OFFICE OF RESEARCH ADMINISTRATION UNIVERSITY OF WATERLOO INCORPORATING THE WATERLOO RESEARCH INSTITUTE

PROJECT NO. 707-10-03

ISOTOPE HYDROGEOLOGY

and

GEOTHERMOMETRY

of the

MOUNT MEAGER GEOTHERMAL AREA

FINAL REPORT

August 1980

Prepared for

Energy, Mines and Resources

Contract Serial Number OSB79-00098

Ian D. Clark Peter Fritz Frederick A. Michel

OPEN FILE DOSSIER PUBLIC GEOLOGICAL SURVEY COMMISSION CERTAIN AMATTO .

This document was produced by scanning the original publication.

Ce document est le produit d'une numérisation par balayage de la publication originale.

ABSTRACT

A substantial survey of stable and radioactive environmental isotopes has been carried out in order to investigate the recharge, thermal history, age and geothermometry of the thermal waters at Mount Meager, B.C., a Quaternary volcano currently the site of active exploration for geothermal resources. Isotope determinations include 18 O, 2 H and 3 H in precipitation, runoff waters, thermal and cold groundwaters and glacier ice, 13 C and 14 C in dissolved inorganic carbon and 18 O and 34 S in dissolved sulphate from thermal and cold groundwaters as well as 13 C and 18 O in hydrothermal calcite crystals. Major ion analyses were performed on thermal and cold spring waters.

Precipitation and cold spring data have been used to define the local meteoric waterline and to document the altitude effect on waters recharging the geothermal system, demonstrating there to be two hydrogeologically separate reservoirs which are recharged at different altitudes. Both pools of geothermal waters have experienced shifts of between +0.5 and +1.5 % in δ^{18} O values indicating a limited degree of 18 O exchange with hot silicate minerals.

Tritium contents indicate these waters to have recharged prior to 1955. Carbon-13 contents in dissolved inorganic carbon and in hydrothermal calcites from drill core demonstrate there to be contamination of the thermal waters with "dead" volcanogenic CO_2 plus carbon exchange with fracture calcite which precludes the possibility of dating the thermal waters using carbon-14.

- ii -

Several chemical and isotopic geothermometers are used to estimate the maximum temperatures experienced by the thermal waters. The fractionation of 18 O between 50 and ${}^{2-}$ and 4 O in these waters gives calculated maximum temperatures of less than 140° C. The dissolved sulphate is shown to comprise inputs from oxidized volcanogenic 4 S and 50 gases and from dissolution of marine sulphate in the metasedimentary basement rocks. The Mg-corrected Na-K-Ca geothermometer shows excellent correlation with the 50 G-H₂O estimates with maximum temperatures less than 120° C. Fractionation of 13 C and 18 O in the systems 62 Co₂ and 62 Gase of subsurface temperatures in excess of ${}^{140^{\circ}}$ C. Silica geothermometer results are not reliable due to equilibrium with amorphous silica phases in the subsurface. The thermal waters are shown to have mixed with up to 15% cold groundwaters with apparently no substantial effect on the geothermometer estimates.

It is concluded that these thermal waters are not deeply circulating and have not experienced temperatures in excess of 140°C.

Résume

Un relevé substantiel d'isotopes stables et radioactifs naturels a été fait pour étudier la recharge, l'histoire thermale, l'âge et la géothermometrie des eaux hydro thermales du Mont Meager, C.B., un volcan Quaternaire qui est maintenaut le lieu d'exploration de ressources geothermales. Les déterminations isotopeques comprenneut le ¹⁸0, ²H et ³H daus la précepetation, daus les eaut de ruissellement, daus les eaux sousterraines thermales et froides, ainsi que le ¹³C et 1^{, 18}0 de la calcite hydrothermales. L'analyse des ions majeurs a été farte sur des échautillions d'eau provenant de sources froides et thermales.

Les donnés obtenus de la précepetation et des eaux de sources ont été utilisés afin de définir la ligue métorique locale et de documenter l'effet d'altitude sur les eaux qui rechargeut le systeme géothermales, démontraut qu'il y a deux réservoirs géothermales géologiquement distincts qui sont à des altitudes différentes. Les deux réservoirs d'eaux géothermoles out subit des altérations allaut de 0.5 et 1.5%, δ^{18} 0 indiquant un degré lemité d'échauge de ¹⁸0 ovec les minéraux silicieux échauffes.

De basses teneurs en ³H indiquent que ces eaux ont rechargies avaut 1955. Les teneurs en ¹³C du carbone inorganique aqueux et des calcites hydrothermales provenaut des carottieres démontrent qu'il of a une contamination des eaux thermiques avec du CO₂ Volcanique "mort" ainsi qu'un échange avec la calcite secondaire des fissures. Ceci elimine la possebèlité de dater les eaux thermales utilisant le ¹⁴C.

Plusseurs géothermomètres chimiques et isotopéques sont utilisés pour estimer les températures maximales subit par les eaux thermoles. La fractionation du ¹⁸0 entre le SO_4^{2-} et le H₂0 dans ces eaux donne des valeurs maximales calculées mourdre que 140° C. Il ist démontré que le sulphate dessous comprend des sources de H₂S oxidé, de SO₂ gaseux et de la dissolution des sulphates marins provenaut de la noche de fond métasédimentaire. Le géothermometre Na-K-Ca corrigé avec le Mg montre d'excellent corrélations avec les estimés du géothermomètre SO₄-H₂O qui indiquent une température enférreur à 120°C. La fractionation du ¹³C et du ¹⁸O dans le systeme CO₂ - CaCO₃ et H₂O -CaCO₃ utilisant de la calcite hydrothermale et des eaux provenant des forages offrent aucune indication des températures au-dela de 140°C. Les resultats du géothermomètre SiO₂ ne sont pas fiables à cause de l'équilibre chimique avec les phases de silice amorphe dans le sousterrain. Il est demontré que les eaux thermiques sont melanges avec jusqu 'a 15% d'eau froide ce qui apparamment, a aucun effet substantiel sur les estimations geothermometriques.

Il est conclu que ces laux thermiques ne circulent pas pro-.fondément et n'ont pas subit des températures au-de la de 140°C.

- v -

ACKNOWLEDGEMENTS

I would like to express my deep appreciation to Dr. Peter Fritz for his guidance and support throughout the course of this study and for his critical review of the manuscript. I also acknowledge the support of Dr. Jeff Turner, Dr. Jim Barker and Dr. John Greenhouse for their review of this manuscript and for their participation on the thesis examination committee.

I wish to thank Mr. Frederick Michel for his preliminary involvement at Mount Meager and for his assistance in the initial sampling and throughout the course of this study. I gratefully acknowledge Dr. Jack Souther of the Geological Survey of Canada as the Scientific Authority responsible for the funding of this study under Energy, Mines and Resources contract number OSB79-00098 and thank him for his valuable assistance as a liason in Vancouver.

Furthermore, I would like to extend my thanks to Mr. Bob Drimmie for his technical assistance and advice in the Isotope Laboratory; to his assistance, Jeanne Berry, Stan Gruszka, Richard Kular and Diana Simpson for the isotope analyses; to Heidi Flatt, Rob Lathe and Ron Kellerman for the chemical analyses and to Dr. Jim Barker for the gas analyses.

A special word of thanks goes to my wife, Diane, for her undaunted assistance during the August field work and to Liz Neil (Reid,Crowther Ltd.) and Brian Fairbank (Nevin, Sadlier-Brown,

- vi -

Goodbrand Ltd.) for their help in sampling precipitation and drill core in my absence. A further word of thanks goes to Brian for maintaining open lines of communication during the concurrent drilling program at Mount Meager and to Mr. Joseph Stauder and B.C. Hydro for our accomodation during the field work.

Finally, I would like to recognize the efforts of my fellow students Stan Feenstra, who afforded me great assistance in the isotope analysis of sulphates and Don Desaulniers, who provided a translation of the abstract.

TABLE OF CONTENTS

					-							Page
ABSTRACT · · · ·	•. •	•••	•	•	• •	•	•	•	•	•	•	11
ACKNOWLEDGEMENTS	• •	• •	•	•	• •	•	•	•	•	•	•	vi
TABLE OF CONTENTS	• •		•	•	• •		•	•	•	•	•	viii
LIST OF FIGURES	• •	•••	•	•	• •	•	•	•	•	•	•	• X
LIST OF TABLES	• •	• •	•	•	• •	•	•	•	•	•	•	xii
INTRODUCTION	• •	• •	•	•	• •	•	•	•	•	•	•	1
PHYSICAL SETTING	• •	• •	٠	•	• •	•	٠	•	٠	•	•	6
SAMPLING AND ANALYSIS	• •	• •	•	•	• •	•	•	•	•	•	•	16
ISOTOPE HYDROGEOLOGY AN	DGEO	OTHEI	RMOM	ETR	Y IN	GEOT	HER	MAL	AR	EAS	•	19
Isotope Hydro	geol	097										19
Geothermometr	у.		•	•	• •	•	•	•	•	•		20
RESULTS AND DISCUSSION	• •		•	•	•••	•	•	•	•	•	•	23
Isotope Hydro	geol	027 (of M	oun	t Mea	lger		•	•	• .	•	23
Meteoric	Wat	ers			• •	•	•	•	•	•	•	~ 24
Cold Spr	ings	٠	•	•	• •	٠	•	•	•	•	•	26
Thermal	Wate	rs •	•	•	• •	•	•	•	•	•	٠	28
. Age of Ground	wate	rs •	•	•	• •	٠	•	•	•	•	٠	37
Tritium	• •	• •		•	• •	•	•	•	•	•	•	37
Carbon-1	.4 and	d Car	rbon	-13	• •	٠	•	•	٠	٠	٠	40
Carbon-13 in	Aque	ous (Carb	ona	te •	٠	•	•	•	•	٠	45
Sulphur-34 in	Aqu	eous	Sul	pha	te •	•	•	•	•	•	•	55
Mixing of The	rmal	and	COT	d G	round	iwate	TS	•	•	•	•	. 20
Geothermometr	y (• •	•	•	• •	٠	•	•	•	•	•	62
The Sul-	bata	Geoti	nerm	Come	ter •	•	*	•	•	•	•	66
The Wate		- we Calo:	ite i	Geo	therm		AF	•	•	•	•	67
The Carb	m = 10	iori	ia _	Ca	loite		the	•	• mot	•	•	73
The Sili	ca G	Poth		met	07 07	: GEO	LIIE.	LIUOI	ue l	GI	•	76
INC SIL		eotin	CI MOI		61 .	٠	•	•	•	•	•	
SUMMARY AND CONCLUSIONS		• •	•	•	• •	•	•	•	•	•	•	80
Origin and Hi	stor	v of	the	Th	ermal	Wat	ets				-	80
Dating of the	The	rmal	Wat	ers								81
Geothermometr	V						•	•				81
REFERENCES			•					•				86

Page

APPENDIX A	SAMPLING	92
	Water Samples	94
	Environmental Isotopes	94
	Chemistry	94
	Carbonate Samples	95
	Aqueous Carbonate	95
	Calcite	96
	Sulphate Samples	96
APPENDIX B	ANALYSIS · · · · · · · · · · · · · · · · · ·	97
	Field Determinations of Chemical Parameters	98
	Chemical Analysis	99
	Stable Isotope Analysis	99
	Oxygen-18 and Deuterium in Water	100
	Oxygen-18 in Sulphate	100
	Sulphur-34 in Sulphate	103
	Carbon-13 in Aqueous Carbonate	103
	Oxygen-18 and Carbon-13 in Calcite .	104
	Radioactive Isotopes	105
	Tritium	105
	Carbon-14	105
APPENDIX C	CHEMICAL AND ISOTOPIC ANALYSES	106
APPENDIX D	GAS SAMPLING AND ANALYSTS	128

ł.

LIST OF FIGURES

Page

1

FIGURE

1	Location of Mount Meager Geothermal Area.	2
2	Location of hotsprings, drillholes and thermal anomalies.	3
3a	Meager Creek Hotsprings site.	10
3Ъ	Pebble Creek Hotsprings Site.	10
4	Location of cold springs at Mount Meager. Also shown are locations of rain samplers and glacier ice samples.	15
5	18 o and 2 H relationship for rain and snow samples.	25
6	18 O - altitude relationship in precipitation.	27
7	18 O - altitude relationship in cold springs.	29
8	18 2 0 and ² H relationship for thermal and cold groundwaters.	34
9	Tritium in precipitation, Ottawa, 1953 to 1977.	39
10	Relationship between discharge temperature and the calculated $\delta^{13}C_{CO_2}(g)$ value for thermal and cold spring waters.	49
11	Ranges of δ^{13} C values for common sources of carbon dioxide.	50
12	$\delta^{13}C_{CO_2}(g)$ - pCO ₂ relationship in thermal and cold spring waters.	53
13	Ranges of $\delta^{34}S$ values for common sources of sulphur in dissolved sulphate.	56
14	Major ions, δ^{18} O and temperature as a function of Cl ⁻ concentrations for hotsprings and artesian boreholes along Meager Creek.	60
15	Na-K-Ca geothermometer shown with data from this study.	64
16	Correction curves for the Na-K-Ca geothermometer with corrections for temperatures presented in this study.	64

Figure

17	Oxygen-18 fractionation curve for the $SO_4^{2-} - H_2O$ geothermometer.	69
18	Oxygen-18 fractionation curve in the H_2^0 - CaCO ₃ system.	72
19	Carbon-13 fractionation curve in the CO_2 - $CaCO_3$ system.	75
20	Solubility of quartz and it's related polymorphs from 0 to 200°C.	77
21	Correlation between the $SO_4 - H_2O$ and Mg-corrected Na-K-Ca septhermometers.	82

•

Page

LIST OF TABLES

,

TABLE		Page
1	Chemical data for thermal and cold spring waters.	12
2	Mineral solubility data for thermal and cold spring waters.	13
3	Environmental isotope data - cold spring waters.	3 0
4	Environmental isotope data - thermal waters.	32
5	Environmental isotope data - glacier ice.	41
6	Carbon-14 activities and $\delta^{13}C$ values for major thermal discharges.	43
7 -	Calculated $\delta^{13}C_{CO_2}$ and pCO ₂ data for thermal and cold spring waters.	48
8	Compilation of all geothermometer temperature estimates.	65
9	Sulphate - water ¹⁸ 0 geothermometer calculations.	68
10	δ^{13} C and δ^{18} O composition of calcite preciptitates at spring vents and in drill core.	71
11	Comparison of geothermometer temperature	83

.

INTRODUCTION

The potential for geothermal power production in Western Canada was recognized in 1973 (Souther, 1975) when the Geological Survey of Canada and the British Columbia Hydro and Power Authority began reconnaissance programs to locate geothermal anomalies. The main focus of interest was Mount Meager (Figure 1) which last erupted 2440 years ago leaving a steep geothermal gradient to which an abundance of hotsprings bears witness.

Exploration for geothermal resources at Mount Meager began in March, 1974, when Energy, Mines and Resources sponsored two shallow (45 and 118 m) drillholes to test the geothermal gradient near the Meager Creek hotsprings, which discharge with temperatures of up to 60° C.

Work continued in 1975 in a program of combined geophysics and drilling conducted by Nevin, Sadlier-Brown, Goodbrand Ltd., Consulting Geologists and sponsored by the B.C. Hydro and Power Authority. A series of geophysical profiles were completed which delineated a low resistivity (high temperature, high porosity) anomaly on the southern side of the complex along Meager Creek (Figure 2). Following this, four additional holes were drilled in this area (Nevin et al., 1975). Geophysical surveys were continued into 1978, and led to the discovery of two more thermal anomalies located on the north flank of the complex and along the Lillooet Valley between the Pebble Creek hotsprings and Meager Creek (Nevin et al., 1977; Figure 2). Drilling in 1978 and 1979 confirmed these anomalies and temperatures as high as 202°C in the south reservoir and 103°C in the northern anomaly were recorded (Nevin et al., 1979; Brian Fairbank, pers. comm.).

Additional studies at Mount Meager include detailed geological



E

٢.

Figure 1. Location of Mount Meager and it's relation to the Garibaldi Volcanic Belt and Pemberton Plutonic Belt.



肥



mapping of the complex (Read, 1975), geochemical analysis of the thermal and runoff waters (Hammerstrom and Brown, 1977) and an environmental isotopic investigation of the hydrogeology (Michel and Fritz, 1978; 1979).

The isotope investigations began in late 1977 with an intent to gain information on the recharge and flow path of the geothermal waters. The studies included analytical determinations of 18 0, 2 H and 3 H contents in thermal, precipitation and runoff waters and dating using carbon-14 in dissolved carbonate. Following these studies, it was felt that a full scale investigation of the isotope hydrogeology of the Mount Meager thermal waters would provide a great deal of information regarding the hydrogeological regime and thermal history, including the reservoir temperatures of the geothermal waters. Therefore, in 1979 a contract was awarded to the University of Waterloo by the Department of Energy, Mines and Resources, to sample and analyze precipitation, runoff, cold springs and thermal springs for stable and radioactive environmental isotopes and geochemistry.

Mount Meager was visited in June and August of 1979 in order to sample the spring thaw recharge event and late summer baseflow. The main focus of the study was threefold: a) a detailed investigation of the recharge environment and subsurface flow path of the thermal waters, through analyses of 18 O, 2 H and 3 H concentrations, to provide information regarding the magnitude of the geothermal resource; b) age dating the thermal waters, through the use of tritium and carbon-14, if possible, to provide information on residence times of thermal and cold groundwaters, and c) the application of a series of geothermometers, aimed at determining reservoir temperatures, and the possible presence

of a commercial supply of thermal fluids or steam at depth.

5

Following an outline of the occurrence and physical setting of the thermal waters at Mount Meager, this thesis discussed the results of these isotope and geochemical investigations as applied to geothermal exploration.

PHYSICAL SETTING

Location and Access

Mount Meager is located 120 km north of Vancouver, B.C. at the headwaters of the Lillooet River in the Coast Range Mountains (Figure 1). Logging roads, running north from Pemberton, B.C. have provided access to the project area as well as to most sampling locations (Figure 2). Samples from areas remote to logging roads were accessed on foot or by a Hillar 12E two passenger helicopter.

Geology and Physiology

The Mount Meager complex sits at the northern end of the Cenozoic Garibaldi Volcanic Belt (Figure 1) which comprises late Tertiary to Quaternary basaltic to rhyolitic volcanoes (Lewis and Souther, 1978). The Garibaldi Belt is considered to be a northward extension of the western United States High Cascades which include the Mount Baker and Mount St. Helens volcanic centers. Regional basement rocks are predominantly granodiorites, diorites and gneisses of the Mesozoic to Tertiary Coast Range Plutonic Complex. To the east of the Garibaldi belt and trending northwest is the Pemberton Belt of late Tertiary and Quaternary quartz monzonite plutons which intersects the Garibaldi Belt at the Salal Creek Pluton in the vicinity of Mount Meager (Figure 1). Both belts are related to subduction of the Juan de Fuca plate although the older Pemberton belt apparently formed when subduction was greatest, during the Miocene (Lewis and Souther, 1978).

Apparently unrelated to the Quaternary volcanics is an extensive fault system developed in the basement rocks along the Lillooet Valley from Harrison Lake to the south. This fault zone, which

- 6 -

intersects the Garibaldi Belt in the vicinity of Mount Meager is host to a series of discharges of deeply circulating geothermal waters which will be discussed below.

The Mount Meager complex consists of a series of predominantly andesitic and dacitic flows and breccias overlying metavolcanics and metasedimentary basement rocks of pre-Tertiary age, indicative of intermittent volcanism within the Tertiary and Quarternary. The volcanic pile is directly underlain by a basal breccia which has incorporated blocks of basement, (ranging up to 20 m diameter) in a tuffaceous matrix, and exceeds 300 m in thickness along the southern side of the complex (Read, 1977). This represents an explosive eruption which has led to extensive fracturing of the local basement rocks (Lewis and Souther, 1978).

Directly above the basal breccia lies an extensive porphyritic andesite flow with associated breccia and comagnatic dykes and which makes up the major part of the complex. Lewis and Souther (1978) report ages of 4.2 ± 0.2 My for these flows, reflecting a long period of intermittent volcanism. Plugs related to these flows form The Devastator and Pylon Peak in the southern portion of the complex where maximum thicknesses exceed 1200 m (Read, 1977).

A younger stage of volcanism occured in the north and central portions of the complex, represented by sequences up to 600 m thick of porphyritic dacites which form the upper sections of Mounts Job, Capricorn, Meager and Plinth.

The final stage of volcanic activity at Mount Meager was the eruption of the Bridge River Ash from a vent on the northeast flank of Plinth Peak. Dacite pumice blocks range in size from up to 4 m in

the valley to 10 cm on Plinth Peak and form ash deposits up to 30 m thick (Nasmith et al., 1967) which have been identified as far east as Banff, Alberta (Westgate and Dreimanis, 1967). The age of this eruption has been placed at 2440 \pm 140 years b.p. by carbon-14 dating a peat sample beneath the ash (Nasmith et al., 1967).

The physiology of Mount Meager is characterized by deeply incised valleys and canyons, unconsolidated and unstable gravel and ash deposits and wide, glaciated cirques and U-shaped valleys grading sharply upwards to craggy spires, remnant of the recent volcanic events. Glaciers presently occupy the valleys between peaks atop the volcanic compex, flowing into outlet glaciers in the upper reaches of the major valleys. Streams are all youthful and discharge, in varying proportions, glacial meltwater, groundwater and precipitation runoff. The treeline generally follows an elevation between 4000 to 6000 ft below which exists a subalpine forest of timber grade Fir, Cedar and Hemlock.

Thermal Springs

The regional settings for the hotsprings of southwestern B.C. can be divided into two groups. The Harrison, Sloquet and Skookumchuck hotsprings are related to the Pemberton Belt and issue from the intrusive rocks or from basement rocks proximal to the intrusives along the Lillooet Valley fault system (Figure 1). This fault system has apparently provided the fracture permeability required for deep circulation of meteoric waters to produce these thermal discharges. The second group includes the Meager Creek and Mount Cayley hotsprings which are related to the centres of Quaternary volcanism. The Pebble Creek hotsprings, occuring at the intersection of these two Tertiary

.8

belts, are related to both groups of thermal springs.

Along the Meager Creek are three sites where thermal waters discharge (Figure 2). The Meager Creek hotsprings at 580 m elevation represent the principal discharge of these thermal waters where as many as twenty-one individual vents have been identified in an area of approximately 1200 m² (Figure 3a), contributing to a metered discharge rate of $\sim 40l/s$ (Lewis and Souther, 1978). These hotsprings, at 45-55°C, issue from coarse fluvial sand and gravel deposits on the south side of Meager Creek, about 7 Km from it's confluence with the Lillooet River, encrusting the sides of the vents and pools with amorphous silica. The Meager Creek sediments in this area are about 18 m thick and overly a fractured local bedrock of quartz diorite. The Placid hotsprings emmanate from the gravel and boulder bank of Meager Creek approximately 1 km upstream from the Meager Creek hotsprings (610 m elevation). The five vents discharge 45°C water at a combined rate of less than an estimated 2%/s. About 5 km further upstream, a series of six vents (No Good Warm Springs) issue 20-40°C water from a grassy bank above a cobble and sand spit on the north side of Meager Creek (715 m elevation). These springs have a combined estimated flow rate of less than 5%/s and represent the most western discharge of thermal waters found at Mount Meager. The title "Meager Creek thermal waters" will herein include the hotspring and drillhole waters in the Meager Creek Valley.

The Pebble Creek hotsprings occur on the northeast side of the Lillooet River 7.5 km upstream from the influence of Meager Creek at an elevation of 550 m (Figure 2; 3b). Two major springs occur towards the back of a 30 m high bench on the bank of the river, issuing into small







Figure 3b. Pebble Creek hotsprings site and location of major vents.

pools which are depositing thick calcite tuffa, stained deep ochre. The bench is formed by a wedge of a welded ash flow lying on fractured quartz monzonite bedrock, and forms a steep face towards the river. Several warm seeps issue from the ash and the underlying fractured bedrock which outcrop on the face of this bench.

The Meager Creek hotspring waters are dominated by an Na-Cl chemistry with Na⁺ and Cl⁻ concentration averaging \sim 400 ppm and \sim 550 ppm respectively (Table 1). Other major ions include Ca²⁺ (\sim 85 ppm), HCO₃⁻ (\sim 475 ppm) and SO₄²⁻ (\sim 150 ppm). Furthermore, they contain \sim 160 ppm SiO₂, and are oversaturated with respect to quartz and amorphous silica. The Placid hotsprings have essentially the same chemistry as the Meager Creek hotspring, being dominantly Na-Cl waters, which possibly indicates a common source and flow path. The No Good warm springs, although considerably lower in total dissolved solids than the above springs, are also dominated by an Na-Cl chemistry and are oversaturated with respect to quartz and amorphous silica (Table 2) indicating that they too are possibly from the same geothermal pool.

The Pebble Creek hotsprings, unlike the Meager Creek thermal waters, are dominated by a Na-HCO₃ chemistry with concentrations for Na⁺ and HCO₃⁻ of \sim 400 ppm and 750-1050 ppm respectively. Other major ions in these waters include Ca²⁺ (\sim 35 ppm), SO₄²⁻ (\sim 300 ppm), Cl⁻ (\sim 80 ppm) (Table 2). Also unlike the Meager Creek thermal waters, these waters are supersaturated with respect to calcite and undersaturated with respect to amorphous silica (SiO₂ \sim 80 ppm; Table 2). The contrasting chemical natures of the Pebble Creek and Meager Creek thermal waters suggests that they may have unrelated sources and that

					-									
Sample Location	Date	Temp.	Hq	Ca ²⁺ ppm	Mg ²⁺ ppm	Na ⁺ ppm	k+ ppm	Fe _{tot}	Mn ²⁺ ppm	S10 ₂ ppm ²	s0 ₄ ррт	C1 C1	HCO3 ⁻	TDS
Hotsprings														
Meager Creek Hotsprings Main Vent Vent #19 Placid Hotsprings No Good Warm Springs Vent #1	Jun/79 Jun/79 Aug/79	50.1 49.8 45.1	6.54 6.24 5.89	81.9 78.0 114 77.0	26.2 24.5 27.6	439 440 433 360	45.5 50.0 53.5 35.0	0.12 0.20 0.35	0.64 0.08 0.76	162 142 138	122 130 174	528 605 674 405	443 437 398	1848 1907 2013
Pebble Creek Hotsprings Main Vent #7	Jun/79 Jun/79 Aug/79	29.5 59.8 57.0	6.82 6.88 6.60	75.6 32.7 35.3	13.7 4.73 5.11	175 426 419	22.4 13.8 14.1	0.13	0.84 0.19 0.15	101 79 67.5	69.0 288 316	196 83.3 62.4	382 763 735	1035 1679 1655
Drillholes							•							
EMR-1 74-H-1 75-H-1 79-H-1	Aug/79 Aug/79 Aug/79 Sep/79	58.4 52.3 10.1 28	6.06 6.23 7.70 6.12	107 223 32.9 210	36.2 90.3 18.0 43.1	424 2390 23.0 9.10	48.4 98.1 6.93 6.82	0.14 0.16 0.1 35.5	1.20 0.67 0.50 0.85	155 104 15.5 23.8	182 2370 222.6 16.1	571 2640 0.56 0.89	526 1270 233 974	2049 9188 353 1266
Cold Springs					•							•		
Boundary Creek Cold Spring #4 Moria Cold Spring #1 CaCO ₃ Cold Spring #3 Problem Cold Spring #1 Fall Creek Cold Spring #1 78-H-1 Cold Spring #1	Aug/79 Aug/79 Jun/79 Aug/79 Jun/79 Jun/79	4.5 9.6 9.0 4.6	8.31 7.91 7.62 7.65 5.92 7.18	12.2 110 98.6 5.40 3.50	5.42 38.5 12.5 44.9 2.60 1.01	4.84 4.50 3.20 11.9 6.00 16.0	0.54 3.31 1.75 5.00 1.80 0.67	0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.01 05 05 05 05 05	6.0 6.7 8.9 10.9 52.8 36.5	2.02 124 8.95 8.55 3.48 3.48	$\begin{array}{c} 0.2\\ 0.34\\ 0.8\\ 0.8\\ 0.8\\ 0.8\\ 0.8\end{array}$	66.3 395 370 594 36.8 40.8	97 682 504 809 114 102

Table 1. Chemical data for thermal and cold spring waters

12

1.23

6.40 7.60

76.2 64.2

968 745

159 128.

483 394

5.99 5.88

28.8 15.0

Sep/79 Sep/79

Mount Cayley Hotspring Mount Cayley Cold Spring

Regional Springs

Table 2. Mineral solubility data for thermal and cold spring waters¹

	*				
Sample Location	So	Jubility Pro	duct - log	(IAP/KT)	
Hotsprings	Calcite	Gypsum	Quartz	Chalcedony	Silica Gel
Meager Creek Hotsprings Main Vent Vent #19 Placid Hotsprings No Good Warm Springs Vent #2 Pebble Creek Hotsprings Main Vent #7 Vent #7	-0.18 -0.52 -0.55 -0.21 0.07	-1.72 -1.72 -1.71 -1.71 -1.77 -1.77	1.08 1.03 1.03 1.03 0.58 0.58 0.58	0.69 0.64 0.68 0.68 0.70 0.22 0.25	0.20 0.14 0.18 0.18 0.20 -0.27 -0.25
Drillholes					
EMR-1 74-H-1 75-H-1 79-H-1	-0.39 0.02 -0.08	-1.51 -0.61 -2.46 -2.14	0.96 0.88 0.65 0.54	0.60 0.50 0.11	0.11 0.00 -0.40 -0.43
Cold Springs					
Boundary Creek Cold Spring #4 Moria Cold Spring #1 CaCO ₃ Cold Spring #3 Problem Cold Spring #1 Fall Creek Cold Spring #1 78-H-1 Cold Spring #1	-0.45 0.76 0.42 0.68 -3.43 -2.30	-3.77 -1.38 -2.46 -1.93 -3.46 -4.03	0.34 0.32 0.49 0.52 1.30	-0.23 -0.23 -0.07 0.72 0.55	-0.75 -0.75 -0.59 -0.54 0.21 0.04
Regional Springs					
Mount Cayley Hotspring Mount Cayley Cold Spring	-0.16 -0.40	-0.37 -0.42	1.14 1.25	0.67 0.73	0.18 0.22
T As determined by WATEQF (Plummer enote: negative values imply undersat	t al., 1976) uration, posit	tive values t	imply oversa	turation.	

at least two independent pools of thermal waters exist.

The chemistries of all the hotsprings in the Mount Meager area are dominated by the transformation of alkali feldspars in the host basement rocks to clay minerals plus inputs of gas related to the recent volcanism. The water/rock interaction is doubtlessly aided by the substantial fracture permeability developed in the basement complex as a result of the explosive eruptions which occurred in the past. Extensive fracturing can be seen in exposed sections of bedrock on the south side of the complex and as well in exposures of the basal breccia described by Read (1975).

Cold Springs

Cold springs in the Mount Meager area range in altitude from 1850' to 6150' (Figure 4), issuing in most cases throughout the complex from unconsolidated soil, gravel and ash deposits. Temperatures range from $-.1^{\circ}$ C to 9° C and chemistries, although generally quite low in TDS can be quite variable with Ca²⁺ concentrations between 3.5 and 110 ppm, HCO₃⁻ between 2.70 and 395 ppm and SiO₂ between 6.00 and 52.8 ppm (Table 1). Cold springs with high carbonate concentrations are precipitating calcite tuffa, as is the case at the CaCO₃ cold springs where approximately 20 m of hillside below the vents is covered by an intricate network of terraced pools.



Figure 4. Location of cold springs at Mount Meager. Also shown are locations of rain samplers and glacier ice samples.

SAMPLING AND ANALYSIS

A wide variety of samples for stable environmental isotope and radioactive isotope analyses were collected at Mount Meager, including ¹⁸0, ²H and ³H in water, ¹³C and ¹⁴C in dissolved inorganic carbon, ¹⁸0 and ³⁴S in dissolved sulphate, and ¹³C and ¹⁸0 in calcite deposits. All analyses were performed in the Environmental Isotope Laboratory at the University of Waterloo. Detailed descriptions of all sampling and analytical technques are found in Appendices A and B and analytical data is in Appendix C.

Water Samples

Oxygen-18, deuterium and tritium in water were determined for all known emanations of thermal water at Mount Meager and other hotsprings. Samples were also taken at a variety of cold springs, at the upper and lower reaches of major creeks, from glacier ice, as well as snow and rainfall. The latter was collected under liquid parafin in precipitation samplers.

¹⁸0 contents in water samples were determined on CO_2 gas equilibrated with the water at 25°C and recalculated to Standard Mean Ocean Water (SMOW) using a fractionation factor $\alpha_{CO_2(g)} -H_20 = 1.0412$. Results are expressed in the conventional delta per mil (parts per thousand) notation ($\delta^{18}0$ %_o) with an analytical precision of ± 0.15 %_o. ²H contents were analysed using H₂ gas produced by the reduction of water vapour by hot (800°C) uranium. ²H concentrations are expressed as δ^{2} H %_o SMOW and have an analytical precision of ± 1 %_o.

Tritium (³H) concentrations were determined by combining

normal nonenriched water samples with a scintillation liquid in a gelling agent which was placed in a liquid scintillation counter with known standards. The results are expressed as T.U. (Tritium Units, where 1 T.U. = 1 3 H per 1 x 10 18 1 H), and where not presented, have an analytical precision of ± 10 T.U.

Dissolved Inorganic Carbon

Dissolved carbonate was sampled for analysis of 13 C and 14 C by precipitation of BaCO₃ from an alkaline solution created by the addition of NaOH until the pH exceeded 10, followed by the addition of excess BaCl₂.2H₂O. Precipitates for 13 C analyses were stripped from 3 ℓ water samples while the substantially larger 14 C samples required stripping the DIC from 60 ℓ water samples.

For ¹³C analyses the $BaCO_3$ was converted to CO_2 by reaction with 100% phosporic acid. The results are expressed in the δ ¹³C %, notation and refer to PDB (Peedee Formation Belemnite Standard), with a reproducibility of ± 0.5 %. Carbon-14 activities were measured by liquid scintillation counting using benzene synthesized from $BaCO_3$. Activities are expressed as pmC (percent modern carbon) defined as 95% of the NBS Oxalic Acid Standard.

Dissolved Sulphate

 $BaSO_4$ was stripped from solution as a co-precipitate of $BaCO_3$ in the manner described above and separated from $BaCO_3$ by acidification with 5% HCl. Sulphate samples were converted to CO_2 for ${}^{18}O$ analysis according to the graphite-reduction method described by Holt (1977) in

which $BaSO_4$ is mixed with powdered graphite and thermally decomposed at $\sim 1150^{\circ}$ C. Analyses are reported as δ ¹⁸0 %, SMOW with a reproducibility of better than ±0.5%, (Feenstra, 1980).

 34 S concentrations in sulphate were analysed by using SO₂ gas produced by the thermal decomposition of BaSO₄ at 1200^oC (Rafter, 1957). Values are reported as δ^{34} S[']%_o CDT (Canyon Diablo meteorite Troilite) with a reproducibility of ±0.3%_o.

Calcite

Calcite was collected from sinter deposits at the mouths of hot and cold springs as well as from hydrothermal deposits in drill core. Samples have been analysed for their 18 0 and 13 C concentrations by conversion to CO₂ through acidification with 100% phosphoric acid at 50°C. The resulting analyses are both expressed relative to PDB with an analytical precision of better than ±0.2%.

Chemistry

At each site sampled for chemistry, temperature, field pH and field alkalinity were recorded. Chemistry samples were filtered through a .45 µ pore diameter filter paper and collected in two 250 ml bottles, one of which was acidified to below a pH of 3 for heavy metal analyses. Water samples for silica determinations were diluted with deionized water to prevent precipitation of amorphous silica.

All chemical analyses referenced in this study were done in the Aqueous Geochemistry Laboratory at the University of Waterloo. Charge balance calculations demonstrated that all analyses have less than 10% discrepancy between anion and cation equivalence concentrations.

ISOTOPE HYDROGEOLOGY AND GEOTHERMOMETRY IN GEOTHERMAL AREAS Isotope Hydrogeology

Until less than two decades ago, the emanations of hotsprings and fumeroles were held by most researchers to represent juvenile water rising from cooling magmas deep within the earth's crust (White, 1957). However, Craig et al. (1956) discovered that the deuterium content of many geothermal waters was the same as the local meteoric waters indicating that they were not necessarily "juvenile" or mantle derived waters. Furthermore, he documented that oxygen-18 concentrations experienced an enrichment from their meteoric levels. In 1963, then, Craig concluded that there was no evidence for juvenile water and that most geothermal fluids represent deeply circulating meteoric waters which have experienced ¹⁸0 enrichment due to exchange with hot silicate minerals at depth. Hydrogen exchange is minimal due to a paucity of this element in most rock forming minerals.

A meteoric source for geothermal fluids then permits the use of 18 O and 2 H to trace these waters to their source and provide an understanding of the hydrogeological regime of many hotsprings. Craig (1966) was able to determine the origin and flow path for the Red Sea and Salton Sea (Lake Mead) geothermal brines in this manner. Arnasson (1977) produced a map of deuterium in rain for the whole of Iceland, and using observed trends, was able to define recharge zones and trace flow paths of thermal waters discharging from boreholes and hotsprings. Sakai and Matsubaya (1976) used environmental isotopes in water and sulphate to investigate the origins of waters in a series of volcanic and thermal systems in Japan, demonstrating that there are inputs from

- 19 -

all three of meteoric, oceanic and magmatic sources.

Isotopic investigations can also be used to qualitatively estimate the magnitude and hence, the power potential of a geothermal resource. Because an ¹⁸0 shift is affected by temperature and length of contact time with reservoir rocks, it can often be considered an indicator of the extent of water-hot silicate rock interaction, which has bearing on the potential of the geothermal system (Truesdell and Hulston, 1980). However, geothermal water in carbonate rocks generally experiences a large ¹⁸0 shift even at moderate to low temperatures owing to exchange with high concentrations of ¹⁸0 (20-30%_o) in the rock (Clayton et al., 1966). Conversely, small shifts have been observed in systems in which the silicate reservoir rocks have been altered by exchange with meteoric waters to lower δ^{18} 0 compositions due to high water/rock ratios and high temperatures over long periods of time as is the case at Wairakei, New Zealand (Truesdell and Hulston, 1960).

Geothermometry

Isotope geochemistry has also been applied in the field of geothermometry by using the temperature dependency of the stable isotope fractionation effects between various aqueous or gaseous species to estimate reservoir temperatures in geothermal systems. In particular, 18 O, 2 H, 13 C and 34 S isotopes have been used because of the great number of species in which they are found and because of their temperature dependent fractionations. Oxygen-18 fractionations in the SO₄²⁻ - H₂O, CO₂ - H₂O and SO₂ - H₂O systems have been investigated as have 2 H in H₂ - H₂O and H₂ - CH₄, 13 C in CO₂ - CH₄ and CO₂ - HCO₃⁻ and

 34 S in the H₂S - SO₄²⁻ system (Truesdell and Hulston, 1980).

The ¹⁸0 fractionation between sulphate and water has been used with success for Wairakei, N.Z. geothermal waters with results substantiated by measured borehole temperatures (Hulston, 1976). McKenzie and Truesdell (1976) have used this geothermometer at three major geothermal fields in the U.S., adopting corrections for subsurface boiling (¹⁸0 enrichment) and near surface dilution. Oxygen-18 fractionation between CO₂ and water vapour has been applied with success at the Larderello geothermal field (Panichi et al., 1976).

The Carbon-13 fractionation between CO_2 and CH_4 was first calculated by Craig (1953) and was subsequently applied with varying degrees of certainty to gases in Larderello, Italy (Panichi et al., 1976) and Wairakei, N.Z. (Hulston, 1976). Difficulties in achieving isotopic equilibrium in experimental work has cast some doubt, however, on the validity of the fractionation factors used (Gunter and Musgrave, 1971). Carbon-13 in the $CO_2(g) - HCO_3^-$ (aq) system has been investigated experimentally (Mook et al, 1974) and has been applied to the thermal waters of Steamboat Springs, Nevada and Yellowstone, Wyoming (Truesdell and Hulston, 1980).

Deuterium fractionation between H_2 and H_20 has been used by Arnasson (1976) to estimate subsurface temperatures in Icelandic geothermal fields, using borehole temperature data for confirmation.

In addition to isotopic, a series of chemical geothermometers have been developed which, often through empirical relationships, can be used to estimate subsurface temperatures. Principally, the relationship between the molar concentrations of aqueous Na^+ , K^+ , Ca^{2+}

and Mg^{2+} have been used (Fournier and Truesdell, 1973; Fournier and Potter II, 1979) to calibrate a widely applied geothermometer. The solubility of quartz and amorphous silica can provide a geothermometer (Fournier and Row, 1966) and based on the relationship between the partial pressures of H_2S , H_2 , CH_4 and CO_2 , deep thermal temperatures have been evaluated (D'Amore and Panichi, 1980). However, these geothermometers can be very sensitive to chemical changes during ascent and cooling and therefore, often produce rather distorted estimates of subsurface temperatures.

RESULTS AND DISCUSSION

Isotope Hydrogeology of Mount Meager

The oxygen-18 - deuterium relationship in a non-thermal groundwater is generally not affected by geochemical or biological processes and, in most cases will reflect the average annual temperature of the recharge area. Higher temperatures of condensation in a vapour mass will input greater contents of heavy isotopes in the precipitation and therefore recharging waters at lower elevations and lower latitudes will be enriched in heavy isotopes relative to waters recharging at higher elevations and latitudes. Because of these variations in recharging waters, the "metoric relationship" between ¹⁸0 and ²H in a groundwater can be used as a tracer to identify its origin.

In geothermal areas, as discussed above, this is not necessarily possible because 18 0 exchange between minerals and water at elevated temperatures often results in an 18 0 enrichment in the water due to high concentrations of 18 0 in most rocks (Craig, 1963; Epstein et al., 1967). Silicate rocks, including granites and diorites have δ^{18} 0 values of +8 to +9 %, while marine carbonates are much higher, at +20 to +30%, SMOW (Truesdell and Hulston, 1980). The resulting "meteoric relationship" between 18 0 and 2 H is then no longer obeyed. However, because deuterium is not affected, the original meteoric waters can be identified and thus, the region or recharge area for the thermal waters can be postulated (Arnasson, 1976). Furthermore, the 18 0 shift can be used to derive information from geothermal waters, because the magnitude of the shift often reflects the magnitude of the geothermal resource (Truesdell and Hulston, 1980).

A detailed analysis of oxygen-18 and deuterium abundances in

- 23 -

meteoric and non-thermal groundwaters is, then, a prerequisite for an understanding of the origin of geothermal waters and the environment through which they have passed.

Meteoric Waters

A survey of 18 O and 2 H in precipitation was initiated during previous studies (Michel and Fritz, 1978), and was intensified within the scope of the present study in order to establish the meteoric relationship between 18 O and 2 H for the area. In any given area this linear relationship generally remains constant for precipitations at various altitudes and times of the year reflecting a consistent origin and history of vapour masses.

It was not possible to operate precipitation samplers during the winter months but some snow samples were collected. However, it could not be ascertained that they remained isotopically unaltered, as evaporation can enrich snow in 18 O and 2 H and thus affect their meteoric relationship (Moser et al., 1970).

Data from precipitation collected at Victoria, B.C. since 1975, which is very similar to Mount Meager precipitation data, was also used to define the local meteoric water line. A curve was fitted to these data using a least squares computer subroutine which generated the equation:

$$\delta^2 H = 6.9 \ \delta^{18} O - 8.1$$

which is illustrated graphically in Figure 5.

Any water sample originating in a vapour mass represented by this equation will then plot on the meteoric water line unless it has changed its isotopic identity through evaporation or exchange. It's location on


the meteoric water line will be a function of temperature of condensation in the original vapour mass. The lower the temperature the lower the heavy isotope contents. This results in seasonal, latitude and altitude effects.

In a localized study area such as this, particularly in a mountain environment, isotopic variations are principally a function of elevation rather than latitude. This effect can be documented with a plot of elevation versus δ^{18} 0 in precipitation which will provide rough estimates of the actual altitude of recharge for various groundwaters.

For the data collected in this study, a plot of oxygen-18 in precipitation versus altitude is shown in Figure 6. It demonstrates that the gradient of the altitude effect is approximately $-0.25\% \delta^{18}$ 0 per 100 m rise. A common value for this effect observed in alpine environments is ~ -0.15 to $-0.5\% \delta^{18}$ 0 per 100 m rise in altitude, (Gat, 1980).

Cold Springs

Where accessible, cold spring water throughout the Mount Meager area were sampled in order to define further the hydrogeological regime.

Because they are not affected by isotopic exchange, cold groundwaters generally reflect the average annual precipitation of the recharge area and plot on the local meteoric water line. However, the shorter the flow system, the more pronounced the seasonal variations in the groundwater discharges will be due to the effects of a smaller reservoir, shorter residence time and less complete mixing of the seasonally varying recharging waters. Thus, a single sampling of a spring which acts as a discharge for a short flow system may not represent the average annual precipitation of the recharge area as would be expected for a spring discharging from a





deeper groundwater reservoir. Furthermore, if springs are sampled in a mountainous area, the discharge altitude indicates little about the recharge altitude.

Cold springs in the Mount Meager area have been sampled at altitudes ranging between 564 m and 1875 m. Of the springs which were sampled in both the spring and late summer sampling trips, the high altitude springs show a seasonal fluctuation of up to 3%, in δ^{18} 0 values while the low altitude springs have variations over the sampling period within the analytical error of $\pm 0.15\%$, (Figure 7; Table 3).

The high altitude cold springs, then, discharge from very limited, shallow flow systems of short residence time while the low altitude cold springs discharge well mixed waters from larger hydrogeological systems of longer residence times. Because these low altitude discharges show no seasonal fluctuations, they should then represent the average annual δ^{18} 0 values of the meteoric waters which recharge their systems. These non fluctuating springs discharge at between 1000 to 1200 in elevation, and therefore, recharge must occur above this level. Hence, meteoric waters recharging above 1000 to 1200 m altitude must have an average annual δ^{18} 0 value of -17.0 to -17.5%. This observation can be useful in assessing the recharge altitude of the thermal springs as will be shown below.

Thermal Waters

Unlike cold groundwaters, thermal waters cannot be expected to plot on the local meteoric water line due to exchange with 18 O in reservoir rocks. The 18 O content of granites and granodiorites is generally in the order of + 8% to + 9% SMOW (Taylor and Epstein,



	Table 3.	Envir	onmental is	otope data - col	d spring water	S	
Sample Location	Altituda	(m)	Date	Temperature	6 180 %	6 ² H %o	
		//	7444	>	1010	HOLD	•••••
Devastation Cold Spring	118	8	Jun/79	10	-17.1	-124	
Boundary Cold Spring #3	120	4	Aug/79	4.5	-16.7	-	
#4			Aug/79	4.5	-17.1		51
CaCO ₂ Cold Spring #1	94	2	Jun/79	5.6	-17.4	-132	43
a #3			Jun/79	5.6	-17.3	-128	
#			Jun/79	6.2	-17.3	-127	42
5#			Aug/79	6.9	-17.2	-126	52
9#0			Aug/79	10	-17.0		25
#1			Aug/79	10	-17.7	-	
Morta Cold Spring #1	114	с С	Aug/79	8.5	-17.5		34
#3			Aug/79	10	-17.4		
Rivendell Cold Spring #1	97	5	Aug/79	10	-17.3		
#2			Aug/79	10	-17.3		
Angel Cirque Cold Spring	# 1 166	_	Jun/79	2	-19.4	-136	24
•	l#		Aug/79	0.3	-16.5	-122	4
	#2		Jun/79	2	-18.1		
	#2		Aug/79	2	-16.4		22
	#4		Aug/79	2	-17.3		
	#7		Aug/79	-0.2	-16.1		
Problem Cold Spring #1	115	_	Jun/79	0.6	-17.7	-127	54
			Aug/79	10	-17.0	-125	13
#2			Jun/79	10	-16.9	-125	23
#2			Aug/79	10	-17.2		
Loggers Cold Spring	82	m	Aug/79	2	-17.7		
Fall Creek Cold Spring #1	20	4	Aug/79	3.9	-17.0		. 26
	-		Aug/79	ŝ	-16.9		
78-H-1 Cold Spring #1	72	æ	Jun/79	4.6	-18.1	-136	
			Aug/79	10	-18.0		
÷.			Jun/79	10	-17.4	*	
Job Cold Spring #1	144	8	Jun/79	. 10	-17.8	-134	40
Job West Spring	152	4	Sep/79	10	-15.8	• -	
Affliction Cold Spring	14 9	4	Jun/79	10	-18.7	-142	213
Mt. Athelstan Cold Spring	181 187	2 2	Jun/79	5	-19.4	-144	29
			Aug/79	1.3	-17.1		
	7.#		Aug/79	1.2	-16.8		28

1962) representing a significant enrichment with respect to most meteoric waters. Exchange of 18 O between water and minerals is facilitated by elevated temperatures and therefore most geothermal waters exhibit a positive shift in δ^{18} O values.

Craig (1963, 1966) has reported positive δ^{18} 0 shifts of 3 to 4.5 %, magnitude for Steamboat Spring and Lassen Park thermal waters and 5 and 7 %, for steam at Larderello, Italy and Hekla, Iceland. These thermal waters are neutral to alkaline, have temperatures generally in excess of 200°C and show no shift in δ^2 H from meteoric waters. Hulston (1976) reports positive shifts of 5 %, in ¹⁸0 as observed in the thermal waters from boreholes at El Tatio, Chile.

However, Hulston also reports values as low as 1-1.5 %, for 18 O shifts at Wairakei and Broadlands, New Zealand. In these cases, however, high water/rock ratios (rapid development of alteration minerals) and rapid circulation of meteoric waters have apparently affected the 18 O shift.

The δ^{18} O - δ^2 H data for the thermal waters at Mount Meager (Table 4) demonstrate this ¹⁸O shift as well but to a lesser degree (Figure 8). The Meager Creek hotsprings show a shift of close to 1.0 %, from meteoric waters with local borehole waters exhibiting a shift of approximately 1.5 %. The Pebble Creek hotsprings are shifted slightly more than .5 %, from local meteoric waters. Apparently, then, none of the thermal waters sampled have had the opportunity to exchange ¹⁸O with reservoir minerals to any great degree. Due to a low water/rock ratio (typical of a fracture porosity) and lack of an observable steam separation, it is unlikely that the low ¹⁸O shift observed here is comparable with that of the New Zealand geothermal systems. More likely,

. . --

3

Table 4 continued. Environmental isotope data - thermal waters

Sample Location	Date	, Temperature °C	δ ¹⁸ 0 % SMOW	δ ² H % SMOW	³ H (T.U.) ± 10 T.U.
Boreholes					
EMR-1	Feb/78	8	-15.6	-127	33
EMR-1	Mar/78	8- 8-	-15.7	-125	
EMR-1	0ct/78		-16.0	-132	
EMR-1	Dec/78	ł	-16.3	-135	26
EMR-1	Jun/79	58,5	-16.2	-126	7
EMR-1	Aug/79	58.4	-16.1		39
EMR-2	Mar/78	1	-16.2	-129	61
74-H-1	0ct/77	:	-15.1	-125	
74-H-1	Feb/78	:	-15.3	-130	
74-H-1	Mar/78	1	-15.0	-126	13
74-H-1	Jun/79	50.5	-15.6	-127	0
74-H-1	Aug/79	52.3	-15.3		
75-H-1	Aug/79	10.1	-17.2	-128	31
PDH-78-3	Sep/78	:	-17.2	-129	16
79-H-1	Aug/79	ł	-17.1		. 44
1-H-62	Sep/79	28.0	-16.7	-125	35



ţ



the small shift indicates that these thermal waters have been in contact with rocks at comparatively lower temperatures (and, hence, less 18 0 exchange) than found at other geothermal systems, possibly due to a more shallowly circulating system. Oxygen exchange with igneous rocks only becomes very significant at temperatures upwards of 150°C (Truesdell and Hulston, 1980).

The difference between the shift seen in the hotsprings along Meager Creek and the local borehole waters (Figure 8) may well reflect the mixing effects of ascending thermal waters and the 18 O depleted, cold, shallow circulating meteoric waters. The deeper borehole samples would be expected to have experienced much less mixing and therefore be more representative of the true local geothermal waters. This is difficult to substantiate with tritium data due to its apparent variability in shallow groundwaters.

Following this, the original δ^{18} 0 value for these water can be established by subtracting the magnitude of these shifts. Accordingly, the Meager Creek thermal waters had an original δ^{18} 0 value of about -17.0 to -17.5 which is very close to the value thought to represent the average annual precipitation recharging the low altitude cold springs discussed above (Figure 7). Recharge for these thermal waters, then, may well occur at as low as 1000 m elevation.

The Pebble Creek thermal waters, however, have ¹⁸0 contents much lower than the Meager Creek thermal waters and, corrected for a positive shift, average to between -19.5 and -20.0 %. Apparently, the Meager Creek and Pebble Creek thermal waters discharge from quite separate geothermal pools. The more negative values for the Pebble Creek thermal waters likely corresponds to a significantly higher altitude recharge zone. They may also possibly reflect more negative δ^{18} 0 values in the Lillooet River drainage basin, within which they recharge. ¹⁸0 data for river waters in the Meager and Lillooet River drainage basins demonstrates the Lillooet waters to be generally 0.5 to 1.0 %, more negative (Appendix C).

Age of Groundwaters

The depth of circulation of meteoric waters in a geothermal system, and hence the recharge and magnitude of the system can often be reflected by the age of the thermal waters. However, dating such waters is difficult and estimates are certainly not regarded without skepticism. The two techniques commonly applied are tritium (³H) and carbon-14 dating, which provide age estimates of up to 30 years and thousands of years respectively. However, while easily bracketing the useful range for geothermal systems, they provide complications which make them applicable in few geothermal situations. Use of non-reactive radioisotopes such as ³⁹Ar (half-life = 269 years) may provide a more confident age estimate but so far, its collection, separation and analysis are very difficult and expensive. (Truesdell and Hulston, 1980).

Tritium

³H is produced naturally in the atmosphere by the bombardment of nitrogen by cosmic radiation and is believed to have a natural abundance of between 5 and 20 T.U. (Brown, 1961) and possibly as low as 1 T.U. as calculate by Grosse et al., (1951). However, between 1952 and 1964, atmospheric testing of thermonuclear bombs resulted in abnormally high amounts of tritium entering the atmosphere. Except for radioactive decay (halflife = 12.35 years), tritium is conservative and not modified by chemical, biological or physical processes. Thus, it's absence in natural groundwaters can identify waters which have entered the flow system prior to 1952. Monthly precipitation samples have been collected at Ottawa since 1953 and analysed for tritium concentrations. The resulting graph, (Figure 9) demonstrates the high input of 3 H into the atmosphere following detonation of thermonuclear devices in 1952, 1953, 1954, 1958 and 1961-62. Yearly oscillations in tritium fallout are due to an apparent annual spring "leak" of 3 H into the troposphere from the stratosphere. Tritium levels, although presently less than 100 T.U., have been in the order of thousands of T.U. which is considerably greater than the estimate of 1-5 T.U. for natural or background levels discussed above.

Precipitation samples collected between 1977 and 1979 at Mount Meager have tritium levels in the order of 20-70 T.U. with an unweighted average of 47 T.U. Cold springs contain just slightly less tritium (Table 3) ranging from 79 T.U. to the detection limit and averaging 33 T.U. The cold springs are then, likely representative of short and rather limited flow systems. However, virtually no information exists on the seasonal variations in tritium fallout at Mount Meager, and it may well be possible to have major precipitation events with very low tritium contents. This argument is based upon precipitation data collected since 1975 at Victoria. Thus very short flow systems may well show low tritium contents at certain times and unless systematic, long term sampling is done, it will not be possible to differentiate older from younger water with certainty.

Also, the input of glacial meltwater into these short flow systems must be known to be able to attach an age to the water because they input essentially tritium free water (Job Glacier (South) and



C

Devastation Glacier = 0 T.U.; Table 5).

The thermal waters at Mount Meager have significantly less tritium than do the cold springs with levels generally at or slightly above the detection limit (Table 3). The Pebble Creek thermal waters show consistently low values at the detection limit while the Meager Creek thermal waters in the springs and boreholes show an apparent variability ranging between detection and 21 T.U. These small amounts of tritium can likely be attributed to mixing with modern near surface waters (which will be discussed below) which implies that the thermal waters are tritium free and therefore, in excess of 25 years old, the Pebble Creek hotspring waters apparently experience less mixing with modern near surface waters, possible because they issue from fractured bedrock 30 m above river level rather than from fluvial sands and gravels as do the Meager Creek hotsprings.

Carbon-14 and Carbon-13

Radiocarbon or carbon-14 is produced in the upper atmosphere through the bombardment of nitrogen by cosmic radiation. Radioactive decay balances this production to provide an atmospheric concentration which is believed to have been constant within a few % for several thousands of years. Carbon-14, incorporated into the hydrosphere as dissolved $^{14}CO_2$ and $H^{14}CO_3^{-}$, will maintain a constant concentration providing the water remains in contact with the atmosphere. In a closed system however, the recharging water becomes isolated from atmospheric CO_2 and radioactive decay reduces the concentration of ^{14}C in the water. The length of time the waters are isolated from the atmosphere will be

Sample Location	ه 18 ₀ گ SMOM	³ н (т.u.) ± 10 т.u.
Job Glacier (south)	-14.9	0
Devastation Glacier (east)	-16.0	0
Cathedral Glacier	-17.4	
Job Glacier (north)	-15.5	
Affliction Glacier	-16.1	11

reflected by a decrease in 14 C activity and thus, comparison of 14 C in a groundwater sample to ¹⁴C in modern or present day water can theoretically render an estimate of the age of that groundwater. If decay is the only mechanism by which the ¹⁴C activity has decreased, then the measured activity can be directly related to age through the halflife of ¹⁴C, 5730 years. However, due to contributions of "dead" carbon from dissolution of secondary calcite and other carbonate minerals along the flow path, as well as contributions from volcanogenic CO₂, the activity of ¹⁴C in DIC in geothermal areas can be significantly decreased, without radioactive decay, appearing unrealistically old. In a previous study, (Michel and Fritz, 1978), carbon-14 dating was attempted on two springs and two boreholes (Table 6). However, because the ¹⁴C activities were suprisingly low and the calculated δ^{13} C values of CO₂ in equilibrium with water was close to magmatic CO2, carbon exchange with hydrothermal carbonate minerals and contamination by volcanogenic CO, was suspected. In the present study, a survey of ¹³C in aqueous carbonate (Table 7; Figure 10) supports that volcanogenic CO2 has indeed equilibrated with the thermal waters. Furthermore, hydrothermal calcite crystals from drillcore in 79-H-1 were analysed for ^{13}C and ^{18}O (Table 10). Calculated fractionation factors between these calcites and the DIC from artesian waters in this drillhole demonstrate that these minerals were in isotopic equilibrium with thermal waters. Therefore, ¹⁴C exchange is undoubtably taking place.

Age dating is also complicated by the effects of mixing waters which have dissolved CO₂ from different sources of different ages. If mixing with near surface cold groundwaters takes place to any signifiTable 6. Carbon-14 activities and $\delta^{13}\text{C}$ values for major

•

S	
U	
D	
5	
g	
2	
C	
S	
-	
d	
Ξ	
Ξ.	
d)	
ě.	
1	

Sample	Date	14c (pmc) ⁸	13 _C % PDB
Meager Creek Hotsprings Main Vent ¹	Feb /78	5.6	-5.2
Pebble Creek Hotsprings Main Vent ¹	Feb /78	0.24	-4.6
No Good Warm Springs Vent #2	Aug /79	19.8	-8.4
EMR-1 ¹	Feb /78	4.6	-7.0
74-H-1 ¹	Feb /78	0.19	-5.3
Mount Cayley Hotsprings	Sept/79	0.4	-1.5

¹Michel and Fritz (1978)

43

,

.

cant degree, then contributions from biogenic or soil CO_2 would be expected. This has been found to be the case for No Good warm spring #2 which discharges at a much lower temperature with lower TDS and higher tritium values than the Meager Creek hot springs (Tables 1 and 4). The ¹⁴C activity for these waters is 19.8 pmC (compared to 5.6 pmC for Meager Creek hot springs; Table 6) indicating that they most likely represent a mixture of thermal waters which are dominated by "dead" volcanogenic CO_2 and cold, shallow groundwaters, which have, at some time, equilibrated with modern CO_2 , probably of biogenic origin.

Thus, due to inputs of volcanogenic CO_2 plus the effects of mixing with near surface waters, dating of these thermal waters with carbon-14 is impossible. The conclusion is substantiated by the following discussion regarding the various sources of CO_2 in the thermal and cold spring waters as determined by a survey of ${}^{13}C_{\rm DIC}$ and pCO₂ data.

Carbon-13 in Aqueous Carbonate

The ¹³C composition of dissolved carbonate can be controlled by a number of processes combining various sources and subsurface histories of carbon. Understanding the controls of the carbon system is important for age dating and geothermometry in geothermal systems and, therefore, warrants investigation.

In most geothermal systems, a significant CO_2 gas phase is present which controls the $\delta^{13}C$ for the DIC. We can calculate the $\delta^{13}C$ for the equilibrium $CO_2(g)$ which can then be used to identify the sources of this gas providing it is an open system with respect to this gas. The per mil difference in ${}^{13}C$ between $CO_2(g)$ and each of H_2CO_3 , HCO_3^- and CO_3^{2-} is represented as:

$$\varepsilon_{aq/CO_2} = (\alpha - 1) \cdot 1000 \simeq 1000 \ln \alpha$$

where α = fractionation factor = $\frac{({}^{13}c/{}^{12}c)_{aq.carb.species}}{({}^{13}c/{}^{12}c)_{c0}}_{2}(g)$

and ε = the enrichment factor $\sim \delta^{13}C_{aq} - \delta^{13}C_{C0_2(g)}$

The value for α is temperature dependent and is determined according to the following experimentally derived equations:

$$1000 \ln \alpha_{H_2CO_3}^{o}/CO_2(g) = 0.373 \times 10^3/T + 0.19$$

(Vogel, Grootes and Mook, 1970)

$$1000 \ln \alpha_{\rm HCO_3}/\rm{CO_2(g)} = 9.552 \times 10^3/T - 24.09$$

(Mook, Bommerson and Staverman, 1974)

$$1000 \ln \alpha_{\rm CO_3}^{2-}/{\rm CO_2(g)} = 9.037 \times 10^3/T - 22.73$$

(Thode, Shima, Rees and Kroshnamurty, 1965)

Using these fractionation factors and the molar concentrations of each carbonate species as determined by WATEQF (a fortran version of the WATEQ PL1 water analysis program, Plummer et al., 1976), an isotope mass balance equation can be written to determine the value of δ^{13} C for the CO₂ gas phase in equilibrium with the water sample.

$$\delta^{13}C_{DIC}:M_{DIC} = M_{H_2CO_3} \cdot (\delta^{13}C_{CO_2} + \epsilon_{H_2CO_3/CO_2}) + M_{HCO_3} \cdot (\delta^{13}C_{1O_2} + \epsilon_{HCO_3}/CO_2) + M_{HCO_3} \cdot (\delta^{13}C_{1O_2} + \epsilon_{HCO_3}/CO_2) + M_{HCO_3} \cdot (\delta^{13}C_{1O_2} + \epsilon_{HCO_3}/CO_2)$$

where $M = Concentration in moles/1000g H_2^0$ $\varepsilon = enrichment factor = 1000 ln \alpha$ DIC = total dissolved inorganic carbon

The carbonate speciation, as determined by WATEQF is also a function of temperature, T, and the equilibrium (dissociation) constant, K, where:

and
$$\log K_1 = 14.8435 - 3404.71 \text{ T}^{-1} - 0.03279 \text{ T}$$

 $\log K_2 = 6.498 - 2902.39 \text{ T}^{-1} - 0.02379 \text{ T}$

(Harned and Davis, 1943)

 K_1 and K_2 are the dissociation constants in the system $H_2CO_3^-$ HCO₃ and HCO₃⁻ - CO₃²⁻ respectively and T is the absolute temperature at which the reaction takes place.

The results of these calculations are tabulated in Table 7 and are graphically described in Figure 10 where calculated δ^{13} C values of the carbon dioxide are compared with discharge temperatures. The inset in this figure and Figure 11 show the various sources which can contribute to the carbon pool of a groundwater. It is noteworthy that little or no difference in ¹³C content exists between atmospheric CO₂ (which has, however, a ¹⁴C activity equivalent of ~ 100 pmC) and mantle derived CO₂ (which is free of ¹⁴C). Their ¹³C's are close to -7 %. (Craig, 1963; Ferrara et al., 1963; Barnes et al., 1978), and thus δ^{13} C values alone cannot be used to distinguish between the two.

However, groundwater recharged by infiltration through vegetated soils will dissolve root respirated, biogenic CO_2 which in these latitudes commonly has a $\delta^{13}C$ value between -21 %, and -26 %, (Rightmire, 1973; Fritz et al. 1978; Figure 11) and will dominate over atmospheric CO_2 . This may then be followed by the dissolution of carbonate minerals. If this dissolution occurs out of contact with CO_2 , this will lead to an increase in ${}^{13}C$ in the aqueous phase. An increased $\delta^{13}C$ of the aqueous phase will then increase the $\delta^{13}C$ of the calculated equilibrium CO_2 accordingly, depending upon pH, which can result in a wide range of values for the calculated $\delta^{13}C_{CO_2(g)}$ and hence, no unique solution exists.

The values of $\delta^{13}C_{CO_2(g)}$ calculated for the hotsprings and thermal borehole waters all fall into the range of -7.4 % - 9.9 %.

Sample Location	T ^o C	рH	HCO ₃ (ppm)	6 ¹³ CDIC	6 ¹³ CC02	log pCO ₂
Hotsprings						
Meager Creek Hotspring Main Vent Vent #19 No Good Warm Springs Vent #1 Vent #2 Pebble Creek Hotspring Main Vent Vent #7	50.1 49.8 38.8 29.5 59.8 56.5	6.54 6.24 6.47 6.82 6.88 6.88	443 437 404 382 763 771	-6.1 -7.3 -7.6 -8.4 -4.6 -6.3	-9.5 -9.7 -11.3 -14.0 -8.2 -9.9	77 48 81 -1.24 79 55
Boreholes ~						۰.
EMR - 1 74-H-1 75-H-1 79-H-1	58.4 52.3 10.1 28.0	6.06 6.23 7.70 6.12	526 1255 233 974	-6.2 -4.9 -10.7 -7.0	-8.4 -7.4 -19.8 -9.2	16 05 -2.42 24
Cold Springs						
Boundary Cold Spring #4 CaCO ₃ Cold Spring #1 #4 Moria Cold Spring #1 Angel Cirque Cold Spring #1 Problem Cold Spring #1 Fall Creek Cold Spring #1 78-H-1 Cold Spring #1 Mt. Athelstan Cold Spring #1	4.5 5.6 6.2 8.5 .3 9.0 3.9 4.6 1.2	8.31 7.71 7.50 7.91 8.72 7.65 5.92 7.18 8.48	66.3 370 351 395 2.70 594 36.8 40.8 12.0	-6.1 0.5 -3.0 -5.0 -7.2 -2.8 -8.6 -13.9 -6.8	-16.3 -10.1 -12.0 -14.5 -18.1 -12.0 9.8 -22.2 -17.4	-3.59 -2.26 -2.14 -2.43 -4.58 -1.99 -1.45 -2.66 -4.49
Runoff						
Job Creek (at glacier)	5.1	7.3	44.7	0.2	-8.9	-2.81
Regional Hotsprings						
Mt. Cayley Hot Spring Mt. Cayley Cold Spring Harrison Hot Spring	28.8 15.0 67.0	5.99 5.88 7.90	1465 1310 26.5	-1.5 -3.3 -17.9	-3.6 -4.9 -21.8	.09 .09 -3.34

Table 7. Calculated $\delta^{13}C_{CO_2}$ and pCO₂ data for thermal and cold spring waters







(Table 7; Figure 10). Because this range is very close to that of volcanogenic CO_2 (Figure 11) it seems likely that they have equilibrated with this source of carbon dioxide. Any component of modern biogenic or atmospheric CO_2 which may exist in the recharging water would then be masked by this source of radiogenically dead CO_2 and thus, age estimates of the waters would be unrealistically old. This case is substantiated by the very low carbon-14 activities of below 6 pmC determined for these waters (Table 6) and by their very high pCO₂ values which will be discussed below.

The cold springs at Mount Meager appear, however, to have experienced quite a different carbonate evolution. As discussed above, a groundwater entering the flow system after equilibrating with biogenic or soil CO_2 can evolve to more positive values of $\delta^{13}C_{DIC}$ and hence, more positive calculated $\delta^{13}C_{CO_2(g)}$ values than in the original gas. (Deines et al., 1974). The process involves carbonate dissolution and results in elevated pH's and lower pCO_2 values. Because of the scatter of $\delta^{13}DIC$ values for the cold springs and because of the generally high pH's and low pCO_2 values, it would appear that these cold groundwaters have evolved in this manner and hence, would likely have considerably greater carbon-14 activities. Certainly they don't appear to have incorporated any significant amount of volcanogenic CO_2 .

It is interesting, then, to note that the calculated $\delta^{13}C_{CO_2}$ values for Mount Cayley thermal waters are significantly more positive (-3.6 %, and -4.9 %, Table 7; Figure 10), than Mount Meager thermal waters. This enrichment in ¹³C can be accounted for by the incorporation of CO₂ derived from marine carbonates ($\delta^{13}C \sim 0.0$ %) during meta-

morphism (by a local high temperature environment or by reaction with a silicate melt) into CO₂ acquired from degassing of the mantle (Barnes et al., 1978); or by carbonate dissolution along the flow path. Both explanations are substantiated by the presence of crystalline limestone in the local metasedimentary basement rocks at Mount Cayley (Souther, 1980).

Partial pressure data for CO_2 (Table 7; Figure 12) can be used to substantiate the above interpretation of CO_2 sources for Mount Meager thermal waters. pCO_2 values are a function of pH, temperature and DIC and are calculated according to the equation:

$$pCO_2 = \frac{(10^{-pH}) \cdot [HCO_3]}{K_{CO_2} \cdot K_{H_2}CO_3}$$

where $K_{CO_2} = -13.417 + 2299.6 T^{-1} + .01422 T$ and $K_{H_2CO_3} = 14.8435 - 3404.71 T^{-1} - 0.03279 T$ (Harned and Davis, 1943)

Atmospheric CO_2 concentration is very low $(pCO_2 = 10^{-3.5} \text{ atm})$ while biogenic CO_2 in the soil horizon has a higher partial pressure $(pCO_2 = 10^{-1} \text{ to } 10^{-2.5} \text{ atm})$ due to oxidation of carbon by micro-organisms and by root respiration (Stumm and Morgan, 1970). Volcanogenic CO_2 , however, can comprise up to 95% of a geothermal gas (Ferrara et al., 1963). Figure 12 demonstrates that the hotspring samples tend to have high concentrations of $CO_2(g)$, reflecting a dominantly volcanogenic source while cold springs have much lower CO_2 partial pressures. Exceptionally low pCO_2 's can be attained through the closed system



evolution of CO_2 as well. The dissolution of $CaCO_3$ along the flow path results in an elevated pH which in turn consumes CO_2 (Deines et al., 1974). This has been documented in at least two cold springs which show pCO_2 values below atmospheric levels. Multiple CO_2 sources are recognized in the warm springs (No Good Warm Springs #1, 2) whose $\delta^{13}C$ DIC fall between biogenic CO_2 and volcanogenic CO_2 . This was substantiated above in the discussion of carbon-14 activities. The mixing of cold groundwaters which evolved from an initial equilibration with modern biogenic CO_2 and thermal waters with volcanogenic CO_2 has resulted in a moderate temperature spring with a ${}^{14}C$ activity of 19.8 pmC.

The dominance of mantle derived CO_2 in the thermal waters can be further substantiated by pCO_2 data from the Mount Cayley and Harrison hotsprings. Mount Cayley, a Quaternary volcano, has a calculated pCO_2 of $10^{\cdot 09}$ (greater than 1 atmosphere pressure) and a δ^{13} C of -3.6 %, for the gas phase in equilibrium with the thermal waters. Clearly these waters contain predominantly volcanogenic CO_2 . Contrasted with this are the Harrison hotsprings which issue from the southern end of a deep fault system delineated by the Harrison and Lillooet River valleys to Mount Meager. The fault system is unrelated to any sites of recent volcanism and, therefore, the low δ^{13} C DIC of -17.9 and low pCO₂ of $10^{-3\cdot 34}$ represent an original equilibration between these waters and modern biogenic CO₂ which implies that they can be dated.

Sulphur-34 in Aqueous Sulphate

Prerequisite to the application of the sulphate-water geothermometer is a source of sulphur which is present in the reservoir in its oxidized state (SO_4^{2-}) . A different sulphate source would substantially reduce the confidence of any temperature estimate if some component of the sulphate has not equilibrated with the water at reservoir temperatures.

The δ^{34} S values for the Meager Creek thermal waters fall within a range of 6.5 to 9.1 %. CDT while the Pebble Creek thermal waters fall within a range of 13.7 to 14.3%. (Table 9). The 6%. difference between these two ranges indicates quite separate sources of sulphate in the reservoirs. However, the narrow range of values for each thermal pool (± 1.5%. and ± 0.5 for Meager and Pebble Creek thermal waters respectively) implies a significant degree of consistency in the sulphur source which justifies the use of the sulphate-water geothermometer.

Two principal sources of sulphate in water are mantle derived H_2S and SO_2 ($\delta^{34}S \sim 0\%$ CDT; Nakai et al., 1967; Faure, 1977; Figure 13) which are oxidized to SO_4^{2-} and solution of marine sulphates for which the $\delta^{34}S$ value has varied over the past 400 my between + 10 and + 35%. CDT (presently marine suphates are $\sim + 20\%$; Faure, 1977).

These values can readily become altered in geothermal systems, however, by fractionation between various sulphur components at the vent (Rafter et al; 1958). Fractionation also occurs as a result of bacteriological activity which can oxidize H_2S to form S^0 and SO_4^{2-} , often accompanied by a drop in pH to values as low as 1.0, or reduce SO_4^{2-} , under anaerobic conditions, to form H_2S (Rafter et al., 1960;



Faure, 1977). This fractionation is often evident by high δ^{34} S values (enrichments of up to 20%, with respect to H₂S; Faure, 1977) in the sulphate and by the presence of H₂S. However, because SO₄²⁻ is the only sulphur species detected at any of the discharge sites at Mount Meager and because of the moderate δ^{34} S values and pH's, it is unlikely that any chemical or biological fractionation is occuring at or near the surface in these thermal waters.

The rather intermediate 34 S compositions (average $\sim 10\%$, CDT) found in all the thermal waters at Mount Meager likely reflect a combined input of sulphur from volcanogenic gases and marine sulphates. The latter may have been incorporated from the local pre-Tertiary metasedimentary rocks through leaching by geothermal waters. Varying inputs to thermal reservoirs from these sources would, then, account for the differences in δ^{34} S values determined for the Meager Creek and Pebble Creek thermal water pools. Furthermore, assuming this mixing occurs within the reservoir and biological fractionation (for which no evidence exists) does not occur, then the temperature estimates calculated with the sulphate-water geothermometer can be considered valid. Mixing of thermal and cold groundwaters

Fundamental to the application of the geothermometers is an assumption that the thermal waters have experienced no mixing with near surface cold groundwaters of a different chemical or isotopic nature. There is evidence that both the Meager Creek and Pebble Creek thermal waters have experienced some mixing, but the degree may be insufficient to affect the temperature estimates.

From before, we can assume the Meager Creek and Pebble Creek thermal waters to be of separate origins and therefore, evidence for mixing in the Meager Creek thermal waters cannot be used for the Pebble Creek hot springs. The only evidence, then, for mixing at the Pebble Creek hotsprings are the small amounts of tritium present which can be attributed to a minor component of near surface groundwaters.

Because the Meager Creek thermal waters discharge from several hotsprings and artesian drillholes, the variations in their chemistries and isotope contents can be used to illustrate the effects of mixing. The chloride ion is considered to be conservative and hence, has been used as an indicator of subsurface mixing (McKenzie and Truesdell, 1976; Mazor et al., 1979) by plotting its concentration vs. major ion concentrations, δ^{18} 0 values or temperature for a series of hotsprings discharging from a geothermal system. Assuming that the effects of mixing are simply dilution of the thermal waters, then the plotted points should follow a straight line with the origin representing 100% shallow groundwaters, while springs further along the line represent less diluted thermal waters. This method assumes that only two end member water types are being mixed rather than three or more unique

waters, which is considered to be valid assumption for the Mount Meager setting.

This has been done for the major discharges of Meager Creek thermal waters (Figure 14) and the resulting relationships demonstrate there to be varying degrees of mixing in these hotsprings and boreholes. Drillhole 75-H-1, which discharges at 10.1° C, has only a trace Cl⁻ and is generally low in all major ions, represents groundwaters with no thermal component. The Placid hotsprings exhibit the least amount of mixing and appear to most closely represent the true geothermal waters in this area. This observation is substantiated by the tritium concentrations in these springs which are below detection. Both EMR-1 and the Meager Creek hotspring discharges have detectable tritium, substantiating figure 14 which demonstrates them to contain an estimated 10-15% cold groundwaters. No Good warm spring vent #2 appears to comprise in excess of 50% cold shallow groundwaters while vent #1, despite its anomalously high Cl⁻, appears intermediary between vent #2 and the Placid hotsprings.

Drillholes 79-H-1 and 74-H-1 do not fit the above mixing relationships. Drillhole 79-H-1 has very low Cl⁻ and Na⁺ concentrations and thus, appears unrelated to the Meager Creek hotspring waters. Furthermore, it has tritium concentrations in the range of that for cold spring waters (Table 3) and has a moderate temperature (28°C). These waters appear, then, to be modern near surface groundwaters which have been warmed by the steep geothermal gradient in the area.

Drillhole 74-H-1 (347.5 m depth) discharges briney thermal waters with major ion concentrations far above those in any of the



Figure 14. Major ions, δ^{18} O and temperature as a function of Cl⁻ concentration for hotsprings and artesion boreholes along Meager Creek. Mixing of thermal and cold ground-waters is shown with borehole 75-H-1 and Placid Hotsprings representing the mixing end members.
other thermal water discharges (Table 1). However, a chemical analysis on artesian water encountered during drilling above the 267 m depth (Nevin et al., 1975) indicates these waters to be chemically similar to the Meager Creek hotsprings. The thermal waters discharging from this drillhole, then, appear dominated by a saline zone which exists below the zone through which flow the Meager Creek thermal waters. The latter zone is considered, on the basis of drill core data, to be the highly fractured bedrock surface which likely controls the lateral, down gradient, outflow of thermal waters seen in the resistivity anomaly (Figure 2).

These relationships show, then, that the major discharges of hot geothermal waters have likely experienced only minor mixing. Furthermore, they are likely to be diluted by waters of Meager Creek or the Lillooet River, along which they discharge and for which the concentrations of SO_4^{2-} and other major ions are low (Hammerstrom and Brown, 1977; see appendix C). Hence, the temperature estimates for most hotsprings and boreholes are not likely to be significantly affected by mixing. The estimates for the No Good warm springs and drillhole 79-H-1, however, should be regarded with skepticism.

Geothermometry

In the exploration for geothermal resources, the only direct method of determining subsurface temperatures is through down hole measurements. However, to get estimates of subsurface temperatures without the commitment that drilling involves, attempts have been made in the past two decades to develop a series of chemical and isotopic geothermometers which require only laboratory analysis of geothermal fluids or gases. (McKenzie and Truesdell, 1977; Fournier and Truesdell, 1973; Fournier and Row, 1966; D'Amore and Panichi, 1980).

In the present study, several of these geothermometers have been applied to the Mount Meager geothermal system with rather consistent results despite the inherent uncertainties of applied aqueous geothermometry.

The Na-K-Ca Geothermometer

Studies on Na⁺ and K⁺ species in hot water systems suggest that the alkali concnetrations are controlled by equilibria with K-feldspars, albite and K-micas (White 1965; Ellis and Mahon, 1967). Fournier and Truesdell (1973) suggested that Ca^{2+} in high concentrations also plays a role in alkali-mineral exchange reactions and derived a semiempirical equation defining the equilibrium constant, K, where:

$$\log K = \log \frac{(Na^{+})}{(K^{+})} + \beta \log \frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^{+})}$$

where
$$\beta = \frac{1}{3}$$
 when $\log \frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^{+})}$ is negative

and
$$\beta = \frac{4}{3}$$
 when $\log \frac{(Ca^{2+})^{\frac{1}{2}}}{(Na^{+})}$ is positive

Shikazono (1976) has attempted to develop a thermodynamic basis for this relationship, and concludes that at elevated temperatures, the basic chemistry of most thermal waters is indeed controlled by feldspars, calcite and associated clay minerals. Log K values, calculated with this equation were then compared to measured temperature from known geothermal fields, resulting in the relationship graphically shown in Figure 15.

This formula was applied to chemical data obtained in this study (Table 1) and the resulting log K values are also plotted on Figure 15. They indicate a range of subsurface temperatures for Meager Creek thermal waters of $184^{\circ} - 200^{\circ}$ C and for Pebble Creek thermal waters of $139^{\circ} - 140^{\circ}$ C. As will be discussed later, the sulphate geothermometer indicates temperatures ranging between $73^{\circ} - 141^{\circ}$ C for the Meager Creek thermal waters and $108^{\circ} - 136^{\circ}$ for the Pebble Creek thermal waters. These temperatures are significantly lower than those determined using the Na⁺ -K⁺ - Ca²⁺ geothermometer.

Reconciling these differences, however, is a magnesium correction factor determined by Fournier and Potter II (1979). They suggest that high magnesium contents in thermal waters play a role in these equilibria and hence must be corrected for. The correction factor is determined by using the equation:

$$R = \frac{(Mg^{2+})}{(Mg^{2+}) + (Ca^{2+}) + (K^{+})} \times 100$$

and a set of empirical curves (Figure 16) to determine a temperature value which must be subtracted from the calculated $Na^+ - K^+ - Ca^{2+}$ estimate. The resulting temperatures show much better agreement with the estimates of other geothermometers and are summarized in Table 8.



Figure 15. Na-K-Ca Geothermometer shown with data from this study.



Figure 16. Correction curves for the Na-K-Ca geothermometer with corrections for temperatures presented in the study (Fournier and Potter II, 1979).

Table 8. Compilation	of all ge	othermomet	er tempe	rature e	stimates		
Sample Location			Tempera	ture °	Celcius		
	Measured	504-H ₂ 0	cac0 ₃ -	cac0 ₃ -	Mg-Na-	Stite	ca
			00	Н,0	K-Ca	Chalc.	Qtz
Hotsprings			- - -	 			
Meager Creek Hotsprings Main Vent	50.1	<u>9</u> 8	t	ı	77	147	164
Vent #19	49.8	*	L	ł	82	136	156
Placid Hotspring Vent #2	45.1	pu	ł	1	94	134	153
No Good Warm Spring Vent #1	38.8	121	1	I	96	126	148
Vent #2	29.5	116	1	8	66		137
Pebble Creek Hotspring Main Vent	59.8	136	62	48	105	95	124
Vent #7	56.5	135	1	1	104	87	118
Drillholes							
EMR]	58.5	87	ł	1	64	142	160
74-H-1	50.5	73	1	1	40	113	138
75-H-1	10.1	pu	8	ł	46	18	40
79-H-1 60-68 m (artesian water)	28.0	*	ı	8	85	37	74
90.5 m (fracture calcite)	53	pu		20	nd	pu	pu
185 m (fracture calcite)	92	pu	67	86	pu	nd	pu
262.5m (fracture calcite)	128	pu	, 7 0	95	pu	nđ	pu.
Regional Hotsprings		ł				0	
Mount Cayley Hotspring	28.8	78	88	18	49	103	131
Mount Cayley Cold Spring	15.0	nd	46	-1.2	52	90	121
Skookumchuck Hotspring	54.5	79		1	nd	pu	nd.
Sloquet Hotspring	66.2	72	ł	ł	pu	pu	pu
Harrison Hotspring	67.0	98	I	ł	pu	pu	pu

.

nd = not determined

- = no calcite sampled

* = inconsistent results

The Sulphate-Water Geothermometer

w

The distribution of oxygen-18 between dissolved sulphate and water is temperature dependent and has been determined experimentally (Lloyd, 1968; Mitzutani and Rafter, 1969; Mitzutani, 1972). The equation defining this relationship is:

here:

$$\alpha = \frac{\delta^{18} O_{SO_4} - H_2 O}{\delta^{18} O_{SO_4} + 1000}$$
(Mitzutani and Rafter, 1969)
(Mitzutani and Rafter, 1969)

In the low temperature environment, the exchange reaction is very slow, but in most geothermal systems it is rapid enough to ensure isotopic equilibrium. McKenzie and Truesdell (1976) estimate that it will take 2 years at 300°C and 18 years at 200°C and pH of 7 for 99.9% isotopic exchange, assuming a first order reaction. Therefore, re-equilibration during the ascent of geothermal fluids due to cooling is probably unimportant.

Provided, then, no gypsum dissolution or precipitation takes place and/or H_2S is not being produced, the waters will have a good stable memory of the reservoir temperature. As discussed above, there was no H_2S detected at any thermal water discharges. Also, the waters are well undersaturated with respect to gypsum (Table 2) and, therefore, it is unlikely that they are actively dissolving or precipitating this mineral. If gypsum existed as a fracture mineral, it would unlikely have persisted for any length of time with these waters.

Sulphate samples collected at various discharges of Mount Meager

thermal waters were analyzed for their ${}^{18}0/{}^{16}0$ ratios and with the $\delta^{18}0$ values for the sample waters, the respective fractionation factors, α , were determined (Table 9). These have been plotted on the experimentally derived fractionation curve (Figure 17) to determine the temperature of equilibration for each sample. Measured water temperatures and calculated reservoir temperatures are compared and it can be seen that the calculated temperatures exceed the measured temperatures indicating cooling of the thermal waters during ascent from the reservoir. Furthermore, these calculated values indicate that the temperatures which exist at depth are likely below about 140° C.

The calculated temperatures for the Mount Cayley Hotsprings and the hotsprings along the Lillooet Valley indicate these areas to have lower subsurface temperatures than Mount Meager.

The Water - Calcite Geothermometer

Equilibrium fractionation of oxygen-18 between water and precipitated calcite is also a temperature dependent reaction and under favourable circumstances can be used to substantiate the temperatures derived from the sulphate-water geothermometer. Unlike the sulphate geothermometer, in which the exchange reaction takes place between two aqueous phases, the oxygen exchange between water and calcite takes place between an aqueous and a solid phase. As a consequence, the calculated temperature will reflect equilibrium at the sampling point and not in the reservoir, and is restricted to hotsprings and drill core with calcite deposits.

It assumes, however, that the isotopic composition of the water

Table 9.	Sulphate	- water ¹⁸) geothermon	leter calcul	ations		
Sample Site	\$04 ²⁻	δ ¹⁸ 0 _{H2} 0	δ ¹⁸ 0504	1000 ln ¤	6 ³⁴ S504	Temper	ature ^o C
	(mqq)	%° SMOM	%° SMOW		%° CDT	Measured	Calculated
Hotsprings							
Meager Creek Hotsprings Main Vent	122	-16.4	+2.1	18.6	7.2	50.1	98
Vent #19	130	-16.2	1	}	9.1	49.8	8 9
No Good Warm Springs Vent #1	114	-16.1	-0.3	15.9	7.4	38.8	121
Vent #2	69.0	-17.2	-1.0	16.3	6.5	29.5	116
Pebble Creek Hotsprings Main Vent	288	-19.5	-5.3	14.3	13.7	59.8	136
Vent #7	316	-19.6	-5.3	14.4	14.3	56.5	135
Boreholes							
EMR-1	182	-16.2	+3.7	20.0	7.1	58.5	87
74-H-1	2370	-15.6	+6.3	22.0	9.1	50.5	73
Regional Hotsprings							
Mt. Cayley Hotsprings	1178	-15.7	+5.4	21.3	12.2	28.8	78
Skookumchuck Hotsprings	413 ¹	-17.6	+3.3	21.1	9.8	54.5	79
Sloquet Hotsprings	360	-15.5	+6.6	22.2	13.8	66.2	72
Harrison Hotsprings	512 ¹	-14.3	+4.1	18.5	14.6	67.0	98

lSouther and Halstead (1973)
-- inconsistant results



is known. For "old" calcites, such as collected from fractures in boreholes, the δ^{18} 0 of the precipitating groundwaters may differ from present ones and, therefore, these temperatures may be rather unreliable.

The experimentally derived equation defining the equilibrium exchange reaction is:

1000 ln α = 2.78 (10⁶/T²) - 3.39 (0'Neil et al., 1969)

where:

$$\alpha = \frac{\delta^{10}O_{H_2O} + 1000}{\delta^{18}O_{CaCO_3} + 1000}$$

10

Samples of calcite from Mount Meager include sinter deposits from both hot and cold springs and hydrothermal crystals taken from fractures in drill core. Their ¹⁸0 and ¹³C contents are summarized in Table 10. Calculated temperatures are plotted on the fractionation curve (Figure 18) and are shown with tie lines to measured water temperatures at the sampling point. The measured temperatures plotted for drill hole 79-H-1 were actual rock temperatures encountered during drilling and not necessarily the temperature of the water from which the fracture calcite was precipitated. Also the waters used for this relationship in 79-H-1 were from an artesian zone at 60-68 m depth.

Isotopic equilibrium between water and precipitating $CaCO_3$ requires increased time at decreased temperatures but even in the temperature range of 50 - 100° C, the reaction requires only days rather than years as does the SO₄ - H₂O oxygen exchange reaction (O'Neil et al., 1969). This is reflected by the hot and cold spring data for which the difference between measured spring temperatures and calculated tempera-

Table 10. δ^{13} C and δ^{18} O composition of calcite precipitates at spring vents and in drill core

Sample Location	5 ¹³ € ‰ PDB	6 ¹⁸ 0 % PDB
Hotsprings		
Pebble Creek Hotsprings Main Vent	-3.4	-26.2
Mount Cayley-Hotspring	+0.5	-16.6
Cold Springs		
Boundary Creek Cold Spring #4	-8.2	-23.3
CaCO ₃ Cold Spring #1 #4 terrace	+2.3 -1.1 -0.3	-13.0 -14.9 -14.4
Moria Cold Spring #1	-3.5	-15.7
Rivendell Cold Spring #2	-3.2	-15.4
Problem Cold Spring #1	-0.5	-13.6
Mount Cayley Cold Spring	+3.2	-11.9
Drill Core		
<pre>79-H-1 70 m (aphanitic calcite) 90.5 " 146 " 185.5 (euhedral calcite crystals) 207.7 (aphanitic calcite) 262.5 (euhedral >2 mm dia) 294.3 (aphanitic calcite) 307.7 " 78-H-1 325.9 "</pre>	-5.8 -8.0 -4.2 -8.2 =4.9 -6.9 -8.9 -6.2	-22.1 -18.2 -22.3 -28.7 -22.0 -29.7 -21.2 -22.7 -26.9



tures are all less than 15 C^o and average close to 7 C^o (Table 8). Conversely, the calculated $SO_4 - H_2O$ temperatures for the cold springs are much higher than the measured temperatures. Evidently a significant disequilibrium exists in this case because the sulphate is likely from a deeper source or has not had sufficient time to attain isotopic equilibrium with these cooler waters.

Of the 79-H-1 data, the samples at depths 185.5 m and 262.5 m were euhedral crystals up to 0.5 cm in size, reflective of a hydrothermal precipitation for which calculated temperatures are in good agreement with the Na-K-Ca geothermometer (Table 8). The remaining drillhole samples were generally aphanitic calcite with associated quartz and clay, possibly related to past metamorphic events rather than representing recent hydrothermal deposits. Their calculated temperatures, then, would, not be expected to reflect an equilibrium hydrothermal precipitation reaction which is clearly substantiated by the discrepancy between their measured and calculated temperatures.

The Carbon Dioxide - Calcite Geothermometer

This geothermometer is based upon the temperature dependence of the carbon-13 fractionation in the exchange reaction between $CO_2(g)$ and $CaCO_3$. It is presented here to substantiate the temperatures derived from the sulphate-water geothermometer and is possibly more reliable than the $CaCO_3-H_2O$ geothermometer because the carbon reservoir was was not subject to changes in isotopic composition as can be expected for the water in the system. However, like the $H_2O - CaCO_3$, the calculated temperature is for the time and location of precipitation of

the calcite and not for the time of sampling.

The equilibrium exchange reaction equation has been determined experimentally to be:

1000 ln
$$\alpha$$
 = 2.9880(10⁶/T²) + 7.6663 (10³/T) - 2.4612
(Bottinga, 1968)

where
$$\alpha = \frac{\delta^{13}C_{CO_2} + 1000}{\delta^{13}C_{CaCO_3} + 1000}$$

The $\delta^{13}C_{CO_2}$ values have been calculated (Table 8), as described above, using the carbonate speciation, the ^{13}C enrichment factor for the carbonate species in isotopic equilibrium with CO_2 and the analysed carbon-13 value for the dissolved inorganic carbon (DIC) of the sample. The results of these calculations are graphically represented in Figure 19.

The calculated temperatures for the hotsprings and calcite precipitates in drill hole 79-H-1 demonstrate that, in most cases, ¹³C equilibrium between $\text{CO}_2(g)$ and CaCO_3 does not exist at the measured temperatures. If this disequilibrium existed at the time of calcite precipitation, then the calculated temperatures may reflect conditions deeper in the system. Conversely, if these were equilibrium reactions, then there may be an error introduced by assuming that $\text{CO}_2(g)$ of a single isotopic composition ($\delta^{13}C_{\text{CO}_2} = -9.2$ % PDB; Table 7) has equilibrated with all the precipitated calcite minerals sampled. Nonetheless, there are no indications by this geothermometer, that temperatures in excess of 140° C may exist at depth.



The cold spring data also demonstrates a disequilibrium precipitation reaction. Calcite precipitation is caused by degassing of CO_2 as the waters discharge, causing a rise in pH and supersaturation of $CaCO_3$. In this process, precipitation is faster than equilibration with respect to ^{13}C resulting in a substantial disequilibrium (Usdowski et al., 1978), which is demonstrated by the higher calculated temperatures for cold springs in Figure 19.

Silica Geothermometer

The increased solubility of quartz and its related polymorphs at elevated temperatures has been well documented (Kennedy, 1950; Kitahara, 1960; Morey et al., 1962; Fournier and Rowe, 1962; Figure 20). Furthermore the rates at which dissolution and precipitation reactions take place are increased at elevated temperatures. Experimental work by Morey et al. (1962) has shown that above about 150°C, equilibrium is rapidly attained but below this temperature quartz precipitation is very sluggish. In many geothermal systems, hot water at depth attains equilibrium with quartz or chalcedony and, due to cooling during ascent and the relatively slow precipitation reactions at lower temperatures, becomes supersaturated at the discharge point. The concentration of silica in solution at the discharge point then should reflect the temperature at which equilibrium with quartz or chalcedony has taken place. Difficulties are encountered, however, if steam separation occurs, which concentrates the silica in solution. Also, mixing with cold groundwaters can either dilute the dissolved silica or quench the thermal waters which encourages precipitation of amorphous silica and thus, calculated temperatures will be too low.

The silica geothermometer has been applied with good success



in high temperature geothermal areas by Fournier and Rowe (1966) using a model to account for steam separation during the ascent and cooling of the thermal waters. Borehole temperatures have confirmed such estimates and equilibrium with quartz at depth was concluded.

Low temperature systems have also been investigated, using the silica geothermometer. Mazor et al. (1980) has found good correlation between hotspring temperatures and calculated temperatures assuming equilibrium with chalcedony and/or quartz and concludes that these springs are fed by waters from rather shallow low temperature aquifers. Arnorsson (1976) has also used this geothermometer in low temperature geothermal areas in Iceland and concludes that above $180^{\circ}C$ quartz equilibrium dominates, below $110^{\circ}C$ equilibrium with chalcedony takes place and between $110-180^{\circ}C$ equilibrium with either polymorph may occur.

The Meager Creek thermal waters have fairly high concentrations of silica in solution which renders temperature estimates between $137^{\circ}C$ and $164^{\circ}C$ assuming quartz equilibrium and 111° to $147^{\circ}C$ assuming equilibrium with chalcedony. The Pebble Creek hotsprings have somewhat lower dissolved silica concentrations with temperature ranges of 118° – $124^{\circ}C$ and 87° – $95^{\circ}C$ for quartz and chalcedony equilibrium respectively (Table 8). The Meager Creek thermal water temperature estimates appear, then, to be somewhat higher than those predicted by the previously discussed geothermometers although the Pebble Creek hotsprings show good correlations with previous estimates. It is then interesting to note that the waters discharging from the Meager Creek, Placid and No Good thermal springs and EMR-1 and 74-H-1 drill holes are near saturation with respect to amorphous silica (Figure 20), which is being deposited at the hotspring vents and on the casing of 74-H-1. The close correlation between these discharges and the solubility line of amorphous silica suggests that these waters are in equilibrium with an amorphous silica phase in the near surface environment rather than with quartz or chalcedony at depth. Furthermore, high silica concentrations can be also controlled by the incongruent alteration reactions of feldspars and hornblende to clay minerals (Fournier and Rowe, 1966; Stumm and Morgan, 1977, p. 397) with the concommitant release of silica. The clay by-products of these reactions have been noted in drill core at Mount Meager by Read (1975). Because the dissolved silica concentrations in the Meager Creek thermal waters appear to be controlled by more than simple equilibrium with quartz or chalcedony, these temperature estimates should be viewed with some skepticism.

Silica concentrations in the Pebble Creek thermal waters are considerably lower than amorphous silica solubility (Figure 20), implying equilibrium with chalcedony or quartz at depth, and thus, the calculated silica temperatures appear quite reasonable.

Most cold springs at Mount Meager have low (< 10 ppm) silica contents reflecting equilibrium with quartz in the low temperature environment. However, Fall Creek and 78-H-1 cold springs have silica contents of 52.8 and 36.5 ppm respectively, which are much higher than would be expected for quartz equilibrium at low temperatures. These high concentrations are most likely due to leaching from the glassy volcanic ash deposits.

In conclusion, despite the uncertainties regarding the reactions which control the silica concentrations, the temperature estimates of the silica geothermometer are in agreement with other geothermometers in offering no evidence for high temperatures at depth.

SUMMARY AND CONCLUSIONS

Origin and History of Thermal Waters

All chemical and environmental isotope data indicate that the Meager Creek and the Pebble Creek thermal waters discharge from completely separate geothermal reservoirs. The Meager Creek thermal waters, corrected for a positive shift in ¹⁸0 contents, have an isotopic composition similar to the average annual precipitation above approximately 1000 m elevation, as determined from cold spring data. The Pebble Creek thermal waters, also corrected for a positive ¹⁸0 shift, are considerably more depleted in ¹⁸0 and ²H than the Meager Creek thermal waters, reflecting a different recharge zone at higher elevations.

The Meager Creek thermal waters have experienced an ¹⁸0 shift of between +1.0 and +1.5 %, through oxygen exchange with hot silicate minerals in the reservoir. The Pebble Creek thermal waters have experienced less exchange, and are shifted by as little as +0.5 %. These shifts are considerably less than have been found at known geothermal fields, indicating that subsurface temperatures at Mount Meager are probably less than 150°, a temperature above which significant exchange is expected to take place.

Mixing of geothermal waters and shallowly circulating groundwaters has been shown to take place at Mount Meager, undoubtedly due, in part, to the location of the thermal discharges in or proximal to major regional discharge channels. The hotsprings have been estimated to contain between 10 and 15% cold groundwaters. This mixing is, apparently, insufficient to seriously affect the geothermometric estimates.

The majority of cold springs at Mount Meager discharge from seasonally variable, shallow flow systems and show a correlation between altitude and lighter isotope contents. The lower altitude cold springs,

- 80 -

including the $CaCO_3$ and Problem cold springs are unique in that they show no seasonal variation and hence, discharge flow systems of sufficient circulation time to ensure mixing of seasonally varying meteoric waters. The ¹⁸O and ²H contents of these waters must, then, represent the average annual precipitation falling above the altitude of these springs.

Dating of Thermal Waters

Tritium contents in the thermal waters are considered to be due to the small degree of mixing with shallow groundwaters. Hence, the thermal waters are tritium free, indicating rechage prior to at least 1955. Carbon-14 activities in the thermal waters are very low, implying unrealistically old ages. However, a survey of partial pressure and δ^{13} C data for dissolved CO₂ and bicarbonate and for calcite precipitates demonstrates there to be a considerable input of volcanogenic CO₂ in the thermal waters as well as exchange of carbon with hydrothermal minerals. These contributions of "dead" carbon have been responsible for the low 14 C activities and therefore, a realistic age estimate for these waters is impossible.

Geothermometry

Reservoir temperature estimates from the geochemical and isotopic geothermometers consistently indicate the Meager Creek and Pebble Creek thermal waters to have experienced only moderate heating. Offering the most confidence in their estmates are the Mg-Na-K-Ca geothermometer (40-105°C) and the SO_4-H_2O geothermometer (73°-136°C), as demonstrated by the excellent correlation in Figure 21. Although the $SO_4 - H_2O$ estimates are consistently 20-30° higher



Figure 21. Correlation between SO4 - H₂O and Mg-corrected Na-k-Ca geothermometers. The line fitted to the data has a 1:1 slope.

Table 11. Comparison of geothermometer

Geothermometer	Meager Creek Thermal Waters	Pebble Creek Thermal Waters
Measured	30 - 50°C	56 - 60°C
so ₄ - H ₂ 0	73 - 116°C	135 - 136°C
Mg-Na-K-Ca	40 - 99°C	104 - 105°C
CaCO ₃ - H ₂ O	20 - 95°C	48°C
$CaCO_3 - CO_2$	67 - 111°C	79°C
SiO ₂ - Chalcedony	113 - 147°C	87 - 95°C
-		

temperature estimates

than the Mg-Na-K-Ca estimates, the relationship follows a 1:1 slope which generates a significant degree of confidence. Despite the uncertainties of the source of dissolved silica and the possibility of equilibrium with an amorphous silica phase in the subsurface, the silica geothermometer estimates $(37^{\circ}-147^{\circ}C$ for equilibrium with chalcedony), fit the range of temperatures determined with the above two geothermometers and substantiate the estimates of moderate temperatures at depth. The $CaCO_3^{-}H_2^{0}$ and $CaCO_3^{-}CO_2$ geothermometers have estimated temperatures for the various depths of sampling in the drill hole 79-11-1 to be less than approximately $100^{\circ}C$. Apparently, during the precipitation of these hydrothermal calcites, moderate temperatures existed in the system. These estimates are roughly correlative with downhole temperatures measured during drilling and fall within the range of estimates of the above geothermometers.

As summarized by Table 11, all the chemical and isotopic geothermometers consistently indicate that neither the Meager Creek or Pebble Creek thermal waters have passed through reservoirs with temperatures in excess of 140°C.

The application of this series of geothermometers to the thermal waters of Mount Cayley has demonstrated these waters to have experienced no temperatures in excess of 100°C. Like Mount Meager, then, Mount Cayley thermal waters have undergone only moderate heating in the subsurface.

All isotopic and chemical evidence indicates that the Meager Creek and Pebble Creek thermal waters are part of separate, shallowly circulating geothermal systems of limited heat capacity. However, this does not preclude the possibility that a more significant heat source

exists at greater depths beneath Mount Meager. Discharging gases of an apparent volcanic origin may be related to such a heat source and thus verify its existence. Furthermore, drilling in the 1979 season, as discussed above, has found temperatures well in excess of the estimates provided in this study. However, because no thermal water or steam has been found at these depths, this thermal reservoir may have insufficient permeability to permit appreciable circulation of meteoric waters. In this case, the innovative techniques of "hot dry rock" geothermal power generation may prove to be better suited to the Mount Meager area than are the more conventional geothermal technologies.

REFERENCES

- Arnasson, B., 1976. The hydrogen-water isotope thermometer applied to geothermal areas in Iceland. Geothermics, 5:75-80.
- Arnasson, B., 1976. Hydrothermal systems in Iceland traced by deuterium. Geothermics, 5:125-151.
- Barker, J.F., 1979. Methane in groundwater a carbon isotope geochemical study. Ph.D. thesis, University of Waterloo, Waterloo, Ontario, 310 pp.
- Barnes, I., Irwin, W.P. and White, D.E., 1978. Global distribution of carbon dioxide discharges, and major zones of seismicity. U.S.G.S. Water-Resource Investigations, 78-39, open file rep., 12 pp.
- Bottinga, Y., 1968. Calculated fractionation factors for carbon and oxygen isotopic exchange in the system calcite-carbon dioxidewater. Jour. Phys. Chem., 72:800-808.
- Brown, R.M., 1961. Hydrology of tritium in the Ottawa Valley. Geochim. Cosmochim. Acta, 21:199.
- Clayton, R.N., Friedman, I., Groff, D.C., Mayeda, T.K., Meents, W.F. and Shimp, N.F., 1966. The origin of saline formation waters, 1, Isotopic composition. Jour. Geophys. Res., 71:3869-3882.
- Craig, H., 1963. The isotopic geochemistry of water and carbon in geothermal areas. In: Tongiorgi, E. (Editor), <u>Nuclear Geology</u> on <u>Geothermal Areas</u>, <u>Spoleto</u>, <u>Sept. 9-13</u>, <u>1963</u>. Consiglio Nazionale dell Ricerche, Laboratorio di Geologia Nucleare, Pisa, pp. 17-53.
- Craig, H., 1966. Isotopic composition and origin of the Red Sea and Salton Sea geothermal brines. Science, 154:1544-1548.
- Craig, H., Boato, G. and White, D.E., 1965. Isotopic geochemistry of thermal waters. Natl. Res. Council Publ., 400:29-38.
- D'Amore, F. and Panichi, C., 1980. Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer. Geochim. Cosmochim. Acta, 44:549-556.
- Deines, P.D., Langmuir, D. and Harmon, R.S., 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate groundwaters. Geochim. Cosmochim. Acta, 38:1147-1164.
- Egboka, B.C.E., 1980. Bomb Tritium in shallow sand aquiters. Ph.D. thesis, University of Waterloo, Waterloo, Ontario, 197 pp.

- Ellis, A.J. and Mahon, W.A.J., 1967. Natural hydrothermal systems and experimental hot water/rock interaction, (Part II). Geochim. Cosmochim. Acta., 37:1255-1275.
- Epstein, S. and Taylor, H.P. Jr., 1967. Variations of ¹⁸0/¹⁶0 in minerals and rocks. In: <u>Researches in Geochemistry</u>. P.H. Abelson (editor), John Wiley, New York, 2:29-62.
- Faure, G., 1977. <u>Principles of Isotope Geology</u>. John Wiley and Sons, Inc., New York, 464 pp.
- Feenstra, S., 1980. The isotopic evolution of sulphate in a shallow groundwater flow sytem on the Canadian Shield. M.Sc. thesis, University of Waterloo, Waterloo, Ont., 152 pp.
- Ferrara, G.C., Ferrara, G. and Gonfiantini, R., 1963. Carbon isotopic composition of carbon dioxide and methane from steam jets of Tuscany (Italy). In: Tongiorgi, E. (editor), <u>Nuclear Geology</u> on Geothermal Areas, Spoleto, Sept. 9-13, 1963. Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, pp. 275-282.
- Fournier, R.O. and Potter II, R.W., 1979. Magnesium correction to the Na-K-Ca chemical geothermometer. Geochim. Cosmochim. Acta, 43:1543-1550.
- Fournier, R.O. and Rowe, J.J., 1962. The solubility of cristobolite along the three phase curve, gas plus liquid plus cristobolite. Am. Mineralogist, 47:897-902.
- Fournier, R.O. and Rowe, J.J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. Amer. Jour. Sci., 264:685-697.
- Fournier, R.O. and Truesdell, A.H., 1973. An empirical Na-K-Ca geothermometer for natural waters. Geochim. Cosmochim. Acta. 37:1255-1275.
- Fournier, R.O. and Truesdell, A.H., 1974. Geochemical indicators of subsurface temperature - Part 2, Estimation of temperature and fraction of hot water mixed with cold water. Jour. Res. U.S.G.S., 2 No. 3:263-274.
- Fritz, P., Barker, J.F. and Gale, J.E., 1979. Geochemistry and isotope hydrology of groundwater in the Strippa granite. Lawrence Berkely Laboratories, University of California, Report LBL 8285, 135 pp.
- Fritz, P., Reardon, E.J., Barker, J., Brown, R.M., Cherry, J.A., Killey, R.W.D. and McNaughton, D., 1978. The carbon-isotope geochemistry of a small groundwater system in northeastern Ontario. Water Resour. Res., 14:1059-1067.

- Gat, J.R., 1980. The isotopes of hydrogen and oxygen in precipitation, Chapter 1. In: Handbook of Environmental Isotope Geochemistry, Volume 1, The Terrestrial Environment, A., Fritz, P. and Fontes, J.C. (editors), Elsevier, 1980, Amsterdam, pp. 21-44.
- Grosse, A.V., Johnston, W.M., Wolfgang, R.L. and Libby, W.F., 1951. Tritium in nature. Science, 113:1-2.
- Gunter, B.D. and Musgrave, B.C., 1971. New evidence on the origin of methane in hydrothermal gases. Geochim. Cosmochim. Acta, 35:113-118.
- Hammerstrom, L.T. and Brown, T.H., 1977. The geochemistry of thermal waters from the Mount Meager Hotsprings Area, B.C. Geol. Surv. of Canada, Open File Report, 34 pp.
- Harhed, H.S. and Davis, R. Jr., 1943. The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°C. Jour. Amer. Chem.Soc., 65:2030-2037.
- Holt, B.D., 1977. Preparation of carbon dioxide from sulphate, sulphur dioxide, air and water for the determination of oxygen isotope ratio. Analytical Chemistry, 49:1664-1667.
- Hulston, J.R., 1976. Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand. Geothermics, 5:89-96.
- Kennedy, G.C., 1950. A portion of the system silica-water. Econ. Geol., 45:629-653.
- Kitahara, S., 1960. Polymerization of silicic acid obtained by the hydrothermal treatment of quartz and the solubility of amorphous silica. Rev. Phys. Chem., Japan, 43:131-137.
- Lewis, T.J. and Souther, J.G., 1978. Meager Mountain, B.C. A possible geothermal energy resource. Geothermal series number 9, Earth Physics Branch, Energy, Mines and Resources, Ottawa, Canada, 17 pp.
- Lloyd, R.M., 1968. Oxygen isotope behaviour in the sulphate-water system. Jour. Geophys. Res., 73:6099-6110.
- McKenzie, W.F. and Truesdell, A.H., 1976. Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulphate and water from hot springs and shallow drillholes. Geothermics, 5:51-61.
- Michel, F.A. and Fritz, P., 1978. Isotope hydrology of the Meager Creek thermal waters. Report for Energy, Mines and Resources, 24 pp.

- Michel, F.A. and Fritz, P., 1979. Isotope hydrology of the Meager Creek thermal waters. Final report for Energy, Mines and Resources, 11 pp.
- Mitzatani, Y., 1972. Isotopic composition and underground temperature of the Otake geothermal water, Kyushu, Japan. Geochem. Jour., Japan, 6:67-73.
- Mitzatani, Y. and Rafter, T.A., 1969. Oxygen isotopic composition of sulphates, 3. Oxygen isotopic fractionation in the bisulphate ion-water system. N.Z. Jour. Sci., 12:54-59.
- Mook, W.G., Bommerson, J.C. and Staverman, W.H., 1974. Carbon isotope fractionation between dissolved biocarbonate and gaseous carbon dioxide. Earth Planet Sci. Letters, 22:169-176.
- Morey, G.W., Fournier, R.O. and Rowe, J.J., 1962. The solubility of quartz in water in the temperature interval from 25 to 300°C. Geochim. Cosmochim. Acta, 26:1029-1043.
- Moser, H. and Stichler, W., 1970. Deuterium measurements on snow samples from the Alps. In: <u>Isotopes in Hydrogeology</u>, Proceed. Symp., I.A.E.A., Vienna, pp. 43-55.
- Nakai, N. and Jensen, M.L., 1967. Sources of atmospheric sulphur compounds. Geochemical Jour., 1:199-210.
- Nasmith, H., Mathews, W.H. and Rouse, G.E., 1967. Bridge River ash and some other recent ash beds in British Columbia. Can. Jour. Earth Sci., 4:163-170.
- Nevin Sadlier-Brown Goodbrand Ltd., 1975. Report on detailed geothermal investigation at Meager Creek, (unpublished) to B.C. Hydro and Power Authority, 18 pp., Appendices.
- Nevin Sadlier-Brown Goodbrand Ltd., 1977. Report on 1976 geothermal investigation at Meager Creek north and northeast flanks of the volcanic complex, (unpublished) to B.C. Hydro and Power Authority, 10 pp.
- Nevin Sadlier-Brown Goodbrand Ltd., 1979. Report on 1978 field work, Meager Creek Geothermal Area, Upper Lillooet River, British Columbia; to B.C. Hydro and Power Authority and Energy, Mines and Resources, Canada, 1978 Joint Venture. 82 pp, Appendicies.
- O'Neil, J.R., Adami, L.H. and Epstein, S., 1975. Revised value for the ¹⁸0 fractionation between CO₂ and water at 25°C. U.S. Geol. Surv. Jour. Res., 3:623-624.
- O'Neil, J.R., Clayton, R.N. and Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. Jour. Chem. Phys., 51:5547-5558.

- Panichi, C., Ferrara, G.C. and Gonfiantini, R., 1976. Isotope thermometry in the Larderello (Italy) geothermal field. Geothermics, 5:81-88.
- Plummer, N.L., Jones, B.F. and Truesdell, A.H., 1976. WATEQF. A FORTRAN IV version of WATEQ. U.S. Geol. Surv. Water Res. Invest. 76-13, 61 pp.
- Rafter, T.A., 1957. Sulphur isotopic variations in nature, Part 1. The preparation of sulphur dioxide for mass spectrometer examination N.Z. Jour. Sci. Tech., Sect. B, 38:849-857.
- Rafter, T.A., 1967. Oxygen isotopic composition of sulphates Part 1. A method for the extraction of oxygen and its quantitative conversion to carbon dioxide isotope ratio measurements. New Zealand Jour. Sci., 10:493-510.
- Rafter, T.A., Kaplan, I.A. and Hulston, J.R., 1960. Sulphur isotopic variations in nature, Part 7 - Sulphur isotopic measurements on sulphur and sulphates in New Zealand geothermal and volcanic areas. New Zealand Jour. Sci., 3:209-218.
- Rafter, T.A., Wilson, S.H. and Shilton, W.B., 1958. Sulphur isotopic variations in nature, Part 6 - Sulphur isotopic measurements on the discharge from fumaroles on White Island. New Zealand Jour. Sci., 1:154-171.
- Read, P.B., 1975. Drill core alteration and sinters, Appendix F. In: Report on detailed geothermal investigation at Meager Creek. Nevin Sadlier-Brown Goodbrand Ltd., B.C. Hydro and Power Authority, internal report.
- Read, P.B., 1977. Meager Creek Volcanic Complex, southwestern British Columbia. Rep. of Activities, Part A. Geol. Surv. Can. paper 77-1A.
- Rightmire, C.T. and Hanshaw, B.B., 1973. Relationship between the carbon isotope composition of soil CO₂ and dissolved carbonate species in groundwater. Water Res. Research, 9:958.
- Sakai, H. and Matsubaya, O., 1976. Stable isotope studies of Japanese geothermal systems. Geothermics, 5:97.
- Souther, J.G., 1975. Geothermal potential of Western Canada. In: Proceedings, Second United Nations Symposium on the Development and Use of Geothermal Resources, 1:259-267.
- Souther, J.G., 1980. Geothermal reconnaissance in the central Garibaldi Belt, British Columbia. In: Current Res., Part A, Geol. Surv. Can. paper 80-1A, pp. 1-11.

- Souther, J.G. and Halstead, E.C., 1973. Mineral and thermal waters of Canada. Energy, Mines and Resources, paper 73-18, 31 pp.
- Stumm, W. and Morgan, J.J., 1970. <u>Aquatic Chemistry</u>. John Wiley and Sons, Inc., New York, 583 pp.
- Taylor, H.P. Jr. and Epstein, S., 1962. Relationship between 0¹⁸/0¹⁶ ratios in coexisting minerals of igneous and metamorphic rocks, part 1: Principles and experimental results. Geol. Soc. Am. Bull., 73:461-480.
- Thode, H.G., Shima, M., Rees, C.E. and Krishnamurty, K.V., 1955. Carbon-13 isotope effects in systems containing carbon dioxide, bicarbonate, carbonate, and metal ions. Can. Jour. Chem., 43:582-595.
- Truesdell, A.H. and Hulston, J.R., 1980. Isotopic evidence on environments of geothermal systems, Chapter 5. In: <u>Handbook of</u> <u>Environmental Isotope Geochemistry, Volume 1, The Terrestrial</u> <u>Environment, A.</u>, Fritz, P. and Fontes, J.C. (Editors), <u>Elsevier, 1980</u>, Amsterdam, pp. 179-219.
- Usdowski, E., Hoefs, J. and Menshel, G., 1978. Relationship between 13C and 18O fractionation and changes in major element composition in a recent calcite-depositing spring-A model of chemical variations with inorganic CaCO₃ precipitation. Earth and Planetary Science Letters, 42:267-276.
- Vogel, J.C., Grootes, P.M., and Mook, W.G., 1970. Isotopic fractionation between gaseous and dissolved carbon dioxide. Zeitschrift fur Physik, 230:225-238.
- Westgate, J.A. and Dreimanis, A., 1967. Volcanic ash layers of recent age at Banff National Park, Alberta, Canada. Can. Jour. Earth Sci., 4:155-161.
- White, D.E., 1957. Thermal waters of volcanic origin. Geol. Soc. Am. Bull., 68:1637-1658.

APPENDIX A

SAMPLING

SAMPLING

With the aim of conducting an intensive analysis of the hydrogeology, age and subsurface temperatures of the Mount Meager geothermal system, a sampling program was designed to accomodate a spectrum of environmental isotopes and chemistry samples. Samples of spring waters, runoff, precipitation and glacier ice were required for oxygen-18, deuterium and tritium determinations to investigate the recharge, and flow path of the hydrogeological system. Carbon-14 and carbon-13 studies required samples of dissolv ed carbon to study the carbonate system in hopes of determining a realistic age estimate of the thermal waters. Estimation of subsurface temperatures using an isotopic and chemical geothermometer required samples of dissolved sulphate and carbonate, precipitated hydrothermal and sinter calcite as well as basic chemistry samples.

Therefore, two sampling trips were made to Mount Meager during the summer of 1979. The initial sampling trip in June was designed to: a) collect groundwater and surface water samples during the major spring than recharge event. b) collect chemistry and precipitated carbonate and sulphate samples at all thermal water discharges. c) distribute a series of precipitation collectors at varying altitudes to be left for the summer.

The results of this preliminary trip provided a basis from which to design a second trip in August, 1979. The timing of this trip was such that, due to an unusually hot and dry summer, it was possible to sample what could be considered to be the baseflow component of discharge from thermal and cold springs. The focus of the second trip was to:

 a) resample all thermal and cold spring discharges and runoff sampled in June to document their seasonal isotopic and chemical variability; b) collect water from precipitation samples installed in June; c) collect water samples from any artesian zones encountered during the concurrent drilling program; d) collect precipitated carbonate samples from specific thermal water discharges for carbon-14 dating; e) collect hydrothermal calcite samples from available drill core.

Water Samples

Environmental Isotopes

To ensure that water samples suffered no alteration in their 18 O, 2 H and 3 H concentrations between the time of collection and analysis, they were collected in 250 ml plastic Nalgene bottles. Sample bottles were rinsed in the water to be collected, filled to overflowing and tightly capped.

Precipitation samples were collected in ½ gallon jugs fitted with a funnel in the cap and a 1 cm thick layer of liquid parafin inside to prevent alteration of the sample through evaporation.

Chemistry

Samples were collected for standard chemistry in a

1 & plastic bottle and were filtered through a 4" diameter, .45 micron pore size filter paper using a vacuum flask and hand pump. The filter and flask were rinsed with the initial 100-200 m& of sample to avoid contamination. Two 250 m& plastic bottles were filled with the filtered sample, one acidified to a pH of 2 with nitric acid prevent precipitation of metals in solution prior to analysis, and one left unacidified for anion and silica analysis. The remaining filtered sample was used to determine alkalinity (Appendix B).

Carbonate Samples

Aqueous Carbonate

The required minimum of approximately 20 mg carbon, as dissolved carbonate, for ¹³C analysis was secured by collecting 32 of water in plastic Nalgene bottles. The sample was then raised to pH>10 by the addition of NaOH, immediately followed by the addition of BaCl₂ to precipitate the dissolved carbonate quantitatively. The amount of BaCl₂ added was estimated from previous determinations of alkalinity and sulphate in solution in spring waters, using approximately .75 g BaCl₂ per 60 ppm HCO₃⁻ and 100 ppm BaCl₂ per 100 ppm SO₄⁻ (BaSO₄ is insoluble at high pH and will precipitate more easily than BaCO₃). The bottle was then rolled to mix and the precipitate allowed to settle at least overnight before decanting into a 500 ml plastic bottle.

A carbon-14 analysis requires substantially more material than does a carbon-13 analysis and therefore, a 60 ℓ volume of water was collected from which was precipitated the BaCO₃ sample in the manor

described above. Proportionatly more $BaCl_2$ was added (15 g per 60 ppm HCO_3^{-1} and 20 g per 100 ppm SO_4^{-2-}) to ensure the quantitative removal of all carbonate. To prevent contamination during the decanting procedure the intake air was drained through a portion of the stripped sample water to absorbed atmospheric CO_2 .

Calcite

Calcite samples were taken for ¹³C analysis from sinter deposits at cold and hot springs available and from drill core. Drill core calcite samples were often large crystals filling 1-5 mm fracture openings or as an aphanitic fracture coating. A minimum of approximately 100 mg of material was required for analysis.

Sulphate Samples

The 100 mg $BaSO_4$ required for both ${}^{18}O$ and ${}^{34}S$ and analyses was co-precipitated from solution in the sampling procedure for ${}^{13}C$ (see above). Material left following ${}^{13}C$ analysis was acidified to remove all $BaCO_3$ and prepared for analysis as described in Appendix B-3.2.
APPENDIX B

ANALYSIS

ANALYSIS

Field Determinations of Chemical Parameters

Field temperature, pH and alkalinity measurements were taken for all springs and boreholes sampled for major ions. Temperature and pH were taken at the discharge sites and alkalinity titrations were performed a short time later following filtering of the sample (see section B.1.2).

Temperature measurements were made using a standard mercury thermometer and recorded for all discharging vents at each spring site. A pH measurement was taken at the vent or vents of strongest discharge of thermal and cold spring waters at each site. Shut in boreholes were allowed to flow freely for a period of time to stabilize the temperature and pH measurement. The instrument used was a Digimatic Pocket pH meter suitable for field work requiring backpacking. Three buffer solutions with pH's of 4, 7 and 10 were carried with the pH meter and the two buffers closest in pH to the sample were used for calibration. The buffers were submerged in the spring water to raise or lower their temperature to that of the spring to ensure an accurate calibration of the meter, using the recommended buffer pH's for the appropriate temperature. Alkalinity titrations were performed on a 20 ml aliquot of the chemistry sample, filtered through a .45 μ pore size paper (Appendix A-2), pipetted into a plastic titration beaker. The sample was titrated with a solution of .01248 normal $\rm H_2SO_4$ to a pH of 4.3 and converted to an alkalinity value as ppm HCO_3 by the equation:

Alkalinity (ppm HCO₃⁻) =
$$\binom{mls \ a \ cid \ x \ 12.48}{mls \ sample}$$
 x 61

Chemical Analyses

All chemical analyses referenced to this study were done in the aqueous geochemistry laboratory at the University of Waterloo. Samples of thermal and cold groundwaters from springs and boreholes were analysed for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe_{total} , Mn^{2+} , $Si0_2$, $S0_4^{2-}$ and Cl⁻. Cation determinations were done using filtered samples, acidified to pH ~ 2 to prevent the precipitation of heavy metals and anion concentrations were determined on filtered unacidified samples.

Charge balance calculations demonstrated all analyses to be precise to better than an acceptable 10% descrepancy between anion and cation concentrations.

Chemical data were then run through the computer program WATEQ-F (Plummer, 1976) for the determination of ion speciation, activities and saturation indices.

Stable Isotope Analyses

All analyses of stable environmental isotopes were carried out in the Isotope Geochemistry Laboratory at the University of Waterloo and are expressed in the conventional & %。 (per mil) notation referenced to an international standard, where:

$$\delta_{\rm m} = \left(\frac{{\rm R}_{\rm sample} - {\rm R}_{\rm standard}}{{\rm R}_{\rm standard}}\right) \times 1000$$

and $R = \frac{18_0}{16_0}, \frac{2_H}{1_H}, \frac{13_C}{12_C} \text{ or } \frac{34_S}{32_S}$

Oxygen-18 and Deuterium in Water

Oxygen-18 concentrations in water samples were measured using the standard technique of equilibrating CO_2 of known isotopic composition with the sample at 25^oC and analysing the CO_2 gas. The accepted $H_2O - CO_2$ fractionation factor of 1.0412 (O'Neil et al, 1975) was used in the subsequent calculation (Figure B-1). All reported values are precise to better than $\pm 0.15\%$.

Deuterium concentrations in water were measured on hydrogen gas prepared by reducing H_2^0 to H_2 through the oxidation of hot (800°C) uranium. Determinations of $\delta^2 H$ are precise to within $\pm 1\%$.

Both 18 O and 2 H reported as per mil (%,) deviation from SMOW (Standard Mean Ocean Water).

Oxygen-18 in Sulphate

The oxygen-18 concentration in sulphate was analysed for the application of the $SO_4^{2-} - H_2O$ isotopic geothermometer. Samples were analysed as CO_2 prepared according to the graphite-reduction method (Holt, 1977; Rafter, 1967) in which a 20 mg sample of BaSO₄ is mixed with an equal portion of powdered graphite placed in a graphite crucible and decomposed at 1150°C in an induction furnace.



Figure B-1. Relationship between SMOW and PDB scales for expressing oxygen-18 values. The CO₂ - H_2O fractionation factor is used in the determination of $\delta^{18}O$ values in water.

The reaction can be written as:

 $BaSO_4 = excess C \rightarrow BaS + CO_2 + 2 CO + C$

The CO is quantitatively converted to CO_2 by a high voltage created between platinum electrodes in a conversion chamber, cooled to liquid nitrogen temperatures to freeze out the CO_2 . Precipitated $BaSO_4$ samples (Appendix A-3) used in this process were acidified to remove any $BaCO_3$, washed repeatedly by decanting with deionized water to remove dissolved salts, dried at 90°C and heated at 500°C for 2 hours to destroy any organics. For a complete description of the analytical technique, see Feenstra (1980). The resulting à ¹⁸O value from the mass spectrometric analysis, referenced to the Isotope Geochemistry lab working standard (SF prior to April 3 1980, COWS after April 3), can be converted to SMO^H by the following respective formulae:

$$\delta_{\text{SMOW}} = 1027.3 \left(\frac{\delta_{\overline{\text{m}}}}{1000} + 1 \right) - 1000$$

for working standard = SF

$$\delta_{\text{SMOW}} = 1004.5 \left(\frac{\delta_{\text{m}}}{1000} + 1\right) - 1000$$

for working standard = COWS

where
$$\delta_{m} = \left(\frac{R_{sample}}{R_{working standard}} - 1\right) \times 1000$$

Repetative analyses of a bottle of Fisher Scientific Reagent Grade $BaSO_4$ have provided an estimate of reproducability of $\pm 0.5\%$. (Feenstra, 1980).

Sulphur-34 in Sulphate

Sulphur-34 concentrations were determined on samples of $BaSO_4$ precipitated from solution and prepared for analysis according to the procedure outlined above (Appendix A-3). SO_2 gas for mass spectrometric analysis was prepared by the thermal degradation of $BaSO_4$ to BaO with the evolution of O_2 and SO_2 gases. A 50 mg sample of $BaSO_4$, is mixed with an equal weight of ground quartz glass wool and placed in a 4 mm diameter quartz glass tube with a glass wool tamp. This arrangement is then placed in a 6 mm quartz glass tube, attached to a vacuum line and heated to the softening temperature of quartz glass (~ 1200^OC). The evolved SO_2 is purified and transferred into a glass sample vessel for isotope analysis. A complete description of the analytical technique used is provided in Feenstra (1980).

Carbon-13 in Aqueous Carbonate

Aqueous carbonate, precipitated as $BaCO_3$ (Appendix A-2), was analysed for its ¹³C content by conversion to CO_2 . The CO_2 gas was evolved under vacuum conditions in a reaction between phosphoric acid and $BaCO_3$.

The CO₂ gas was analysed for its ¹⁸0 content as well as its ¹³C content in order to apply a correction factor for ¹⁷O, which, having an isotopic abundance of 0.0337% (Faure, 1977), contributes to the mass 45 peak. The formula converting the $\delta_{\rm m}$ values to the international carbonate standard, PDB (Pee Dee Bellemnite), are as follows:

$$\delta^{13}$$
C PDB = $(\delta_m^{13}$ C · 1.0674) - $(\delta_m^{18}$ O · 0.0337) - 3.3
for working standard = SF

$$\delta^{13}$$
C PDB = $(\delta_m^{13}C \cdot 1.0291) - (\delta_m^{18}O \cdot 0.03312) - 37.11$
for working standard = COWS

Reproducibility of these results are \pm 0.3%.

Oxygen-18 and Carbon-13 in Calcite

Calcite was analysed for its 18 O and 13 C contents by acidifying finely ground ~ 100 mg samples under vacuum at 50^O to produce CO₂ gas. The reaction between calcite and acid, can be written as:

$$CaCO_3 + H_3 PO_4 \rightarrow CO_2 + H_2O + Ca^{2+} + HPO_4^{2-}$$

The CO₂ gas was then analysed for its ¹⁸0 and ¹³C contents. The resulting machine values (δ_m) were converted to values relative to PDB with a precision of about ± 0.2%, by the following equations:

$$\delta^{18}$$
0 PDB = ($\delta_{\rm m}$ ¹⁸0 · 0.9661) + (0.0087 · $\delta_{\rm m}$ ¹³C) - 35.36
 δ^{13} C PDB = ($\delta_{\rm m}$ ¹³C · 1.0291) - (0.03312 · $\delta_{\rm m}$ ¹⁸0) - 37.11

These equations have been derived from the per mil differences between the laboratory working standards SF and COWS and the NBS No. 20 Solenhofen limestone standard ($\delta^{18}O_{PDB} = -4.14$) following reaction at $50^{\circ}C$.

Radioactive Isotopes

Tritium

Tritium is one of the rare isotopes with a naturally occuring concentration of only a few T.U. where $1 \text{ T.U.} = {}^{3}\text{H}/{}^{1}\text{H} \times 10^{18}$. Higher "bomb tritium" levels are more readily detected and are analysed for in the Isotope Geochemistry Laboratory at the University of Waterloo using a liquid scintillation counting technique on natural non-enriched water samples. The liquid scintillator with a gelling agent (INSTAGEL) was mixed with the water sample and placed in a counter for up to one week. Disintegrations are then counted by the detectable release of light energy. Counting statistics of reference samples are used to determine the analytical error for each sample. The error, in the order of ± 10 T.U. is presented with the tritium data.

Carbon-14

Carbon-14 activities were measured using a liquid scintillation counting technique on benzene synthesized from dissolved carbonate samples which were precipitated as $BaCO_3$ (Appendix A-2). For a detailed description of the analytical technique, refer to Fritz et al., (1979). The activity of ¹⁴C is expressed as a percent modern carbon (pmC) which has been defined as 95% of the National Bureau of Standards (NBS) oxalic acid standard.

APPENDIX C

CHEMICAL AND ISOTOPIC ANALYSES

- note: Analyses for each sample are referenced as follows:
 - 1. Nevin, Sadlier-Brown, Goodbrand (1975)
 - 2. Hammerstrom and Brown (1977)
 - 3. Michel and Fritz (1979)
 - 4. Present Study

Meager Cr. Hot Spring Main Vent 74/10/30 ¹ 76/8/3 ² 76/11	74/10/30 ¹ 76/8/3 ² 76/11	76/8/3 ² 76/11	76/11	/30 ²	78/2 ³	78/12/12 ³	79/6/25 ⁴	79/8/19 ⁴
C	58	58 6.6	48.5	50.0	50 6.6		50.1 6 54	54.2 6 45
	0.2	0.0	+.0	00.0			443	469
	81	51	92.0	92.0		85	81.9	
	25	15	24.8	31.0		26	26.2	
-	450	330	347	390		435	439	
	47	54	44.0	48.5		55.7	45.5	
	675	600	428	500		661	528	
	110	190	65	145		152	122	
	468	504	450	595		330	464	
	164	150	80.5	102.0		189	162	
			0.00	0.00			.12	
			.32	. 34			,64	
			-					
0 "to SMOW					-16.0		-16.38	-15.72
7r SMOW					-126		-127	-124
tium (T.U.)					17±9	29+12	19±10	3±10 .
C % PUB					-5.2		-6.1	
C 7. PDB								
74 PDB								
\$ modern					5.6			
MOMS •7. 0					6.3		2.1	
7.• CD T			*				7.2	

					-		-																		°_		
	79/8/18 ⁴	40.4	6.34	409																	-						
	79/6/25 ⁴	38.8	6.47	404															-16.1	-125		-7.6				-2.4	
No Good Warm Spring Vent #1	76/8/2 ²	30.0	6.80		83.5	17.1	248	27.0	295	50		54.0						n.d.									
				1																			-				
Placid Hot Spring Vent #2	79/8/21 ⁴	45.1	5.89	398	114	27.6	433	53.5	674	174	398	138	.35	.76	52.7	8.7	38.6	.04	-16.0								
	79/8/19 ⁴	51.2																	-16.2		13±10						
Meager Cr Hot Spring Vent #19	79/6/25 ⁴	49.8	6.24	437												5			-16.4		36±10	-7.3					
		°C		mqq	bpm	mqq	mqa	uidd	ավն	mqq	under	undd	mqq	uidd					5 0 7 SMOW	SD 7, SMOW	Tritium (T.U.)	5 ^{1.3} C 7, PDB	5 ¹³ C % PDB	5 ^{-1 0} 7 PDB	14 _C % modern	5 ¹⁸ 07. SMOW	5 ³⁴ S 7.e CD T
Sample	Date	Temp	Hq 11 Hq 11 Hq		Ca ²⁺	Mg ²⁺	Na ²⁺	K+	c1 [°]	²⁻²	11C03	Si02	Fe total	+ + UB	ліс 2	0 0 0	C02	CH ₄	H ₂ 0 (H ₂ 0 6	H ₂ 0	DIC	caco ₃	E CaCO ₃	DIC	sot sot	H SO4

																				,					;	<u>109</u>		
-																												
-																											-	
																							-					
		-											-															
		79/8/18 ⁴	29.9	6.65	· 379														.b.n	-16.5		38±10				20	-	
		79/6/25 ⁴	. 29.5	6.82	382	75.6	13.7	175	22.4	196	69.0	382	101	. 25	.84					-17.2	-128	13±10	-8.4				-1.0	6.2
		76/8/2 ²	31.4	6.50		92.0	15.4	165	23.7	133	25	503	56.0	.45	.45													
	No Good Warm Spring Vent #2	74/10/30 ¹	33	6.7		40	7.6	150	32	275	76	387	108															
			°C		ppm	mqq	mqq	mqq	mqq	mdd	mqq	undd	mdd	undi	mqq				are .	18 5 0 7. SMOW	SD 7. SMOW	<pre>Tritium (T.U.)</pre>	5 7, PUB	1 ³ C % PDB	2. 0 7. PDB	14 _C % modern	1 ¹⁸ 0 7/ SMOW	134 S 7. CDT
	ple	Ð	Temp	Hd Hd	A HCO ₃ 1	Ca ²⁺ 1	Mg ²⁺	Na ²⁺ I	K ⁺ 1	C1 [~]	504 ²⁻ I	11C03	Si02 F	Fetotal I	Mn ⁺	N ₂	02	c0 ₂	CH ₄	H ₂ 0 6	H ₂ 0 δ	H ₂ 0 1	DIC	CaCO ₃ 6	CaCO ₃ §	DIC 1	S04 5	SO_ 6

																	_					-		- UL			
	79/9/9 ⁴	59.1	6.54	786														tr	10 2								
	79/6/24 ⁴	59°8	6,88	763	32.7	4.73	426	13.8	83.3	288	763	79	.13	. 19					201	-146	20±10	-4.6	-3.41	-26.2		-5.3	13.7
	78/12/12 ³				33.2	4.7	388	16.4	86.6	317	718	78.6															
	78/10/9 ³				33,3	4.7	423	17.3	81.8	329	724	84.9															
	78/2 ³	59	67	1															C 01	-146	23+10	-4.6			.24	-	
	76/11/30 ²	. 59.0	6 . 70		32.5	7.0	405	18.9	71	385	1053	60,0	.15	.11													
-	76/9/1 ²	59.0	6.85		42.5	6.1	396	18,2	67	275	992	43.0	.15	.1													
Pebble Cr. Hot Spring Main Vent	74/1 ^{1.}	60.0	7.9-8.1		30,0	4.7	425.0	14.5	100	-1.0	757.0	75.5		10													
Sample Pebble	Date	Temp °C	Hq 51 Hq 51	E B IICO ppm	Ca ²⁺ ppm	Mg ²⁺ ppm	Na ²⁺ ppm	K ⁺ ppm	C1 ⁻ ppm	S0 ₄ ²⁻ ppm	a IICO 3 ppm	Si02 ppm	Fetotal ppm	ad Mn⁺ ppm	mic Z 2	5 02 \$	C02 \$	CH4 \$	H_0 6 0 1 SMOW	H ₂ 0 &D 7, SMOW	H ₂ 0 Tritium (T.U.)	2 DIC & 13C 7, PDB	CaCO ₃ 6 ¹³ C % PDB	ξ caco ₃ δ ¹ 0 7. PDB	b, DIC 14 _C \$ modern	6 S0 = 8 ¹⁸ 0 72 SMOW	H S0 ² 6 ³⁴ S 7.4 CD T
																										· ·	

.

		Pebble Cr. Hot Springs						
mplo		Vent #7				-		
te		76/9/1 ²	76/11/30 ²	79/6/24 ⁴	⁴ 6/6/6L			
Temp	°C	53,5	50.5	56.5	57.0			
PH Hd	-	7.70	8,00	6.85	6,60			
B HC03	ndq			171	, 735			
Ca ²⁺	mqq	44.0	39.0		35,3			
Mg ²⁺	mqq	6.6	7.0		5.11			
Na ²⁺	udd	410	418		419			
K+	udd	13,8	18,9		14.1			
່ເວ	ppm	72	72		62.4			
50_{4}^{2-}	mqq	315	340		316			
HCO3	udd	992	1068		735			
Si02	mqq	40.0	44.0		67.5		-	
An Fe tota	al ppm	0°00	0°*00		<,1			
+ Wu Mu	bpm	60*0	•00		.15			
N N MIC	96							
0 07	%							
c_{0_2}	46							
CH4	40							
][
H_2^0	6 0 7. SMOW			-19.6	-19,5			
11 ₂ 0	5D 72 SMOW	٢		-145				
Н ₂ 0	Tritium (T.U.)			2±10	16+10			
DIC	6 ^{1.3} C 7, PUB			-6,3				
CaCO ₃	6 ¹³ C % PDB		-					
E CaCO ₃	8 0 7. PDB							111
DIC	14 _C % modern							-
so4	6 ¹⁸ 0 7, SMOW			-5.3	•		·	
н S04	8 ³ * S 7.• CDT			14.3		-		

•

¢

•

.

								-																-11	2		,
	79/8/19 ⁴ .	58.4	6.06	526	107	36.2	424	48.4	571	182	526	155	.14	1.20	64.7	22.5	12.8	0.03	1 7 1	1.01-	37±10	-6.2				3.7	7.1
	79/6/25 ⁴	58.5	6.17 N.	531															C 71	-126	7±10					-	
	78/12/12 ³				109	37	423	529	697 .	189	413	169															
	78/10/9 ³				108	37	423	51.9	652	182	521	170															
	78/2 ³	58	6.15	1						-									_15 K	-127	33±10	-7.0			4.6		
	76/11/30 ²	.56.5	6.15		105.0	40.5	410	52.0	500	180	686	96	.30	.65		-		, ,									
	76/8/3 ²	56.0	6.05		97.0	34.1	377	46.2	466	170	458	92	.15	.65													
EMR-1	74/3/29 ¹ »	59			85		430	27	650		513	151															
Boreholes		°C		nudel	udd	ppm	uidd	mqq	udd	wdd	bpm	bhm	mqq 1	udd	•• ••	عبن	de	**	6 0 22 SMOW	6D 77, SMOW	Tritium (T.U.)	δ ^{1.3} C 7, PDB	6 ¹³ C % PDB	6 ¹⁸ 0 7. PDB	14 _C % modern	6 ¹⁸ 0 % SMOW	δ ³⁴ S 7.• CDT
Sample	Date	Temp	61d		Ca ²⁺	Mg 2+	Na ²⁺	+	c1 ⁻	5042-	8 11C0_	si Si O ₂	Ana Fetota	Is +nM	si∎ 22	0 0	C02	CH ₄	0 H	2 Н ₂ 0	H ₂ 0	es DIC	LaC0.	E CaCO ₃	DIC	sot	н S04

,

•

. _

Samp Le		74-H-1 406'-877'	406 1140				75-H-1 65'-300'		79-H-1 60-68 m
Date		75/1/31 ¹	75/2/21 ¹	78/2 ³	79/6/25 ⁴	79/8/21 ⁴	75/9/18 ¹	79/9/9 ⁴	79/8 ⁴
Temp	Ĵ,	55	55	. 52	50.5	52.3	10.5	10.1	
Hq 11		1	7.34	6.3	6.41	6.23		7.70	7.09
	udd	-			, 1255	1273		233	
Ca ²⁺	udd	150	380			223	3,1	32.9	209
Mg 2+	mqq	24.0				90.3	14.0	18.0	41.4
Na ²⁺	mqq	910	2300			2390	20.8	23.0	10.1
K ⁺	ррт	52.1	06			98.1	7.8	6.93	6.82
c1	udd	1		-		2640	• 3	•56	-89
S04	mqq	-	1880	*		2370	12	22.6	16.1
% HCO3	uidd	1	1396			1273	183	233	883
St02	mqq	41.0	80.5	-		104	40	15.5	22.9
Fetot	al ppm	8	-			.16		<,1	<.1
Mn +	udd					.67		.50	.69
N N 2	-							80*9	
م 10 10	510							3,9	
C02	die							15.8	
CH ₄								n.đ	
Н ₂ 0	6 0 7 SMOW			-15.3	-15.6	-15.3		-17.2	-17.1
H ₂ 0	6D 7. SMOW			-127	-127			-128	
H ₂ 0	Tritium (T.U.)				-8+10	23±10		31+10	44±10
es DIC	6 ¹³ C 7, PUB			-5,3	-4,9			-10,7	
alys alys	δ ¹³ C "Zo PDB								
E CaCO ₃	δ ¹⁰ 0 7. PDB			-					
DIC	14 _C % modern			.19					
so to	6 ^{1,8} 07. SMOW				6.3		•		113
H SO4	δ ³⁴ S 7. cDT				9.1			•	ŀ

.

· · · · · · · · · · · · · · · · · · ·

_

																										+	
																											-
						-																					
									-	· .																	
														<u> </u>													
				-																							
	⁹ /8 ⁴	8	.12	74	10	3.1	.10	.82			74		5,5	85.				ų	16.7	25	10	0.1					
	79/		9	6	5	4	6	0			6		3	•							354	-					
																			MOMS	MOMS	(T.U.	PDB	PD8	PDB	odern	MOMS	CDT
		°C		mqq	ppm	ppm	mdd	ppm	ррш	mqq	unded	udd	udd	ndq	**	ela	*		δ 0 %	6D %	Tritium -13	6 °C %	6 ¹³ C %	5 0 7a	14 _C % m	5 ¹⁸ 07,	8 ' S 7
		cmp	Ŧ	co ₃	a ²⁺	5 +7	4+7 B	+	,	0, ²⁻	c0 ₃	10 ₂	total	+_			2	4	0.	0	0	5	c0 3	C0.3	0	-	
Sample	hate		iei ata <u> </u>	Di E	ũ	N.	ž	M	0	S(≚ sə:	s A I	snA 5	I.S.	2 Z	ംപ സ	3	5	112	H ₂	H ₂	599	sily:	N S		toz I S	SO

. . . .

.

.

	1														Í		1		11-	1					Ť	115	-
		a																									-
	79/8/17 ⁴	6.9	7.49	354						-						-			-17.2	-126	52±10						
caco ₃ spg. #4	79/6/22 ⁴	6.2	7.50	351															-17.3	-127	42+10	-3.0	-1.1	-14.9			
caco ₃ spg. #3	79/6/22 ⁴	5.6	7.62	,370	98.6	12.5	3,20	1.75	<0,8	8,95	370	8,9	<.1	<.005					-17.3	-128						-	
CaCO ₃ Spg.∶ #1	79/6/22 ⁴	. 5.6	7.71	370												-			-17.4	-132	43±10	5	2.3	-13.0			
ca ∞_3 Spgs.	75/9/30 ¹	8,5	7.96	44 MB	95	96	3.2	0,16	0,5	44	278	21.0															
Boundary Cold Spring #4	79/8/30 ⁴	4.5	8.31	66.3	12.2	5.42	4.84	0.54	<,2	2.02	66.3	6.0	<.1	.01					-17.1		51+10	-6.1	-8.2	-23.3			
old Springs		°C		udd	udd	mqq	mqq	mqq	mdq	udd	mqq	mqq	nl ppm	ppm	910		8	día	δ 0 % SMOW	6D 7, SMOW	Tritium (T.U.)	6 ^{1 3} C 7, PDB	6 ¹³ C % PDB	8 0 7. PDB	14 _C % modern	6 ¹⁸ 0 7, SMOW	6 ^{3*} S 7. CDT
Sample C	Date	Temp	E1 E1 Hq	HCO3	Ca ²⁺	Mg ²⁺	Na ²⁺	K ⁺	_13	504 ²⁻	4 11C0_3	Si02	Ana Fe tote	4 Wu+	N2 N2	ت 2 0	C02	CH ₄	0,11	H ₂ 0	H ₂ 0	es DIC	alys	E CaCO ₃	DIC	so so a	п S04

.

																				11]		Π				11	6
	·	79/8/20	1.2	8.48	12.0															-17.1			-6.8					
	Mt.Athelstan Cold Spring #1	79/6/24												1						-19.4	-144	29±10						
	78-H-1 Cold Spring	79/6/24	4.6	7.18	40.8	3,5	1,01	16.0	0.67	<0.8	3,48	40.8	36.5	<,01	<0,05					-18.1	-136		-13.9					
•	Fall Creek Cold Spring #1	79/8/26	3.9	5.92	36,8	5,40	2,60	6,00	1.80	0.50	8,55	36.8	52.8	<,1	•03					-17.0		79+10	-8.6					
-	Problem Cold Spring #1	79/6/23	6	7.65	, 594	106	44.9	11.9	5.0	<0.8	36.1	594	10.9	<0,1	<0,05					-17.0	-127	54±10	-2,8	5	-13.6			
-	Angel Cirque Cold Spring #1	79/8/26	E• .	8.72	2.7	-														-16.5	-122	4±10	-7.2					
	Rivendell Cold Spring #2	16/8/31																		-17.3			-3.0	-3.2	-15.4		-	
	Moria Cold Spring #1	19/8/31	8°5	7.91	395	110	38.5	4.50	3, 31	0.34 .	124	395	6.7	<,1	•03					-17.5		34+10	-5,0	-3.5	-15.7			
-			63		anc.	m	m	L.	E.	E.	un de la companya de	ur.	E.	H.	Ĕ					B To SMOW	WOWS 22	itium (T.U.)	BUR To PUB	³ C 7‰ PDB	0 7. PDB	C & modern	BO 7. SMOW	1
	c		Temp °(pH	llC0 ₃ pF	Ca ²⁺ pp	Mg ²⁺ pp	Na ²⁺ pp	K ⁺ pp	c1 pp	so ₄ ²⁻ pp	lico ₃ pp	Si0 ₂ pp	Fetotal Pp	Mn ⁺ pp	N2 \$	0 ₂ %	c02 \$	CH4 S	1,0 6 ¹	H ₂ 0 &D	H ₂ 0 Tr	DIC &	caco ₃ 6	CaCO ₃ &	01C 14	30 ⁴ 6 ¹	Contraction of the second seco
	ampł	ate		811	Da Da		. —	- ^		. –		sa	j xe	SIA	[B	orua	οųσ	. –	. –				sə	eīys	τυ Υυτηγ	əđo		, 1

	1 1											Ì							11				-			- 11	7 -
Lillooet River L-1	76/11/15 ²	1.3	7.75		14.1	2.5	3.5	1.1	. 46	24	46	4.5	• 30	•03													
	76/11/30 ²	0.0	7.40		15.7	3.0	13.5	1.7	1,01	39	76	10.0	0*30	•04													
Lillooet < River L-4	76/9/2 ²	5.0	7.20		7.0	2.2	2.0	1,1	. 44	15	31	2.0	1.45	.05									-				
Meager Creek M-6	74/10/30 ¹	4			6,8	1.8	5.	1.1				9.4														-	
Meager Cr. Hot Springs Creek	76/11/30 ²	-1.0	7.50		15.4	1.0	2.0	1.5	<,18	16	3	1.7	10.	0.0										•		-	-
Angel Creek	76/8/2 ²	. 7.5	7,50		7.4	2.2	2.9	1,1	.37	S	46	11.0	.3	10.		-											
	76/11/30 ²	0*0	7.50		16.9	4.5	5.5	1.3	1.38	25	1	1.7	.15	0*0													
Meager Creek M-9	74/10/30 ¹	4			7.8	2	1.4	0.7				8,3															
urface Waters		°C			bpm	bpm	uudd	udd	udd	udd	udd	mqq	udd 1	bpm	de	4.	76	440	6 0 % SMOW	6D 7. SMOW	Tritium (T.U.)	6 ^{1 3} C 7, PUB	δ ¹³ C % PDB	8. 0 7. PDB	14 _C % modern	6 18 0 74 SHOW	δ ³⁴ S 7. CD T
Sample S	Date	Temp	ejd Hq Hq	E B HCO3	Ca ²⁺	Mg ²⁺	Na ²⁺	K+	C1	504 ²⁻	M HCO3	Si02	And Fe tota	+ uW	Sim N 2	تە 12	C02	CH ₄	Н ₂ 0	H ₂ 0	H ₂ 0	S DIC	al ys	E CaCO ₃	ope DIC	sot sot	н S0 ₄ =
				+															• .							, .	

, `

,

Mosaic Creek at Glacier	²⁵⁴ 79/9/7 ¹	1+5																	7.9 –16.6		10	22 -6.8		-		1	
	79/6/			45															-		51	+	-				
	76/11/13 ²	0.0	7.80		47.0	10.5	8.0	2.0	.61	75	183	8.5	1.60	.50													
	76/11/13 ²	5.0	7,20		7.0	2.2	2.0	1.1	. 44	15	31	2.0	1.45	.05												÷	
Job Creek at Glacier	76/10 ¹	0*0	6,38		26.0	6.0	7.9	2.9	0.3	44	41.0	22.0		300													
	76/11/30 ²	6.0	7.30		3, 3	0.5	2.0	1.0	. 45	e	38	18.0	00*0	0,00				•									
Pebble Cr. Hot Springs Creek	76/9/1 ²	7.0	7,10		3.9	1,1	2.5	1.1	0.27	10	23	22.0	00*00	0.00													
Lillooet River L-11-5	76/11/15 ²	2.0	7,75		16,3	3,0	5,5	1.2	1.56	25	53	3.0	, 25	.02													
		D.		udd	mqq	mqq	uidd	mqq	mqq	udd	uidd	. udd	n ppm	udd	96	96	40	-	δ 0 2 SMOW	6D 7, SMOW	Tritium (T.U.)	6 ^{1 3} C 7, PUB	δ ¹³ C 2 PDB	δ ^{1 σ} 0 7. PDB	14 _C % modern	6 180 76 SMOW	10 4 4 C 4
Sample	Date	Temp	eld Fig		Ca ²⁺	Mg ²⁺	Na ²⁺	K+	c1	804 ²⁻	11C03	Si02	Ana Fe tota	4uW+	отш N 2	0 0	C02	CH ₄	н _, 0	H ₂ 0	H ₂ 0	e DIC	al ys	E CaCO ₃	DIC	504 =	

.

•

,

•	r-i				1 I			-	<u> </u>					Í	_	·										1	19
																										-	
																											•
																							-				
				1			•																-	-			
					-													-			-						
Mt. Cayley Cold Spring	79/9/11 ⁴	15.0	5,88	1310	394	128	745	64.2	720	984	1310	72.7	7.6	1.73				n.d.	-15.7		10+10	-3,3	3.2	-11.9			10.7
Mt. Cayley Hot Spring	79/9/11 ⁴	28,8	5,99	1465	483	159	968	76.2	1077	1178	1465	90.5	6.4	1,23				n.d.	-15.7	-118	14+10	-1,5	• 2 ·	-16.6	. 4	5.4	12.2
umt Cayley		° C		wdd	mqq	mqq	mqq	mdd	udd	mqq	mqq	bpm	l ppm	bpm	-			010	δ 0 1 SMOW	6D 7. SMOW	Tritium (T.U.)	6 1.3C 1, PUB	6 ¹³ C % PDB	8 "0 7" PDB	14 _C % modern	6 ¹⁸ 0 7% SMOW	δ ³⁴ S 7.e CD
Sample Mc	Date	'ſemp	eld Fg Hg		Ca ²⁺	Mg ²⁺	Na ²⁺	K†	C1	s04	11C03	Iys Si02	And Fe tota	4uW	oim 2 2	02	C02	CH ₄	Н ₂ 0	H ₂ 0	H ₂ 0	a DIC	alys	A CaCO ₃	DIC	sot	r so ₄ =

. . . .

T.U.)																			6													1	.20	,
TRI' (±10	C E	39								49					72		36		22+									49					15	26
δ ² H ⁰ /oo SMOW	-116	-112	1110	-110	-103	-111		- 97	- 99	- 100	-128		-111			-108	-100		-71														-113	-135
δ ¹⁸ 0 ⁰ /00 SMOW	-16.2	-15.7	-14.8	-15.3	-14.1	-15.2	-15.0	-12.6	-12.3	-11.9	-17.3	-17.3	-15.0	-14.6	-13.9	-15.5	-12.7	-14.1	-9.2	-8.5	-10.4	-8.5	-13.1	-10.9	-13.5	-9.5	-6.2	ı	- 6.8	-12.4	-11.7	-14.2	-14.9 ·	-17.8
DATE	Jul-Aug/79	Sep//9	Sen/79	Jul-Aug/79	Sep/79	Jul-Aug/79	Sep/79	Jul-Aug/79	Sep/79	Jul-Aug/79	Jul-Aug/79	Ju1-Aug/79	Jul-Aug/79	Sep/79	Sep/79	Sep/79	Sep/79	Sep/79	0ct/77	79/7/12 - 79/8/17	79/8/17 - 79/8/22	79/8/22 - 79/9/1	79/9/1 - 79/9/4	79/9/4 - 79/9/7	79/7/6 - 79/7/9	79/7/9 - 79/7/10	79/7/10 - 79/7/13	79/8/17 - 79/8/22	79/8/22 - 79/9/1	79/9/1 - 79/9/4	79/9/4 - 79/9/8	79/9/8 - 79/9/10	79/10/12 -79/11/1	79/11/1 -79/12/1
SAMPLE NAME	Sampler # 1, 8300'	# 1, 8300' # 2 6300	# 2, 6300	# 3, 7900	# 3, 7900*	# 4, 6200	# 4, 6200	# 5, 1400'	# 5, 1400'	# 6, 2800 ¹	# 7, 7650'	# 8, 7250'	# 9, 5500'	# 9, 5500'	# 10, 5000'	# 10, 5000'	# 11, 3150'	# 11, 3150'	Pebble Creek Camp	MC - 1S0 - 1	- 2	- 3	- 4	- 5	LR - 1S0 - 1	- 3	- 4	- 5	- 6	- 7	- 8	- 10	- 11	- 12
	긝																																	

ISOTOPE DATA FOR PRECIPITATION, SURFACE AND SUBSURFACE WATERS, MOUNT MEAGER, B.C.

•

120

RAINFAL

	ISOTOPE DATA FOR PRECIPITATION, 3	SURFACE AND SUBSURFACE	E WATTERS, MOUNT N	EAGER, B.C.	
FIONS	SAMPLE NAME	DATE	δ 0 ⁰ /00 SMOW	δ ² H ⁰ /00 SMOW	TRITIUM (±10 T.U.)
MONIC	Sampler Site #1, 8300'	Jun/79	-15.9		
	#1, 8300'	Sep/79	-15.1	-103	32
	#2, 6300'	Jun/79	-17.6		33
	#3, 7900	Jun/79	-16.1		
	#3, 7900'	Sep/79	-13.2	-94	
	#4, 6200	Jun/79	-18.2		
	Sampler Site #8, 7250'	Jun/79	-19.0.		
	Sampler Site #9, 5500'	Jun/79	-15.6		
	Mt. Athelston, 6200'	Jun/79	-18.0		
	Devastation Glac.	Feb/78	-18.4	-128	81
	EMR-1, 1850'	Feb/78	-17.9	-128	52
	74-H-1, 2300'	Feb/78	-16.1	-120	73
	Pylon Peak, 6600'	Mar/78	-15.7	-121	22±11
					•
GLACIER ICE	Job Glacier (North)	Aug/79	-15.5		
	Affliction Glac.	Aug/79	-16.1		11
	Devastation Glac. (East)	Aug/79	-16.0		0
	Job Glacier (South)	Sep/79	-14.9		0
	Cathedral Glacier	Aug/79	-17.4		
RUNOFF	Meager Creek Ml	Feb/78	-17.3	-128	54
	TM	Jun/79	-18.2	-130	11
	IW	Aug/79	-16.4		53
	. M4 .	Jun/79	-18.2		
	M4 .5	Aug/79	-16.2		
	M4 .5	Sep/79	-15.5		1
	MS	Feb/78	-16.2	-127	58
	MS	Mar/78	-16.6		36
	M6	Jun/79	-18.0		
	M6.5	Aug/79	-16.2		-
	M7	0ct77	-16.8	-126	121
	- M7	Feb/78	-16.5	-130	
	MB.	Jun/ Junr	-18.2	-131	

.

	(· N																																		14	. 2	
	TR (T T T T T T T T T T T T T T T T T T				27										39	24											50	ы		38	32±8	•	11			28	12
MEAGER, B.C.	8 ² 11 ⁰ /00 SMUW				-135			-140										-134												-133	-130	-140		-143		-129	
URFACE WATERS, MOUNT	δ ¹⁰ 0/00 SMOW		-18.1	-16.0	-18.3	-17.2	-14.9	-17.4	-16.2	-16.3	-16.3	-16.8	-17.9	-15.8	-17.4	-17.1	-17.6	-17.1	-16.8	-16.8	-17.3	-17.0		-19.3	-17.6	-15.9	-17.7	-16.3	-15.6	-17.6	-17.7	-19.0	-17.0	-18.8	-16.9	-18.8	-18.1
SURFACE AND SUBS	INVIII:	6	Jun/79	Aug/79	Jun/79	Jun/79	Sep/79	Jun/79	Sep/79	Aug/79	Aug/79	Sep/79	Jun/79	Aug/79	Jun/79	Aug/79	Jun/79	Aug/79	Jun/79	Jun/79	Jun/79	Aug/79		Jun/79	Jun/79	Aug/79	Jun/79	Aug/79	Sep/79	Feb/78	Sep/78	Jun/79	Aug/79	Jun/79	Aug/79	Jun/79	Jun/79
ISOTOPE DATA FOR PRECIPITATION,	SAMPLJ: NAMI:		Meager Creek M10	0 I W	M12	Devastation Creek (top)	(top)	(bottom)	(bottom)	Boundary Creek (top)	(bottom)	No Good Creek (top)	(bottom)	(bottom)	Angel Creek (top)	(top)	(bottom)	(bottom)	Problem Creek (upper)	. (lower)	Camp Creek' (bottom)	(bottom)	Meager Creek Hot	Springs Creek (bottom)	Canyon Creek (bottom)	(bottom)	Capricorn Creek (bottom)	(bottom)	(bottom)	Lillooet River		Lillooet River Ll	L1	. L4	L4	L9]	L10

41.4.7 A 18. A 18.

	NDT ATA HOURD	PRECEPTIATION, SI	JRFACE AND SUBSURFACE	WATTERS, MOUNT N	EAGER, B.C.	
	SAMPLE NAME		DATE .	δ ¹⁸ 0 ⁰ /00 SMOW	δ ² H ⁰ /oo SMOW	TRITIUM (±10 T.U.)
	Pebble Creek		0ct/77 Feb/78	-17.5 -17.7	-129 -135	56±9 87
			Mar/78 Jun/79	-17.0	-128	25
	Dead End Creek Pebble Creek Hot	(top)	Jun/79	-18.7		
	Springs Creek	(upper)	Jun/79	+16.8		
	Salal Creek	(JAMOT)	Jun/79	-1/.0		
	Job Creek	(top)	Jun/79	-17.9		S
		(top) (bottom)	Sep/79 Jun/79	-16.3 -17.8		18
		(bottom)	Aug/79	-15.6		
	Spire Creek	~	Aug/79	-16.8		
	South Spire		Aug/79	-17.6		
	Afflication Creek	(top)	Aug/79	-16.7		27
		(bottom)	Jun/79	-18.1		
	Poly Creek	(bottom)	Jun/79	-18.6		
	Mosaic Creek	(top)	Aug/79	-16.6		32
	Manatee Créek	(bottom)	Jun/79	-18.8		
	#8 Creek		Jun/79	-18.3		
HOT SPRINGS	Meager Creek Hot					
	Springs Main Vent		0ct/77	-15.8	-121	11±9
	44 44		Feb/78	-16.0	-126	17±9
	5.8 6.8		Mar/78	-15.7	-125	
	46 48		Dec/78	-16.2	-126	29±12
	88 88		Jun/79	-16.4	-127	19
	44 44		Aug/79	-15.7	-124	3
	Vent #2		Feb/78	-16.6	-132	58
	#2		Mar/78	-16.0	-127	
	# 2 #		$\operatorname{Mar}/78$	-15.7	-125	34
	£15		67 Jun	-10.5	-125	

SAMPLE NAME	DATE	18 0/00 SMOW	6 ² H ⁰ /00 SMOW	TRITIUM (<u>±10 T.U</u> .)
Vent #15	Aug/79	-15.8		
#17	Jun/79	-14.6		24
#17	Aug/79	-15.8		36
#19	Jun/79	-16.4		13
•	Aug/79	-16.2		
Placid Hot Springs				
Vent #1	Aug/79	-16.0	-124	0
# 3	Aug/79	-15.1		
#5	Aug/79	-16.1		0
No Good Warm Springs				
Vent #1	Jun/79	-16.1	-125	
2#	Jun/79	-17.2	-128	13
#2	Aug/79	-16.5		38
#5	Jun/79	-17.0		
#5	Aug/79	-16.7		
Pebble Creek Hot Springs				
Main Vent	Oct/77	-19.0	-140	
14 - 11	Feb/78	-19.3	-146	23
88 88	Mar/78	-19.0	-143	*
88 88	0ct/78	-19.8	-151	
. 56 65	Dec/78	-19.3	-147	
88 88	Jun/79	-19.5	-146	20
11 11	Aug/79	-19.3		
Vent #2	Feb/78	-19.0	-144	
5#	Mar/78	-19.2	-141	
5#	Jun/79	-18.0		23
5#	Sep/79	-18.9		0
L#	Jun/79	-19.6	145	2
L#	Aug/79	-19.5		16

ISOTOPE DATA FOR PRECIPITATION, SURFACE AND SUBSURFACE WATERS, MOUNT MEAGER, B.C.

	ISOTOPE DATA FOR PR	RECIPITATION, SU	JRFACE AND SUBSURFACE	WATERS, MOUNT M	EAGER, B.C.	
	SAMPLE NAME		DATE	δ ¹⁸ 0 ⁰ /00 SMOW	δ ² H ⁰ /00 SMOW	TRITIUM (<u>±10 T.U</u> .)
COLD SPRINGS	Devastation		Jun/79	-17.1	-124	
	Boundary	#3	Aug/79	-16.7		
		#4	Aug/79	-17.1		51
	CaCO ₇ Springs	1#	Jun/79	-17.4	-132	43
	n I	#3	Jun/79	-17.3	-128	
		#4	Jun/79	-17.3	-127	42
		#4	Aug/79	-17.2	-126	52
	J	#6	Aug/79	-17.0		25
		.#7	Jun/79	-17.7		
	Moria	#1	Aug/79	-17.5		34
		#3	Aug/79	-17.4		
	Rivendell	14	Aug/79	-17.3		
		#2	Aug/79	-17.3		
	Angel Cirque	. I#	Jun/79	-19.4	-136	24
		#1	Aug/79	-16.5	-122	4
		#2	Jun/79	-18.1		
		#2	Aug/79	-16.4		22
		#4	Aug/79	-17.3		
		#7	Aug/79	-16.1		
,	Angel Creek Spring	#1	Jun/79	-17.5		
	Problem Springs	#1	Jun/79	-17.7	-127	54
	I	#1	Aug/79	-17.0	-125	13
		#2	Jun/79	-16.9	-125	23
		#2	Aug/79	-17.2		
	Loggers Springs		Aug/79	-17.7		
	Fall Creek Springs	#1	Aug/79	-17.0		79
	,	#4	Aug/79	-16.9		
	78-H≟l Springs	#1	Jun/79	-18.1	-136	
		#1	Aug/79	-18.0		
*		#3	Jun/79	-17.4 -		
	Job Spring	#1	Jun/79	-17.8	-134	40
	Job West Spring		Aug/79	-15.8		12

من

	ISOTOPE DATA FOR PRECIPITATION,	SURFACE AND SUBSURFACE	E WATERS, MOUNT MEAGER, B.C	
	SAMPLE NAME	DATE	¹⁸ 0 ⁰ /00 SMOW δ ² H ⁰ /00 SI	TRITIUM (±10 T.U.)
REGIONAL HOTSPRINGS	Skookumchuck Hotsprings Sloquet Hotsprings Harrison Hotsprings	Jun/79 Jun/79 Jun/79	-17.6 -15.5 -14.3	Ģ
NOTE:	1) All sample locations are sh	own on figures 2 and 4.		

Analyses having dates prior to June, 1979 are referenced to Michel and Fritz (1979). 2)

127

.

APPENDIX D

r

GAS SAMPLING AND ANALYSIS

.

GAS SAMPLING AND ANALYSIS

Geothermal gases have been used in many investigations of geothermal fields for geothermometry (Ferrara et al., 1963; Arnasson, 1976; Hulston, 1976; Panichi et al., 1976; D'Amore and Panichi, 1980). In particular, fractionation of ¹³C between CO_2 and methane, H² between any of H₂O, H₂S, H₂, CH₄ and NH₃, and ³⁴S between H₂S and a number of aqueous sulphur species have been investigated. As well the molal concentrations of H₂S, H₂, CH₄ and CO₂ have been used to estimate subsurface temperatures.

An attempt was made at Mount Meager to sample the thermal gases to evaluate the potential for applying any of the above geothermometers. During August, 1979, samples were collected at all hotsprings and artesian drillholes by both of two methods. Pure gas samples were collected by filling a 250 ml glass bottle and inverting it underwater over the vent to allow emmanating gases to displace the water. A small amount of water was left in the bottle which was then sealed with Saran Wrap, tightly capped and stored inverted. Gases dissolved in the thermal waters were collected by completely filling a 250 ml glass bottle with the water, sealing with Saran Wrap and capping.

Analyses were conducted in the Isotope Geochemistry laboratory at the University of Waterloo using a gas chromatograph and a helium carrier gas. For a more detailed description of the technique see Barker (1979, unpublished Ph.D. thesis). Water samples were analysed for dissolved CH_4 , reported as µmoles/ ℓ while gas samples were analysed for the major gases present as % volume. Results are presented in table D-1.

The principle gases found in the thermal waters of Mount Meager are, in order of importance, N_2 , CO_2 , O_2 and a trace of CH_4 . H_2S , detectable to the parts per billion range by its characteristic smell, was not found in any samples. If this gas is present in the geothermal waters at depth, it may well be oxidized to SO_4^{2-} . The high percentage of CO_2 in the geothermal gases confirms the p CO_2 data discussed in the above text, alluding to a non-atmospheric or biogenic source.

The results of this investigation indicate that the potential exists for the application of a few of the above mentioned geothermometers, particularly the CO_2 - CH_4 geothermometer. However an intensive gas sampling program would be required to collect sufficient sample for isotopic analysis. Also, although H_2S was not readily detectable, it is apparently present in parts of the geothermal system in copious amounts as evidenced by the strong smell prevalent through-out Job Creek valley on the north side of the complex. Further exploration may well reveal this source, leading to further potential for the application of gas phase geothermometers.

water	Samples				
	Sample Location		CH ₄	(µmoles/l)	
	Meager Creek Hotsprings Mai	n Vent		<0.2	•
	No Good Warm Spring Vent #1			<0.2	
	Vent #2			<0.2	
	Pebble Creek Hotsprings Mai	n Vent		tr	
	EMR-1			tr	
	79-H-1			tr	
	Mt. Cayley Hotspring			<0.2	
	Mt. Cayley Cold Spring			<0.2	
	tr =	0.2~ 0.5			
	<0.2	= not det	ected		
Gas S	amples				
	Sample Location	Volume	% (recal	culated to	100%)
		0 ₂	N ₂	c0 ₂	CH4
	Placid Hotspring Vent #2	8.7	52.7	38.6	0.04
	EMR-1	22.5	64.7	12.8	0.03

3.9

80.9

15.8

74-H-1

Table D-1 Gas analyses of thermal waters

0.20

L