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GEOCHEMISTRY AND GEOTHERMOMETRY OF SPRING WATER FROM THE BLACKFOOT RESERVOIR REGION, SOUTHEASTERN IDAHO

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ABSTRACT

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The Blackfoot Reservoir region in southeastern Idaho is recognized as a potential geothermal area because of the presence of several young rhyolite domes (50,000 years old), Quaternary basalt flows, and warm springs. North- to northwest-trending high-angle normal faults of Tertiary to Holocene age appear to be the dominant structural control of spring activity. Surface spring-water temperatures average 14°C except for a group of springs west of the Reservoir Mountains which average 33°C. Chemical geothermometers applied to fifty water samples give temperatures less than 75°C except for eight springs along the Corral Creek drainage. The springs along Corral Creek have Na-K-Ca temperatures that average 354°C, a direct result of high potassium concentrations in the water. A correction for carbon dioxide applied to the Na-K-Ca geothermometer lowers the estimated temperatures of the anomalous springs to near the measured surface temperatures, and Na-K-Ca-Mg temperatures for the anomalous springs are near 100°C. Mixing model calculations suggest that hot water with a temperature of approximately 120°C may be mixing with cooler, more dilute water in the springs from the Corral Creek drainage, a temperature supported by Na-K-Ca-Mg temperatures and mineral saturation temperatures.

Stability relations of low-temperature phases in the system indicate that the large concentrations of potassium in the eight anomalous springs are derived from reactions with the potassium-bearing minerals muscovite and K-feldspar. Carbon dioxide and hydrogen sulfide gases may be derived through the oxidation of organic matter accompanied by the reduction of sulfate. Concentrations of major and minor elements, and gases found in springs of the Blackfoot Reservoir region are due to water-rock reactions at temperatures less than 100°C.

Based on spring geochemistry, a geothermal reservoir of 100°C up to 120°C may exist at shallow (less than 2 km) depths in the Blackfoot Reservoir region.

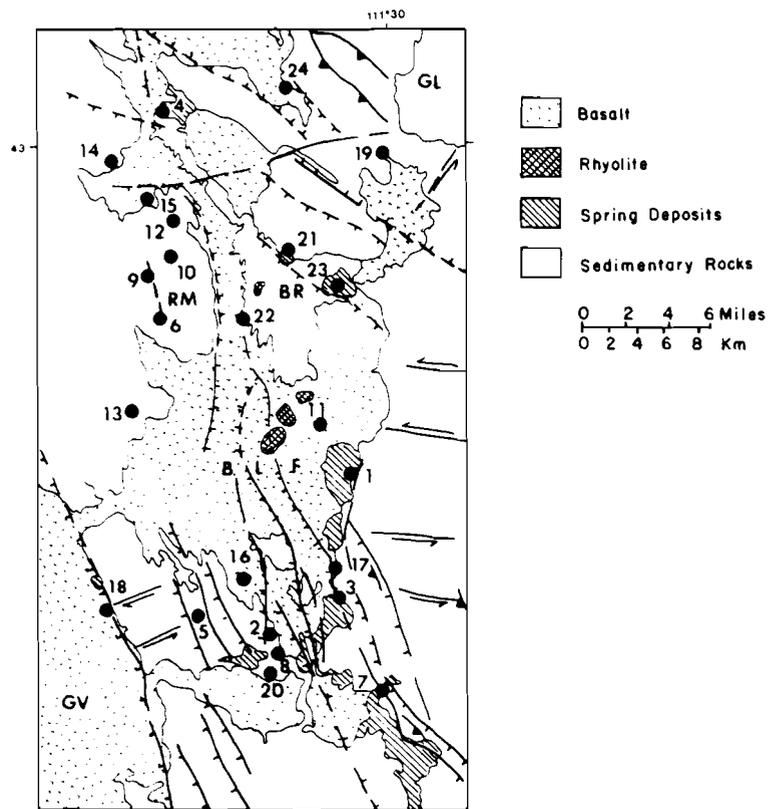*Present address: 1201 Searchlite Court, Reno, Nevada 89503

Fig. 2. Geology of the Blackfoot Reservoir region showing spring sampling locations numbered as in Table 1. Geology generalized from Dion (1974). Abbreviations are: *GV* = Gem Valley; *BR* = Blackfoot Reservoir; *BLF* = Blackfoot Lava Field; *RM* = Reservoir Mountains; *GL* = Gray Lake.

flows, but Middle Cone contains inclusions of an older basalt (Fig. 2). China Hat and Middle Cone have been dated at less than 0.1 m.y. by K-Ar methods (Armstrong et al., 1975) and at about 0.05 m.y. by K-Ar, thermoluminescence and hydration rind methods (Leeman and Gettings, 1977). Two islands in the Blackfoot Reservoir are composed of older rhyolite which has been dated by Phillips Petroleum Company. Rhyolitic tuff from Sheep Island, in section 11 and 14, T. 6 S., R. 41E., gives a K-Ar age of 1.4 ± 0.2 m.y. Rhyolitic vitrophyre from the smaller island immediately south of Sheep Island in section 14, T. 6 S., R 41E., gives a similar age of 1.5 ± 0.6 m.y. (D. Haymond, pers. commun. to W.P. Nash, 1979). Several exposures of rhyolite occur in the northern part of the study area. In the Cranes Flat 15-minute quadrangle, three stubby flows or flat domes (Mansfield, 1927) of rhyolite cover a total area of approximately 3 square miles (0.8 km²). Two of the exposures have been dated by K-Ar methods at the University of Utah. Rhyolite from the SW 1/4 NW 1/4 sec. 33, T. 4 S., R. 42 E. (sample

BFR-3A), gives an age of 1.59 ± 0.06 m.y. and rhyolite from the NE 1/4 NE 1/4 sec. 25, T. 4 S., R. 41 E. (sample BFR-5A), gives an age of 1.41 ± 0.15 m.y. (S. Evans, pers. commun., 1979). A small exposure of rhyolite tuff at the north end of the Chesterfield Range in sec. 20, T. 5 S., R. 40 E., has been dated by Phillips Petroleum Company at 10.7 ± 0.5 m.y. (D. Haymond, pers. commun. to W.P. Nash, 1979).

Quaternary travertine spring deposits are widespread and delineate areas of past and present spring activity (Fig. 2). The exposures vary in size up to about 12 km² and occur primarily along the edges of the lava fields adjacent to upper Paleozoic and lower Mesozoic calcareous rocks.

Westward-dipping thrust faults have long been recognized and were originally described by Richards and Mansfield (1912) as a single large folded thrust fault which they named the Bannock overthrust. Later work resulted in the recognition of several discontinuous, separate thrust faults. Current interpretation of the Bannock thrust zone by Armstrong and Cressman (1963) stems from the recognition of a westward-dipping imbricate thrust zone extending from southwestern Montana to north-central Utah, and the presence of tear faults and younger block faults as progressive stages in the tectonic development of the region. Thrusting occurred from Late Jurassic through Cretaceous time, preceded and accompanied by the development of large north-trending folds. Individual thrust faults are younger to the east, as are the rocks exposed in the overriding western plates (Armstrong and Cressman, 1963; Armstrong and Oriel, 1965). In the Soda Springs area, the Paris fault is exposed near Cavanaugh Siding approximately 17 km southeast of Soda Springs where Cambrian Brigham Quartzite and Triassic Thaynes Limestone are juxtaposed (Mabey and Oriel, 1970). The trace of the Paris fault is covered to the north. The Meade fault places Mississippian limestone over Jurassic and Cretaceous strata and is exposed to the east of Georgetown where it bends to the north and splays into several slices (Maybey and Oriel, 1970).

Two principal sets of high-angle faults have been recognized: an east- to northeast-trending set thought to be tear faults originating in response to differential eastward movement among the thrust plates (Armstrong and Cressman, 1963), and a set of high-angle, north- to northwest-trending block faults (Armstrong and Oriel, 1965). Gem Valley, Bear River Valley, and Slug Creek Valley are grabens. Steep northwest-trending normal faults cutting basalt and one of the rhyolite domes in the Blackfoot Lava Field, and the presence of fault scarps on modern alluvial fans, attest to the youth of block faulting. Travertine deposits located along the east side of the Bear River Valley and similar deposits elsewhere in the region are associated with the north- to northwest-trending block faults and not with thrust faults.

Springs in southeastern Idaho have been described by Mansfield (1927, 1929) as normal springs (non-saline and non-mineral depositing) which grade into mineralized and thermal springs of four types: calcareous, iron-bearing, sulphureted, and saline. Springs in the Soda Springs—Blackfoot Reservoir

area are various combinations of the first three types, all of which are carbonated. Most of the sulfur springs and vents are concentrated along the eastern edge of the Bear River Valley. Saline springs occur to the east in the Crow Creek and Freedom 7½ minute quadrangles.

Young and Mitchell (1973), and Mitchell (1976) have identified geothermal potential in the Blackfoot Reservoir area based on the geologic setting and anomalous subsurface water temperatures predicted by the Na-K-Ca geochemical thermometer. Mitchell (1976) concludes that there is a possibility of deep geothermal resources or shallow low-temperature geothermal energy in the region.

WATER COLLECTION AND ANALYSIS

Fifty water samples were collected from an area of approximately 900 km² surrounding the Blackfoot Reservoir in southeastern Idaho. Sample locations are shown in Fig. 2. Sampling procedures of Brown et al. (1970) and Presser and Barnes (1974) were followed. The water was filtered through a 0.45-micrometer pore diameter filter and four 500 ml samples were collected from each site in polyethylene bottles with polyseal caps. Two of the samples were acidified to below pH 2 with hydrochloric and nitric acid. The third sample was diluted 10:1 to prevent polymerization of silica, although analysis later showed that the concentrations of silica were so low that the dilutions were unnecessary. Undiluted samples were actually used for silica analysis to eliminate any error introduced by dilution. Temperature, pH, and bicarbonate were measured in the field. The high CO_2 content of the water and the rapid re-equilibration of aqueous carbonate species made it necessary to perform the bicarbonate titration as quickly as possible at the sample site. Even so, the calculated bicarbonate contents are probably slightly lower and the pH measurements slightly higher than those of the actual springs.

Major dissolved cations were determined by atomic absorption. Sulfate was determined by an indirect atomic absorption method in which sulfate is precipitated as barium sulfate, and excess barium is measured. Chloride and fluoride were measured with a specific ion electrode, and chloride was checked by Mohr titration. A phosphomolybdate method was used to determine orthophosphate colorimetrically. Total orthophosphate is reported as PO_4.

Activities, fugacities, activity ratios, and activity products of solution species were calculated using WATEQF (Truesdell and Jones, 1974; Plummer and others, 1976). Temperatures of last water—rock equilibria were calculated for each water analysis using the basic tools provided by Fournier and Row (1966, 1967), Fournier and Truesdell (1973), Paces (1975), Fournier (1977) and Fournier and Potter (1979). The assumptions made in estimating subsurface temperature from spring water chemistry are (Fournier et al., 1974): (1) temperature-dependent chemical reactions occur in the subsurface; (2) reacting mineral phases are abundant in excess; (3) equilibrium is

attained between water and reacting minerals; and (4) water composition does not change, or re-equilibrate significantly, or changes in a predictable way on its path to the surface. These basic assumptions are often not valid in the Blackfoot Reservoir springs due to low spring temperatures, high carbon dioxide content, cold water mixing, and other processes as discussed in the following sections.

Silica and Na-K-Ca temperatures were calculated using equations from Fournier (1977) and Fournier and Truesdell (1973). Thermodynamic parameters have been developed for these equations by Benjamin et al. (1983) who observed that the solution composition may be buffered by various alteration phases, but the temperature-composition correlation is preserved. We have chosen to retain the original parameters of Fournier and Truesdell for consistency with CO_2 and Mg corrections described by Paces (1975) and Fournier and Potter (1979).

WATER CHEMISTRY

Table 1 summarizes the surface temperatures, pH, and concentration of major and minor elements present in water samples from the Soda Springs—Blackfoot Reservoir area. Arithmetic mean values are presented for groups of springs with similar characteristics. Most of the waters are neutral to very slightly acidic. Approximately 85% of the samples are between pH 6.2 and 7.0. Major cations present are sodium, potassium, calcium, and magnesium. Silica concentrations are generally low, averaging 11 mg/l Si. Hooper Springs contains 33 mg/l Si, the largest amount measured in the region. The relatively high silica at Rh Spr. 1 and 2 was expected because these springs flow directly from glassy rhyolitic rocks. Mole percents of the major cations are plotted on a portion of the (Ca + Mg)-Na-K triangular diagram in Fig. 3. Most of the springs contain very little potassium relative to other cations, are high in calcium and magnesium, and contain varying amounts of sodium. The most noticeable exceptions are SP 104, SP 114, SP 117, and Corral Creek 1, 2, 3, 4, and 6, which contain unusually high concentrations of potassium.

Major anions present are bicarbonate, sulfate, and chloride. The eight springs that contain anomalous amounts of potassium also contain the largest amounts of sulfate and bicarbonate. Mole percents of the anions are plotted on a portion of the HCO_3—Cl—SO_4 triangular diagram in Fig. 3. Bicarbonate is the dominant anion in springs in this region. SP 100 contains anomalous concentrations of fluorine and phosphate, which is part of the reason for its unusual position within the triangle, as these elements are not considered when calculating the mole percentages. This spring is located less than one mile from the Monsanto Company's elemental phosphorus plant and is probably contaminated with water draining from the tailings and wastes.

Minor elements that make up less than one weight percent of the total dissolved solids include strontium, barium, aluminum, iron, boron, lithium,

TABLE 1

Chemical composition of spring water from the Blackfoot Reservoir region, southeastern Idaho in mg/l

Map No.[a]	Sample No.	T, °C	pH	Na	K	Ca	Si	Mg	Sr	Cl	F	PO4	SO4	HCO3
1	Woodall, 1, 2, 3, 4	13	6.41	5	2	166	7	43	0.2	7	0.5	0.1	20	872
2	Hooper	10	5.85	29	13	110	33	116	0.3	11	0.5	0.5	49	1200
3	Formation	12	6.65	4	1	146	5	39	0.1	4	0.3	0.0	32	763
4	Poison Creek 1, 2, 116	19	6.70	26	3	95	8	32	0.1	31	0.7	0.0	42	499
5	Big	12	6.69	9	1	79	13	18	0.1	9	0.2	0.4	3	409
6	Corrall Creek 1, 2, 3, 4, 6	33	6.71	89	217	618	12	240	5.0	39	1.4	0.0	832	3250
7	Sulfur 1, 2	16	6.29	8	2	254	14	47	0.3	8	0.4	0.2	120	1200
8	100, 101, 102	14	7.09	38	11	102	20	83	0.2	42	2.0	0.4	126	768
9	103	12	6.59	24	32	175	10	53	0.5	26	0.4	0.3	110	882
9	104	22	6.74	95	241	635	10	258	5.0	37	1.2	0.0	890	3580
10	105, 106, 107	8	7.01	4	0.4	61	5	7	0.03	10	0.1	0.05	0	255
11	108	13	6.50	6	1	68	7	17	0.1	5	0.2	0.2	8	341
12	109	10	6.26	7	1	51	8	22	0.1	12	0.2	0.1	6	304
13	110, 111, 112, 113	13	6.88	5	2	68	9	10	0.05	5	0.1	0.1	3	309
14	114, 117	23	6.43	145	203	620	9	266	7.0	64	1.3	0.0	1240	2940
14	115	11	6.30	14	2	91	7	18	0.1	39	0.1	0.05	37	349
15	118	8	6.32	9	1	51	9	20	0.3	12	0.2	0.1	9	309
16	119	10	6.18	20	8	62	26	63	0.1	9	0.3	0.4	12	628
17	120	10	6.36	11	1	80	6	18	0.1	15	0.2	0.1	19	351
18	121	16	6.52	23	12	332	13	126	0.6	12	0.1	0.0	160	1860
19	Chubb	13	7.50	21	1	60	6	22	0.1	25	0.3	0.04	60	284
20	Soda	30	6.74	12	22	887	15	169	3.0	5	0.4	0.1	750	3250
21	Lone Tree	24	6.61	26	15	220	9	73	0.4	24	1.6	0.0	80	1280
22	Hopkins Landing	9	6.40	20	2	37	14	17	0.1	15	0.2	0.2	18	246
23	Henry 1, 2, 3, 4, 5	19	6.73	20	4	177	8	51	0.3	20	0.9	0.0	71	906
24	Rh Spr. 1, 2	11	6.84	9	3	9	26	4	0.03	11	0.4	0.1	2	74

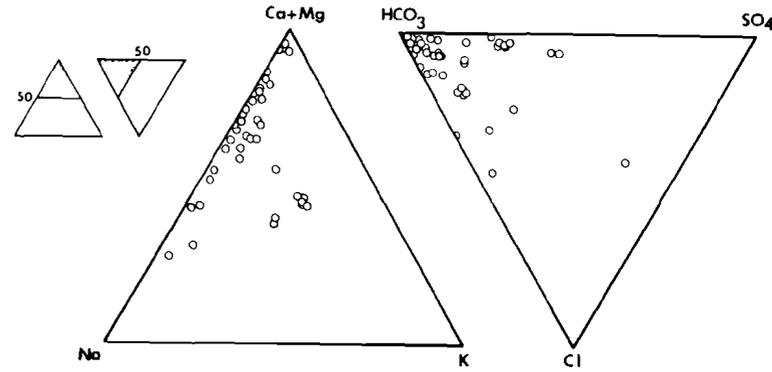[a] Number refers to the numbers shown in Fig. 2.

Fig. 3. Mole percentages of major cations and anions in spring and well water from the Blackfoot Reservoir region, southwestern Idaho.

fluorine, and phosphate. The largest concentrations of strontium (3—7 mg/l), boron (0.1—0.6 mg/l), lithium (0.1—0.9 mg/l), and fluorine (Table 1) are found in waters from the Corral Creek springs, SP 104, SP 114, SP 117, and Soda Springs.

CHEMICAL TEMPERATURES

Springs sampled in southeastern Idaho vary in surface temperature from 8°C to 40°C, with an average of 16°C. The warmest waters occur at a group of springs and wells drilled by FMC Corporation from 1966 to 1970 that are located on the west side of the Reservoir Mountains in the Corral Creek drainage. The relatively low temperatures and lack of evidence of steam fumaroles in the area indicate primarily conductive cooling of the water during ascent rather than cooling by steam separation.

Quartz and chalcedony saturation temperatures assuming no steam loss during cooling were calculated from the measured silica content of the springs and are shown in Table 2. Estimated temperatures vary from 43°C to 119°C for quartz saturation, and from 8°C to 89°C for chalcedony saturation. The calculated temperatures are only moderately high for the springs with the highest surface temperatures. In some cases, the chalcedony temperatures are similar to the measured surface temperatures. Two cold springs flowing through rhyolite to the northeast of the Blackfoot Reservoir (Rh Spr. 1 and 2) give high (100°C) calculated temperatures of quartz equilibration probably due to silica dissolved from volcanic glass, but these springs are below saturation with respect to amorphous silica. Estimated silica temperatures are realistic only if water has reached equilibrium with quartz or chalcedony and has not re-equilibrated or mixed with cooler water on its upward path. In the springs of the Blackfoot Reservoir region equilibrium with quartz or chalcedony may not have been reached due to low temperatures or rapid movement of water through the rocks. The SiO_2 content may be controlled by aluminosilicates rather than a pure silica phase. Most of the warm

springs have a rapid flow, which may mean little re-equilibration has occurred; however, mixing with cooler, more dilute waters may be partly responsible for low silica content.

Na-K-Ca temperatures are also shown in Table 2. The estimates vary from −27°C to +74°C, except for eight springs which give anomalously high temperatures averaging 354°C. Geothermometer temperatures below the measured spring temperatures are the result of deviations from the basic assumptions of mineral—water equilibria. In such cases the measured spring temperature is the best temperature estimate. The springs with high calculated temperature include Corral Creek 1, 2, 3, 4, and 6, SP 104, SP 114, and SP 117. They are roughly aligned in a north-northwesterly direction along the valley of Corral Creek. The anomalous temperatures are a result of large potassium concentrations which are several times greater than any other springs in the area. There may be an abundance of feldspar minerals in the rocks; however, at lower temperatures the amount of Na, K, and Ca in the water may be controlled by reactions between minerals other than feldspars such as micas, clays, and carbonates.

An important characteristic of the springs in the Blackfoot Reservoir region, and one which is not taken into account in the silica or Na-K-Ca geothermometers, is the presence of large amounts of bicarbonate in the water. Concentrations range from less than 100 mg/l to over 3500 mg/l, with the highest amounts found in the Corral Creek springs, SP 104, SP 114, SP 117, and Soda Springs. A correction for the CO_2 content in the water with high Na-K-Ca temperature drastically lowers the Na-K-Ca temperatures. The Corral Creek springs, SP 104, SP 114, and SP 117 show CO_2-corrected Na-K-Ca temperatures that average 32°C, very close to their measured surface temperatures (average 29°C). Most of the Blackfoot Reservoir area springs, other than those mentioned above, have Na-K-Ca-CO_2 temperatures below 0°C, suggesting that a steady-state may exist, not between feldspars, but between other Na, K, and Ca-bearing minerals. Re-equilibration betweeen the water and minerals in the upflow may also be occurring.

A magnesium correction was applied to ten Na-K-Ca temperatures according to the recommendations of Fournier and Potter (1979). The corrected temperatures of eight anomalous Na-K-Ca temperatures are near 100°C. The Na-K-Ca-Mg temperatures (Table 2) are three to four times greater than the measured surface temperatures of the springs. The Mg correction is empirical and based on known water chemistry-temperature pairs (Fournier and Potter, 1979). None of the analyzed waters used in the development of the empirical correction were high bicarbonate waters similar to the Corral Creek samples.

Thermal waters are often enriched in Li as well as other alkalis, and the molar ratio Na/Li may be used as a geothermometer for surface waters (Fouillac and Michard, 1981). The concentration of Li is below the limit of detection (0.04 mg/l) in many of the Blackfoot Reservoir springs, but we have calculated Na/Li temperature for those springs with the highest mea-

TABLE 2

Chemical geothermometers indicating temperatures of last water—rock equilibria for spring spring and well waters in the Blackfoot Reservoir region, southeastern Idaho

Sample	Map No.	Measured temp. T, °C	Quartz (cond.) T, °C	Chalcedony (cond.) T, °C	Na-K-Ca T, °C	Na-K-Ca-CO_2 T, °C	Na-K-Ca-Mg T, °C
Woodall 1	1	12	43	8	−19	−59	
Woodall 2	1	14	53	19	−16	−57	
Woodall 3	1	17	58	23	−6	−52	
Woodall 4	1	8	53	19	−2	−42	
Hooper Spr.	2	10	119	89	58	−15	
Formation Spr.	3	12	43	8	−19	−57	
Poison Ck. 1	4	19	53	19	16	−23	
Poison Ck. 2	4	14	58	23	18	−32	
Big Spr.	5	12	77	43	−6	−46	
Corral Ck. 1	6	40	77	43	366	34	114
Corral Ck. 2	6	38	77	43	365	34	106
Corral Ck. 3	6	32	74	40	367	35	107
Corral Ck. 4	6	28	82	49	368	32	111
Corral Ck. 6	6	25	62	28	347	23	101
Sulfur Spr. 1	7	21	95	63	2	−46	
Sulfur Spr. 2	7	11	58	23	−15	−58	
SP 100	8	10	93	61	74	11	31
SP 101	8	21	103	71	49	6	
SP 102	8	12	91	58	43	−18	
SP 103	9	12	66	31	74	5	70
SP 104	9	22	66	31	370	36	108
SP 105	10	8	43	8	−22	−50	
SP 106	10	8	43	8	−20	−56	
SP 107	10	8	48	14	−24	−53	
SP 108	11	13	53	19	−6	−46	
SP 109	12	10	58	23	−8	−49	
SP 110	13	2	48	14	−27	−61	
SP 111	13	26	48	14	20	−23	
SP 112	13	9	80	46	6	−30	
SP 113	13	9	71	37	−9	−45	
SP 114	14	18	48	14	324	32	83
SP 115	14	11	53	19	3	−41	
SP 116		25	58	23	31	−24	
SP 117	14	28	71	37	325	33	81
SP 118	15	8	62	28	−1	−43	
SP 119	16	10	107	76	50	−13	
SP 120	17	10	48	14	−11	−51	
SP 121	18	16	77	43	34	−25	
Chubb Spr.	19	13	48	14	10	−25	
Soda Spr.	20	30	82	49	28	−27	
Lone Tree Spr.	21	24	62	28	47	−14	
Hopkins Lod.	22	9	80	46	25	−24	
Henry 1	23	15	53	19	1	−40	

TABLE 2 (*continued*)

Sample	Map No.	Measured temp. T, °C	Quartz (cond.) T, °C	Chalcedony (cond.) T, °C	Na-K-Ca T, °C	Na-K-Ca-CO₂ T, °C	Na-K-Ca-Mg T, °C
Henry 2	23	16	58	23	−1	−42	
Henry 3	23	18	53	19	7	−39	
Henry 4	23	20	62	28	16	−34	
Henry 5	23	24	71	37	42	−19	
Rh Spr. 1	24	11	109	78	48	4	
Rh Spr. 2	24	10	105	73	47	1	

sured Li concentrations (Corral Creek, SP 104, SP 114, SP 117, and Soda Springs). Calculated Na/Li temperatures are 210—226°C for Corral Creek springs, SP 104, SP 114, SP 117 and 264°C for Soda Springs and are discordant with other temperature estimates.

The springs near Corral Creek exhibit variations in surface temperature, silica content, and other constituents, thus indicating that they may be of a mixed origin. Mixing models were calculated for six springs assuming cold water temperature is 8°C and silica content is 6 mg/l, similar to several of the coldest springs in the vicinity of Corral Creek. Mixing models conserving enthalpy and dissolved silica are shown on Fig. 4. The estimated temperature of the hot water component ranges from 84°C to 163°C and the fraction of cold water varies from 0.87 to 0.73 (Fig. 4). The best temperature estimate from Fig. 4 is 121°C.
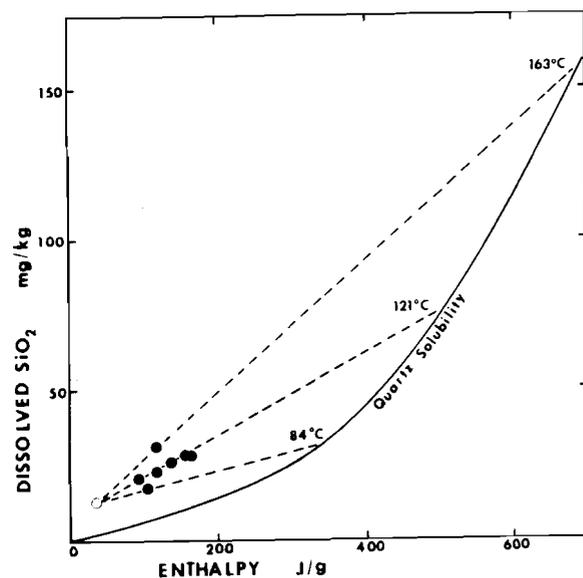
Fig. 4. Dissolved silica versus enthalpy diagram for springs in the Corral Creek area show·

CHEMICAL EQUILIBRIA

Activity diagrams are used to interpret some of the chemical characteristics of the spring waters in relation to the stability of minerals which may be in contact with the water. Carbon dioxide has been shown to be an important component of the springs in the area; therefore, reactions between minerals have been written involving CO_2 and H_2O as reactants and bicarbonate (HCO_3^-) as a product.

The relative stability fields of phases in the K_2O-Al_2O_3-SiO_2-H_2O-CO_2 system at 25°C and 1 atmosphere and 120°C and 2 atmospheres (boiling curve pressure) have been plotted in Fig. 5. P_{CO_2} is assigned a value of 0.26 atmospheres, which is an average value for the Blackfoot Reservoir springs. Thermodynamic data and equilibrium constants for the reactions are computed using the program SUPCRT (Helgeson et al., 1978). All of the springs have silica activities between those of quartz saturation and amorphous SiO_2 saturation, as is typical of many ground waters (Garrels and Christ, 1965; Stumm and Morgan, 1970). Most of the waters plot in the stability field of kaolinite. The cluster of points near the muscovite-K-feldspar junction at 120° (dashed line) represent Corral Creek 1, 2, 3, 4, and 6, SP 104, SP 114, and SP 117. The high concentrations of potassium in these springs could be due to reactions among muscovite, feldspar and carbon dioxide. A trend of
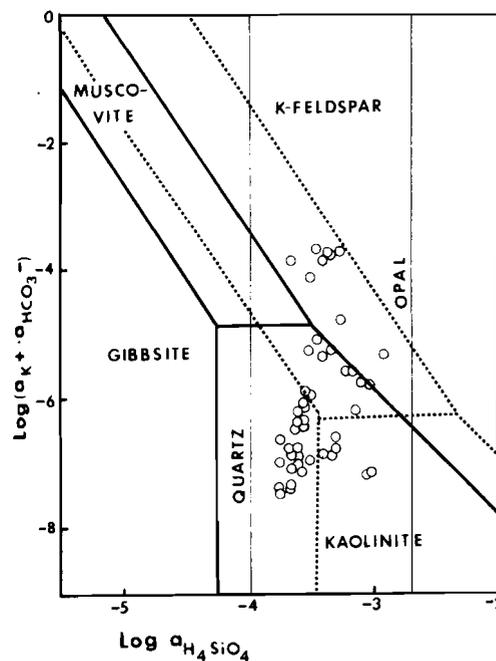

Fig. 5. Logarithmic activity diagram showing log $(a_{K^+})(a_{HCO_3^-})$ versus log $(a_{H_4SiO_4})$, stability of mineral phases at 25°C, 1 atm (solid lines) and 120°C, 2 atm (dashed lines) and water compositions for the Blackfoot Reservoir region (open circles), P_{CO_2} = 0.26 atm.

increasing potassium and silica concentrations in the spring-water activities within the kaolinite stability field, may be due to irreversible reactions of the water with muscovite and feldspar.

Stability relations of analcite, albite, kaolinite, and gibbsite in the system Na_2O-Al_2O_3-SiO_2-H_2O-CO_2 at 25 °C and 1 atmosphere at 120° and 2 atmospheres (boiling curve pressure) are shown in Fig. 6. The spring compositions fall well within the stability field of kaolinite at both temperatures, thus the amount of sodium in the water does not appear to be controlled by equilibrium between Na-feldspar and kaolinite. The sodium could be the result of irreversible reactions of the water with Na-feldspar or of reactions of other low-temperature Na-bearing minerals such as smectites.

The abundance of carbonate rocks throughout the Blackfoot Reservoir region make it highly probable that the calcium and magnesium in solution is derived from reactions with limestone, dolomite, and other carbonate rocks. The springs containing high amounts of bicarbonate also contain the most calcium and magnesium.
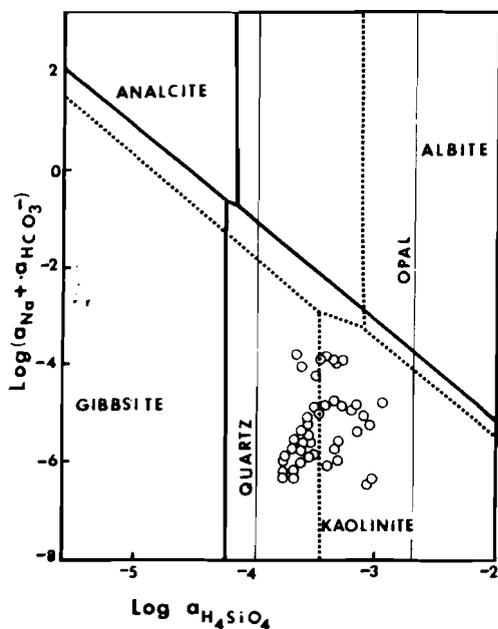

Fig. 6. Logarithmic activity diagram showing $\log (a_{Na^+})(a_{HCO_3^-})$ versus $\log (a_{H_4SiO_4})$. stability of mineral phases at 25°C, 1 atm (solid lines) and 120°C, 2 atm (dashed lines) and water compositions for the Blackfoot Reservoir region (open circles), P_{CO_2} = 0.26 atm.
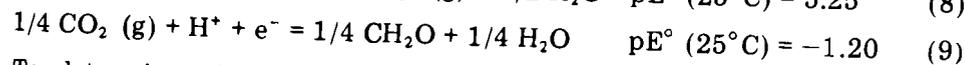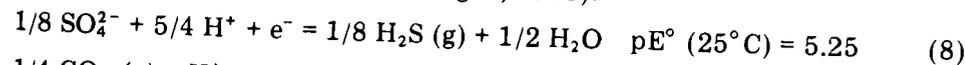
GASES

All of the sampled springs in the Blackfoot Reservoir area are characterized by large amounts of carbon dioxide. There are also a few areas of noticeable sulfur deposition and H_2S odor. Sulfur Springs is located approxi-

mately four miles (6.5 km) east of Soda Springs on the western edge of the Aspen Range at the mouth of Sulfur Canyon. The sulfur and associated small gypsum crystals occur as the cement of a fault breccia composed of tuff, limestone, and quartzite fragments (Richards and Bridges, 1911). Hydrogen sulfide can also be detected in the Blackfoot Reservoir where it is associated with underwater springs and gas seeps. Sulfur-cemented rhyolite fragments were found on the small island south of Sheep Island. Gas bubbles can be seen extending from this island in a southeasterly direction, past the eastern edge of Cinder Island toward the southern end of the reservoir. The eastern side of Cinder Island is a near-vertical cliff which appears to be a fault scarp. The northwest—southeast orientation of the islands and gas bubbles is similar to that of other normal faults to the south and west of the Blackfoot reservoir.

There are several ways to account for the presence of hydrogen sulfide and carbon dioxide gases. Previous authors (Mansfield, 1927; Richards and Bridges, 1911) have suggested a volcanic source for the gases due to the proximity of volcanic centers. The possibility may not be entirely ruled out; however, it is far more likely that the gases, in addition to the aqueous species discussed previously, are derived from reactions of water with the enclosing rocks.

A simple model proposed here is the oxidation of organic matter accompanied by the reduction of sulfate. The two half-cell reactions are (thermodynamic data from Stumm and Morgan, 1970):

$$1/8\ SO_4^{2-} + 5/4\ H^+ + e^- = 1/8\ H_2S\ (g) + 1/2\ H_2O \qquad pE° \ (25°C) = 5.25 \qquad (8)$$

$$1/4\ CO_2\ (g) + H^+ + e^- = 1/4\ CH_2O + 1/4\ H_2O \qquad pE° \ (25°C) = -1.20 \qquad (9)$$
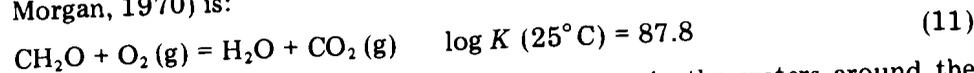
To determine whether the reaction is thermodynamically possible under actual conditions, we can calculate the free-energy change for the reaction, $\Delta G = 2.303\ RT \log(Q/K)$. ΔG is the free-energy change for the reaction, K is the equilibrium constant at 25°C, and Q is the reaction quotient at the same temperature. We will assume that P_{CO_2} = 0.435 atm, the activity of H_2O = 1, the activity of SO_4 = 5.82 × 10^{-4}, and pH = 6.22 (from Sulfur Spr. 1). Stumm and Morgan (1970, p. 283) suggest that the concentration of organic matter in natural waters ranges from 0.1 to 10 mg/l. This corresponds to CH_2O concentrations of about $10^{-5.5}$ to $10^{-3.5}$ moles/l. In the Blackfoot Reservoir area, the actual concentration is probably somewhere between the extremes, due to the abundance of organic-rich sedimentary rocks. Organic matter averages 2.1 weight percent of the Phosphoria Formation (Gulbrandsen, 1967), whose thickness ranges from approximately 75 to 150 m in the Soda Springs area. Other black shale and limestone units are scattered throughout the stratigraphic section. P_{H_2S} can be estimated between 10^{-2} and 10^{-8} atmospheres for springs with a noticeable sulfur odor (Stumm and Morgan, 1970, p. 364). For the reaction:

$$SO_4^{2-} + 2\ CH_2O + 2\ H^+ = H_2S\ (g) + 2\ CO_2\ (g) + 2\ H_2O \qquad (10)$$
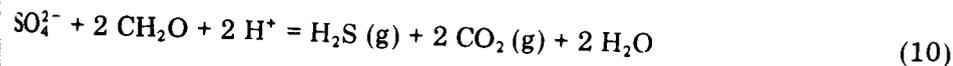
$Q = 10^{14}$ to 10^{24}, $K = 10^{51.6}$, $Q/K = 10^{-38}$ to 10^{-28} and $\Delta G = 2.303\ RT$ log $(Q/K) = -51$ to -38 kcal/mole. The oxidation of organic matter and reduction of sulfate is clearly favored thermodynamically under the conditions given.

Depending upon the oxidation potential, pH, and the presence of biological mediators, the oxidation of organic matter to CO_2 may also be accompanied by the reduction of oxygen, nitrogen, manganese, or iron species. The oxidation reaction most favored thermodynamically (Stumm and Morgan, 1970) is:

$$CH_2O + O_2\,(g) = H_2O + CO_2\,(g) \qquad \log K\,(25°C) = 87.8 \qquad (11)$$

To determine whether the reaction could occur in the waters around the Blackfoot Reservoir, ΔG must be estimated. The concentrations used in the calculation are $P_{CO_2} = 0.26$ atm and $(CH_2O) = 10^{-5.5}$ (minimum value).

A rough estimate of P_{O_2} for use in the calculation can be made at Sulfur Springs, where the amount of sulfate and pH is known, and an estimate (10^{-2} to 10^{-8} atm) can be made for P_{H_2S}. Using reaction (8) where $pE°\,(25°C) = 5.25$ (Stumm and Morgan, 1970):

$$pE = 5.25 + 1/8 \log (SO_4^{2-}) - 5/4\ pH - 1/8 \log P_{H_2S} = -2.20 \text{ to } -2.95 \qquad (12)$$

From the relation:

$$2\,H_2O = 4\,H^+ + O_2 + 4\,e^- \qquad (13)$$

where $pE°\,(25°C) = 20.75$ (Stumm and Morgan, 1970), the partial pressure of O_2 can be calculated from:

$$\log P_{O_2} = -4\,(pE°) + 2 \log (H_2O) + 4\ pH + 4\ pE = -67 \text{ to } -70. \qquad (14)$$

Therefore, for Sulfur Spring 1, P_{O_2} is approximately 10^{-67} to 10^{-70} atm. For the oxidation reaction (11) $Q = 10^{64}$, $Q/K = 10^{-24}$, and $\Delta G = 2.303\ RT$ log $(Q/K) = -33$ kcal/mole. The oxidation reaction is favored thermodynamically under these minimum conditions.

Similar calculations could be made for other redox processes if the concentrations and oxidation states of other elements and gases were known. Mitchell (1976) reports nitrate (NO_3) up to 0.4 mg/l and ammonia (NH_3) up to 2 mg/l in spring waters from this area, which suggests that other reduction processes are also occurring. Buddingtonite, an ammonium feldspar, has been reported to occur in the Phosphoria Formation in southeastern Idaho as an alteration product of volcanic glass or its intermediate products (Gulbrandsen, 1974). The ammonium is thought to be derived from the decomposition of organic matter which is abundant in the phosphatic shale.

The source of the sulfate in Blackfoot Reservoir spring water may be gypsum in the Twin Creek, Nugget, Preuss, or other sedimentary units that occur in western Wyoming and southeastern Idaho. These units do not crop out in the Blackfoot Reservoir region perhaps because of volcanic cover, complex overthrusting, and normal faulting.

High sulfate content in water may also reflect sulfate-rich organic matter in shales or limestones. Hembree et al. (1952) report 1212.0 mg/l SO_4^{2-} in a tributary of the Powder River, Wyoming, flowing over a shale substrate. Subsurface waters flowing through shale, siltstone, limestone, and dolomite commonly contain up to several hundred parts per million sulfate (White et al., 1963). An analysis of drainage water (13°C) from a phosphate mine in the Phosphoria Formation in Garrison, Montana, showed 40 ppm SO_4, 2.0 ppm Cl, 0.9 ppm F, 0.8 ppm NO_3, and 0.45 ppm PO_4 (White et al., 1963). The SO_3 content of phosphorite in the Phosphoria Formation ranges from 1.07 wt.% in the Retort Shale member to 2.17 wt.% in the Meade Peak Shale member (Gulbrandsen, 1967).

The large amounts of sulfur present at Sulfur Springs may be derived from hydrolysis of buried sulfur deposits ($4\,S + 4\,H_2O = 3\,H_2S + H_2SO_4$) (Ellis and Mahon, 1964). Although it may be possible that gypsum beds are hidden in fault blocks beneath the Blackfoot Lava field, it is more probable that the source of sulfate lies within the organic-rich sedimentary rocks common to the region and perhaps in localized sulfur deposits.

SPRING DEPOSITS

Extensive spring deposits are found near the edges of the Blackfoot Lava Field in the Soda Springs, Henry, and Cranes Flat 15-minute quadrangles (Fig. 2). The spring deposits consist of travertine which forms ledges, mounds, or cones, that appear to be associated with north- to northwest-trending normal faults, and are adjacent to calcareous and carbonaceous rocks of Triassic, Permian, Pennsylvanian, and Mississippian ages. Present spring activity and deposition are not nearly as widespread as the magnitude of the spring deposits suggests for earlier Quaternary time.

X-ray diffraction analysis of the acid-insoluble residues revealed that quartz, apatite, and gypsum are nearly ubiquitous minerals. The spring waters are supersaturated with respect to apatite. The spring waters are undersaturated with respect to gypsum and anhydrite. Other minerals identified in travertine include pyrite, geothite, gibbsite, a phosphate, and a zeolite (?). The phosphate minerals other than apatite are difficult to identify because they are present in small amounts, have a large range of cation substitution, and can be hydrated or partially hydrated.

HEAT FLOW, GEOTHERMS, AND WARM WATER

Maximum surface spring-water temperatures in the Blackfoot Reservoir region average 40°C at the Corral Creek springs and temperature of last equilibration with minerals is estimated at 100—120°C. The water may be heated to this temperature by deep circulation without invoking the presence of an igneous body at depth.

The depth to which the water must circulate to reach 100—120°C may be

estimated from the observed thermal gradient in southeastern Idaho. Brott et al. (1981) tabulate geothermal data from 248 drill holes in southeastern Idaho. Gradient estimates and therefore heatflow estimates for the Snake River Plain are complicated by the presence of the Snake Plain aquifer, but thermal gradients on the southeastern margin average $66 \pm 6°C$ per km which leads to estimated heat flow of 124 ± 13 m W m^{-2}. The mean annual surface temperature of the Blackfoot Reservoir region is $5°C$. Water of the Corral Creek springs would be required to circulate to a depth of 1.75 km to reach $120°C$. The regional heat flow values (Blackwell, 1978) imply a lower thermal gradient and a greater circulation depth to reach $120°C$.

Estimation of geotherms, heat flow, and circulation depths is complicated by the presence of young basalt flows, rhyolite domes, and shallow aquifers. It appears reasonable that water can be heated to the moderate temperatures estimated for the Blackfoot area by circulation along faults to depths of a few kilometers.

SUMMARY AND DISCUSSION

There is considerable geologic evidence that geothermal resources are present in the Blackfoot Reservoir region of southeastern Idaho. Thick Quaternary basalt flows occur in the western part of the area in Gem Valley, the Blackfoot Lava Field, and the Willow Creek Lava Field. Abundant basaltic cinder and lava cones and related basaltic intrusive bodies located within the lava fields imply a local source. Three young rhyolite domes (about 50,000 years old) at the southern end of the Blackfoot Reservoir coincide with gravity and magnetic anomalies. The anomalies may be alternatively explained by: (1) deep Tertiary valley fill and thick basalt flows and related basaltic intrusives; (2) a volcanic collapse structure; or (3) a large, shallow, laccolithic silicic magma body. The first explanation has been verified for other geophysical anomalies in the area, and there is no additional evidence for a volcanic collapse structure or magma body in the Blackfoot Reservoir region.

North- to northwest-trending high-angle normal faults of Tertiary to Holocene age appear to be the dominant structural control of spring activity in the area, as attested to by travertine deposits along the east side of the Bear River Valley and Blackfoot Lava Field.

The Blackfoot Reservoir region lies in a zone of high heat flow which parallels the Snake River Plain to the north. From regional heat flow data it is possible to estimate temperature-depth profiles and calculate that circulating meteoric water may reach temperatures up to $100°C$ within a few kilometers of the surface. If additonal heat sources are present, such as a cooling magma body, the depth of circulation would be much less. More detailed heat flow data near the Blackfoot Reservoir would be helpful in distinguishing variations in heat flow and assessing the presence of local heat sources.

Chemical geothermometers used to calculate temperatures of last water—

rock equilibrium must be used with full understanding of the basic assumptions inherent in the method. Quartz- and chalcedony-saturation temperatures average $67°$ and $34°C$, respectively, for springs in the Blackfoot Reservoir region. Unless substantial mixing and re-equilibration with cooler shallow waters has occurred, these temperatures indicate that a hot-water reservoir is probably not present at shallow to moderate depths. Mixing models based on the silica and enthalpy of warm and cold springs in the Corral Creek drainage denote a hot water component with a temperature of about $120°C$ present in the subsurface.

Na-K-Ca temperatures vary up to $74°C$, except for eight springs along the Corral Creek drainage that average $354°C$. Activity diagrams depicting stability fields of several common minerals show that the sodium and potassium in the waters are not derived from equilibrium reactions among feldspars and other minerals. Exceptions are the high concentrations of potassium in the eight springs mentioned above, which appear to be derived from reactions between the potassium-bearing minerals muscovite and potassium-feldspar. The anomalous chemical temperatures are a direct result of the large potassium concentrations. It appears that for most of the Blackfoot Reservoir springs, a basic assumption of the Na-K-Ca geothermometer has not been met and the calculated subsurface temperatures have little significance. If the effects of carbon dioxide, which is abundant in springs of the region, are considered, the predicted subsurface temperatures of the eight anomalous samples are lowered to an average of $32°C$ which is close to the measured surface temperature. In using the carbon dioxide or magnesium corrections to the Na-K-Ca geothermometer, the same basic assumptions are inherent in the methods as with the original geothermometer.

Bicarbonate is the major anion present in the Blackfoot Reservoir springs. Many of the springs appear to be "boiling" due to the vigorous release of the gas at surface pressures. The bicarbonate acts as an acidifying agent which increases the reaction rate between rock and water. This is particularly evident in the large concentrations of calcium and magnesium seen in the waters, which are derived from reaction of limestones and other carbonate rocks abundant in the region. As the calcium carbonate-saturated water reaches the surface, CO_2 gas is released due to the decreased pressure and the pH increases causing calcium carbonate to be precipitated.

A thermodynamically feasible mechanism to account for the presence of carbon dioxide and hydrogen sulfide gases is through the oxidation of organic material by the reduction of sulfate. Abundant organic material and sulfate is available from the Phosphoria Formation and other dark shales and limestones in the area. It is both possible and probable that the gases are derived from water—rock reactions and are not volcanic emanations.

CONCLUSIONS

There are several conclusions which can be made concerning geothermal potential in the Blackfoot Reservoir region of southeastern Idaho from this study of the spring-water chemistry:

(1) Major and minor elements found in the spring water are derived from water—rock reactions which may be enhanced by carbon dioxide and sligthly increased temperatures at depth. There is no need to invoke a volcanic or magmatic source for any of the constituents.

(2) CO_2 and H_2S gases are also derived from water—rock reactions and are not products of subsurface volcanic activity.

(3) Chemical thermometers must be used with caution in low-temperature CO_2-rich environments. The silica geothermometer may be the most useful in these cases.

(4) Based on spring geochemistry, a geothermal reservoir of less than 100°C may exist at shallow (less than 2 km) depths in the Blackfoot Reservoir region. There is no evidence of a high-temperature component in the warm springs. Additional heat-flow data may indicate that temperatures hot enough for local use (space heating, etc.) can be found at exploitable depths in the region. Normal faulting provides conduits for water circulation; however, travertine deposition may result in impedance of the flow within the channels or in pipes.

ACKNOWLEDGEMENTS

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HYDROTHERMAL HISTORY OF PITON DES NEIGES VOLCANO (REUNION ISLAND, INDIAN OCEAN)

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ABSTRACT

Rançon, J. Ph., 1985. Hydrothermal history of Piton des Neiges volcano (Reunion Island, Indian Ocean). *J. Volcanol. Geotherm. Res.*, 26: 297—315.

The Piton des Neiges volcano on Reunion Island represents a unique example of an oceanic volcano where the extreme development of amphitheatre-headed valley erosion has led to the formation of three large cirques. They are so large that the island's volcanostructural and petrological history can be traced from its emergence to the latest stages of its sub-aerial evolution (> 2.1 m.y. to 22,000 years ago).

The various magmatic series of the Piton des Neiges are, moreover, abundantly invaded by hydrothermal mineralization. It is this post-magmatic feature, represented by the hydrothermal alteration of the series, which is examined here.

Mineralogical studies (X-ray, microprobe, scanning electron microscope) reveal a large number of hydrothermal species. Of these, zeolites are the most common and five are described here for the first time in Reunion (gonnardite, levynite, erionite, garronite, herschelite).

Six hydrothermal facies characteristic of weak metamorphism are defined: chabazite-phillipsite, natrolite-thomsonite, analcime-thomsonite, laumontite-thomsonite, albite-prehnite and prehnite-pumpellyite. The paleo-temperatures covered by these facies range from 0 to 380°C.

On the basis of these data and supporting field observations, three main hydrothermal phases were determined and fitted into the known chronostratigraphy. These three phases have succeeded one another over the last two million years in the Piton des Neiges massif. The extent and mineralogical facies of each phase can be related to the volcanotectonic structures. This sequence has been directly linked to the geological evolution of the massif. The progressive restriction with time of the hydrothermal manifestations to the present Piton des Neiges occurred alongside the focusing of volcanism centralized on this same relief. An attempt is made to reconstruct the island's hydrothermal history.

GEOLOGICAL SETTING

The island of Reunion, part of Mascarene archipelago, lies in the western Indian Ocean, between the Mid-Indian Ocean Ridge and Madagascar. Reunion is a typical intraplate volcano which developed independently from the other Mascarene islands, Mauritius and Rodrigue (Perroud, 1982), and