observed at the hotsprings site include patterned ground, frost heave and frost shatter (see Appendix 5). Groundwater discharge from subpermafrost sources, through taliks, generally have relatively *constant* flow rates, total dissolved solid (TDS) concentrations and temperatures (van Everdingen, 1974), as is the case at Rabbitkettle. Carbonate-saturated waters, able to flow to the surface, initially cemented the local glacial sediments into a conglomerate, then continued to form travertine-lined conduits to the surface, creating vents which were built up from many years of travertine precipitation. The circulation of the water and the absence of precipitation within the conduits keep the spring vents open. The continued deposition of travertine eventually resulted in coalescence of the individual spring mounds into a larger terraced structure.

At some time during this development, a meander in the Rabbitkettle River cut a terrace in front of the travertine structure and exposed the underlying glaciofluvial gravels. Afterwards the present north mound began to develop. A fluvial origin for the terrace is supported by airphoto interpretation, remobilization of large boulders deposited earlier by the creek and /or from the overlying till, and the presence of large boulders of travertine-cemented conglomerate downstream

from the spring deposit. Large travertine blocks buried under vegetation at the base of the south-mound terrace are believed to have fallen off the mound during the undermining process; this is similar to what has occurred along the edge of the north mound where it has been undercut by more recent migration of the river.

The springs do not discharge at the lowest point in the valley, which today is the level of the Rabbitkettle River. Since the time of spring formation, Hole-in-the-Wall Creek has relocated and the Rabbitkettle River has incised deeper into the valley floor. The springs will maintain their present locations as long as the underlying conduits or taliks are maintained, since these remain the easiest paths to the surface. Excess leakage or fractures in the conduits could provide alternative routes. Local evidence of smaller seepages, perched water tables, pooled water, patterned ground and the more recent development of the fourth cooler spring suggest that the hydraulics of the site may be continuing to change (Chapter 6).

The actual hydraulic head of the springs could not be determined. However, a leveling survey conducted on July 21, 1991 (Table 4), determined that the water level is highest in vent 003, followed in order by vent 002, the extinct vent⁴, vent 001 and vent 004. There is a decrease in elevation of 60.3 centimetres from the south vent to the north vent, which is due to the different ages of the vents, the different mound ages and to different rates of travertine accumulation (Chapter 5).

⁴ Elevation is measured from the top of the debris pile and is not based on an actual water level

Table 4. Surveyed water levels (July 21, 1991)

Spring Vent	Height above Datum* (brass disc on north mound)	Height above Rabbitkettle River
(001	-0.038 m	27.35 m
(002	+0.269 m	27.65 m
Extinct Vent	+0.191 m	27.57 m
(003	+0.565 m	27.95 m
(004	-21.11 m	6.27 m

*Note: Datum is shown as point C in Figure 19a.

4.6 Discharge

The mean residence time for water in the aquifer, based upon tritium analysis, is between 10 and 25 years. This refers to the lag in time from precipitation and snowmelt recharging the aquifer to when the water discharges at the spring vents. By definition, discharge is the volume of water that flows from the aquifer via the spring vents in a given period of time. At Rabbitkettle, changes in the flow system appear to be reflected with a minor time lag in the discharge volumes at the springs.

From the limited discharge data available and presented in Table 5, a few observations can be made. First, the data reveal that discharge from the north spring is always the greatest, averaging about 60 percent of the total water discharged from the site. Second, the data show that total discharge within the three main springs (measured during the summer months only) has fluctuated by slightly more than 50 percent over the years. The data also indicate a general trend of increased discharge between early and late summer. Total discharge measured in July of 1978 was between 4 and 6 litres/second (Brown and Wright,

1979). Between mid-July and mid-August of the same year, the total discharge doubled, reaching 10 litres/second. During the summer of 1991, the total measured discharge of the three main springs showed a moderate increase from 5.2 to 6.1 litres/second between early July and early August. Water-level fluctuations within some of the shallow travertine pools on the mounds, also support the occurrence of increased discharge during this time. Tiny channels and connecting pools that were water-filled in late June were dry by mid-July and refilled again by early August. The fact that these channels and pools were water-filled in June indicates higher discharge levels during the spring. These pools are not the result of snow melt because they only appear close to the vents connected by tiny channels.

Table 5. Discharge (Litres/second)

Date	Vent 001	Vent 002	Vent 003	Vent 004
92-Jun-29	5.9	1.0	2.4	-----
91-Aug-08	3.4	0.8	1.9	0.3
91-Jul-01	3.1	0.5	1.6	0.3
90-July-15	3.25	0.5	1-1.5	Hamilton (1990)
	North Vent	South Vents		
86-July		9	(Total Discharge)	
78-Aug-21	7	3	Brown and Wright (1979)	
78-Aug-11	6	3		
78-Jul-25	4	2		
78-Jul-21	3	1		

Observations from time-lapse photographs taken over the fall and winter, and from conversations with Park staff indicate that the springs continue to flow over the winter months. The warm temperature of the water keeps the vents open, even though the mounds become extensively buried in snow. Although difficult to tell visually, discharge during the winter is believed to decrease. This can be supported by the lack of winter recharge, by increases in silica concentrations (section 4.4 i) and by declines in year-long calcium carbonate precipitation rates (section 5.1). Factors controlling discharge, which are also factors that influence the hydraulic head or water levels, can result from a variety of hydrologic phenomena. Barometric pressures can cause day-to-day fluctuations in discharge but go relatively unnoticed at Rabbitkettle, especially since discharge was not measured on a daily basis. Rainstorms that last several days in the recharge zone may also cause changes in discharge. However, at Rabbitkettle, seasonal changes have the most significant effect on discharge fluctuations. These fluctuations can only be due to changes in input to the recharge zone, as mixing with another subsurface groundwater component does not occur. External loading to the system, such as earthquakes, can also cause increased water levels (Freeze and Cherry, 1979), although this phenomenon has not been observed at Rabbitkettle.

The hydrogeologic system at Rabbitkettle consists of episodic recharge events and seasonal drainage. The groundwater reservoir undergoes a decline in storage due to drainage of the aquifer during the long frozen winters. During spring melt and frequent summer rains, there is a gain in storage.

High discharge rates are common during the spring, which may be due to the melting of snow in the recharge zone. However, early-summer discharge measurements at the springs are variable as a result of the rate at which the

recharge zone has thawed. A slow onset of spring will result in a gradual snowmelt and a sluggish input of water into the flow system. This input will show up as a moderate increase in spring discharge. Such conditions were observed in the moderate discharge fluctuations of 1991. A rapid melt results in the input of a large slug of water and more rapid discharge fluctuations at the spring vents. In 1992, spring was late in arriving but then warmed quickly (personal communication, Nahanni National Park staff, 1992). A late spring meant a delayed input of the spring slug of water. That resulted in much higher June-to-early-July discharges in comparison with other years. In fact, water levels in all the rivers were higher than usual during this time, in contrast to previous years (personal communication, Nahanni National Park staff, 1992).

The observed rise in discharge during the summer months may be associated with higher precipitation rates common in the month of July (Burns, 1973). In 1991, the rise toward the end of the summer follows considerable rainfall during the last two weeks of July. Therefore, seasonal contributions of rainfall and snowmelt seem to have had the most obvious influence on discharge conditions at the springs.

CHAPTER 5 ORIGIN OF THE MOUNDS

5.1 Chemical Controls on Travertine Deposition and Rates of Deposition

Travertine refers to accumulations of calcium carbonate from any nonmarine environment, such as springs, rivers, lake bottoms and karstic cave waters (Julia, 1983; Turi, 1986). The term travertine comes from an old Roman word, Tivoli, the name of a town in Italy known today as Tibur. This town is well known for its extensive deposits of "tivistino" or travertine (Julia, 1983; Turi, 1986).

Much of the travertine surrounding the springs at Rabbitkettle, forming their characteristic mound structures, is porous. Porous travertine is also referred to as tufa (Turi, 1986). This tufa is buff to tan in colour when freshly precipitated but weathers to a dirty grey in time. The highly porous texture results from the precipitation of travertine on vegetation such as algal mats, mosses, leaves and other plant debris. As the plants decay, the porosity emerges. Samples of the tufa from Rabbitkettle were digested in dilute hydrochloric acid, and more than 98 percent of the material was soluble. The insoluble residue consisted of organic material and silt-sized particles, predominantly algae. The travertine itself is nearly pure calcium carbonate. Some samples show traces of Fe, Mg and Sr, but more than 99 percent is calcium carbonate (Brown and Wright, 1979). A sample reported by van Everdingen (1973) contained 98 percent calcium carbonate (CaCO_3) and traces of magnesium and calcium sulphate (CaSO_4). The calcium sulphate may be from evaporation within shallow abandoned pools (van Everdingen, 1973). Only calcium carbonate is precipitating in the active flow area, as will be seen later.

Travertines precipitate from calcium-bicarbonate waters that have come into contact with the atmosphere (Turi, 1986). Due to their geochemical evolution, these waters have acquired partial pressures of carbon dioxide greater than atmospheric values ($10^{-3.5}$ atm). When carbon dioxide dissolves in groundwater, it produces a very aggressive acidic solution according to the following reactions:

This solution is able to dissolve large quantities of carbonate along its flow path:

When the water reaches open-air conditions, carbon dioxide escapes, forcing reaction 18 to proceed left and precipitate CaCO_3 . Upon degassing, H^+ ions are consumed, producing a rise in pH, and an equal amount of HCO_3^- ions are lost from solution.

Calcium carbonate does not precipitate instantaneously when saturation is reached. Instead, the solution becomes progressively supersaturated as a result of the degassing of carbon dioxide. This is because crystallization is inhibited at first by kinetic effects. The formation of a crystal by precipitation from solution initially requires an increase in free energy because of the excess energy needed to create new surface area (Nielsen, 1964). A critical degree of supersaturation must be attained to overcome this nucleation barrier (Stumm and Morgan, 1981; Lorah and Herman, 1988). This usually occurs when the solution is 5 to 10 times greater than its saturation point --the saturation index is greater than 0.5-- (Jacobson and

Usdowski, 1975; Usdowski *et al.*, 1979; Dandurand *et al.*, 1982; Turi, 1986; Lorah and Herman, 1988). Once nucleation is acquired, degassing and precipitation occur simultaneously (Michaelis *et al.*, 1985).

Carbon dioxide, bicarbonate and calcium concentrations, as well as conductivity, pH and temperature values, were measured at 5-metre intervals away from spring 001 for a distance of 40 metres (Appendix 3). At the 20-metre mark, the surface of the mound changes from relatively flat to sloped. The water cascades over the slope until it reaches the edge of the mound (at 40 metres) where it forms a waterfall. All measured parameters decrease over the surface of the mound, except pH, which increases. The initial 20 metres, the flat stretch, reveals very little change in calcium and bicarbonate concentrations, and in some cases there is even a slight increase in calcium. This is in accordance with calcium carbonate's inability to nucleate until supersaturated conditions are attained.

At all the spring vents, the water is saturated or very close to saturation with respect to calcium carbonate, dolomite, barite and various iron-bearing oxides and hydroxides (Appendix 3). With increasing distance from the vents, the water becomes supersaturated with respect to the above minerals, and saturated with respect to aragonite and magnesite. Saturation increases with distance along the stream. At 20 metres, calcium carbonate saturation is between 0.3 and 0.5 (Appendix 3); beyond this point, the index increases to values greater than 1. However, only calcium and bicarbonate concentrations in solution show any variation with distance, which is to be expected because only calcium carbonate is precipitating. Slight declines in barium, strontium and iron reflect trace losses of these elements to the carbonate being precipitated. All other species were

constant, indicating that there was no notable evaporation of the spring water as it flowed over the surface of the mound.

Rapid losses of carbon dioxide occur initially as the water leaves the vent, resulting in a decline in bicarbonate and advancement of the solution toward supersaturated conditions. Numerous researchers have observed that agitation resulting at cascades or rapids allows for great amounts of carbon dioxide to degas (Dandurand *et al.*, 1982; Herman and Lorah, 1987; Lorah and Herman, 1988). Turbulence causes water to become dispersed, which increases the surface area of solution in contact with the atmosphere, and allows for a high rate of carbon dioxide escape at the liquid-gas interface (Lorah and Herman, 1988). In turbulent areas, the rapid increase in degassing rates allows kinetic inhibitions on crystallization to be overcome. As a result, the greatest losses of calcium and bicarbonate ions from solution, the greatest rates of calcium carbonate precipitation, and the largest increases in pH occur where the greatest volumes of carbon dioxide are lost: along pool rims, on steep gradients (beyond 20 metres) and at the falls.

The most rapid increase in saturation, and also the greatest calcium carbonate precipitation, occurs from the top of the slope to the falls and from the crest of the falls to below the falls. Precipitation rates reached maximums just beyond the break in surface slope and below the falls. Travertine deposits are most extensive at and below the falls, coating everything with a travertine crust. The lowest calcium carbonate precipitation rates are seen at the beginning of the stream as the water leaves the vent and flows over the flat surface of the mound. On the south mound, a much lower maximum is reached halfway along the discharge streams where the water leaves the carved channels and disperses over

the surface of the mound. Variation in precipitation rates are substantially lower on this mound, because there is a gradual change in slope. Minimal variation is seen in precipitation rates of spring 003 runoff, as the slope here is negligible.

To summarize the above observations from this and other studies, the amount of travertine precipitate is greatest where the water is the most turbulent or flowing the fastest (Jacobson and Usdowski, 1975; Usdowski *et al.*, 1979; Dandurand *et al.*, 1982). This, of course, occurs where there are surface irregularities and increased slope. Surface irregularities or projections cause excess diffusion of carbon dioxide, travertine precipitation and the eventual development of rims. These rims become self-perpetuating, building up to form dams that pool the water behind them (Figure 11). Such rim and pool structures, also known as rims and gours, have developed extensively over the surface of both mounds, ranging from a few centimetres to more than 4 metres in depth. Their appearance is a function of the gradient, which determines the rate at which carbon dioxide is lost from solution. On gentle slopes, the basins are long and shallow; steep slopes have deeper pools and more sizable dams.

The rate of travertine precipitation is a function not only of the rate of diffusion of carbon dioxide, but also of the volume of discharge from the springs. In comparing discharge volumes at Rabbitkettle, it was observed that the larger the volume of water, the greater the losses of calcium and carbon dioxide from solution and the greater the amount of precipitation (Figure 12). The north mound emits more than 60 percent of the water discharging at the site and is building at a much faster rate than the south mound. However, this is not evidence of increased precipitation associated with higher discharge, in itself, as it has already been

Figure 11.

Travertine precipitation is dominantly controlled by the loss of carbon dioxide from solution, due to vegetation, temperature change and turbulence, the latter being the most important. Rapid loss of carbon dioxide along slopes and obstructions in the flow path result in stratified deposits and/or dam development. Calm water or pooled water results in porous travertine.

Travertine Precipitation Rates

Figure 12.

Measured precipitation rates from accumulations of travertine on glass slides placed along the discharge path. The greatest rates of precipitation are associated with the steepest slopes and generally the greatest discharge rates. However, spring 003 has a greater discharge than spring 002 but has substantially lower precipitation rates. This is because the greater slope associated with spring 002 over compensates the lack of discharge.

*Indicates an estimate of the percentage of total flow that is flowing over the studied portion of the mound.

observed that the slope conditions of this mound are significantly steeper than those existing on the south mound. Precipitation rates were measured at two locations on the north mound. One side of the mound receives approximately 75 percent of the total discharge and deposits considerably more travertine than the other side, where slope surface conditions are essentially the same.

It is important to remember, however, that the balance between discharge and slope is critical. In comparing springs 002 and 003, discharge is greater for the latter, but precipitation rates are much lower. Even though spring 002 has a lower rate of discharge, it has a greater sloped surface for dispersing the water and diffusing carbon dioxide. In this case, the greater slope compensates for its lower discharge rate.

Relative rates of calcite precipitation along travertine-depositing streams can be determined by measuring changes in Ca^{2+} concentration (converted to calcite) with distance downstream (Jacobson and Usdowski, 1975; Dandurand *et al.*, 1982). Rates can also be estimated from the mass of calcite that precipitated on objects placed in the streams. The average rate of precipitation onto glass slides for the north mound was 24 grams per square metre of mound surface per day ($\text{grams.metre}^{-2}.\text{day}^{-1}$). The south mound is much less, at an average of 9.4 $\text{grams.metre}^{-2}.\text{day}^{-1}$. The maximum measured precipitation rates for the three discharge areas are 55.41 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for spring 001, 16.5 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for 002 and 1.35 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for 003. Precipitation based upon loss of calcium from solution yields average rates of 31 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for the north mound and 14 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for the south mound in 1991. In 1992, the calculated precipitation rates were 92 $\text{grams.metre}^{-2}.\text{day}^{-1}$ and 48 $\text{grams.metre}^{-2}.\text{day}^{-1}$ for the north and south mounds, respectively. The higher

calculated precipitation rates for the 1992 data are in conjunction with higher measured discharge rates for all springs. Brown and Wright (1979) calculated a mean rate of deposition from a loss in calcium of 200 mg/L as the waters flowed over the north mound. The rate of precipitation is roughly 1.25 milligrams of calcite per square metre per second or $108 \text{ grams.metre}^{-2}.\text{day}^{-1}$. This rate is high and probably reflects high discharge rates in the summer of 1978 (as noted earlier in section 4.6).

Temperature is another factor that could slow down the outgassing rates, because the solubility of carbon dioxide increases with decreasing temperature. Therefore, the downstream rate of degassing should decrease as should the precipitation rate, although the drop in temperature as the spring water flows over the mound is minimal during the summer and its effects are likely exceeded by rapid loss of carbon dioxide and rising pH. However, this may become a substantial problem during the winter months. Glass slides which were left on the mound surface over the winter and were retrievable from the 38-metre and 40-metre locations showed an annual precipitation rate (for that location) of 9.64 and $4.80 \text{ grams.metre}^{-2}.\text{day}^{-1}$, respectively. This is approximately 50 percent lower than summer estimates for the same locations. Precipitation rates calculated during the summer are based on high seasonal discharge rates and minimal temperature change as the water flows over the surface of the mound. Therefore, these estimates are not applicable to the entire year, as lower temperatures and lower discharge rates are associated with the winter months.

The relative importance of algae in the formation of tufa has been historically controversial. Some researchers believe bacteria, algae, moss and other photosynthetic plants uptake significant amounts of carbon dioxide from the

stream waters during metabolic processes. It was once believed that the process was mainly the result of algal colonization, particularly in the development of riffle structures (Julia, 1983) (Appendix 7). At Rabbitkettle, algal growth is directly associated only with the spring vents and the physical and chemical conditions play much more important roles.

However, vegetation does play a role in the precipitation of travertine; the abundance of tufa or porous travertine provides considerable evidence. Vegetation or organic debris helps to enhance the degassing process by providing a nucleation site rather than the metabolic uptake of carbon dioxide. In treed areas of the mound, increased rates of travertine deposition have resulted in the development of little mound structures around tree bases (Plate X). Not only do the trees provide nucleation sites, but more importantly they create zones of turbulence which enhance precipitation.

Large reductions in calcium and bicarbonate concentrations along the steeper portions of the north-mound slope indicate a relatively rapid rate of mineral deposition. It also shows that the terrace is growing in an outward rather than an upward direction. In-field measurements of calcite precipitation, based on glass-slide precipitation, indicate that the north mound is building outward, along its slopes, at an average rate of 2.7 millimetres/year. It is growing upward from the top at less than 0.2 millimetres/year. The south mound is building at an average rate of 1 millimetre/year, focused around the most northerly of the two vents (002). These estimates are based on 1991 data, assuming a 50 percent drop in precipitation over the winter. When integrated over the flow areas, as shown in Appendix 6, the north spring deposits roughly 5400 kg/year on top of its mound; spring 002 deposits 750 kg/year and spring 003 deposits only 12 kg/year.

Rates of travertine accumulation based on radiocarbon dates are approximately 24 percent higher than rates determined in 1991 by precipitation onto glass slides (Table 6). These data suggest that rates of travertine deposition on the south mound may have declined. This decline in precipitation may be the result of a loss in slope and more channelling adjacent to the vents as a result of travertine buildup, or it could possibly suggest a decline in discharge from these vents. The appearance of numerous small seepages along the north face of the south mound and the relatively recent development of spring vent 004 could support a decline in discharge due to changing internal hydraulics. However, the evidence is *not* conclusive.

Table 6. Rates of travertine accumulation.

<u>Vent</u>	<u>Present (glass slides)</u>	<u>Past (carbon-14)</u>
001	2.7 mm/year	not available
002	1 mm/year	3.9 mm/year
003	0.2 mm/year	0.8 mm/year

5.1.i. Isotopic Composition of Travertine

The stable isotopic composition of travertine may provide an indication of the physiochemical and environmental conditions under which the travertine precipitated (Craig, 1953; Gonfiantini *et al.*, 1968; Friedman, 1970). For instance, the main source of oxygen-18 in travertine is the water from which it precipitated. Thus, oxygen isotopes may indicate the physical conditions and isotopic composition of the source waters. Variations in oxygen-18 within travertine are related to the temperature of the formation waters and equilibrium-disequilibrium conditions under which precipitation took place (Turi, 1986). Carbon-13 in the travertine is affected by kinetic isotope effects and temperature differences during

deposition. The carbon in travertine is from carbon dioxide which may have originated from organic matter, the atmosphere, igneous or metamorphic sources or the dissolution of carbonate rocks. It has already been established that carbon dioxide at the Rabbitkettle springs originates from soil-atmospheric sources and the decarbonation of limestone. Carbon-isotope ratios in the travertine can reflect these carbon dioxide sources as well as providing insight into the factors controlling travertine precipitation, such as the rate of precipitation. Such information will help decipher the origins and relationships of travertine throughout the site.

Oxygen-18 values at Rabbitkettle for fresh travertine are between +7.41 and +8.75 ‰ SMOW (Figure 13). These values are quite depleted when compared to the average oxygen-18 contents of travertine from all over the world which range from +20 to +26 ‰ (Turi, 1986). This depletion is a function of a cold northern climate where the oxygen-18 content of the waters is low (~ -22.5 ‰ SMOW).

Carbon-13 values of the fresh travertine are +2.57 to +5.81 ‰ PDB, compared to worldwide travertines which vary between -26 to +6 ‰ PDB (Turi, 1986). Carbon-13 rich travertine reflect enriched carbon dioxide, which generally results from the dissolution of carbonate strata or a metamorphic source (Turi, 1986).

At isotopic equilibrium, CaCO_3 (travertine) is isotopically heavier in ^{18}O than the water from which it precipitates, according to the equation:

$$1000 \ln \alpha_{\text{CaC}^{18}\text{O}_3 - \text{H}_2^{16}\text{O}} = 2.78 \times 10^6 / T^2 - 2.89 \quad (19)$$

(Bottinga, 1968; Friedman and O'Neil, 1977). Travertine becomes isotopically

heavier with respect to carbon-13 than the $\text{CO}_{2(g)}$ which is released, according to the equation:

$$1000 \ln \alpha_{\text{CaCO}_3-\text{CO}_{2(g)}} = 1.435 \times 10^6 / T^2 - 6.13 \quad (20).$$

(Gonfiantini *et al.*, 1968; Bottinga, 1968). All fractionations are a function of the temperature of travertine precipitation (Friedman, 1970). At 20°C, as at Rabbitkettle, calcite will be enriched in ^{18}O by 29.4 ‰ over water and enriched in ^{13}C by 10.5 ‰ over CO_2 . However, isotopic equilibrium is rarely reached in the deposition of travertine due to the rapid outgassing of $\text{CO}_{2(g)}$ from the spring water (Gonfiantini *et al.*, 1968; Herman and Lorah, 1988). The slower the rate of escape of $\text{CO}_{2(g)}$, the closer the travertine will be to expected isotopic-equilibrium values (Turi, 1986). Rapid degassing results in the preferential loss of light isotopes of both carbon and oxygen from solution, and produces travertine isotopically heavier than expected. When the spring water first reaches the surface vent, it is believed to be in isotopic equilibrium. Upon discharge, and outgassing of $\text{CO}_{2(g)}$, disequilibrium conditions are observed. The system subsequently evolves toward new equilibrium conditions as the water migrates away from the vent (Gonfiantini *et al.*, 1968; Turi, 1986). Calcium carbonate precipitated along the spring's discharge path is commonly in isotopic disequilibrium with respect to the dissolved carbon. In many studies, the calcium carbonate has the same isotopic composition as the $\text{HCO}_3^-_{(aq)}$, although it should be 2.3 ‰ heavier if formed at isotopic equilibrium (Dandurand *et al.*, 1982; Michaelis *et al.*, 1985).

At Rabbitkettle, the travertine in equilibrium with the emerging spring waters⁵ should have $\delta^{18}\text{O}$ values close to +7 ‰ SMOW and $\delta^{13}\text{C}$ values near +2.5 ‰ PDB (Figure 13). Analyses of travertine sampled near spring vent 003

⁵ Equilibrium refers to an equilibrium with the reservoir waters of an average oxygen-18 composition of -22.5 per mille (SMOW) and carbon dioxide with an average carbon-13 value of -8 per mille (PDB).

Isotopic Composition of Travertines

Figure 13.
This is a plot of the isotopic compositions of various travertines at the site. It demonstrates their isotopic relationship to travertines precipitated at isotopic equilibrium with the present spring waters. The arrow demonstrates enrichment as a result of precipitation at increasing distance from vent 001. (HITW means Hole-in-the-Wall Creek)

2

PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

are close to the calculated equilibrium values, probably because this spring has a small discharge volume and a low gradient, resulting in very slow $\text{CO}_{2(g)}$ diffusion rates and thus slow rates of travertine precipitation. All other fresh precipitate sampled at the site is at disequilibrium because of rapid discharge, higher surface gradients and faster degassing from the vents. The travertine approaches new equilibrium values away from the vents. As the distance from the vent increases, the travertine becomes isotopically heavier because lighter $\text{CO}_{2(g)}$ is preferentially diffused from solution and the initial rapid outgassing diminishes as the water cools slightly. The waters eventually reach a new equilibrium with their surroundings, and a more enriched gas phase exists in the water at the time of precipitation. Since $\delta^{18}\text{O}$ values are strongly dependent upon temperature (Turi, 1986), the slight decline in temperature as Rabbitkettle spring waters flow over the surface of the mounds results in small variations in the $\delta^{18}\text{O}$ values for freshly precipitated travertine. Very little evaporation is taking place on the mounds, and thus is not having an effect on oxygen enrichment of the waters and the resultant travertine. Evidence for this lack of evaporation are constant chloride and fluoride concentrations in the waters as they flow over the surface of the mounds.

Three travertine samples were taken from the base of the north mound. One was taken from the underlying conglomerate unit, and two others were taken just above the contact with this unit. These samples turned out to be isotopically depleted with respect to carbon-13, and isotopically enriched with respect to oxygen-18, in comparison to modern travertine. Travertine deposited at higher temperatures is more depleted in carbon-13 (Friedman, 1970). Higher oxygen-18 values indicate isotopically enriched groundwater, which is in agreement with higher temperatures. Therefore, these "fossil" travertines (possibly the oldest at

spring 001) must have precipitated from spring waters with temperatures greater than 20°C. Spring water temperatures may have been more than double what they are at present, given the larger spread in their $\delta^{18}\text{O}$ values, as larger variations in $\delta^{18}\text{O}$ values are only possible in springs that have higher temperatures (Gonfiantini *et al.*, 1968).

An overgrown block of travertine at the base of the south mound is isotopically similar to old travertine of the south mound. In Figure 13 the composition of this block appears within the equilibrium area of modern travertines. However, when this block was part of the mound it would have been a substantial distance away from a vent. Given what is known about the change in isotopic composition of travertine as it is precipitated at increasing distances from the spring vents --that is a shift toward the right in Figure 13-- this travertine should be isotopically enriched with respect to oxygen and carbon isotopes from the originating spring water. If such is the case, this travertine has also precipitated from higher-temperature waters than those being released today.

A stratified travertine deposit along the ridge above Hole-in-the-Wall Creek (see travertine deposit identified in Figure 4) was sampled and analyzed for its isotopic composition. Isotopically this travertine falls within the same range as the older travertines at the present site. This supports the theory, based on its geographical location along the fault trace, that this travertine was deposited from the same groundwater system as the Rabbitkettle springs.

Calcium carbonate muds from areas adjacent to the mounds that were sampled for their isotopic content show slight enrichment over equilibrium values. This suggests that the waters that precipitated these muds also may be from the same groundwater reservoir as the springs. Isotopic enrichment probably reflects

evaporation as the water slowly seeps to the surface and is held in stagnant pools; evaporation causes the isotopic enrichment of both the water and the resultant travertine.

5.2 Age of the Mounds

The maximum and relative ages of the mounds can be determined from the ages of their underlying terraces. The south mound resides upon glacial till which has been incised by past migration of Hole-in-the-Wall Creek. The incision is believed to be the result of a Late-Wisconsinan glacial meltwater channel (Brown and Wright, 1979) or possibly postglacial fluvial down-cutting. Regardless, since the mound would have appeared following glacial retreat, its maximum possible age is roughly 10,000 years. The exact age of the mound depends on how long after glacial retreat the creek carved out the terrace; a fact that remains unknown. The north mound rests upon unconsolidated glaciofluvial deposits from a much earlier glaciation that have been exposed during postglacial down-cutting of the Rabbitkettle River. The age of this down-cutting is also unknown, but it occurred after the migration of Hole-in-the-Wall Creek. This suggests that the north mound is the youngest of the two mounds and is much less than 10,000 years old.

Additional physical evidence supports the age relationship between the mounds. For instance, the south mound has built up to a higher elevation than the north mound and is at present building at a much slower rate, which suggests that it is older. The fact that the south mound has been subjected to more extensive degradation and vegetation overgrowth may also be, in part, a function of time.

The age of the north mound was estimated by two methods, both of which involved approximating the volume and density of the mound as well as travertine-

deposition rates. The first method derived a rate of deposition based upon average discharge volumes and average losses of calcium (converted to calcite) from solution over the surface of the mound. The second method was based upon actual measured rates of travertine accumulation onto glass slides (1991) and the measured thickness of the north mound. Both methods gave a calculated age for this mound of approximately 6,850 to 7,000 years (Appendix 6). Both methods used summer travertine-deposition rates reduced by 50 percent, to account for the decline in precipitation during the winter months, as determined by a comparison between year-long and summer accumulations of travertine onto glass slides. These methods also assume relatively constant average discharge rates and precipitation rates over the lifetime of the mound. As there are significant errors involved in these assumptions, the accuracy of this age is questionable. However, the fact that both methods give a similar age is encouraging, as well as the fact that they support an age that is less than 10,000 years.

The age of the south mound was impossible to determine by these methods, as the error involved is too great. The thickness of this mound is unknown, with the best estimate falling between 3 and 7 metres, based upon the depths of the existing vents and the elevation of the adjacent terrace ridge. The present unvegetated area is roughly 11,900 square metres, but a considerable quantity of travertine had been deposited distally from the main exposed mound. Therefore, the calculated volume of this travertine pile is unreliable. There is also the problem of incorporating into the calculation, discharges and associated precipitation rates for two spring vents, and an extinct vent that was once an important contributing factor.

Future research into the ages of these mounds will have to come from the U-Th dating of the travertine itself. This technique is expensive and was not available for this study due to time constraints. Carbon-14 dates from the base of the mounds were also not possible, due to the absence of any datable material. Wood fragments deep within the travertine were found to be travertinized. Some algal material from the older travertine was acquired by dissolving away the travertine with dilute HCl, but unfortunately, not enough datable material was recovered during an extensive period of dissolution time. Furthermore, any algae may have metabolized "dead" CO₂ from the spring water, rendering it undatable.

5.2.i. Ages and History of the Spring Vents:

Determining the age relationships between the vents is important to understanding the hydraulic changes over the lifetime of the system. For instance, carbon dating of entrapped wood suggests that the present vents on the south mound are not the original vents. Changing and possibly weakening hydraulics have resulted in "vent switching." Wood was *not* found within spring vent 001, nor was there any attempt to swim to the bottom of the vent in search of any. However, as there is no physical evidence suggesting the existence of any other vent; its age is considered to be concurrent with the age of the mound. This makes vent 001 the oldest active vent on the site, even though it is part of the youngest mound.

The age relationship between vents 002 and 003 was determined from carbon-14 dates on tree branches that had fallen across the vents during the accumulation of travertine. A large piece of wood entrapped at 121 centimetres within vent 002 was dated at 310 ± 65 years (WAT 2605). Based on the age and

depth of the entrapped wood, the average rate of build-up for this vent is 0.39 ± 0.1 centimetres/year. Since the vent is 186 centimetres deep, it would have taken approximately 500 ± 100 years to build to its present elevation. Wood entrapped in vent 003 at 55 centimetres below the surface was dated at 700 ± 110 years (WAT 2646). Since this vent is 130 centimetres deep and building at an average rate of 0.08 ± 0.01 centimetres/year, it is approximately 1625 ± 230 years old. Therefore, vent 003 is the elder of the two existing vents; a relationship supported by the fact that vent 003 is building at the slowest rate, yet has built to the highest elevation. This assumes, however, that precipitation has been relatively constant at both vents.

The elevation difference between the extinct vent and vent 003 is 37.4 centimetres. Since the rate of growth for vent 003 is 0.08 ± 0.01 centimetres/year, the time of extinction of the former vent can be estimated at 468 ± 63 years. Since the time to build up vent 002 (500 ± 100 years) is close to this estimate, it is possible that the extinction of this vent was accelerated, or even caused by, the appearance of spring 002. Spring 002 likely started as a down-slope seep that became more aggressive in drawing head away from the former vent. This may be similar to the more recent appearance of the smaller spring 004 (see chapter 6) that sits hydraulically lower than the other vents. The actual age of spring 004 remains undetermined.

5.2.ii. History of Surface Flow

Insight into past surface-flow directions are important to understanding the historical development of the mounds. The following discussion deals with both the old and more recent surface flow. A lack of datable material within the

travertine has limited conclusions regarding older flow directions. Conclusions are often inferred from field observations, such as pool orientation, and from air-photo interpretation. Surface flow is best documented in the most recent history from descriptions in references and the availability of photographs. Photographs in 1974 were taken by G.W. Scotter; the 1978 reference is from Brown and Wright (1979).

The oldest deposits on the site have succumbed to frost and vegetation, and have likely originated from the now-extinct vent, making them much more than 500 years old. Such deposits are located on the east side of the south mound, 10 to 15 metres into the forest and directly across from the extinct vent (area H in Figure 14). Here, the occurrence of large travertine-conglomerate boulders, containing smaller fragments of travertine cemented together, indicate changing flow sequences. Travertine was once precipitated in this area from discharge originating from the now-extinct vent. The area was then abandoned and subjected to frost; the frost-shattered-travertine fragments were then cemented together in response to the later return of calcium carbonate-rich waters. Again the water was diverted, leaving the area exposed to frost and overgrowth.

Travertine deposits on the low terrace immediately north of the south mound (area J in Figure 14) are also remnants of older deposits that originated from the now-extinct vent. Since the deposits are not continuous down the adjacent slope of the south mound but are disrupted by vegetation and other inorganic debris, they did not originate from the more recent vent 002. Entrapped wood fragments here are travertinized. However, some of the fresher surface deposits occurring close to the embankment are from small recent seeps positioned along the undercut face of the south mound.

Figure 14. Detailed geomorphological map of the site.
Letters are referenced in text.

Flow from the extinct vent also discharged toward the northwest through the Hole-in-the-Wall Creek "cut", depositing travertine down the embankment that separates the two mounds (toward area E in Figure 14). The deposits along this slope remain quite intact, but those in the region above suffer considerable degradation (Appendix 5).

Historically vent 003 discharged in a northerly direction. The oldest deposits associated with this spring are exposed within the Hole-in-the-Wall Creek "cut" to the west of the vent (area V, Figure 14), where they are now extremely frost-damaged and heavily-vegetated. On the southeast portion of the mound (area W, Figure 14) amongst thick vegetation, are well-preserved rimstone pools up to 30 centimetres deep. The deep rims suggest deposition associated with a steep slope; possibly prior to the infilling of the topography with travertine originating from spring 002. This would put the age of these deposits at more than 500 years.

Deposits to the north of vent 003, within a radius of 20 to 30 metres (area X, Figure 14), are all less than 500 years old because they partly overlie deposits from the extinct vent and vent 002. Carbon-14 dates of wood trapped along the flow path are in agreement with this hypothesis as sample C14-7 (Figure 19b) was dated at 270 ± 70 years (WAT 2604) and sample C14-6 was modern (less than several hundred years old).

Today, vent 003 discharges toward the south into the forest. In recorded history, 1964 to present, this has always been the main direction of flow. In 1974, flow also exited the vent from channels on the north side, which flooded extensive areas on the north and west side of the vent. In 1978, flow distribution had changed very little. Between 1978 and the present, flooding on the north and west

side of the vent terminated, except for minor pooling during higher-discharge periods.

Flow from spring 002 has extended in all directions for extensive periods of time. All of its associated deposits are less than approximately 500 years old (area Y, Figure 14). Today, spring 002 discharges toward the east, flowing over the surface of the mound for about 25 metres. In 1974, the dominant flow from this vent was also toward the east, sinking into the ground at 32 metres (Marsh and Scotter, 1976). At this time, however, water also overflowed in a roughly circular fashion for 10-to-20 metres away from the vent. Short channels, indicated by iron-staining, radiated in all directions from the vent. By the summer of 1978, flow was dominantly towards the east, as it remains today.

Today, water flows from the most northern vent (001) via three channels that flow down the northwestern slope toward the river. Flow has diverted very little from its present channels since 1978. The earliest photographs of the north mound, in the summer of 1974, reveal extensive short-radial channel development, indicated by iron-staining around the vent; two larger channels exited on the northwest and southeast sides at 180°. Flow was dominantly toward the river; however, there was extensive overflow onto the mound surface from the southeast channel. This overflow was responsible for submerging nearly half the surface area on top of the mound. In 1964, Atchison noted that water flowed over the surface of the mound and disappeared into it, indicating flow similar to that photographed in 1974. He made no mention of flow towards the falls. Photographs taken in 1991 from the same locations as those in 1974, show dry weathering pools in areas previously occupied by wet freshly-precipitated pools. Brown and Wright (1979) observed that the centre line of the actively-growing

sector of flow had systematically shifted through a 30° arc between the years 1973 and 1978. They did not mention the direction of change, but photographic evidence suggests that it was clockwise toward the north.

5.3 Regional Travertine-Precipitating Springs

Numerous travertine-precipitating springs can be found in the region (Figure 15; Appendix 4), most of which have a fault association (Hamilton, 1990) and all of which are located within carbonate terrane. All of the springs are chemically dominated by $\text{Ca}^{2+}\text{-HCO}_3^-$ concentrations with pHs that are slightly acidic to slightly basic, increasing as the water flows away from the vents (Hamilton, 1990). Typically the travertine-precipitating springs of this region form crumbly-deposits (Hamilton, 1990) which can cover substantial areas. Most, however, have *not* developed the extensive travertine terracing found at Rabbitkettle. Old Pot (028), now a cool spring which is no longer depositing travertine, historically deposited similar travertine structures to Rabbitkettle, which are now largely covered by vegetation.

A number of the travertine-precipitating springs are located along the fault-controlled Flat River valley. A group located in the centre of this valley (017, 055, 056, 058, 059) have high partial pressures of carbon dioxide and temperatures below 9°C (Hamilton, 1990; Hamilton *et al.*, 1991; Timlin, 1991). The travertine-precipitating springs, located at the eastern end of this river valley (028, 027, 029, 030, 031), have lower partial pressures of carbon dioxide and temperatures ranging from 10° to 25°C (Hamilton, 1990; Hamilton *et al.*, 1991).

Figure 15.
Locations of regional travertine-precipitating springs.
Numbers correspond to those of Hamilton (1990).

Travertine-precipitating springs along the Broken Skull Fault in the South Nahanni River valley (001, 002, 003, 004, 040, 041, 023, 026, 046, 047) consist of a mixture of both thermal and nonthermal springs with temperatures ranging from 3.8° to 49°C. Two additional travertine-precipitating springs are located adjacent to the fault-controlled South Nahanni River valley (021, 043), with temperatures of 17° and 44°C, respectively. These isolated springs are believed to be controlled by faults or fractures associated with local anticlinal structures (Hamilton, 1990).

Figure 16 shows that Rabbitkettle waters chemically cluster with the Flat River springs. This is likely a result of two factors, the most important being that the geology along the Flat River is similar to that at Rabbitkettle. North along the South Nahanni River, the local rocks show much more variability. This would explain why the resultant springs are Ca^{2+} - HCO_3^- dominated but are proportionally rich in sulphate, chloride, and why some, particularly the ones to the north, have high potassium concentrations. The second factor is the addition of excess carbon dioxide in the Flat River springs which has caused the dissolution of more carbonate, resulting in high Ca^{2+} and HCO_3^- concentrations. Rabbitkettle waters are isotopically very similar to the waters of springs 040 and possibly 041. These springs are located at the north end of the Broken Skull Fault along the South Nahanni River valley, an area that has been associated with considerable seismic activity. The concentrations of carbon dioxide and the isotopic signatures of springs 040 and 041, demonstrated in Figure 17, are likely controlled by a similar system to that of Rabbitkettle. The same is true for spring 030, on the farthest extension of the Flat River Fault. Biogenic carbon dioxide is introduced into the groundwater from the recharge zone and mixed with a metamorphic source of carbon dioxide from the decarbonation of limestone; accessing the

Figure 16.

Trilinear plot of local travertine-precipitating spring water chemistries. $\circ$, open circles represent Kabbitkettle spring water chemistries for 001. Closed-circles represent high $p\text{CO}_2$ springs along the Flat River Valley. Other Flat River Valley springs are represented by open diamonds. Squares represent springs associated with the South Nahanni River Valley (Data from Hamilton, 1990).

Figure 17.
 $^{13}\text{C}_{\text{CO}_2}$ and pCO_2 for local travertine-precipitating springs. Plot locations show the probable carbon dioxide source.

groundwater through a fault. The springs in the centre of the Flat River valley (017, 055, 056, 058) are dominantly enriched by metamorphic CO_2 . Springs 023, 028 and 046 have low partial pressures of carbon dioxide and are depleted in $\delta^{13}\text{C}_{\text{CO}_2}$, which suggest that the carbon dioxide in these springs is strictly biogenic. The remaining springs (027, 029, 031, 043), which are all thermal, do not have access to a deep CO_2 source. Their positions in Figure 17 likely reflect soil inputs of carbon dioxide under open- and partially closed-system conditions, where the $\delta^{13}\text{C}_{\text{CO}_2}$ becomes enriched by the dissolution of carbonate rocks. Lower pCO_2 could also be the result of the precipitation of carbonate prior to discharge; however, the resultant $\delta^{13}\text{C}_{\text{CO}_2}$ values would be more enriched as a result of the loss of isotopically lighter carbon dioxide.

With so many travertine-depositing springs in the region, why are so few of them developing the extensive terracing seen at Rabbitkettle? This is an important question, and answering it requires an understanding of the conditions at Rabbitkettle that differ from the other locations. From earlier discussion it became apparent that, in general, the major controls on the deposition of travertine are: the chemistry of the water in terms of calcium carbonate saturation; the rate of escape of carbon dioxide from solution; and the prevailing hydraulic conditions.

All of the springs in the region are chemically similar and are at, or close to, saturation with calcium carbonate. The greatest variable between the springs is temperature. Hamilton (1990) noted that the thermal travertine-precipitating springs in the region have more extensive travertine deposits. The importance of this relationship is that carbon dioxide is more soluble in cooler waters and slower to diffuse from solution upon discharge. The effect is slower rates of travertine precipitation from cooler waters. Rate of discharge, as discussed earlier, is

another important variable which controls travertine-precipitation rate. So, even though the springs of the Flat River valley have high $p\text{CO}_2$ and resultant high Ca^{2+} - HCO_3^- contents, their low discharge temperatures and low discharge rates result in deposits which are accumulating at a slower rate, often over large areas. The slower rate of accumulation also makes these deposits less noticeable because vegetation is able to overgrow all but the most active portions.

The development of extensive terraced travertine deposits like Rabbitkettle also require the right structural and hydrogeological conditions. Rabbitkettle waters are part of a deep-flow system which is recharging in the mountains and discharging topographically low along the river valley. These conditions establish a high hydraulic head at the springs; allowing the mounds to build up high above their terraces. Cooler springs often indicate that the waters have not migrated to any depth within the subsurface. Deep circulation often goes hand-in-hand with a strong hydraulic driving force. Deposits with lower hydraulic head will often 'spread out', lacking the potential for height and the development of deep terraces.

Slope, or lack thereof, is another important factor determining the extent of travertine terrace buildup. The Rabbitkettle springs discharge beside a river upon a level terrace. Many of the other travertine-precipitating springs of the region are discharging high along valley slopes where the water is forced to move downslope very quickly. Excessive slope rapidly forces the water to supersaturated conditions upon discharge, and develops thin asymmetric deposits. A number of the Flat River valley springs form deposits which are thinly smeared over a steep-sided valley. Springs which deposit most of their travertine at a distance from their vents, due to lower gradients, form broad flat-topped deposits. Brown and Wright (1979) observed that smaller pools develop on steeper slopes and deeper

pools occur where there is a shallow upstream slope meeting a steeper slope. For this reason, at Rabbitkettle, the largest and deepest pools occur near the outer edges of the mounds. Therefore, to develop large terrace structures, discharge must begin on lower gradients.

In summary, the ideal conditions for the development of an extensive terraced travertine deposit require thermal carbonate-saturated groundwater, which has been deeply circulated, to be forced to the surface by way of a fracture or fault, and the resultant spring vents must discharge large volumes of the saturated water onto a low gradient surface. In addition, deposition rates must be significant enough so that the accumulation is not in competition with vegetation, and accumulation must proceed over thousands of years.

CHAPTER 6 DEGRADATION OF THE MOUNDS

6.1 Natural Degradation

In the future, Rabbitkettle Hotsprings may eventually cease to flow from the present vents. However, more pending threats to survival of the mound structures are the chemical and mechanical weathering processes associated with discontinuous permafrost and negative mean annual air temperatures.

Travertine-terrace development in warmer climates, such as Pamukale in Turkey and Mammoth Hotsprings in Yellowstone Park, undergo considerably less degradation due to weathering. The fresh white appearance of these travertine deposits is sustained with age. At Rabbitkettle, chemical attack by rainwater and melting snow and physical attack due to harsh temperatures, result in the discolouration of the travertine to grey only a few years after the spring water is diverted. In a subarctic climate, not only is the rate of travertine buildup slower (as precipitation of travertine decreases with decreasing temperature), but the rate of breakdown of the travertine is faster due to dramatic external temperature changes that result in frost damage.

The porous nature of travertine makes it extremely susceptible to frost-shatter, which is the most dramatic form of degradation to the mound structures. Layers of travertine are being exfoliated from the mounds, as trapped moisture undergoes thermal expansion. The release of this compressive stress, due to the expansion of freezing moisture, generally occurs at the apex of the travertine rims. As a result, the mounds show extensive destruction of the beautiful rimstone-pool structures (Plate XI). Frost shatter is a more common phenomenon to the terraces of the north mound, as this structure is younger and in an earlier stage of

degradation, and it exhibits significantly larger rimstone pool structures. Constant deterioration of the rimstone pools by frost shatter, over the thousands of years of this mound's existence, has resulted in extensive accumulation of travertine debris around its base. The rate of terrace deterioration is relatively quick, setting in only a few years after diversion of the water. Wet terraces of the north mound photographed in 1974, were photographed again in 1991. The recent photographs show dry, weathered terraces that have become extensively frost-shattered. Over the winter of 1992, new frost-related damage, in the form of freshly broken rims, was observed in two places on the north mound. As disheartening as this may sound, however, it is obvious that the break-down process remains much slower than the accumulation process.

The south mound is an older-travertine pile dominantly in a later stage of degradation. This mound, and some of the travertine-debris piles around the site, (Appendix 5) show evidence of frost stirring which is associated with permafrost. As frost shatter continues to reduce the size of the travertine fragments, frost stirring redistributes them into polygons and stripes.

Patterned ground forms as a result of water held within the travertine undergoing freeze-thaw, and is most evident in areas experiencing lower-temperature gradients due to underlying permafrost. Theories on the mechanical origin of patterned ground are varied, and are discussed in detail in a paper by Washburn (1956). All the patterned ground at Rabbitkettle is confined to areas where the water level is not far below ground surface. In the central portion of the south mound, water is close to the surface because of the loss of an older vent, resulting in leakage and unconfined subsurface flow. In other areas exhibiting

patterned ground, water flows close to the surface as a result of perched water tables. These areas are described in detail in Appendix 5.

The most impressive polygonal structures can be seen on the surface of the south mound, only a few metres away from vent 002 (Plate XII). Here, clusters of sorted circles, polygons and stripes exhibit coarse borders with fines in the centre. Generally, the stripes are oriented perpendicular to the steepest available slope; being most obvious along the edges of the extinct vent rubble pile. Other more subtle frost-related structures occur in the bottoms of abandoned pools in the form of frost plugs, patterned mosses and small frost-induced mud piles. These may represent the early stages of more destructive frost action that will result in breakdown of the travertine and the eventual formation of patterned ground.

With the continued disintegration by frost, some of the distal travertine areas that were once terrace structures have become susceptible to forest overgrowth. The degradation process continues, enhanced by the mechanical breakdown by vegetation, until eventually the travertine is transformed into calcareous soil.

River damage is another naturally induced form of degradation. In the past, the Rabbitkettle River has been a destructive force against the mounds. In recent history, a minimum of 300 years ago, the river undermined the north mound on its northern side. This estimate is based upon the ages of trees growing between the present river water level and the edge of the mound (Marsh and Scotter, 1976). Large metre-sized blocks have fallen off of the mound since it was undercut by the river. This has created huge overhangs and a waterfalls for the spring waters flowing off the top of the mound. The potential for falling debris is high, and thus this area is dangerous. Over the winter of 1991/1992, a large part of this overhang

was overcome by gravity and tumbled to the ground. The debris buried a long-abandoned trail that was once used to tour this side of the mound. Close observation of the "break" point revealed miniature-stalactitic structures which formed a band across the break (Plate VIII). These structures are believed to be the result of pooling rainwater and melting snow on the surface of the mound. The water infiltrates through stress fractures in the travertine, which originated by the undercutting of the river, causing dissolution and reprecipitation of the original travertine.

Local evidence suggests that at a much earlier period of substantially higher river water levels, the meander of the Rabbitkettle River that the north mound sits upon may have demolished an earlier travertine formation when it carved out the lower terrace. Abundant travertine debris and travertine-cemented boulders on the down current side of the north mound are evidence for this conclusion. The travertine-cemented boulders downstream of the north mound (Area B, Figure 14) are similar to the cemented travertine-fluvial gravels beneath the north mound, and along the terrace ridge to the northwest of the existing mound. This meander managed to undercut the south mound, resulting in the buried travertine boulders at its northern base.

Minor damage to the mounds is the result of animals, as large mammals like moose are drawn to the site for its mineralized water. Substantial moose tracks, moose-derived broken rims and diggings have been observed in and around the hotsprings of the south mound. The north mound is less accessible to animal traffic, except humans and birds of prey, and consequently has insignificant animal-induced damage.

6.2 Human Degradation

Humans have added a recent stress to the mounds as tourist traffic results in trampling of the trails and fragile travertine structures. Damage by humans becomes more threatening as more and more tourists gain knowledge of the site. In an eight-week period during the summer of 1978, the mounds were visited by 124 tourists (Brown and Wright, 1979). The average number of people visiting the mounds in 1988 and 1989 was 190; in 1990, the total visitation was 270, and in 1991 it was as high as 403. Total visitation thus has more than doubled in the last few years.

In the past, access to the mounds was not regulated. However, in 1984, controlled visitation was put into effect because of the fear of rapid deterioration of the site. Visits to the mounds today are guided by Park staff on designated trails. These trails took very little time to become permanent scars on the local landscape. A trail up the southeast side of the north mound was abandoned more than ten years ago, and still remains quite visible. Despite this obvious disadvantage, the trails help to localize damage and minimize long-term degradation. Therefore, continued use of the *existing* trails is important. The most substantial damage occurs during the first few years of establishing the trails. It was noted by the author, that between the summers of 1991 and 1992, damage to the existing trails was minimal. However, widening of the trail should be deterred by encouraging a strict single-file approach.

In order to explore the summit of the north mound, *all* persons must do so barefoot, walking up only along the wet slope. This is a particularly good policy as it prohibits people from scrambling up the travertine-scrree slopes, which would result in their premature deterioration. The wet zone is continually precipitating

travertine, and even though the fresh-travertine riffles often give way beneath your feet, they are repaired by fast precipitation rates. Close observation of riffles along this trail revealed that this was indeed happening. As well, no trail has become visible even though the same section of the mounds is always used, and trail marker stones on the mound quickly became buried by the newly formed travertine. Once on top of the north mound, more damage is done to your feet than to the surface of the mound. However, walking around should be restricted. People should *not* step in the iron-rich channels or the iron-rich deposits, as these areas are often unconsolidated and are subject to faster erosion. Standing too close to the vent may destroy travertine overhangs and send someone for an unexpected swim.

To date, these policies have been effective. Visitors show considerable interest in the mounds and take great care in watching their step. Visitation at its present level does not seem to be having a noticeable adverse impact on the site. However, a close watch is necessary, particularly if tourism increases. Quantifying the rates of degradation due to humans has proved to be quite difficult. Estimates of damage were based solely on week-to-week visual comparison and long-term photograph comparison. In the summer of 1992, as part of the ongoing monitoring program, three-centimetre diameter platelets were installed along the trail leading up the north mound. It is the hope that these platelets will provide indicators of buildup or breakdown along this trail during the next five years (see Appendix 9).

6.3 Potential Degradation

One of the greater concerns for the Park, in terms of potential degradation to the Rabbitkettle mounds, has been the threat imposed by the Rabbitkettle River. Historically, the river has caused substantial damage when water levels were metres higher than at present. Water levels were higher because the river had not yet incised deeply into the underlying unconsolidated sediments. Today, the river still has substantial chemical and physical erosion capacity, because it is undersaturated with respect to calcium carbonate and discharges rapidly at approximately 10,000 litres/second. Also, water levels within the river can fluctuate dramatically in a matter of days during the spring and after heavy rains. These high water levels have resulted in erosion of the river bank. However, erosion is moderate at best, and has not offered any great threat to the north mound for some time. Substantial threat to the mounds can only arise from extensive water level increases (more than we see today), or drastic river migration in the direction of the mounds.

To anticipate the future migration path of the Rabbitkettle River and its potential effect on the mounds, it is important to observe the river's past migrations. Figure 18 documents the meandering of the river to as far back as 1949. Somewhere between 1976 and 1982, the river cut off the closest meander to the spring site, forming an oxbow. The water now flows directly through the shoot, causing extensive flooding just above the hotsprings. Before this event, the mounds had been located on the outer bend of the river where erosion is always the greatest. Now, the erosive potential of the river has decreased due to pooling of the water upstream. This loss in force, in combination with the fact that the northern bank is now heavily armoured by a coating of travertine and other

Figure 18a.
The geomorphological changes of the Rabbitkettle River from 1949 to 1966.

Figure 18b.
The geomorphological changes of the Rabbitkettle River from 1976 to 1992.

debris, should slow down the gradual breakup of the riverbank by deflection of the currents. In time, the flooded region will straighten out and the greatest erosional power will be on the river bend upstream of the hot springs. At this time, the river should continue to be deflected by the armoured riverbank. Therefore, the present and predictable future threat of the river has decreased; its threat could only increase with drastic water level rises resulting from extreme and unpredictable climate change.

A passive form of degradation to the hot spring mounds will result as the mounds grow to a height equal to their artesian hydraulic head. There is no way of determining what this maximum height might be, but when reached, the springs will no longer flow. The loss of flow would eventually result in the precipitation of calcium carbonate within the conduit, a reduction in upwelling, and the eventual blocking of the vent as it dries up or becomes a seep. Similar travertine-depositing springs are located near Midway, Utah. Some of the structures contain actively flowing springs; some form water-filled-crater structures that do not overflow, while others form shallow dry craters or mounds consisting of solid travertine (Baker, 1968). These structures are believed to be in various stages of development as a result of differing hydraulic conditions. Similar circumstances at Rabbitkettle have resulted in the extinction of a vent in the middle of the south mound. An open vent no longer exists here. Instead, water gurgles and seeps close to the surface of a travertine-debris pile. This spring vent became extinct because it reached a maximum head imposed on it by a loss of water to spring 002.

Potential changes in the internal hydraulics of the underlying spring system will have the greatest impact on the site. Breakthroughs in conduits can result in: new internal flow directions; new spring and seep discharge points; the reduction

of discharge to the main vents; increased potential for mixing with cooler subsurface waters; and increased losses of groundwater flow directly into the Rabbitkettle River from the subsurface. Evidence that internal hydraulic change has already occurred beneath the south mound are: the appearance of seeps along its northern face; the extinction of one of its vents; extensive frost-related damage and patterned ground; and by the more recent development of vent 004. Vent 004 sits topographically 21.0 to 21.6 metres lower than the other three spring vents. In future, more of the spring water may be drawn toward this vent as a result of this head difference, and could result in decreasing discharge from the three main springs. In fact, similar circumstances may have been the cause for the extinction of the vent on the south mound. At present, discharge is apparently *not* being lost to the Rabbitkettle River, as the chemistry of the river upstream and downstream of the mounds shows no change. However, since the river has such high volume and discharge, it is possible that an influx of considerably less carbonate-rich waters may have an insignificant effect upon the chemistry.

Since the spring system is holding at a delicate state of equilibrium, a pumping test, which would have contributed to a more detailed understanding of the hydraulics, was cancelled. It was felt that the system may be sufficiently sensitive to undergo irreversible damage to the internal hydraulics if this were pursued.

Future and unpredictable causes of hydraulic change may result from large-scale influences such as global warming or earthquakes. Climate change could result in the melting of permafrost and the breakdown of the existing taliks. This event would increase the potential for leakage and/or groundwater mixing with shallow waters. Mixing with cooler waters which are undersaturated with respect

to calcium carbonate could lead to *no* precipitation of calcium carbonate upon discharge. Also, as Rabbitkettle Hotsprings is located in a seismically-active region, the threat of damage by an earthquake is not out of the question. A severe earth tremor could fracture the conduits or mounds, changing their hydraulics forever.

LEGEND FOR FIGURE 19.

Flow Areas:

1974

1978

1991

1992

time-lapse camera location

heavily vegetated areas

reference point (permanent brass platelet)

brass platelets: I.D. number; (thickness in millimetres)

(1.1) elevation below reference point C (metres)

sample location

Travertine:

rimstone pools (height < 10 cm)

rimstone pools (height 10 - 50 cm)

rimstone pools (height 50 - 100 cm)

rimstone pools (height > 100 cm)

remnant pools

patterned ground (carbonate muds or fine sands)

patterned ground (fine, medium and coarse grained travertine)

fine-grained travertine debris (light coloured)

stripes

iron-rich channels

Figure 19a. Surface-characteristic map of the North Mound.

Figure 19b. Surface-characteristic map of the South Mound.

CHAPTER 7. CONCLUSIONS

The calcium-carbonate-saturated waters of Rabbitkettle Hotsprings are depositing spectacular travertine-terrace structures despite severe climatic conditions. Similar and considerably larger travertine structures are found throughout the world, but generally have the advantage of developing in milder climates. In the Nahanni region, the numerous other travertine-precipitating springs do not provide conditions consistent with the development of structures comparable to those at Rabbitkettle.

Rabbitkettle Hotsprings are located within the southern Mackenzie Mountain Fold Belt, and are associated with folded Paleozoic carbonate rocks. A gentle syncline exposes Sunblood Formation carbonates on the mountain spur 3 to 6 kilometres southeast of the hotsprings. Along this exposure, at an average of 1,000 metres above sea level, meteoric waters infiltrate into the aquifer through fractures and solution openings. As the water incorporates carbon dioxide and oxygen from the recharge zone, it begins to dissolve minerals from the predominantly fossiliferous, pyritic and argillaceous limestones.

As the water descends within the Sunblood Formation, it becomes forced under artesian pressure beneath the impermeable Road River shale. Gradually heated with depth, the mineralized water reaches a little more than 1 kilometre below the subsurface. Heating is the result of an above average geothermal gradient associated with the local quartz monzonite intrusions, possibly from the radioactive decay of minerals.

Beneath the mounds, the limestone aquifer intercepts the Broken Skull Fault. This fault provides a conduit for the hot water to migrate toward ground

surface. It also provides a means for carbon dioxide, from the decarbonation of limestones at depth, to mix with the groundwater on its upward migration. This influx of carbon dioxide increases the carbonate-dissolution capacity of the water. The water migrates up through the bedrock fault and continues through taliks that have been maintained in the overlying unconsolidated deposits. Through its travels, the water drops in temperature between 40° and 50°C by conductive cooling with the surrounding wall rock and sediment. When the warm mineralized water reaches the surface, the drop in confining pressure results in the loss of dissolved carbon dioxide from solution, and the deposition of calcium carbonate as travertine. The time from recharge to discharge is between 10 and 25 years.

This process has continued uninterrupted for thousands of years. The chemical consistency indicates that the waters are in a state of equilibrium prior to discharging. Historically, the temperature of the main springs has remained close to 20°C. However, isotopes from old travertine suggest that a significant drop in the discharge temperature has occurred since the early development of the mounds. The present consistency of the discharging spring water indicates that there is no subsurface mixing with other water sources. Fluctuations in discharge are the result of weather conditions in the recharge zone; seasonally adding to or subtracting from storage within the aquifer. Since the water temperature shows little change with discharge fluctuation, it is believed that heating and cooling within the subsurface is dominated by conductive processes.

Four springs discharge at the site and emanate from the same groundwater reservoir. The cooler spring, however, discharges topographically lower, and its chemistry suggests a loss of calcium carbonate and amorphous iron prior to

discharging. This spring may have resulted from an internal leak in the conduit system beneath the south mound.

Travertine has been deposited on this site for close to 10,000 years. The north mound has developed on a lower more recently cut terrace; making it the youngest of the two mounds. Current rates of deposition estimate that this mound has been precipitating travertine for close to 7,000 years. The north mound is also building at a faster rate, possibly by stealing a substantial portion of head from the other mound, which will eventually allow it to close the elevation gap.

Even though the north mound is the youngest, its vent is the oldest of the active vents. Radiocarbon-dating of entrapped wood within the south-mound vents suggests that these vents are not the original points of discharge. Vents on this mound have been subject to "switching" as a result of changing hydraulics within the underlying system. The first identifiable vent is the now-abandoned vent, located in the centre of the mound and is estimated to have become extinct 468 ± 63 years ago corresponding to the appearance of spring 002, 500 ± 100 years ago. Spring 003 appeared 1625 ± 230 years ago. The age of spring 004 remains undetermined; however, it is definitely the youngest.

Rates of travertine precipitation were measured from the loss of calcium in solution as the water flows over the surface of the mound, and from precipitation of calcium carbonate directly onto glass slides. All studies indicate that only calcium carbonate is precipitating on the mounds, and precipitation begins only after supersaturated conditions exist. The greatest rates of precipitation occur where carbon dioxide is rapidly released from solution, causing the solution to become supersaturated. This happens where there is the greatest turbulence. However, volume of discharge, vegetation and temperature also have an effect.

The rate of loss of carbon dioxide from solution also determines whether the travertine is precipitated at isotopic and chemical equilibrium. Faster rates lead to conditions of disequilibrium. At present, the north mound is accumulating travertine at an average rate of 2.7 mm/year. The south mound is building upward at 1 mm/year adjacent to spring 002, and at 0.2 mm/year adjacent to spring 003.

The mounds will exist for many years to come if degradation can be minimized, and care is taken when visiting the site, since human impacts can potentially be controlled. Natural forms of degradation to the site result from extensive frost action that show up as frost shatter, spalling of the travertine rimstone structures and patterned ground; another form includes animal traffic which is specific to the south mound. Destruction by the Rabbitkettle River has historically caused substantial damage to the mound structures. However, the recent meander cut-off has decreased the destructive potential by flooding upstream of the site. The most real threat to the system comes from the possibility of more change in the internal hydraulics which would result in losses of hydraulic head within the three main springs. Evidence suggests that these events are taking place, albeit slowly. The best way to observe the changing conditions at the site is by monitoring them year-by-year. Recommendations along with a detailed monitoring program are outlined in Appendix 9.

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Appendix I Spring Water Chemistry

Constituent	Gabrislee et al. 26-Jul-63	van Everdingen 13-Jun-73	Ford 1974	Crandall 15-Aug-76	Brown et al. 1979	Hamilton 1986	Hamilton 1988	Gulley 27-Jun-91	Gulley 27-Jun-92
SiO ₂ (ppm)	15	13		40		16	5.6	6.0	7.2
Al (ppm)	0.1							0.017	<0.2
Pb (ppm)	0.11	0.12				0.128	0.02	0.114	0.5
Mn (ppm)		0.01		0.001		0.013	0.005	0.007	<0.02
Cu (ppm)	44.8 (113)*	218	212*	200	150*	197	198	198	248
Mg (ppm)	41.2	38.7		39.8	37.7*	38.2	42	41	44.3
Na (ppm)	3.9	4.2		3.85		3.9	11	10	4.1
K (ppm)	4.9	4.9		4.94		4.9	6	4.7	5.9
HCO ₃ (ppm)	317	322		404		788	635	786	958
SO ₄ (ppm)	32.2	38		36		32.6	32.3	33.5	31.5
Cl (ppm)	4.1	0.7		0.7		1.21	1.508	2.3	1.62
F (ppm)	0.25	0.13				0.53		<0.10	0.06
N-NH ₃ (ppm)	0.2	<0.01					0.127	<0.10	<0.10
CO ₂ (atm)	0.003**	0.17		0.135**		0.106	0.156**	0.217	0.190
Ba (ppb)				138		200		188	188
Ag (ppb)						<2		<50	<10
Cu (ppb)		<1		2		3		2	<20
Pb (ppb)		<5		5				70	<100
Zn (ppb)		8				8	67	15	<20
Mn (ppb)						13		<50	<50
Co (ppb)						<2		6	<20
Cr (ppb)								16	<20
V (ppb)				8				<10	<20
As (ppb)						0.3		<200	<200
Mo (ppb)						<2		8	<20
Bi (ppb)								21	<200
Te (ppb)								<100	<200
Cd (ppb)						<2		<2	<20
La (ppb)								<10	<50
Se (ppb)								<100	<200
Ge (ppb)								10	<200
Sm (ppb)								<200	<200
Br (ppb)				265		700	788	620	880
Y (ppb)								<10	<20
U (ppb)						6.4			
Hg (ppb)				<1					
W (ppb)						<2		<100	<200
S (ppb)				10					
Ti (ppb)				3					
Br (ppb)							<50		
Li (ppb)								38	48
Temperature °C	20.5	22	21	21	21	21	21	21	21
Conductivity (µS/cm)		1100			1080		1130	1080	1160
pH	7.88***	8.61	8.45	7.28***	8.42	8.85	7.81***	8.50	8.43
OR (mV)		381					341	357	

* Calculated from Hardness Data

** Calculated using estimated field pH

*** Laboratory pH

Appendix 1 Spring Water Chemistry

Constituent	910627-001	910712-001	910728-001	910808-001	920311-001	920827-001	920787-001
SiO ₂ (ppm)	6.0	---	---	---	45.6	7.2	6.7
Al (ppm)	0.017	<5	<5	<5	<0.2	<0.2	<0.2
Fe (ppm)	0.114	<5	<5	<5	0.3	0.5	0.4
Mn (ppm)	0.007	<5	<5	<5	<0.02	<0.02	<0.02
Ca (ppm)	198	188	187	185	165	249	238
Mg (ppm)	41	40	40	39	17.5	44.3	42.4
Na (ppm)	10	10	10	10	3.8	4.1	4
K (ppm)	4.7	<5	<5	<5	2.9	5.9	5
HCO ₃ (ppm) Tc	796	757	753	742	664	958	909
HCO ₃ (ppm) T	637	692	692	812	664	844	736
SO ₄ (ppm)	33.5	34.2	34.3	34.4	33	31.5	32.3
Cl (ppm)	2.3	2.53	2.64	2.38	3.11	1.62	1.9
F (ppm)	<0.10	0.92	0.96	1.21	<0.10	0.66	0.72
n-NO ₃ (ppm)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
CO ₂ (atm)	0.217	0.212	0.235	0.181		0.302	0.281
Ba (ppb)	183	179	174	182	176	188	186
Ag (ppb)	<50	<50	<50	<50	<10	<10	<10
Cu (ppb)	2	<50	<50	<50	<20	<20	<20
Pb (ppb)	70	<200	<200	<200	<100	<100	<100
Zn (ppb)	15	<20	<20	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50	<50	<50	<50
Co (ppb)	8	<10	<10	<10	<20	<20	<20
Cr (ppb)	16	<50	<50	<50	<20	<20	<20
V (ppb)	<10	<10	<10	<10	<20	<20	<20
As (ppb)	<200	<200	<200	<200	<200	<200	<200
Ni (ppb)	8	<50	<50	<50	<20	<20	<20
Bi (ppb)	21	39	21	26	---	<200	<200
Te (ppb)	<100	<100	<100	<100	<200	<200	<200
Cd (ppb)	<2	4	<2	<2	<20	<20	<20
La (ppb)	<10	<10	<10	<10	<50	<50	<50
Sb (ppb)	<100	<100	<100	<100	<200	<200	<200
Sc (ppb)	10	<10	<10	<10	<200	<200	<200
Sn (ppb)	<200	<200	<200	<200	<200	<200	<200
Sr (ppb)	620	605	618	613	600	690	684
Y (ppb)	<10	<10	<10	<10	<20	<20	<20
W (ppb)	<100	<100	<100	<100	<200	<200	<200
Li (ppb)	39	---	---	---	37	48	46
Temperature (°C)	21	21	21	21	20.5	21	21
Conductivity (uS/cm)	1030	1130	1060	1160	1130	1160	1170
pH	6.50	6.49	6.44	6.55	6.92	6.43	6.44
Eh (mV)	367	338	290	315	---	---	---

Appendix 1 Cont.

Constituent	910627-002	910712-002	910728-002	910808-002	920311-002	920627-002	920707-002
SiO ₂ (ppm)	---	---	---	---	45.2	7.1	6.8
Al (ppm)	<5	<5	<5	<5	<0.2	<0.2	<0.2
Fe (ppm)	<5	<5	<5	<5	0.2	0.6	0.6
Mn (ppm)	<5	<5	<5	<5	<0.02	<0.02	<0.02
Ca (ppm)	198	189	187	186	162	247	238
Mg (ppm)	42	40	40	40	17.6	44.4	43
Na (ppm)	10	10	10	10	3.7	4	3.9
K (ppm)	<5	<5	<5	<5	2.7	5.7	5
HCO ₃ (ppm) Tc	803	761	754	751	668	949	919
HCO ₃ (ppm) T	645	696	732	692	668	760	756
SO ₄ (ppm)	33.4	34.3	34.5	34.6	33	32.2	29.5
Cl (ppm)	2.3	2.62	2.64	2.32	2.83	1.43	2.18
F (ppm)	<0.10	0.86	0.96	1.15	<0.10	0.72	0.3
N-NO ₃ (ppm)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
CO ₂ (atm)	0.167	0.207	0.178	0.172		0.321	0.308
Ba (ppb)	177	175	173	176	186	183	180
Ag (ppb)	<50	<50	<50	<50	<10	<10	<10
Cu (ppb)	<50	<50	<50	<50	<20	<20	<20
Pb (ppb)	<200	<200	<200	<200	<100	<100	<100
Zn (ppb)	27	<20	<20	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50	<50	<50	<50
Co (ppb)	<10	<10	<10	<10	<20	<20	<20
Cr (ppb)	<50	<50	<50	<50	<20	<20	<20
V (ppb)	<10	<10	<10	<10	<20	<20	<20
As (ppb)	<200	<200	<200	<200	<200	<200	<200
Ni (ppb)	<50	<50	<50	<50	<20	<20	<20
Bi (ppb)	<20	20	21	<20	36	<200	<200
Te (ppb)	<100	<100	<100	<100	<200	<200	<200
Cd (ppb)	3	<2	<2	2	<20	<20	<20
La (ppb)	<10	<10	<10	<10	<50	<50	<50
Sb (ppb)	<100	<100	<100	<100	<200	<200	<200
Sc (ppb)	15	<10	<10	<10	<200	<200	<200
Sn (ppb)	<200	<200	<200	<200	<200	<200	<200
Sr (ppb)	628	618	616	623	603	701	692
Y (ppb)	<10	<10	<10	<10	<20	<20	<20
W (ppb)	<100	<100	<100	<100	<200	<200	<200
Li (ppb)	---	---	---	---	36	46	45
Temperature (°C)	20	20.5	20.5	20	19.4	21	20
Conductivity (uS/cm)	1130	1130	1130	1130	1120	1150	1170
pH	6.61	6.50	6.56	6.57	6.75	6.40	6.40
Eh (mV)	233	316	266	209	---	---	---

Appendix 1 Cont.

Constituent	910027-003	910712-003	910720-003	910800-003	920311-003	920627-003	920707-003
SiO ₂ (ppm)	---	---	---	---	47.2	7.0	6.8
Al (ppm)	<5	<5	<5	<5	<0.2	<0.2	<0.2
Fe (ppm)	<5	<5	<5	<5	0.2	0.7	0.6
Mn (ppm)	<5	<5	<5	<5	<0.02	<0.02	<0.02
Ca (ppm)	199	187	186	185	172	246	238
Mg (ppm)	42	40	38	39	18.3	44.3	43
Na (ppm)	10	10	10	9	3.8	4	3.9
K (ppm)	<5	<5	<5	<5	3.1	5.5	5.2
HCO ₃ (ppm) Tc	808	754	740	739	688	947	928
HCO ₃ (ppm) T	680	688	688	692	688	760*	716
SO ₄ (ppm)	33.7	34.3	34.3	34.5	31	31.6	22
Cl (ppm)	0.82	2.23	2.3	2.35	3.06	1.39	1.4
F (ppm)	<0.10	1.16	1.12	1.2	<0.10	0.72	0.29
N-NO ₃ (ppm)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
CO ₂ (atm)	0.185	0.200	0.187	0.182		0.316	0.311
Ba (ppb)	177	172	173	175	172	181	180
Ag (ppb)	<50	<50	<50	<50	<10	<10	<10
Cu (ppb)	<50	<50	<50	<50	<20	<20	<20
Pb (ppb)	<200	<200	<200	<200	<100	<100	<100
Zn (ppb)	<20	<20	<20	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50	<50	<50	<50
Co (ppb)	<10	<10	<10	<10	<20	<20	<20
Cr (ppb)	<50	<50	<50	<50	<20	<20	<20
V (ppb)	<10	<10	<10	<10	<20	<20	<20
As (ppb)	<200	<200	<200	<200	<200	<200	<200
Ni (ppb)	<50	<50	<50	<50	<20	<20	<20
Bi (ppb)	30	<20	20	35	38	<200	<200
Te (ppb)	<100	<100	<100	<100	<200	<200	<200
Cd (ppb)	6	<2	<2	<2	<20	<20	<20
La (ppb)	<10	<10	<10	<10	<50	<50	<50
Sb (ppb)	<100	<100	<100	<100	<200	<200	<200
Sc (ppb)	10	<10	<10	<10	<200	<200	<200
Sn (ppb)	<200	<200	<200	<200	<200	<200	<200
Sr (ppb)	631	611	589	616	618	697	682
Y (ppb)	<10	<10	<10	<10	<20	<20	<20
W (ppb)	<100	<100	<100	<100	<200	<200	<200
Li (ppb)	---	---	---	---	39	47	46
Temperature (°C)	20	20.5	20	20	19.3	20	20
Conductivity (µS/cm)	1120	1080	1130	1050	1120	1180	1150
pH	6.57	6.51	6.53	6.54	6.77	6.40	6.40
Eh (mV)	209	272	266	263	---	---	---

Appendix 1 Cont.

Constituent	916627-004	916712-004	916729-004	916906-004	920627-004	920707-004
SiO ₂ (ppm)	---	---	---	---	7.9	7.7
Al (ppm)	<5	<5	<5	<5	<0.2	<0.2
Fe (ppm)	<5	<5	<5	<5	0.5	0.4
Mn (ppm)	<5	<5	<5	<5	<0.02	<0.02
Ca (ppm)	153	141	138	136	186	170
Mg (ppm)	41	39	39	39	43.7	41.3
Na (ppm)	10	10	9	10	4.1	4
K (ppm)	<5	<5	<5	<5	6.5	6.1
HCO ₃ (ppm) Tc	662	611	600	603	765	703
HCO ₃ (ppm) T	560	524	540	580	614	584
SO ₄ (ppm)	32.6	34.3	33.3	33.9	30.9	31
Cl (ppm)	2.02	2.04	1.97	2.04	1.32	1.38
F (ppm)	<0.10	0.82	0.6	0.6	0.28	0.26
N-NO ₃ (ppm)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
CO ₂ (atm)	0.021	0.027	0.022	0.020	0.026	0.024
Ba (ppb)	179	173	181	180	176	172
Ag (ppb)	<50	<50	<50	<50	<10	<10
Cu (ppb)	<50	<50	<50	<50	<20	<20
Pb (ppb)	<200	<200	<200	<200	<100	<100
Zn (ppb)	<20	<20	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50	<50	<50
Co (ppb)	<10	<10	<10	<10	<20	<20
Cr (ppb)	<50	<50	<50	<50	<20	<20
V (ppb)	<10	<10	<10	<10	<20	<20
As (ppb)	<200	<200	<200	<200	<200	<200
Ni (ppb)	<50	<50	<50	<50	<20	<20
Bi (ppb)	33	22	26	21	<200	<200
Te (ppb)	<100	<100	<100	<100	<200	<200
Cd (ppb)	<2	<2	<2	<2	<20	<20
La (ppb)	<10	<10	<10	<10	<50	<50
Sb (ppb)	<100	<100	<100	<100	<200	<200
Sc (ppb)	<10	<10	<10	<10	<200	<200
Sn (ppb)	<200	<200	<200	<200	<200	<200
Sr (ppb)	627	598	611	604	678	655
Y (ppb)	<10	<10	<10	<10	<20	<20
W (ppb)	<100	<100	<100	<100	<200	<200
Li (ppb)	---	---	---	---	48	48
Temperature (°C)	10.5	11	12.5	12	10	11
Conductivity (uS/cm)	850	850	830	850	790	800
pH	7.36	7.25	7.32	7.37	7.29	7.15
Eh (mV)	209	272	266	283	---	---

Appendix 1 Cont.

Constituent	930312-001	930312-002	930312-003	930312-004
Al (ppm)	<0.2	<0.2	<0.2	<0.2
Fe (ppm)	<0.2	0.3	0.2	0.2
Mn (ppm)	<0.02	<0.02	<0.02	<0.02
Ca (ppm)	164.8	160.5	167.6	137.4
Mg (ppm)	20.1	20.8	20.6	23.8
Na (ppm)	6.4	3.2	3.2	3.4
K (ppm)	<0.5	<0.5	<0.5	1.6
HCO ₃ (ppm) Tc	577	586	580	505
SO ₄ (ppm)	33.2	34.6	34.2	32.5
Cl (ppm)	1.08	1.02	1.02	1.92
F (ppm)				
NO ₃	<0.10	<0.10	<0.10	<0.10
CO ₂ (atm)				
Ba (ppb)	180	170	172	141
Ag (ppb)	<10	<10	<10	<10
Cu (ppb)	<5	<5	<5	<5
Pb (ppb)	<100	<100	<100	<100
Zn (ppb)	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50
Co (ppb)	<20	<20	<20	<20
Cr (ppb)	<20	<20	<20	<20
V (ppb)	<20	<20	<20	<20
As (ppb)	<200	<200	<200	<200
Ni (ppb)	<20	<20	<20	<20
Bi (ppb)	<200	<200	<200	<200
Te (ppb)	<200	<200	<200	<200
Cd (ppb)	<20	<20	<20	<20
La (ppb)	<50	<50	<50	<50
Sb (ppb)	<200	<200	<200	<200
Sc (ppb)	<200	<200	<200	<200
Sn (ppb)	228	201	<200	<200
Sr (ppb)	612	616	621	589
Y (ppb)	<20	<20	<20	<20
W (ppb)	<200	<200	<200	<200
Temperature (°C)	20.5	18.7	18.6	1.5
Conductivity (uS/cm)				
pH	6.82	6.94	6.89	7.53
Eh (mV)				

Appendix 1 Cont. Field Data

Sample	Temperature C	pH	HCO ₃ ⁻ (mg/L) T	Conductivity (μS/cm)	Eh (mV)
910626-001	21	6.50	637	1030	367
910706-001	21	6.57	684	1130	340
910712-001	21	6.49	892	1130	338
910720-001	21	6.47	854	1180	331
910728-001	21	6.44	892	1080	290
910803-001	21.5	6.57	756	1130	277
910808-001	21	6.55	812	1160	315
920627-001	21	6.43	844	1160	
920629-001	21	6.55	648		
920701-001	21	6.50	680		
920703-001	21	6.45	680		
920707-001	21	6.44	736	1170	
930219-001	20.5	6.82			
930312-001	20.5	6.82			
910626-002	20	6.61	645	1130	233
910706-002	20	6.64	700	1110	292
910712-002	20.5	6.50	686	1130	316
910720-002	20	6.45	728	1130	314
910728-002	20.5	6.56	732	1130	266
910803-002	20	6.57	700	1130	268
910808-002	20	6.57	692	1130	209
920627-002	21	6.40	760	1150	
920629-002	21	6.53	646		
920701-002	21	6.42	658		
920703-002	20	6.45	682		
920707-002	20	6.40	756	1170	
930216-002	18.3	6.97			
930312-002	18.7	6.94			
910626-003	20	6.57	680	1120	209
910706-003	20	6.54	682	1080	288
910712-003	20.5	6.51	688	1080	272
910720-003	20	6.45	724	1080	282
910728-003	20	6.53	688	1130	266
910803-003	20	6.54	700	1080	250
910808-003	20	6.54	682	1050	283
920627-003	20	6.40	760	1160	
920629-003	21	6.45	712		
920701-003	21	6.41	644		
920703-003	20	6.45	856		
920707-003	20	6.40	716	1150	
930216-003	18.1	6.90			
930312-003	18.6	6.89			
910626-004	10.5	7.38	560	850	227
910706-004	11	7.43	568	830	312
910712-004	11	7.26	524	850	308
910720-004	11	7.05	528	850	293
910728-004	12.5	7.32	540	830	245
910803-004	12.5	7.44	632	840	272
910808-004	12	7.37	560	850	223
920627-004	10	7.29	614	790	
920707-004	11	7.15	584	800	
930312-004	1.5	7.53			

Appendix 1 Cont.

Constituent	Rabbitkettle Lake 920626-AKL	South Nahanni River 920626-SNR	Rabbitkettle River upstream 920628-AKRU	Rabbitkettle River downstream 920628-AKRd	Emerald Lake 920628-EL
SiO ₂ (ppm)	4.6	2.0	2.0	1.9	0.4
Al (ppm)	<0.2	<0.2	<0.2	<0.2	<0.2
Fe (ppm)	0.2	0.2	<0.2	0.2	<0.2
Mn (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02
Ca (ppm)	39.3	36.8	38.7	36.8	39.3
Mg (ppm)	30	7.2	5.2	4.9	11.7
Na (ppm)	3	<0.2	<0.2	<0.2	0.9
K (ppm)	5.3	2.4	2.6	2.7	3.5
HCO ₃ (ppm)	260	116	119	113	135
SO ₄ (ppm)	21.3	28.7	21.3	22.1	36.8
Cl (ppm)	0.89	0.31	0.36	0.25	0.36
F (ppm)	0.19	<0.10	<0.10	<0.10	<0.10
N-NO ₃ (ppm)	<0.10	0.1	0.13	0.12	<0.10
CO ₂ (atm)	0.002	0.001	0.001	0.001	0.005
Ba (ppb)	355	<40	<40	<40	42
Ag (ppb)	<10	<10	<10	<10	<10
Cu (ppb)	<20	<20	<20	<20	<20
Pb (ppb)	<100	<100	<100	<100	<100
Zn (ppb)	<20	<20	<20	<20	<20
Mo (ppb)	<50	<50	<50	<50	<50
Co (ppb)	<20	<20	<20	<20	<20
Cr (ppb)	<20	<20	<20	<20	<20
V (ppb)	<20	<20	<20	<20	<20
As (ppb)	<200	<200	<200	<200	<200
Ni (ppb)	<20	<20	<20	<20	<20
Bi (ppb)	<200	<200	<200	<200	<200
Te (ppb)	<200	<200	<200	<200	<200
Cd (ppb)	<20	<20	<20	<20	<20
La (ppb)	<50	<50	<50	<50	<50
Sb (ppb)	<200	<200	<200	<200	<200
Sc (ppb)	<200	<200	<200	<200	<200
Sn (ppb)	<200	<200	<200	<200	<200
Sr (ppb)	286	118	101	94	157
Y (ppb)	<20	<20	<20	<20	<20
W (ppb)	<200	<200	<200	<200	<200
Li (ppb)	<20	<20	<20	<20	<20
Temperature (°C)	17	8	8	8	21
Conductivity (uS/cm)	280	160	140	150	220
pH	8.24	8.42	8.28	7.6	7.26

Appendix 1 Cont.

Bicarbonate Corrections

The chemical results revealed unacceptable charge balance errors of greater than 5 percent. In all cases, the charge concentration of the cations exceeded that of the anions. Most of the analyses were performed in a laboratory and are considered to be quite accurate. The source of error is believed to be HCO_3^- since it was the only ion to be determined from infield titration methods.

Bicarbonate concentrations were corrected assuming the unequal charge balance was due to error incurred during field titrations. All the charts within this appendix show field titrated bicarbonate values as T, and corrected bicarbonate values as Tc.

The main source of error is believed to be from the rapid diffusion of carbon dioxide from solution. Since bicarbonate concentrations are controlled by the concentration of carbon dioxide in solution, the agitation of the sample while titrating would aid in the diffusion of carbon dioxide and indicate a lower bicarbonate concentration. Other potential sources of error are mechanical and human. Mechanical error may originate from improper calibration of the digital titrator or improper release of acid from air bubbles. The majority of the samples were titrated by the same person; however, human error may be incurred in some of the samples as a result visual interpretation of the "end point" by colour change. Any procedural error or "end point" error was amplified by the fact that titration values were multiplied by four to determine the final values.

Appendix 2 Isotope Data

Water Sample	$^{18}\text{O}(\text{H}_2\text{O})$ ‰ (SMOW)	$^2\text{H}(\text{H}_2\text{O})$ ‰ (SMOW)	$^3\text{H}(\text{H}_2\text{O})$ (T U)	$^{13}\text{C}(\text{CO}_2)$ ‰ (PDB)
90-003				-8.49
910627-001			27	-8.34
910706-001			28	
910712-001	-22.68	-175.4		-8.05
910720-001			31	
910728-001	-22.99	-176.5	29	-8.48
910808-001	-22.89	-175.8	32	-8.51
920311-001	-22.86	-172.0	35	
910712-002	-22.76	-176.4		-8.12
910728-002	-22.99	-176.1		
910808-002	-22.99	-175.2	29	-8.41
920311-002	-23.03	-170.8		
920629-002				-8.90
910712-003	-22.67	-175.5		-8.46
910728-003	-22.87	-177.1		-8.18
910808-003	-22.97	-174.9	26	-8.55
920311-003	-22.87	-171.2		
920629-003				-9.16
910712-004	-22.61	-176.8		
910728-004	-22.59	-176.7		
910808-004	-22.81	-173.9	22	
NIC-SNOW (0-20 cm)	-27.34	-210.9		
NIC-SNOW (20-40 cm)	-25.75	-190.8		
910629-SNR	-22.65			
910802-SNR	-22.30	-169.3		
910807-SNR	-22.44	-172.0		
910716-SNR	-22.75	-171.6		
910713-HITW	-22.12	-172.4		
910807-HITW	-22.34	-172.4		
910630-RKR	-23.45	-175.6		
910710-RKR	-22.92	-175.6		
910715-RKR	-22.77	-174.3		
910629-RKL	-12.36			
910711-RKL	-12.46	-128.6		
910807-RKL	-12.32	-127.3		
910713-EL	-18.05	-154.7		
910701-RAIN	-17.25	-140.3	21	
910709-RAIN	-19.30	-150.5		
910719-RAIN	-26.78	-209.0	13	
910725-RAIN	-22.44		12	

NIC, Nahanni Ice Core; SNR, South Nahanni River; HITW, Hole-in-the-Wall Creek;
RKR, Rabbitkettle River; RKL, Rabbitkettle Lake; EL, Emerald Lake

Appendix 2 Cont.

Water Sample	^{13}C (DIC) ‰ (PDB)	$^{34}\text{S}(\text{SO}_4)$ ‰ (CDT)	$^{18}\text{O}(\text{SO}_4)$ ‰ (SMOW)
86-001	-2.32		
90-001	-1.4	...	
91-001	-1.701	+4.24	-8.44
91-002	-2.04	+4.02	-8.28
91-003	-2.07	+4.22	-7.64
91-004	+0.29	+4.83	-7.57

Travertine Sample	$\delta^{18}\text{O}$ ‰ (SMOW)	$\delta^{18}\text{O}$ ‰ (PDB)	$\delta^{13}\text{C}$ ‰ (PDB)
Travertine block	+7.32	-22.84	+2.46
Area A mud	+9.80	-20.44	+3.74
Area B mud	+10.26	-19.99	+3.15
Cement-conglomerate	+12.60	-17.72	+1.23
Contact (T3-001)	+9.38	-20.84	+1.08
Contact (T4-001)	+8.68	-21.52	+1.61
V001 (T5-001)	+9.87	-21.24	+4.28
86-001		-22.10	+2.90
V001 (T10-001)	+9.14	-21.07	+5.49
V002 (T1-002)	+9.25	-20.97	+5.63
V003 (T1-003)	+8.45	-21.75	+2.73
V001-pool (14.5m)	+8.75	-21.45	+5.37
V001-25m	+7.41	-22.76	+2.57
V001-33m	+7.50	-22.67	+3.04
V001-38m	+8.16	-22.02	+4.73
V001-48m	+8.39	-21.80	+5.81

Rock Sample	$\delta^{18}\text{O}$ ‰ (SMOW)	$\delta^{13}\text{C}$ ‰ (PDB)
Rabbitkettle Formation	+18.8	-1.80
Rabbitkettle Formation	+17.20	+0.70
Sunblood Formation	+22.50	-1.80
Sunblood Formation	+21.80	-2.80
Road River Formation	+22.60	-7.10

Appendix 3 Chemistry Changes over the Surface of the Mounds

Distance	Temperature °C	pH	HCO ₃ ⁻ (mg/L)	Conductivity μS/cm	CO ₂ (mg/L)
91-July-12					
<u>Vent 001</u>	21	6.49	892	1130	239
5 m (nw)	20.5	6.73	680	1130	155
10 m (nw)	20.5	6.83	680	1160	155
15 m (nw)	20	6.88	696	1140	148
20 m (nw)	20	7.01	704	1150	155
25 m (nw)	19	7.47	704	1070	106
30 m (nw)	18	7.79	616	950	88
35 m (nw)	16.5	7.80	552	900	81
40 m (nw)	16	7.95	508	830	85
91-July-20					
<u>Vent 001</u>	21	6.47	864	1150	253
5 m (nw)	21	6.48	700	1140	151
10 m (nw)	21	6.56	688	1140	211
15 m (nw)	21	6.64	700	1150	148
20 m (nw)	21	6.80	696	1140	151
25 m (nw)	21	7.28	648	1030	84
30 m (nw)	21.5	7.67	576	920	84
35 m (nw)	21	7.80	504	870	77
40 m (nw)	21	7.80	488	810	84
92-June-27					
<u>Vent 001</u>	21	6.43	844	1160	
20 m (nw)	21	6.83	700		
40 m (nw)	12	7.27	608		
Falls (nw)	17	9.52	580		
20 m (sw)	20	7.24	680		
40 m (sw)	17	7.66	496		
Falls (sw)	14	7.64	416		
<u>Vent 002</u>	21	6.40	760	1150	
23 m (250°)	25	7.54	556		
24 m (315°)	25	7.36	456		
<u>Vent 003</u>	20	6.40	760	1160	
End	19	7.39	640		
<u>Vent 004</u>	10	7.39	614	790	
End	18	7.85	468		
92-July-07					
<u>Vent 001</u>	21	6.44	736	1170	
20 m (nw)	21	6.79	700	1170	
40 m (nw)	18	7.55	652	670	
Falls (nw)	16	8.00	528	700	
<u>Vent 002</u>	20	6.40	760	1170	
23 m (250°)	19.5	7.75	376	520	
<u>Vent 003</u>	20	6.40	716	1150	
End	19.5	6.73	628	1180	
<u>Vent 004</u>	11	7.15	584	800	
End	13	7.64	460	790	

Appendix 3 Cont.

Parameter	910712-001	10m	20m	30m	40m	Falls
pCO ₂ (atm)	0.212	0.086	0.058	0.008	0.005	
HCO ₃ (ppm)	892	680	704	616	508	
SiO ₂ (ppm)		0.7		0.7		
Fe (ppm)	<5	0.7	<5	0.8	<5	
Ca (ppm)	188	203	193	161	129	
Mg (ppm)	40	52.3	41	52.5	41	
Na (ppm)	10	3.8	10	3.8	10	
K (ppm)	<5	4.6	<5	5	<5	
SO ₄ (ppm)	34.2	32	34.1	33	34.1	
Cl (ppm)	2.53	1.67	2.16	1.57	1.58	
F (ppm)	0.92	0.3	0.66	0.3	0.13	
Ba (ppb)	179	188	180	176	159	
Sr (ppb)	605	644	615	617	569	

Parameter	910720-001	10m	20m	30m	40m	Falls
pCO ₂ (atm)		0.162	0.094	0.011	0.005	0.002
HCO ₃ (ppm)	864	688	696	576	488	352
SiO ₂ (ppm)		0.7	0.7	0.7	0.8	0.7
Fe (ppm)	<5	0.8	0.9	0.7	0.6	0.5
Ca (ppm)	188	202	202	157	131	125
Mg (ppm)	40	52.3	52.5	52.5	54	53.2
Na (ppm)	10	3.8	3.8	3.8	3.9	3.8
K (ppm)	<5	4.5	4.8	5.1	5.4	4.9
SO ₄ (ppm)	34.2	32	33	32	33	35
Cl (ppm)	2.53	1.56	1.57	1.56	1.54	1.67
F (ppm)	0.92	0.29	0.3	0.3	0.3	0.31
Ba (ppb)	179	187	187	174	168	164
Sr (ppb)	605	641	642	615	605	594

Parameter	920707-001	10m	20m	30m	40m	Falls
pCO ₂ (atm)	0.281		0.1		0.026	0.003
HCO ₃ (ppm)	736		700		652	528
SiO ₂ (ppm)	6.8		6.9		7.5	7.5
Fe (ppm)	0.4		0.4		0.4	0.4
Ca (ppm)	238		242		121	116
Mg (ppm)	42.4		43.1		46.2	45.7
Na (ppm)	4		4.1		4.3	4.2
K (ppm)	5		5.6		6.7	6.5
SO ₄ (ppm)	32.3		31.6		32.2	31.7
Cl (ppm)	1.9		1.4		1.43	1.37
F (ppm)	0.72		0.28		0.25	0.24
Ba (ppb)	186		188		153	153
Sr (ppb)	684		691		621	609

Appendix 3 Cont.

92-July-07

Parameter	Vent 002	002-END	Vent 003	003 END	Vent 004	004 END
HCO ₃ (ppm)	656	276	716	628	584	460
SiO ₂ (ppm)	6.8	5.8	6.8	6.9	7.7	7.7
Fe (ppm)	0.6	0.3	0.6	0.5	0.4	0.4
Ca (ppm)	238	76	238	243	170	155
Mg (ppm)	43	35.1	43	43.9	41.3	41.5
Na (ppm)	3.9	3.1	3.9	4.0	4.0	4.0
K (ppm)	5.0	5.4	5.2	5.4	6.1	6.1
SO ₄ (ppm)	29.5	24.8	22	32.4	31	28
Cl (ppm)	2.18	0.96	1.40	1.42	1.38	1.34
F (ppm)	0.30	<0.10	0.29	0.28	0.26	0.23
Ba (ppb)	180	103	180	180	172	166
Sr (ppb)	692	460	692	696	655	646
Li (ppb)	45	38	46	46	48	48

Appendix 3 Cont.**Calcite Saturation** **Dolomite Saturation**

Saturation = $\log(I.A.P./K_{sp})$; where I.A.P. is the ion activity product and K_{sp} is the equilibrium saturation. At $S.I. = 0$ the solution is saturated, positive values indicate supersaturated conditions and negative values indicate undersaturated conditions.

Appendix 3 Cont.**Aragonite Saturation** **Barite Saturation**

Appendix 3 Cont.**Magnesite Saturation** **Carbon Dioxide**

Appendix 3 Cont.

Bicarbonate

Calcium

Appendix 3 Cont.**Temperature** **Conductivity**

Appendix 4 Travertine-Precipitating Springs

Spring	Temp	pH	HCO ₃ ⁻ (mg/L)	δ ¹³ C _{DIC} (‰ PDB)	δ ¹³ C _{CO2} (‰ PDB)	log CO ₂ (atm)
Flat River						
017	5.5	6.3	2428	-0.5	-4.9	+0.18
055	1.6	5.9	1100	0.9	-1.9	
056	7.7	6.1	2236	+2.5	-1.2	+0.19
058	8.9	6.2	1918	+0.4	-3.7	-0.03
027	25	7.3	497	-2.10	-9.1	-1.59
028	10	7.6	206	-7.23	-16.1	-2.34
029	14	7.2	546	+0.60	-7.1	-1.48
030	18	6.8	445	-5.15	-10.9	-1.11
031	12	7.7	445	-1.73	-10.6	-2.13
South Nahanni River						
001	21	6.6	812	-1.7	-8.5	-0.70
023	3.8	7.2	293	-8.8	-17.3	-1.87
026	18	6.4	212			
040	49	6.5	431	-3.62	-7.9	-0.65
041	30.5	7.0	726	-2.0	-7.9	-1.12
046	6.0	7.8	239	-7.8	-17.2	-2.49
047	13	8.2	258			
021	17	7.0	477	-5.56	-12.5	-1.37
043	44	6.9	202	-3.59	-8.3	-1.45

Spring	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	SO ₄ (ppm)	Cl (ppm)
Flat River						
017	685	57.0	45.6	8.10	55.3	3.05
055	345	42.0	10.1	3.40	126	5.25
056	579	111.3	84.9	38.0	283	22.4
058	530	54.5	29.1	5.60	38.0	3.76
027	129	26.6	1.30	2.70	29.5	0.40
028	55.3	10.3	0.7	0.7	12.9	0.34
029	140	26.3	1.50	3.30	15.1	0.71
030	128	31.2	6.0	2.8	93.0	1.98
031	114	24.4	1.80	3.10	24.9	0.78
South Nahanni River						
001	185	39	10	4.7	34.4	2.38
023	72.4	31.6	0.6	0.7	69.2	0.55
026	46.0	23.1	1.90	1.50	45.5	3.48
040	168	51.8	49.7	33.3	396	23.4
041	218	68.0	68.0	33.7	389	23.6
046	57.4	24.4	1.80	1.40	45.9	3.69
047	65.9	26.9	1.50	1.40	57.0	2.47
021	251	65.2	19.2	15.3	540	2.58
043	109	25.4	21.9	23.2	219	32.2

(data from Hamilton, 1990; Hamilton *et.al.*, 1991)

Appendix 5

Geomorphology and Periglacial Effects of Areas adjacent to the Hotsprings

Rabbitkettle is located within the zone of discontinuous permafrost (Brown, 1970) and has a mean annual air temperature of -8°C (Burns, 1973). Hay River, which is of similar latitude, has a 12 metre thick layer of permafrost and a 1 to 3 metre thick active layer (Brown, 1970; Brown and Wright, 1979). Although the actual thickness of the permafrost layer is unknown at Rabbitkettle, being of higher elevation than Hay River, permafrost is likely to be considerably thicker. The thickness of the active layer was estimated by Brown and Wright, (1979) to be approximately 1.3 metres. Many of the deposits in the Rabbitkettle area are coarse grained and ice poor. Thus, determination of the actual active layer depth is not easy.

As a result of the presence of permafrost, numerous periglacial features can be observed around the spring site and on the travertine mounds. The two main processes associated with permafrost are: frost shattering, which breaks down larger fragments to silt size that ultimately become incorporated into the soil; and frost stirring which produces patterned ground. At Rabbitkettle, frost shatter is the most dramatic periglacial process in effect; the porous nature of the travertine makes it extremely susceptible to frost damage. The presence of patterned ground on the surface of the mounds along with the large accumulations of snow during the winter months indicates that subsurface heat from the water is not being transmitted through the travertine.

Two types of patterned ground occur at Rabbitkettle: stripes and stone nets. Theories on the mechanical origin of patterned ground were discussed by

Washburn (1956). Although the theories are varied, all agree that the main conditions contributing to the development of patterned ground are the intensity and frequency of freeze-thaw cycles, and the existence of perennially frozen ground. At Rabbitkettle, patterned ground is confined to areas where the water level is close to the ground surface; particularly over perched water tables and areas of extensive spring "leakage." These areas promote freeze-thaw conditions.

The following is a detailed description of the Rabbitkettle Hotspring site including descriptions of surface material, periglacial effects and local geomorphology. "Area" locations are in reference to Figure 14.

Area A.

This area is located in a clearing to the east of and on the same terrace as the north mound. The western and eastern edges of the clearing are dominated by extensive travertine-rich soils and fragmented-travertine debris. Here, non-sorted variably-sized fragments and travertine muds form hummocky elongate stripes. These stripes are from 3 to 17 metres in length and are a little over a metre in width. They are dominantly subparallel, and their alignment may reflect the underlying incline of the ground surface and/or the direction of drainage.

Circular piles or sorted stone nets up to one metre in diameter cover the remainder of the area (Plate XIV). The central portion of the clearing is dominated by roughly-sorted stone nets; these nets consist of variable-sized travertine debris with finer material concentrated in the centres, surrounded by larger clasts (6-15 centimetres) on the perimeters. Circular piles at the northern and southern edges of the clearing are non-sorted, with clasts up to 30 centimetres in size. The smaller material making up these forms is dominantly travertine. The

larger particles consist of variable-sized boulders which are similar to the those dispersed throughout the area. Vegetation grows between the forms but not on them, indicating that the forms are still active.

At the east end of this clearing, piles of loose boulders are exposed through the overlying travertine-rich soil. These boulders originated from Hole-in-the-Wall Creek, and range from a few centimetres to half-a-metre in diameter. They are dominantly composed of quartz monzonite, but include minor rock types such as shales and quartzites. Some of the rock piles are partially submerged in water, and the boulders are being coated with calcium carbonate. Along the perimeter of the clearing are piles of carbonate mud; these areas are also wet and result from the rapid break-down of travertine.

The travertine found in area A has been broken by frost shatter. It has either weathered in-situ or has been remobilized. In-situ weathering suggests that the travertine debris originated from either the present flow zones at a time when discharge was significantly higher, or is part of an old flow zone which has been abandoned. Brown and Wright (1979) observed 1.2 metres of decomposed travertine overlying remnants of what they believed to be a travertine dam. Underlying this "dam" is 15 centimetres of calcareous soil sitting on top of terrace gravels. The considerable amount of travertine debris in this clearing may have also originated from the breakdown and remobilization of travertine which has been dragged downstream by changing water levels of the Rabbitkettle River. In this case, the apparent "dam" structure may be a build-up of travertine debris, blocking groundwater flow and creating a perched water table.

Area B.

A large boulder and rubble pile occupies the centre of this area. The boulders range from 10s of centimetres to more than a metre in size. Most of the boulders are travertine-cemented conglomerates (clasts range from dominantly pebbles, of less than 5-centimetres, to small boulders of less than 25-centimetres). The composition of the rounded clasts are dominantly granitoids⁶ and shale. These conglomerate-boulders have originated from the underlying glaciofluvial deposits where they have been cemented by travertine-precipitating spring water. In fact, the entire ridge from area B to area I consists of these cemented deposits. The remaining boulders of area B consist of granitoid with minor shales, slates and quartzites, that have originated from the underlying Hole-in-the-Wall boulder alluvium.

Roughly-sorted circular piles occur at the perimeter of the boulder ground. These forms consist of variable-sized water-rounded pebbles, cobbles and boulders. Most of the pebble- and cobble-sized clasts are coated in travertine, having resulted from the breakdown of the larger travertine-cemented boulders. The centres of the forms are dominated by boulders; again predominantly granitoids and shales derived from the underlying terrace material. The boulders are surrounded by fine calcareous material of pebble- to sand-sized or less.

The boulder ground extends to the riverbank where spring 004 emerges. The upper portion of this slope exposes boulders and gravels in calcium-rich soils (dominantly quartz monzonite boulders under 30 centimetres). Below this zone are old weathered-travertine terraces, that are being covered by fresh precipitate from spring 004 to the west. The fresh deposits extend down to the riverbank,

⁶ General term for rocks of diorite, monzonite, granodiorite and granite compositions

covering an estimated 10 square metres. Below this zone are river deposited silt-sized soils.

Area C

This area is a continuation of area B, but consists of non-sorted, vegetated circular debris piles composed dominantly of fragmented travertine that form a friable pavement.

Area D

This area is similar to area B, except with non-travertine and travertine-cemented conglomerate boulders present in non-sorted circular piles. The non-travertine clasts are of small size and are often coated with travertine, as they originated from the underlying terrace deposits. There is also an abundance of angular-travertine fragments; frost-shattered remnants of the north mound.

Closer to area E, there are roughly-sorted stone nets with fines in the centre and an average diameter close to 1 metre. The material is mainly travertine, with a minor portion of larger water-rounded boulders of granitoids, shale and slate composition. The margins of these nets are heavily vegetated; suggesting that they are inactive (Brown and Wright, 1979).

The slope of the ridge extending upwards to area E, is armoured with old travertine. These travertine deposits originated during a time when the south mound springs flowed in this direction (see section 5.3).

Area E

At the top of the ridge, the area is covered by a layer of friable travertine up to 33 centimetres thick, overlying ancient Hole-in-the-Wall Creek boulder alluvium. Variable-sized boulders, dominantly quartz monzonite, are covered by crumbly calcium carbonate-rich soils, patterned ground and wet zones of calcareous muds. The patterned ground is the same as that found on top of the south mound in Area G. Decomposed travertine makes up sorted polygons that average about 10 centimetres in diameter. Fine travertine material occupies the centres of the polygons, coarsening toward the edges.

Large circular debris piles also occur in this vicinity (> 1 metre diameter) consisting of larger clasts of granitoids, quartzite and shales (20 to 80 centimetres) surrounded by finer travertine fragments. Large boulders, greater than 2 metres in diameter, are surrounded by calcium carbonate muds and roughly sorted piles of travertine, with fragments averaging less than 1 centimetre. A lack of vegetation on these forms suggests that they are still active.

Area F

This area lies within the "cut" in the glacial till, which resulted from the past migration of Hole-in-the-Wall Creek. The bottom and sides of this channel are littered with large granitoid boulders (1-3 metres) that have been eroded out of the surrounding till. Along the bottom of the channel, water-rounded granitoid boulders form loose piles which are somewhat overgrown with vegetation. Most of these piles are partially submerged in water; the boulders have become coated with thick layers of calcium carbonate where they sit below the water line.

Area G

The entire central portion of the south mound is covered in patterned ground. The patterns are composed of small-diameter stone nets (roughly 10 cm in diameter) and stripes that grade from fines in the centres to larger flat fragments on the perimeters. The fines are sand-sized that grade toward granule. The larger flat fragments average between a couple of centimetres and a few 10s of centimetres and are generally upended. All the fragments were derived from frost shatter of the originating travertine structures.

In the centre of the mound, near the extinct vent, the fines are dominantly white instead of a weathered grey. White fines represent more active frost areas where weathering is unable to take hold against continual stirring. These areas are subject to more frost action because water is percolating very close to the surface.

Stripes occur in the central region of the south mound; particularly associated with the extinct vent. Here, they are inclined to the slope of the extinct vent pile. Stripes occur up to 1-metre in length with the finest material in their centres.

Area H

This area is 10 to 15 metres into the forest at the edge of the south mound, due east of the vegetation 'island'. Occurring in this area are slabs of upheaved travertine boulders and non-sorted debris piles or hummocks. The debris piles are composed of calcium carbonate-rich soil, variable-sized travertine debris and quartz monzonite boulders. The travertine slabs are composed of smaller fragments of travertine that have been cemented together. These slabs suggest that frost in this area has been active for quite some time. When spring waters flowed

in this area, travertine was precipitated. The area was abandoned with a diversion in flow and became subject to frost action. Frost-shattered travertine fragments were then cemented together when the calcium carbonate-rich spring waters returned. After the waters had diverted for the last time, frost action took over again. The final diversion of the spring waters may have been less than 100 years ago, as the largest of these frost heaved blocks is split and leaning upright against a tree of this approximate age. The tree is believed to have pushed this block upwards as it grew.

Area I

The fluvial terrace deposits, which are now travertine-cemented conglomerates, can be traced all along this river-undercut ridge. In area I, the ridge exposes the cemented conglomerates at the base, overlaid by remnant travertine terraces. The framework of the conglomerate varies in size all along this ridge, but at this exposure it is dominantly less than 5 centimetres. The terraces have likely resulted from extensive seepage along the face of the ridge; seeps that no longer are active. The area above the ridge appears to be an old meander scar of the Rabbitkettle River.

Area J

This area is adjacent to the south mound and consists of two low travertine terraces on either side of a heavily vegetated area. The low terraces have remnants of old travertine rims, with most of the area covered by gravel-sized fragmented travertine debris and calcareous muds. The surface material is roughly organized

into small nets (< 10 centimetres diameter); similar to but not as obvious as those described in Area G.

The travertine comprising these terraces resulted from spring water flowing off of the south mound. However, the flow would have been ancient. This is apparent not only because of the extent of frost damage to these deposits but because of the lack of continuity within the travertine deposits on the northern face of this mound. Deposition of ancient travertine and more recent travertine was interrupted by erosion of the north bank.

Modern travertine, however, continues to be deposited in this area from a number of seeps occurring on the flat portions of the terraces and along the north facing ridge of the adjacent south mound. One of the larger seeps is depositing fresh travertine over a 3 x 1.5 metre area.

The region located between these travertine terraces contains large angular blocks of travertine that are overgrown with moss and other vegetation. These angular blocks, which are metres in size, have broken off of the south mound, possibly when this mound was undermined by the Rabbitkettle River; as it carved out the lower river terrace. This undermining may have also resulted in the erosion of the bank above the travertine terraces.

Area K

This area is along the river edge and below the north mound. The mound was undercut by the Rabbitkettle River more than 300 years ago, as some of the trees growing in this zone are approximately 300 years old (Marsh and Scotter, 1976). Today the area is heavily littered with large blocks of travertine which have broken off the north side of the mound. Trees have broken off and fallen

over as a result of falling debris and possibly from high water levels and ice movement during spring breakup. Most of the fallen debris on the western edge of the slope, below the falls, is covered in travertine.

North Mound

The most spectacular periglacial evidence at the site is the spalling or exfoliation of the travertine rimstone pools most prevalent on the north mound (Plate XI). Exfoliation is the result of entrapped moisture within the travertine being subject to repeated freeze-thaw events. The release of the compressive stress, due to the expansion of freezing moisture, concentrates along the apex of the rimstone pools. Continual exfoliation of this mound over the years has resulted in a buildup of fragmental travertine debris along its base.

Standard clast-size classification:

Boulders	>256 mm	Granules	4 mm to 2 mm
Cobbles	256 mm to 64 mm	Sand	2 mm to .05 mm
Pebbles	64 mm to 4 mm		

Appendix 6 Age Determinations of Mounds based on Deposition Rates

The age of the north mound was estimated by two methods, both of which involved approximating the volume of the mound and the rates of travertine deposition. The first method, derived a travertine-deposition rate based upon the loss of calcium from solution (converted to calcium carbonate) over the surface of the mound. The second method, is based upon an average rate of travertine-deposition calculated from its precipitation onto glass slides that were placed within the discharge area. Both methods utilize estimated *year-long* precipitation values which are 50 percent of precipitation rates measured during the summer. The reduction of 50-percent, was calculated from glass slides left in the flow path for one year.

North Mound	Volume of 81,000 m ³
	Mass (@ density of 1500 kg/m ³) would be 1.2 x 10 ⁸ kg
	Average Thickness 18.5 metres

Method 1.

The average discharge based on past measurements gives $Q = 296 \text{ L/min}$.

Loss of calcium over the surface of the mound averages 90 mg/L.

Converted to calcium carbonate: $90 \text{ mg/L} \times 2.497 = 224 \text{ mg/L}$.

Extrapolated deposition: $224 \text{ mg/L} \times 296 \text{ L/min} = 66300 \text{ mg/min}$ or 34900

kg/year. Since discharge and temperature decrease away from the vent in winter a 50 % reduction in precipitation will be allotted for these months decreasing the annual rate to 17450 kg/year.

An age estimate for the north mound, based on the above data, would be 7000 ± 800 years.

Appendix 6. Cont.

Method 2.

The north mound has an average precipitation rate during the summer of 24 g/m²/day (based on precipitation onto glass slides).

Converted to cm/year, the average rate of build up for the north mound is:

$$24 \text{ g/m}^2/\text{day} * \text{m}^2/10000 \text{ cm}^2 * 365 \text{ day/year} * \text{cm}^3/1.5 \text{ g} = 0.58 \text{ cm/year}$$

Over the entire year this rate should decrease by 50% to 2.7 mm/year.

At an average thickness of 18.5 metres it took $18.5 \text{ m} / 0.0027 \text{ m/year} = 6850 \pm 300$ years to build up to this point.

Assumptions:

1. Density of all precipitated travertine average 1500 kg/m³ (this number is based on an average of measured samples).
2. Average estimated *year-long* precipitation value is 50 percent of precipitation rates measured during the summer.
3. Constant average discharge from the vents over the lifetime of the mound.
4. Constant chemistries and a constant loss of calcium over the mound in all directions.
5. Method 1 allows for an estimated error in dimensions and density of 10 percent. Method 2 allows for an estimated error in thickness and precipitation rates of 5 percent.

CALCULATIONS OF THE RATE OF BUILD UP:

North Mound

The north mound has an average precipitation rate during the summer of 24 g/m²/day.

$$24 \text{ g/m}^2/\text{day} * \text{m}^2/10000 \text{ cm}^2 * 365 \text{ day/year} * \text{cm}^3/1.5 \text{ g} = 0.58 \text{ cm/year}$$

From assumption 2, over the entire year this value should decrease by 50 percent to a rate of 2.7 mm/year.

Over an estimated 1230 m² (the area covered by water as it flows over the mound surface) this average rate of precipitation would result in roughly 5400 kg of travertine per year being deposited on top of the mound. This estimate does not include the substantial deposition going on along the river bank below the falls. To include this would more than double the estimate.

South Mound

Vent 002 of the south mound has an average precipitation rate during the summer of 9.4 g/m²/day.

$$9.4 \text{ g/m}^2/\text{day} * \text{m}^2/10000 \text{ cm}^2 * 365 \text{ day/year} * \text{cm}^3/1.5 \text{ g} = 0.21 \text{ cm/year}$$

From assumption 2, over the entire year this value should decrease by 50 percent to a rate of 1.0 mm/year.

Over an estimated 440 m² (the area covered by water as it flows over the mound surface) this average rate of precipitation would result in roughly 750 kg of travertine per year being deposited due to this vent.

Vent 003 of the south mound is building up at roughly 1.35 g/m²/day.

$$1.35 \text{ g/m}^2/\text{day} * \text{m}^2/10000 \text{ cm}^2 * 365 \text{ day/year} * \text{cm}^3/1.5 \text{ g} = 0.03 \text{ cm/year}$$

From assumption 2, over the entire year this value should decrease by 50 percent to a rate of 0.2 mm/year.

Over an estimated 50 m² this average rate of precipitation would result in roughly 12 kg of travertine per year being deposited due to this vent.

Note: Precipitation rates used for the above calculations were based upon average rates measured over the entire flow paths.

Appendix 7 Travertine Structures

Travertine and tufa refer to calcareous deposits of lakes, rivers and springs. The precipitation of calcium carbonate is due to inorganic processes such as turbulence, temperature, evaporation and organic processes such as the regulating of carbon dioxide by photosynthesis, evapotranspiration, and the availability of substrate. The texture and shape of the deposit is governed by the morphology at the point of precipitation. Calcareous tufa, the name for the highly porous, spongy textural variety, results from significant interaction with vegetation, particularly algae and mosses. Travertine also occurs in compact laminated or concretionary forms, generally when physical and chemical conditions predominate. The following section will describe the various structures and textures found within Rabbitkettle's travertine/tufa deposits.

Rimstone Dams and Pools

These structures form the unique terracing found at Rabbitkettle, and have developed extensively over the surfaces of both mounds; ranging from a few centimetres to more than 4 metres in depth. The development of rims are brought about by an interruption of the flow due to surface irregularities, projections or organic litter which cause excess diffusion of carbon dioxide from the water, excess travertine precipitation and the eventual development of rims. The rims themselves then act to increase the surface area of the water, allowing for greater carbon dioxide diffusion. The process becomes self-perpetuating and dams are formed which pool the water behind them (Plate III).

At first glance, rare asymmetric structures found on the river undercut section of the north mound, appear to be folds. However, they are not folds but are rather cross-sections of rimstone dam structures, which have been exposed by the river undercut (Plate VII).

Riffles

Innumerable miniature basins or riffles are superimposed onto all slopes and along all the faces of the larger rimstone-dam structures, forming an intricate, delicate latticework (Plate IV). The method of deposition of these tiny rim and pool structures is similar to the larger terrace structures. Flowing waters--down gradient--result in varying rates of diffusion of carbon dioxide. On gentle slopes, the little basins are larger and the dividing walls are thin because the rate of carbon dioxide diffusion is slow. On steep slopes, such as down the sides of the larger rim structures, the ridges are thick and close together, due to rapid rates of carbon dioxide diffusion. Historically, it was believed that these structures were the result of colonization by algae (cyanophyceae) (Julia, 1983). However, numerous recent studies, including this one, indicate that although algae may have a minor influence, it is insignificant in comparison to physical and chemical changes which result in the loss of carbon dioxide.

Tuffaceous Texture

This is a highly-porous texture which results from travertine precipitation encrusting vegetation such as algae, mosses, leaves and other plant debris. The porosity emerges after the plant material decays, leaving voids in the travertine.

Lamination or Layering

Two main types of layering can be distinguished within the travertine. There is vertical, subvertical and overhanging laminae associated with the travertine dams and horizontal or subhorizontal laminae associated with flow channels and gentle slopes. Lamination manifests itself by colour changes and textural changes, which are related to porosity. Many authors believe this layering to be seasonal. Cooler waters during the winter have increased solubility of carbon dioxide producing dense bands of precipitate. These bands may also originate, in part, by the winter die off of algae, where it is a factor, resulting in denser winter laminae and porous summer laminae.

Flowstone Drapery

These structures are found along the edges of some of the deeper rimstone structures (Plate V). They are similar to but not entirely like stalactitic-flowstone structures seen in karstic caves, the difference being that these structures are attached to terrace walls along their entire length, and are not formed along central channels. Cross-sections of these structures reveal horizontal layering. They are formed from the overflow of calcium carbonate-rich waters dripping along terrace faces.

Pisolites

Pisolites are small spheroidal accretionary structures formed within circulating waters. Two types of pisolite structures occur at Rabbitkettle. The larger of the two types have an average size of 1.5-to-2 centimetres and are found only within the pools at the base of the falls. They have smooth surfaces and

concentrically laminated internal structures, which indicate movement and abrasion as a result of rapidly falling water into shallow, turbulent pools. No nuclei were visible within the pisolites which were split open. The smaller pisolites are all less than 1-centimetre in diameter and consist of crystalline calcium carbonate throughout (Plate VI). These structures occur only within shallow travertine pools and riffles. They have originated from water circulation that is only strong enough to cause position shifts during calcium carbonate precipitation. The resultant structures have granular rather than smooth surfaces, and lack internal lamination as they have formed in a slower less-active environment.

Miniature Stalactitic Structures

These structures were only noticed within freshly fallen travertine blocks of the north mound and the fresh exposure of the break on the mound (Plate VIII). This may be due to the fact that these structures are delicate and do not last long after exposure. The structures appear to have occupied voids within the travertine along the breakage area, and may be the result of dissolution and reprecipitation of travertine from water circulating through stress fractures which originated from the undercutting of the mound by the river.

Appendix 8 Origin of Carbon Dioxide - Model

Dissolved inorganic carbon (DIC) in the water comes from carbon dioxide and the dissolution of carbonate. Concentrations of the carbonate species in solution (H_2CO_3 , HCO_3^- and CO_3^{2-}) can be calculated from the following equations:

$$K_1 = [\text{H}_2\text{CO}_3]/p\text{CO}_2 \quad (1).$$

$$K_2 = [\text{HCO}_3^-][\text{H}^+]/[\text{H}_2\text{CO}_3] \quad (2).$$

$$K_3 = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-] \quad (3).$$

where K are respective temperature-dependent equilibrium constants.

The ^{13}C enrichment factors between $\text{CO}_{2(g)}$ and each aqueous carbon species are temperature dependent and are represented by the following empirical equations:

$$\epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2} = (9.483 \times 10^3/T) - 23.89 \quad (4).$$

(Mook *et al.*, 1974)

$$\epsilon_{\text{HCO}_3-\text{CO}_2} = (-0.373 \times 10^3/T) + 0.19 \quad (5).$$

(Mook *et al.*, 1974)

$$\epsilon_{\text{CO}_3-\text{CO}_2} = (0.87 \times 10^6/T^2) - 3.4 \quad (6).$$

(Deines *et al.*, 1974)

where T is in °K. The aqueous phase CO_3^{2-} is considered to be essentially absent due to the low pHs of this study and is therefore not represented in subsequent equations.

The following equation represents the isotopic equilibrium conditions for any solution of given molalities of dissolved inorganic carbon:

$$\delta^{13}\text{C}^*m_{\text{DIC}} = [m_{\text{H}_2\text{CO}_3}^* (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3}^* (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{HCO}_3-\text{CO}_2})] \quad (7).$$

Where: m = molality, ϵ = enrichment = $1000 \ln \alpha$, (α = fractionation factor).

It shows that the per milie difference between $\text{CO}_{2(g)}$ and DIC is related to the $\delta^{13}\text{C}$ of the gas under equilibrium conditions.

Plant-life in a recharge zone such as the one in this study area will range from lichen on the rocks to spruce trees. Plant respiration and the decomposition of organics will contribute soil-derived CO_2 with carbon-13 compositions in the range of -15 to -23 ‰ and gas concentrations in the range of 10^{-1} to $10^{-3.0}$ atmospheres (Freeze and Cherry, 1979). The associated $\delta^{13}\text{C}_{\text{DIC}}$ at calcium carbonate saturation would fall between -5 to -13 ‰, assuming predominantly open-system conditions and an enrichment $\epsilon_{\text{CO}_2\text{-HCO}_3}$ of approximately 10 ‰. Carbonate is assumed to be dissolved predominantly under open-system conditions.

Similar values were observed from carbonate springs in the Nahanni region which are believed to have no additional CO_2 inputs above and beyond soil- CO_2 . The $\delta^{13}\text{C}_{\text{CO}_2}$ for these springs range between -16 and -18 ‰; the final $\delta^{13}\text{C}_{\text{DIC}}$ values are in the range of -7 to -10 ‰ (Hamilton, 1990; Hamilton *et al.*, 1991). Soil- pCO_2 values range from $10^{-1.5}$ to $10^{-2.5}$ atmospheres.

Metamorphic CO_2 due to the decarbonation of limestone by intrusives, can mix with the CO_2 saturated groundwater causing a decrease in the pH and enabling more carbonate to be dissolved, thus adding to the DIC pool in the range of the original rocks. Close to 99-perc nt of the CO_2 discharging from the Flat River springs is from the decarbonation of carbonates. Therefore the ^{13}C composition of the spring data in the Flat River area is representative of the isotopic value of the local metamorphic CO_2 source. The $\delta^{13}\text{C}_{\text{DIC}}$ contribution based on the high- pCO_2 springs in the Flat River should have final values between

-0.5 and +2.5 ‰ and final $\delta^{13}\text{C}_{\text{CO}_2}$ between -4.9 and +0.7 ‰ (Hamilton, 1990; Hamilton *et al.*, 1991). All theoretical and regional values are summarized in Table 2.

In establishing a usable model it must be taken into consideration that the final concentrations of carbon dioxide and $\delta^{13}\text{C}$ values for Rabbitkettle spring waters will fall between the local soil-input and the metamorphic estimates. From solubility calculations based on an estimated temperature of recharge of 7°C (average groundwater temperature, Hamilton, 1990), it was determined that for soil- pCO_2 in the range of $10^{-1.5}$ to $10^{-2.5}$ atmospheres, bicarbonate concentrations at calcium carbonate saturation will fall between 134 and 298 mg/L.

Equation 7 is the basis for this model as it takes into account both total dissolved inorganic concentrations and relevant $\delta^{13}\text{C}$ values. Equation 7 has been modified to show the relationship between each contributing carbon dioxide source:

$$\delta^{13}\text{C}_{\text{DIC}(f)} * m_{\text{DIC}(f)} = [m_{\text{H}_2\text{CO}_3(s)} * (\delta^{13}\text{C}_{\text{CO}_2(s)} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3(s)} * (\delta^{13}\text{C}_{\text{CO}_2(s)} + \epsilon_{\text{HCO}_3-\text{CO}_2})] + [m_{\text{H}_2\text{CO}_3(m)} * (\delta^{13}\text{C}_{\text{CO}_2(m)} + \epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2})] + [m_{\text{HCO}_3(m)} * (\delta^{13}\text{C}_{\text{CO}_2(m)} + \epsilon_{\text{HCO}_3-\text{CO}_2})] \quad (8).$$

which can be simplified to:

$$\delta^{13}\text{C}_{\text{DIC}(f)} * m_{\text{DIC}(f)} = [m_{\text{DIC}(s)} * \delta^{13}\text{C}_{\text{DIC}(s)}] + [m_{\text{DIC}(m)} * \delta^{13}\text{C}_{\text{DIC}(m)}] \quad (9).$$

(Where: f, final; s, soil; m, metamorphic).

Numerous iterations were performed to determine the values which will satisfy equations 8 and 9 within the constraints of the local data presented in Table 2 and the relevant water temperatures. The following table lists the relevant values that satisfy the equations, in this case an average soil- pCO_2 of $10^{-1.9}$ atmospheres was used (bicarbonate at calcium carbonate saturation with this soil- pCO_2 is equal

to 3.5×10^{-3} mol/L). Final proportions have an estimated variability of ± 4 percent based upon the use of average final $\delta^{13}\text{C}_{\text{DIC}}$ values and final pCO_2 values.

1991 Data

	m_{DIC} (mol/L)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰ PDB)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ PDB)	Proportion
Final	2.0×10^{-2}	-7	-1.9	100 %
Soil	4.3×10^{-3}	-17	-10	20 %
Metamorphic	1.6×10^{-2}	-4	1	80 %

1992 Data

	m_{DIC} (mol/L)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰ PDB)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ PDB)	Proportion
Final	2.7×10^{-2}	-6.5	-1.9	100 %
Soil	4.3×10^{-3}	-17	-10	16 %
Metamorphic	2.3×10^{-2}	-4.9	+0.1	84 %

Maximum using 1991 Data

	m_{DIC} (mol/L)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰ PDB)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ PDB)	Proportion
Final	2.0×10^{-2}	-7	-1.9	100 %
Soil	3.8×10^{-3}	-17	-10	18 %
Metamorphic	1.7×10^{-2}	-5.0	-.05	82 %

Minimum using 1991 Data

	m_{DIC} (mol/L)	$\delta^{13}C_{CO_2}$ (‰ PDB)	$\delta^{13}C_{DIC}$ (‰ PDB)	Proportion
Final	2.0×10^{-2}	-7	-1.9	100 %
Soil	6.8×10^{-3}	-17	-10	30 %
Metamorphic	1.4×10^{-2}	-2.7	2.1	70 %

Appendix 9 Monitoring Program

This monitoring program has been designed so that the majority of the data collection can be performed by Park Staff. Surveying should be performed by someone with previous experience (staff or other), and the final data analysis and interpretation will be performed by a geological consultant. If available, all data collected can be stored in a computer data base for future reference. All observed points (platelet location and new seeps) which are to be plotted on the surface maps can be transferred to a GIS system when this system becomes available.

The most important aspects of Rabbitkettle to be monitored over the long term are:

1. Geochemistry (alkalinity, temperature, pH, conductivity, Eh, major ion chemistry) at all 4 spring vents. Geochemistry sampling and measurements are to be done at the beginning and end of each summer (If possible do chemistry for the 4 spring vents in the winter as well).
 - Changes in chemistry and discharge of the springs provide insight into the amount of travertine being deposited (rebuilding potential) and any changes that may be occurring within the internal hydraulics of the system.
2. Discharge will be measured at each spring in terms of its rate and cross-sectional area of flow. All discharge measurements are to be done at the beginning and end of each summer.
 - Monitoring discharge can provide insight into hydraulic changes.
3. Sedimentation and degradation rates will be monitored. Brass platelets (about the size of a loonie) have been placed along the path and discharge zone (July, 1992) of the north mound. Each platelet is coded and located on Figure 19. At the end of 5 years they will be relocated with the help of a metal finder and the surface map. Rates of accumulation and/or degradation within the discharge area can be assessed at this time. At the beginning and end of each summer the discharge area should be scouted for the appearance of the platelets. The exposed platelets should be located on a dated copy of Figure 19a.
 - If the platelets are exposed, then either accumulation is too slow or degradation is too rapid.
4. Photograph around the north mound at 360° (as specified in instruction section).
 - This provides a means for year to year comparison of surficial degradation to the structures of this mound.

5. Photograph spring vents, showing discharge channels. Photographs will be taken from fixed bench marks (metal platelets) which are identified on Figure 19.
 - Fixed photographs provide a basis of reference to visually assess changes in discharge and can be used in combination with calculated discharge volumes to assess any changing patterns of flow.
6. Photograph each mound from the air.
 - To observe changes in flow directions and forms of degradation over time.
7. Aerial photographs of river meander.
 - To follow any year to year changes in the river migration or water levels that may have long-term consequences for the north mound.
8. Photograph all trails leading to vents at beginning and at the end of summer.
9. Survey of mound elevations to be carried out at the end of 5 years.
 - Location of platelets and a survey of the mound elevations will provide information about modern accumulation rates.

Note: All photographs can be taken once during the summer except where otherwise specified (winter aerial photographs are desirable when possible). Document for all photographs, the date they were taken, time of day and all other significant details such as spring number, bench mark and direction of photograph.

Recommendations

- Maintain restricted access and guided tour policy.
- Retain use of the *existing* trails, as the scars are permanent; the *existing* trails localize damage and minimize long-term degradation.
- Walk strictly single file along the trails to prevent widening of the trails.
- Provide access only to vent 003 and 001, but prevent wandering away from the vents; access to vent 002 and patterned ground areas should be restricted due to the extreme fragile nature of this portion of the south mound (frost polygons can be pointed out to tourists along the trail immediately adjacent to this section of the mound).
- Maintain trails up the north mound in areas with the greatest discharge.
- Maintain barefoot policy and walking up wet side of the north mound.
- Edges of all vents should be approached with caution or completely avoided due to the significant overhang of these features.
- Do *not* step in or on the edges of the iron-rich channels as they are extremely fragile.

- Do *not* step in the iron-rich deposits (reddish-brown areas) while walking up the wet area of the north mound; these deposits tend to be unconsolidated.
- Monitor degradation of the north mound by having wardens watch for signs of metal platelets and/or the appearance of wear along the chosen wet path (wear, refers to the ability to see the development of a trail which visibly stands out from the surrounding area; it may appear as broken non-consolidated travertine and a visual discolouration of the area in question). Traffic is too heavy if the platelets become re-exposed. If this should happen, immediately restrict access to the north mound until such signs disappear. Record the date and location of the exposed platelet(s) on a copy of figure 19a. At the current rates of visitation, such damage by tourist traffic is not likely to become a problem. Problems may result, however, if visitation should double over the next few years.
- For the purpose of "healing" it is possible at times of heavy traffic to syphon water from the spring vents (using a small diameter plastic tube) and allow it to trickle over damaged portions of the mound. This will rebuild deterioration by allowing fresh travertine to precipitate. (Note: As this is a non-passive recommendation it may not fall within park policy for non-interference; then the solution would be to restrict access).
- Keep records (date and location) of the appearance of new seeps that may be noticed in passing. All current seeps are documented in the main thesis.
- Place wooden stakes at the high-water mark along the edge of the Rabbitkettle River below the north mound. By the end of 5 years there should be five dated stakes, which may or may not indicate a trend in water-level fluctuations.

Equipment

- thermometer
- pH meter and calibration fluid
- conductivity meter
- Nalgene bottles (50 ml , 250 ml)
- water filter holders and syringes, filter paper (45 μ m pore size)
- flow testing kit (toothpicks, stop watch, plastic ruler, measuring tape)
- metal platelets
- alkalinity titration kit (Hack Kit)
- camera 50 mm and 28 mm lenses

- 4 to 5 rolls of *print* film (100 to 200 a.s.a.) per year
- compass
- rental of small metal detector (end of 5 years)
- rental of surveying equipment (end of 5 years)
- A diary which will contain all field measurements, photograph identifications, sample numbers, dates and any other relevant observations.
- Masking tape, electrical tape, waterproof markers

Implementation Schedule

- Summer 1993
 - Park begins outlined monitoring exercises.
 - Park may wish to survey in, additional erosion/sedimentation meters.
- Summer 1993 to Summer 1998
 - Park manages outlined monitoring exercises.
- Summer 1998
 - Ground survey for vent elevations and water levels (and elevations to any additional erosion/sedimentation meters installed).
 - Locate and determine depths to original metal markers for determination of traffic erosion rates and sedimentation rates.
 - Complete evaluation of all collected photographs and data.

Expense Schedule

Start up Costs:

- Field chemical equipment and other items not already owned by the Park.

Yearly Expenses:

- Chemical analyses of all samples; (8 sets of samples in the summer; a possible 4 sets in winter).
- Film and processing
- Flight time for aerial photographs

Five Year Expenses

- Rental of small metal detector and survey equipment.
- Hiring of a consultant to interpret accumulated data.

Instructions

A. How to sample for chemistry.

The following procedure is to be carried out at **each** of the **4** springs at the beginning and end of each summer.

1. Label two of the 250 ml sample bottles and one 60 ml sample bottle. If the bottles do not have labels wrap them with masking tape and write labels with a waterproof marker. In the diary, record each sample number (RKHS-dy/mth/yr-(00#)), the date, spring number (# 1 to 4) and the days weather.
2. Rinse syringe once with distilled water and 2 more times with the spring water about to be sampled. Make sure you pour the rinse water well away from the vent.
3. Draw water into the syringe from the spring vent, *then* attach the filter attachment to the syringe (do *not* forget to place the filter paper inside the filter attachment).
4. Slowly discharge the water from the syringe through the filter into a 250 ml Nalgene sample bottle. Remove the filter attachment and repeat steps 3 and 4 until the two labelled 250 ml sample bottles are filled. (The same filter paper can be used for an entire set of samples at an individual spring).
5. To the second 250 ml bottle, add 10 ml of dilute HCl or HNO₃ (this procedure can be performed at the site or immediately upon returning to camp at the end of the day). Make sure that the acidified bottle is labelled as such.
6. Fill the labelled 60 ml Nalgene bottle directly from the spring (no filtering required). Leave no air gaps in the bottle before putting on the cap (sampling for isotopes).
7. Close caps to all bottles tightly and wrap with electrical tape (or other) to ensure caps will not loosen in transport.
8. Measure and record temperature, conductivity, Eh, pH and alkalinity for the spring (see enclosed instructions for measuring alkalinity with the Hack Kit or Hardness Test).
9. Repeat above procedure for all four springs at their vents. In all four, sets will be collected *twice* during the summer; each set includes two 250 ml bottles, one acidified and one not, and one 60 ml isotope sample.
10. Send the 250 ml bottles for determination of major and trace ion analysis. Send the 60 ml bottles to be analyzed for oxygen-18 and deuterium isotope content and have the isotope sample for spring 001 also analyzed for tritium.

B. How to measure and calculate discharge.

The following procedure is to be carried out at **each** of the 4 springs at the beginning and end of each summer.

1. Identify each channel that exits from the main spring vent (this may vary over the years). If more than one channel exists at a vent, discharge must be calculated for each. The results are then tallied to determine the total discharge for the spring vent.
2. For **each** of the individual channels: Lay a measuring tape along the longest and straightest portion of the channel. Make sure there are no distributary channels located above the measured channel segment as it is important that the final results incorporate all of the flow. At 5- or 10-centimetre intervals along this segment of channel, calculate the cross-sectional area. This is done by assuming the channel is rectangular (a fair assumption for these channels) and by measuring (with a ruler) the width of the channel at each point and the depth of the channel at each point. The depth is measured from the bottom centre of the channel to the water surface. Record the numbers on a copy of the discharge chart (page 179). Averages of these numbers will enable the calculation of the average cross-sectional area of the channel. (Formula: $A = \Sigma \text{average width}_i \times \text{average depth}_i / n$)
3. Record the length of the channel segment used. Calculate the velocity (centimetres/second) or the time it takes for a small object to be carried by the stream over the measured segment of channel. This is done by using a stop watch and any tiny object that floats (i.e. tiny stick or toothpick fragment). Measure the velocity 5 or more times (or until you have 5 or 6 reasonably consistent trials where the object has floated freely along the length of the channel without "hangups"). Record all numbers on a copy of the discharge chart (page 179). (Formula: $\text{Velocity} = \Sigma \text{distance}/\text{time}_i / n$).
4. Discharge(Q) for each individual channel can be calculated from the average estimated cross-sectional area of the channel multiplied by the average velocity from all the trial runs (Formula $Q = vA$). For each spring vent, total discharge Q_T , is the sum of measured discharge from each individual channel. This may only apply to spring 001 which can have three or more measurable channels. The other springs generally have one.

Note: To ensure consistency make all the above distance measurements in centimetres and all time measurements in seconds. As no actual channel exits vent 004 the above

technique may not be useful, therefore, this spring vent should be photographed at close range using a scale reference.

5. All of the discharge areas (wet areas) for each spring should be measured (in metres) using a measuring tape and compass; measuring the lengths and direction from the vent to the farthest extent of flow; make all compass directions with respect to known reference points. Provide description of measurements and directions with respect to a rough sketch.

C. Required photographs.

Airborne photographs:

1. Aerial photographs of the North Mound and discharge zone (at an elevation below 500 metres--- depending on the angle of the lens used; just be sure to incorporate the entire mound in the photograph)
2. Aerial photographs of the North Mound and river undercut bank at elevations below 500 metres.
3. Aerial photographs of both vents and discharge zones on the South Mounds (at an elevation below 500 metres).
4. Aerial photograph of the entire site (at an elevation greater than 500 metres).
5. Aerial photograph from the north of the site which includes the River meander and the North Mound (at an elevation greater than 500 metres).

Note: While in the air, finish the roll of film with additional photographs from various other vantage points.

Surface photographs:

1. Photograph the entire north mound by walking 360° counterclockwise around it. Take the first photograph at the site where tourists remove their shoes, and overlap each photograph with the previous. The distance will vary around the mound unavoidably, but try to incorporate as much of the mound as possible while still getting coverage and detail. This generally works best by standing on the path and photographing, moving along frame by frame. Make sure you place an object or person in every picture to use as a reference scale.
2. Photograph each vent close-up (showing the entire vent perimeter).
3. Photograph discharge areas for each vent from designated reference points (reference points are located on Figures 19a and 19b, where brass platelets have been placed)

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

Photograph vent 003 from reference point A, in a direction 206° from north.

Photographs may be taken of the discharge area from reference point D from the vantage point of the tree (tree has been trimmed), incorporating as much of the discharge area as possible (may need to overlap photos). Photograph discharge area of vent 002 from reference point B, in directions 030°, 070° and 110° from north.

Photographs may be taken of the discharge area from reference point E from the vantage point of the tree (tree has been trimmed) incorporating as much of the discharge area as possible (may need to overlap photos). Photograph vent 001 from reference point C, in directions 200°, 300° and 005° from north with a wide angle lens (28 mm). Also take photographs from reference point F at 216° and 260°.

4. Photograph the "trail" leading to the top of the north mound; choose a vantage point at the bottom of the mound looking up. Do this at the beginning and end of the summer. Photograph the last section of the trail leading to vent 003 (reference point D, in the bushes). Photograph the trail only, in a northeast direction. Do this at the beginning and end of the summer.

Note(s):

All photographs are to be taken with a 28 mm lens in designated directions; these directions are to be located with a compass which has been set for the proper declination.

If the discharge zones have widened, take additional photographs which include these areas, making sure to document the directions of each.

Spring 004 has no designated reference point; it can be photographed from the base of the ridge close to the river.

For all the surface photographs place a small recognizable object or person in the picture for a reference scale.

Keep a record in the diary of each photograph taken; include the date, roll# (keep a running record of each roll taken during a summer) and the picture number; also include a brief description of the photograph taken, such as direction from a noted reference point (i.e. roll#1, pic24, refA/265°).

Discharge Chart

Date		Spring number		
Channel number	Velocity Test	Distance (cm)	Time (seconds)	Velocity (distance/time)
	trial 1			
	trial 2			
	trial 3			
	trial 4			
	trial 5			
Average velocity (v)				
Measure channel width and depth at intervals (i.e. 5-10 cm intervals)				
Interval	interval width		interval depth	
1				
2				
3				
4				
5				
Average width of channel				
Average depth of channel				
Average channel cross-sectional area $A=wd$				
Total discharge for the channel, $Q = Av$				

Note: Total discharge for a spring is the sum of all the individual channel discharges ($Q_T = Q_1 + Q_2 + \dots + Q_n$)

LIST OF PHOTOGRAPHIC PLATES

- Plate I.** Rabittkettle Hotspring Mounds and mountain spur alignment.
- Plate II.** Rabbitkettle Hotsprings Mounds and the Rabbitkettle River.
- Plate III.** Travertine-precipitated pools and rimstone dam structures.
- Plate IV.** Riffle structures
- Plate V.** Flowstone drapery.
- Plate VI.** Pisolite structures within shallow travertine riffles.
- Plate VII.** Cross-section of rimstone dam structures.
- Plate VIII.** Miniature stalactitic structures.
- Plate IX.** Iron-rich channels carved on the surface of the north mound.
- Plate X.** Travertine buildup around the base of a former tree.
- Plate XI.** Exfoliation of travertine rims along the face of the north mound.
- Plate XII.** Frost polygons on the surface of the south mound.
- Plate XIII.** Undercut and waterfalls of the north mound.
- Plate XIV.** Circular debris piles or stone nets of periglacial areas.
- Plate XV.** Close-up of spring vent 001.
- Plate XVI.** Close-up spring vent 002
- Plate XVII.** Close-up of spring vent 003
- Plate XVIII.** Discharge area of spring 004.
- Plate XIX.** Wet rimstone pool structures on top of the north mound in 1976.
- Plate XX.** Frost damaged rimstone pool structures of the north mound in 1991.

Plate I. Aerial photograph of Rabbitkettle Hotsprings showing the alignment with the mountain spur in the background.

Plate II. Aerial photograph of Rabbitkettle Hotsprings showing the north and south mounds. The Rabbitkettle River is towards the north.

Plate III. Rimstone dam and pool structures on the northwest side of the north mound.

Plate IV. Innumerable miniature basins or riffles are superimposed onto all slopes and along all the faces of the larger rimstone-dam structures.

Plate V. Flowstone drapery found along the edges of some of the deeper rimstone structures.

Plate VI. Pisolite structures within shallow travertine riffles.

Plate VII. Cross-section of rimstone dam structures. Tuffaceous textures seen on the left side of the photograph are characteristic of the inner-pool-basin deposits. Laminated textures seen on the right side of the photograph compose the rimstone dams.

Plate VIII. Freshly exposed miniature stalactitic structures seen along the northern face of the north mound where the Rabbitkettle River once undercut.

Plate IX. Iron-rich channels carved on the surface of the north mound.

Plate X. Travertine buildup around the base of a small tree that has long since died.

Plate XI. Exfoliation of travertine rims along the face of the north mound.

Plate XII. Frost polygons on the surface of the south mound (camera lens cap for scale).

Plate XIII. The Rabbitkettle River once undermined the north mound. Now the spring waters form a waterfall as they flow off of the surface of the mound. The waterfall creates rapid degassing of carbon dioxide and extensive travertine deposition below.

Plate XIV. Circular debris piles or stone nets common to periglacial affected areas referred to in Figure 14. These are photographed from Area A (Figure 14).

Plate XV. The spring vent on top of the north mound (001) is 15.85 metres at its deepest point and is roughly 6 to 7 metres in diameter. The photograph was taken facing west with the Rabbitkettle River Valley in the background.

Plate XVI. Spring vent 002 is located on the south mound and has a maximum depth of 1.85 metres and averages 2.5 by 3.1 metres in diameter. The photograph was taken facing east, in the direction of discharge. A time-lapse camera can be seen in a tree in the background.

Plate XVII. Spring vent 003 is referred to by Park Warden's as the Japanese Gardens. It is the oldest of the vents on the south mound. It is a maximum of 1.3 metres deep and approximately 7.2 metres long by an average of 1.3 metres in width. Carbon dioxide bubbles can be seen rising to the surface of the vent. The photograph was taken facing south-southwest in the direction of discharge.

Plate XVIII. Discharge from spring 004 through a 5-centimetre diameter vent has precipitated travertine over an area of approximately 10 square metres, down the River bank.

Plate XIX. This photograph taken in 1976 shows wet terraces on top of the north mound. The photograph was taken facing west toward the Rabbitkettle River Valley (photograph courtesy of Parks Canada).

Plate XX. This photograph was taken in 1991 from the same location as Plate XIX. The once-wet pools are dry and showing signs of frost degradation.

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