STATE OF ALASKA

DEPARTMENT OF NATURAL RESOURCES

DIVISION OF GEOLOGICAL AND GEOPHYSICAL SURVEYS

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Report of Investigations 83-15
PROGRESS REPORT - THERMAL FLUID INVESTIGATIONS OF THE MAKUSHIN GEOTHERMAL AREA

By
R.J. Motyka, M.A. Moorman,
and Robert Poreda

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PROGRESS REPORT - THERMAL FLUID INVESTIGATIONS
OF THE MAKUSHIN GEOTHERMAL AREA

By
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ABSTRACT

The number, variety, and distribution of thermal areas indicates the existence of a significant and widespread geothermal resource at Makushin. The Makushin geothermal system appears to consist of a deep boiling hot-water reservoir overlain by a shallow, discontinuous vapor-dominated zone that discharges steam and fumarolic gases at elevations above 360 m. The distribution of thermal springs, fumaroles, and heated ground indicates the hydrothermal system extends from beneath Makushin Volcano outwards to its southeastern flank and along a prominent northeast-trending lineament east of the volcano. The late-Pleistocene to Recent collapse caldera at the summit of Makushin Volcano and the locations of Recent satellitic volcanic cones suggest the hydrothermal system is driven by an elongate, shallow magmatic heat source or perhaps by a series of discrete magma bodies lying along the northeast-southwest trend. The host reservoir rock for the hydrothermal system is a granodioritic intrusion that glacier erosion has extensively exposed on the southeastern flank of the volcano. Numerous fumaroles and associated low-Cl thermal springs rich in HCO_3 and SO_4 emanate from exposed portions of this pluton. Volcanic flows and unfractured or self-sealed upper parts of the pluton apparently serve as cap rocks elsewhere on the system. Thermodynamic considerations of a 152°C superheated fumarole indicate steam separates from the main reservoir at temperatures ≥185°C. Gas geothermometry gives reservoir temperatures ranging from 235°-300°C. A bottom-hole temperature of 195°C was measured in a thermal-gradient hole drilled to a depth of 460 m (90 m below sea level) in upper Makushin Valley, confirming that reservoir temperatures exceed at least this temperature. Enrichments of Li, F, Ag, S (±Hg) found in rock cores recovered from the well indicate alkaline or neutral water-dominated conditions prevailed at the bottom of the hole. Halite deposits were found in association with hydrothermal alteration on and within recent moraines at the head of Glacier Valley in an area that now displays only fumarolic and low-Cl thermal spring activity. These deposits, which indicate alkali-chloride thermal spring activity, suggest that the underlying hot-water reservoir may have recently undergone a rapid depletion of water.

Fumarolic gases evolving from the geothermal system are predominantly CO_2, H_2S, N_2, and H_2 with CO_2:H_2S ratios ranging as high as 7.5. The ^3He:^4He ratios of the fumarolic gases range from 4.5 to 7.8 times atmospheric. These isotopic compositions confirm a magmatic influence on the geothermal system. $\delta^{13}C$ compositions of CO_2 range from -10.2 to 13.0 parts per thousand (permil). The δD compositions of H_2 and steam from the superheated fumarole are near equilibrium for the fumarole outlet temperature of

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152°C. Isotopic composition of deep reservoir waters in equilibrium with the superheated steam is estimated to be $\delta^{18}O \sim -8$ permil and $\delta D \sim -80$ to -86 permil. This range in D values is similar to that in local stream waters and indicates that meteoric waters that charge the deep hot-water system originate from the flanks of the composite volcano. The numerous low Cl, HCO_3 - SO_4 thermal springs that occur in upper Glacier and Makushin Valleys originate from the circulation of local meteoric waters along fractures in the Makushin pluton and appear isolated from any deep hot-water reservoir. A thermal-gradient well indicates that lateral flow of thermal waters in upper Glacier Valley extends to depths of 150 m below sea level. The waters are heated by steam and hot gases ascending from the deep reservoir and by conduction from wall rock. Alkali-chloride, HCO_3-SO_4 rich thermal spring waters in lower Glacier Valley appear to be mainly derived from subsurface downvalley flow of HCO_3-SO_4 thermal waters that originate on the flanks of Makuskin Volcano. The increased concentration of Cl and other constituents could be accounted for by seawater contamination or perhaps by passage of the thermal waters through the Unalaska Formation. However, the possibility of leakage and mixing of Cl-rich hot-water from a deep reservoir cannot be dismissed.

INTRODUCTION

Unalaska Island, second largest in the arcuate chain of Aleutian Islands, is located between latitudes 53°15' and 54°N. and between longitudes 166° and 168°W., 200 km southwest of the Alaska Peninsula (fig. 1). Unalaska village lies on the southern shore of Illiuliuk Bay near the head of Unalaska Bay. The village has a permanent population of about 1,000 people.

Because of the excellent deep-water harbor located at Unalaska Bay (one of the few protected harbors in the Aleutians), the village of Unalaska has naturally evolved into the major base of operations for the Bering Sea fishing industry. Thirteen fish processors operate in the area and bring in as many as 2,000 seasonal employees during the height of crab-fishing season. Unalaska is known as the crab capital of the world.

Unalaska will undoubtedly continue to grow. Recent offshore oil and gas exploration in the Bering Sea has already begun to tax the harbor facilities at Unalaska. The imminent entry of Alaskan fishermen into the Bering Sea bottom fishery will produce additional demands on the village.

To help support its growing service industries, the village is actively seeking a dependable energy base. Electrical power needs of the village and the processors are presently met through oil-fired generators at a cost of 34¢ per KWH. The area lacks any reasonable potential for large-scale hydroelectric.

In 1980, in a search for an alternative energy source, DGGS began investigating the geothermal energy potential of the surrounding area. Attention focused on Makushin Volcano, located 20 km west of Unalaska village (fig. 1). Fumarole fields and thermal springs which occur on the flanks of the active volcano indicated the presence of a high-temperature geothermal resource that, if developed, could be used by the village. Geological and geophysical investigations of the area were initiated by J. Reeder of DGGS (Reeder, 1982;

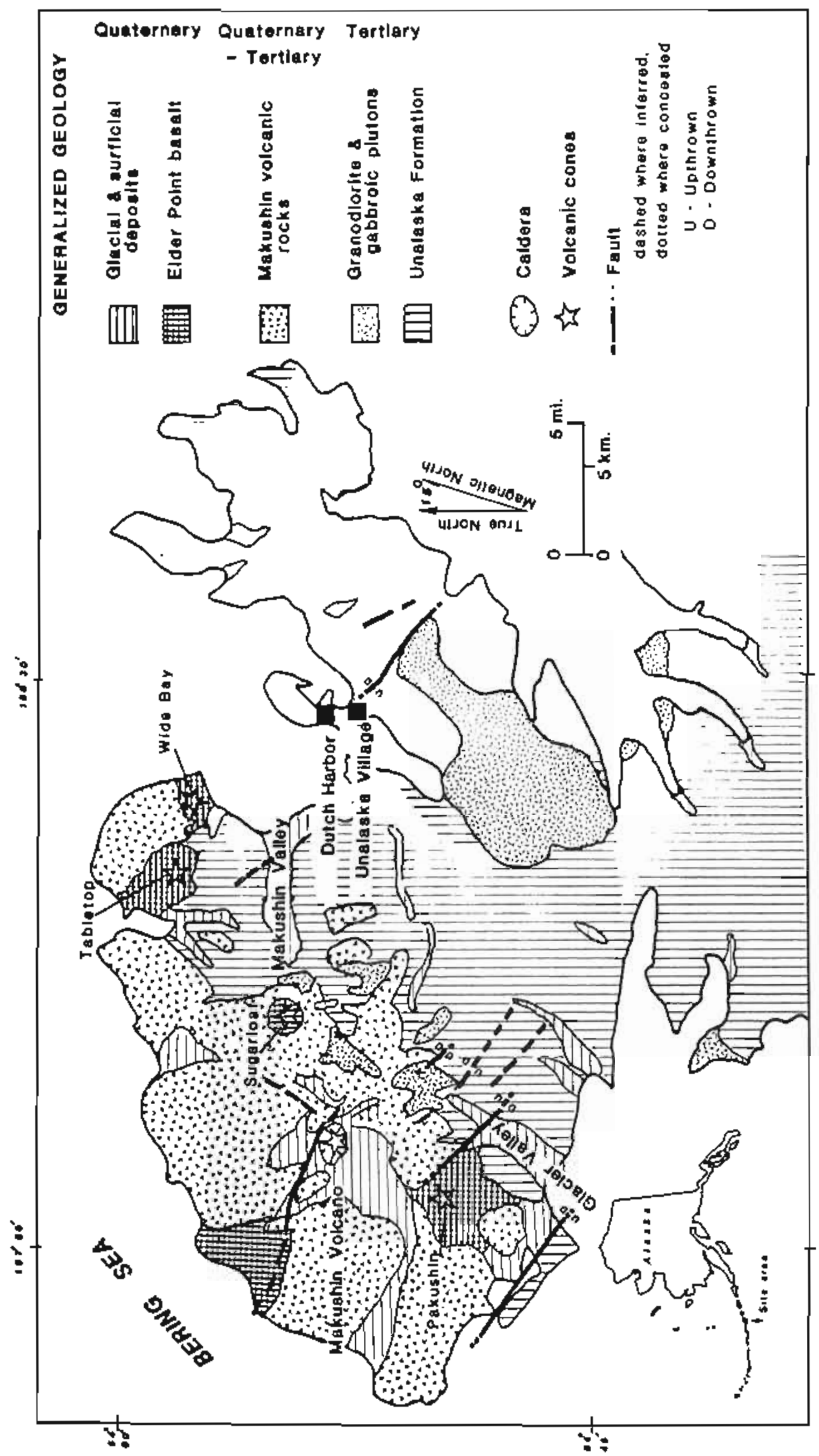

Figure 1. Site map and generalized geology of northern Unalaska Island. Geology adapted from Drewes and others (1961) and Henning and Reeder (1983).

personal commun., 1982). Investigations of fluids associated with the thermal fields were undertaken by the authors to help assess the nature and extent of the underlying hydrothermal system and to provide estimates of reservoir temperatures. The results of these earlier investigations indicated the presence of an extensive shallow vapor-dominated zone as manifested by numerous low-Cl thermal springs that are also rich in HCO_3 and SO_4 and by widespread fumarolic activity at the heads of both Glacier and Makushin Valleys (Motyka and others, 1981; 1982). Initial gas geothermometry suggested deep reservoir temperatures of 230°-280°C. However, the depth of the steam zone, its lateral extent, and the nature of the subsurface system feeding the steam zone (boiling hot-water reservoir or vapor-dominated system) could not be resolved.

Based partially on the findings of DGGS studies and on economic and political factors, the state of Alaska funded a major exploratory drilling program---managed by the Alaska Power Authority (APA)---at Makushin. Republic Geothermal, Inc. (RGI), of California was chosen as the prime contractor. After conducting additional geophysical and geochemical investigations at Makushin Volcano, RGI sited and drilled three 460-m-deep (1,500-ft) thermal gradient holes during the summer of 1982, one of which had a measured bottom-hole temperature of $\sim$195°C.

In conjunction with the exploratory drilling phase, DGGS has cooperated and acted in an advisory capacity to both APA and RGI. In addition, DGGS expanded its investigations of geothermal fluids associated with the Makushin geothermal area. The preliminary findings of these studies are the subject of this interim report. Details on geological and geophysical aspects are covered elsewhere (Reeder and others, 1982; Republic Geothermal Report, in preparation, 1983).

As part of this expanded study, the authors have sampled and are completing analysis of waters, gases, sinter deposits, and hydrothermal alteration products from most of the known thermal fields located on Makushin volcano, including the fumaroles associated with the summit volcanic vent. The data acquired thus far have helped further the understanding of the subsurface hydrothermal system and deep reservoir characteristics, reservoir temperatures, the source of volatiles in the system, the source of waters in the system, and geohydrological conditions. These data are also important in providing pre-exploitation baseline information on the geothermal resource. One vital purpose of these studies is to help guide the siting of the deep test well scheduled for drilling during the summer of 1983.

The observations discussed below support a model of the Makushin geothermal system in which meteoric waters on the flanks of Makushin Volcano charge a deep hot-water reservoir where waters are heated by a cooling magma body to temperatures of 250°-300°C. The geothermal waters boil at temperatures between 190° and 235°C to form a vapor-dominated zone. Steam and gases ascending from this zone feed numerous fumaroles on the southern and eastern flanks of the volcano and give rise to HCO_3 - SO_4 thermal springs.

GEOLOGIC SETTING

The Aleutian chain of active volcanoes lies immediately north of the Aleutian Trench, a convergent boundary between the North American and the Pacific lithospheric plates. This convergence produces one of the most seismically active belts in the world, with much of the seismicity originating from the Benioff zone, the subcrustal region where the Pacific plate is being actively subducted under the North American plate. The eruption of Aleutian magmas appears to be intimately related to this subduction process. The direction of motion of the Pacific plate is northwesterly. In the central Aleutians, this motion is nearly perpendicular to the strike of the volcanic arc with a rate of convergence of $\sim$6.6 cm/yr.

The western part of the arc has been built on oceanic crust that is younger than Cretaceous (Cooper and others, 1974; Kay and others, 1982), whereas the eastern part overlies the Mesozoic continental basement of the Alaska Peninsula (Reed and Lanphere, 1973). Unalaska Island and Makushin Volcano lie on the transition zone separating oceanic and continental subduction domains. Generally, the rocks that form the Aleutian Islands fall into three informal units as defined by Marlow and others (1973), Delong and others (1978), and summarized by Perfit and others (1980): a) an 'early series,' as old as Eocene, composed of marine clastics, volcaniclastics, volcanic flows (predomintly submarine), and associated plutons that have been slightly deformed and metamorphosed to greenschist facies, b) a middle unit of plutonic rocks with radiometric ages primarily between 10 and 15 m.y. B.P., and c) a 'late series' (≤5 m.y. B.P.) consisting of interbedded 'andesitic' volcanic rocks and volcaniclastics that are unmetamorphosed and lie unconformably over the older units.

On Unalaska Island, the Unalaska Formation constitutes the oldest and most extensive group of rocks on the island and consists of a thick sequence of coarse and fine sedimentary and pyroclastic rocks intercalated with dacitic, andesitic, and basaltic flows and sills, cut by numerous dikes and small plutons (Drewes and others, 1961) (fig. 2). The formation, which is exposed over two-thirds of the island, is at least as old as early Miocene (Perfit and others, 1980) and is probably correlative with the 'early series' that occurs elsewhere in the Aleutians. The formation has been extensively folded, faulted, and intruded by plutonic rocks, with moderate hydrothermal alteration occurring near the plutons.

Three well-exposed plutons---Captains Bay, Shaler, and Beaver Inlet---and several smaller plutons intrude the Unalaska Formation. Marlowe and others (1973) reported a K-Ar date of 11.1 ± 3.0 m.y. B.P. for the Shaler pluton; Lankford and Hill (1979) quote an unpublished K-Ar age of 13 m.y. B.P. (D.W. Scholl, USGS, Menlo Park) for the Captain's Bay pluton. The chemistry of the plutons follow calc-alkaline trends (Kay and others, 1982). The Captain's Bay pluton, which is typical of the larger granodiorite plutons along the arc, is crudely zoned from a narrow rim of two-pyroxene gabbro and diorite to a heterogeneous central region of hornblende-biotite granodiorite that is intruded by aplite dikes (Perfit and others, 1980).

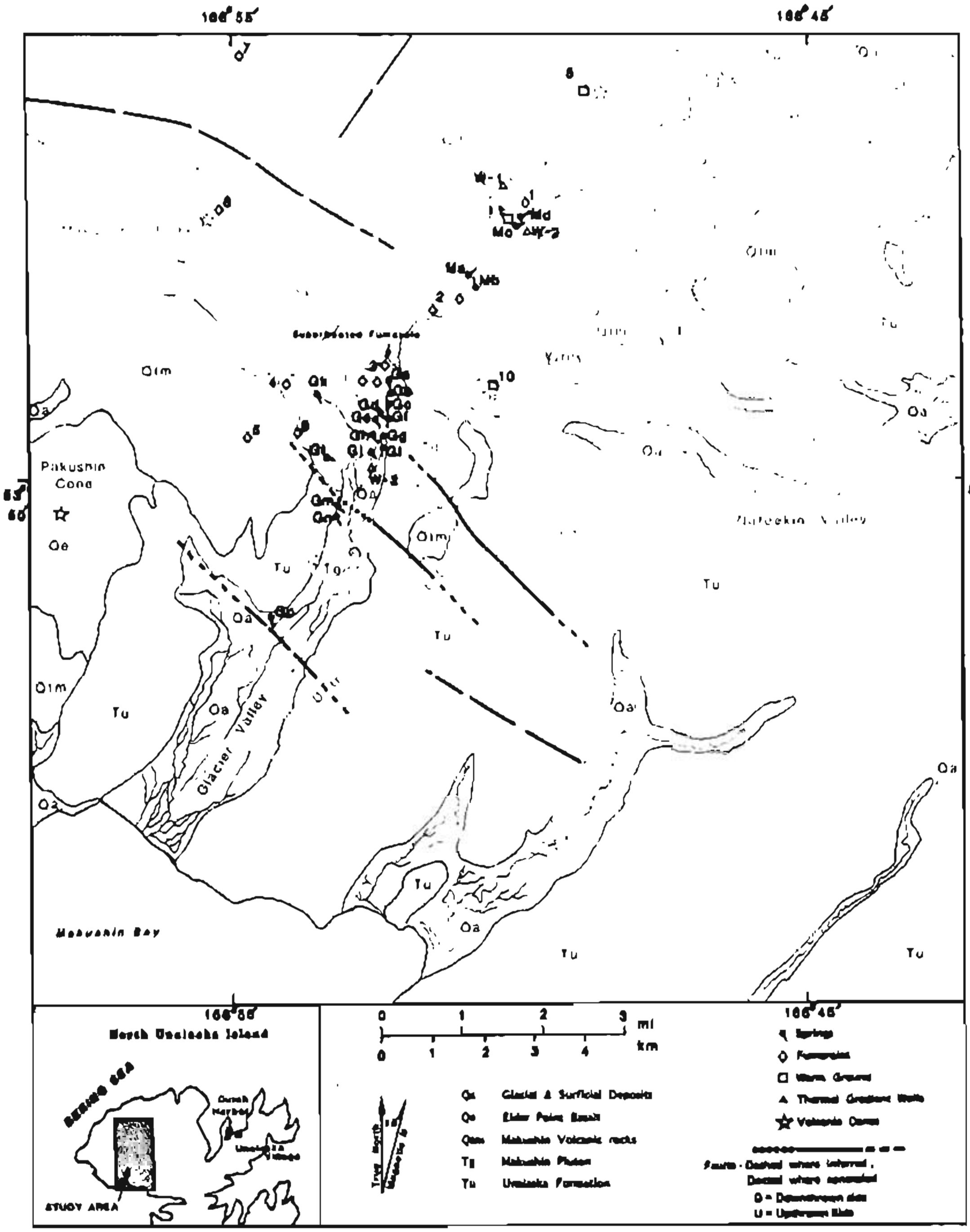

Figure 2. Location map of thermal springs, fumaroles, and hot ground in the Makushin geothermal area. Geology from Drewes and others (1961), Henning and Reeder (1983), and P. Parmentier, RGI, personal commun., (1982).

Recent studies by Reeder and others (1982) on a pluton exposed at the heads of Makushin and Glacier Valleys suggest this intrusion is similar in composition to the Captain's Bay pluton. Chemical analyses on the Makushin intrusive showed an east-southeast trend in silica content, which ranged from

51 percent in Makushin Valley to 62 percent in Glacier Valley, with quartz monzodiorite predominating. The age of this pluton is unknown but is probably correlative with intrusions elsewhere on Unalaska Island.

The Makushin pluton is known to extend northward at least as far as W-1 (fig. 2), where it was encountered beneath 372 m of volcanic flows in a thermal-gradient well (C. Isselhardt, RGI, personal commun. 1982). Preliminary interpretations of gravity data suggest the pluton dips to the northwest beneath Makushin Volcano at a moderately steep angle (Reeder and others, 1982). Most of the thermal activity observed at the surface on the flanks of Makushin Volcano occurs within the exposed portion of this dioritic intrusion.

The western part of northern Unalaska is dominated by Makushin Volcano (2,035 m), a major volcanic center in the Aleutian arc. The broad dome-shaped summit has a small caldera and is capped by a glacier with tongues that descend the larger valleys to elevations as low as 300 m. Four associated late Pleistocene to Recent volcanic cinder cones and composite cones form a roughly northeast-southwest trend that cuts across the heads of Makushin and Glacier Valleys. Volcanic rocks from Makushin Volcano and the associated smaller volcanic cones are here collectively termed the Makushin volcanic field.

Basalt and andesite flows and pyroclastic rocks that compose the Makushin volcanic field unconformably overlie the Unalaska formation and the plutonic rocks that intrude it (Drewes and others, 1961). Marsh (1982) estimates the total volume of Makushin volcanic rocks at 200 km^3. Kay and others (1982) reported the Makushin volcanic rocks have both tholeiitic and calc-alkaline affinities. More recently, Swanson (personal commun., 1983), on the basis of a much larger data base, found the Makushin volcanic rocks to be almost exclusively tholeiitic. Whole-rock and trace-element analyses suggest that the volcanic rocks constituting the Makushin volcanic field have a common magmatic source and that a single magma chamber underlies the field at a relatively shallow depth (Swanson and others, 1983).

Drewes and others (1961) estimated the onset of Makushin volcanism to be late Tertiary or Early Pleistocene, but that the bulk of the volcano was formed in the late Pleistocene. K-Ar determination of absolute age of volcanic rocks from the Makushin area was not possible because of alteration problems and the apparent youth of the volcanism (Reeder, DGGS, personal commun., 1982). Based on the detection limits of the age-dating equipment used, three of the samples are considered to be younger than 0.5 m.y. B.P. and one sample is less than 50,000 yr B.P. (Stan Evans, ESL, U. of Utah, personal commun., 1982).

The lack of erosion of the caldera rim suggests that the Makushin summit caldera formed in late Pleistocene or Recent times. Valley-filling pyroclastic flows and mud-flow deposits occur at the head of Makushin Valley and in a valley south of Bishop Point; they may be related to the caldera-forming eruption. In Makushin Valley these deposits form a flat, uniform surface and overlie glacial till that may have been deposited during a neoglacial advance.

Makushin Volcano is still active and is known to have erupted at least 14 times since 1760, the most recent a minor eruption in 1980 (Coats, 1950; SEAN, 1980). The Wide Bay cones, Table Top Mountain, Sugarloaf Cone, and Pakushin Cone have all probably been active since the last major glaciation.

THERMAL AREAS

Active volcanic systems, shallow magmatically heated rock, and deep, penetrating fracture and fault systems caused by the convergence of two major lithosphere plates combine to provide a favorable setting for the development of hydrothermal systems throughout the Aleutian arc (Motyka, 1982).

At Makushin Volcano the surface expression of such hydrothermal systems are the numerous thermal springs and solfatara fields that occur on the eastern and southeastern flanks of the mountain. Fumarolic activity and areas of geothermally heated ground have now been identified at 12 different locations on and near Makushin Volcano (fig. 2, table 1). Eight of these sites (1-8) were found during previous field investigations (Maddren, 1919; Drewes and others, 1961; Motyka and others, 1981; 1982; Reeder, 1982); four additional sites (9-12) were found during the summer of 1982 (this report; M. Henning, DGGS, personal commun., 1982; P. Parmentier and C. Isselhardt, RGI, personal commun., 1982). In addition, thermal springs are known to occur at 15 localities in Glacier Valley and its tributaries and in four localities at and near the head of Makushin Valley (fig. 2). Several of these sites---including the chloride springs Gm, Gn, and Gp (table 2) in Glacier Valley---were discovered during the summer of 1982.

The most extensive regions of fumarolic activity on the flanks of Makushin Volcano occur at the heads of Makushin Valley (sites 1, 2, and 11, table 1; fig. 2) and Glacier Valley (sites 3, 4, 9). These areas, together with fumarole fields 5 and 7, form an arcuate zone of fumarolic activity on the southeastern flank of the mountain. Fumaroles on the flank of the volcano range in elevation from 360 m (field 1) to 870 m (field 5). High pressure fumaroles were found at sites 3, 5, and 6. One of these is a super-heated fumarole at 152°C, located near the upper end of site 3. Several vents at site 5 were slightly above boiling. The high-pressure fumaroles at the summit could not be measured for temperature because of ice hazards and noxious gases, but are probably superheated.

Numerous HCO_3-SO_4 thermal springs occur in association with the fumarole fields both at the heads of Glacier and Makushin Valleys and immediately downvalley. Spring temperatures range from 40°C to boiling. Warm Mg-Cl springs that are also rich in bicarbonate and sulfate are located along the west side of lower Glacier Valley. The lowest Mg-Cl spring (Gp) lies at about 75 m.

Fumarole field 2 (head of Makushin Valley) and all fumaroles at the head of Glacier Valley lie at the eastern edge of the Makushin volcanic field and occur within the Makushin pluton. Thermal springs Ga-Gl and Ma and Mb emanate from the diorite, whereas spring Mc occurs near the contact of Makushin volcanic rocks with the diorite. Although many of the fumaroles at these sites lie close to the contact with Makushin volcanic flows, the surface expression of fumarolic activity does not extend beyond the contact boundary.

Table 1. Description of fumarole fields and areas of geothermally heated ground at and near Makushin Volcano.

Site	Description
1	Fumarole field: Located in Makushin Valley about 4 km SW of Sugarloaf Cone (fig. 2). The site occurs on the steep northern valley wall at 360 m elevation and consists of a 2,500-m^2 area of mild boiling-point fumarolic activity, mudpots, and heated ground. Hot springs occur immediately below the fumaroles. The fumaroles emanate from colluvium overlaying Recent Makushin volcanic flows.
2	Fumarole field: Located on a steep southeast-facing slope at the head of Makushin Valley between elevations of 640 and 820 m. Thermal activity consists of numerous, boiling-point, mildly pressurized fumaroles covering an area of 0.25 km^2. The vents tend to occur in linear clusters oriented 310°, which suggests that fractures control the fumarolic conduit system. The fumaroles emanate from the Makushin diorite, which has been fractured and intensely hydrothermally altered in this vicinity. The west end of the fumarole field is capped by Makushin volcanic flows.
3	Fumarole field: Located at the head of Glacier Valley on a steep bluff that lies between two deep canyons. Several zones of fumarolic activity and hydrothermally altered ground cover an area of $\sim$0.5 km^2 between elevations of 370 and 600 m. The fumaroles emanate from the Makushin pluton. A highly pressurized superheated fumarole (152°C) occurs beneath a steep cliff of capping Makushin volcanic flows at an elevation of $\sim$600 m. A neighboring fumarole with much lower pressure measures 105°C. Fumaroles elsewhere on the bluff are mildly pressurized and at the boiling point.
4	Fumarole field: Located at $\sim$630 m near the margin of a glacier that descends into a western tributary valley of Glacier Valley. Fumarolic activity and mudpots cover several hundred square meters and emanate from a Recent lateral moraine. Bedrock above the moraine is Makushin diorite. Two of the fumaroles are highly pressurized and spew jets of hot water and steam as a result of stream water infiltrating into the vents. These two vents could not be reached for temperature measurement; other vents in the vicinity were at boiling point.
5	Fumarole field: Located on the south flank of Makushin at 870 m elevation. The fumaroles occur in a 100-m-dia hole melted through a thin cover of glacier ice. Vent temperatures were slightly superheated (99°-100°C). One fumarole is highly pressurized and periodically ejects jets of hot water and steam. The geyserlike activity is probably caused by meltwaters flowing into the superheated vent. Rocks in the glacier hole are bedded volcaniclastics, possibly part of a debris flow.

Site	Description
6	Fumarole field: The largest and most prominent area of thermal activity, located at the active volcanic crater near the center of the otherwise ice-filled summit caldera of Makushin Volcano. Maddern (1919) reported sulfur deposits in and around the crater and observed several loud, high-pressure fumaroles, one of which he measured at 150°C. Several high-pressure fumaroles on the flanks of the active crater and a conspicuous vapor plume emanating from the crater were observed during a reconnaissance to the summit in July 1982 by one of the authors (Motyka). Sulfur deposits ringed several of the vents and sulfur fallout from the crater plume coated the snow surface downwind of the crater. Ice hazards and noxious gases prevented temperature measurements of the high-pressure fumaroles in 1982, but the vents are thought to be superheated. Temperatures of small steam vents in an adjacent ice-free ridge were all at the boiling point.
7	Fumarole field: Located on the north flank of Makushin at an elevation between 820 and 860 m. The site is reported to consist of mild boiling-point fumarolic activity covering $\sim$1,000 m^2 (Reeder, 1982). Rocks in the vicinity are Makushin volcanics.
8	Warm ground: Located on a ridge about 1/2 km southwest of Sugarloaf Cone at an elevation of 525 m (Wescott and others, 1982). The site consists of $\sim$100 m^2 of anomously warm ground. Temperatures measured as high as 85°C at 0.75 m depth. The knoll of warm ground lies on a ridge composed of late Quaternary basaltic flows.
9	Fumarole field: Located at an elevation of 475 m in a western tributary valley of Glacier Valley, south of fumarole field 4. The site consists of mudpots and mild fumarolic activity covering $\sim$100 m^2. The fumaroles emanate from a Recent moraine. Bedrock exposed above the moraine is Makushin diorite.
10	Warm ground: An area of hydrothermally altered ground with a sulfurous smell was reported by M. Henning (DGGS, personal commun., 1982) and P. Parmentier (RGI, personal commun, 1982.) at the head of Makushin Valley at an elevation of $\sim$800 m. Bedrock in the vicinity is believed to be Makushin diorite.
11	Steaming ground: An area of hydrothermally altered ground was reported to be "steaming" by P. Parmetier and C. Isselhardt (RGI, personal commun., 1982) on the northeast-facing slope of Fox Canyon.
12	Snow-free ground: An anomalously snow-free area of ground was reported by Parmentier and Isselhardt (personal commun., 1982) to exist about 2 km north of Sugarloaf Cone. Ground temperatures several centimeters below the surface measured 20°C.

Table 2. Description of thermal spring sites, Makushin geothermal area.

Code	Location	Bedrock	Temp (°C)	Flow (lpm)*	Characteristics
G-a	Upper east fork Glacier Valley near superheated fumarole	Fractured Makushin diorite	70-96	(20)	Acid springs issuing near superheated fumarole.
G-b	Upper east fork Glacier Valley	Fractured Makushin diorite			Springs issue from bluff wall.
G-c	Upper east fork Glacier Valley	Makushin diorite	50-55	(40)	Waters issue from recent glacial till on steep bluff-side.
G-d	Confluence of two upper drainages of Glacier Valley	Makushin diorite	76-99	(200)	Acid springs and HCO_3-SO_4 waters with low Cl emerge at base of fumarole field 3; channels near vents lined with 1-2 cm calcite; strong H_2S odor.
G-e	Upper Glacier Valley	Makushin diorite	40-68	(20-25)	Waters emerge from west side of valley; base of wall thoroughly calcite-cemented alluvium and colluvium; thin calcite apron covering ground below vents.
G-f	Upper Glacier Valley	Makushin diorite	17-78	(50-60)	HCO_3-SO_4 waters with low Cl issue from colluvium at base of east valley wall, mainly as seeps; one spring emanates from a small calcite sinter cone; calcite-coated channels and ground indicate previous large flow rate.
G-g	Upper Glacier Valley	Makushin diorite	50-64	(35)	Waters issue from recent glacial moraine on east side of valley.
G-h	Upper Glacier Valley	Makushin diorite	40-62	(50-60)	Springs emerge from boulders along stream bank on west side of valley; abundant calcite in channel; several warm, swampy ponds.
G-i	Upper Glacier Valley	Makushin diorite	63	(20)	Springs issue from recent medial moraine; some calcite sinter.

*Values in parentheses are visual estimates.

Code	Location	Bedrock	Temp (°C)	Flow (lpm)*	Characteristics
G-j	Upper Glacier Valley	Makushin diorite	40-55	(40-60)	Waters flow from three vents 5-6 m apart on west side of valley; calcite-travertine deposits 1-3 cm thick near orifices of all vents.
G-k	Upper North Fork of Glacier River	Makushin diorite	99-100	(10)	Acid springs, mud pots, and hydrothermally altered ground occur along a fissure trending 104°-110°; springs located near margin of glacier.
G-l	West Fork Glacier River	Makushin diorite	50-64	310-340	Numerous springs emerge from cliffs above north bank of stream just beyond a bedrock constriction of stream channel; 43°C warm marsh 50 m upvalley.
G-m	Near mouth of lower west fork to Glacier Valley	Unalaska Formation	38-44	(20)	Cl waters emerge in warm pond along stream channels.
G-n	Glacier Valley	Unalaska Formation	27-33	(10)	Cl springs emanate from marshy area with lush vegetation.
G-p	Intersection of Pakushin Valley and Glacier Valley	Unalaska Formation	40	(10)	Cl springs issue into shallow pools in marshy area.
M-a	Upper Makushin Valley	Makushin diorite with pyrite and chalcopyrite	99	(20)	Acid waters issue from fissures in bedrock near fumarole field 2; other springs in area 90°C and others unreachable.
M-b	Upper Makushin Valley	Makushin diorite	80-88	(40)	HCO_3-SO_4 water, slightly acidic, emerges in small bowl in glacier drift with reddish oxide staining adjacent rocks.
M-c	Upper Makushin Valley west tributary	Makushin diorite basalt and Makushin volcanics	40-54	(20)	Springs emanate from base of cliff into pond on stream terrace.
M-d	Upper Makushin Valley west tributary	Makushin volcanics	35-67	(50-60)	HCO_3-SO_4 waters issue from colluvium accumulated on a bench 75 m above stream; springs adjacent to fumarole field 1.

Much of the surficial thermal activity appears to be largely controlled by the exposure of the Makushin pluton and the occurrence of capping Makushin volcanic flows. The volcanic flows may also be deflecting some of the fluids that ascend near the center of the volcano laterally outwards toward exposed portions of the pluton. A tuff member located within the Unalaska Formation appears to act as a cap on the eastern boundary of the Glacier and Makushin Valley thermal fields (M. Henning and C. Nichols, DGGS, personal commun., 1982).

Hot springs located in Glacier and Makushin Valleys and thermal areas 1, 2, 3, 8 and 12 (table I, fig. 2) appear to follow a roughly linear northeast trend, which suggests that their distribution may be structurally controlled. The trend is coincident with a major lineament visible on aerial photos and Landsat images; the lineament is defined by Glacier Valley, the head of Makushin Valley, and a valley east of Driftwood Valley. Although some indication of faulting was found in diorite exposed near the head of Glacier Valley, no offset has yet been recognized along the trace of the lineament, which does not appear to be fault related (Henning, DGGS, personal commun., 1982). The lineament may reflect an older structural feature subsequently accentuated by glacier erosion. Glacier erosion probably exposed the pluton at the heads of Glacier and Makushin Valleys.

Occurrence of hydrothermal alteration and relict geothermal vents on and within Recent moraines in Glacier Valley indicates thermal activity was more widespread in the recent past. The moraines are probably no older than 3,000-4,000 yr B.P.---the age of a neoglacial advance which occurred elsewhere in the Aleutians (Black, 1975)---and perhaps much younger. X-ray diffraction analyses identified halite in hydrothermally cemented samples obtained from at least two localities in upper Glacier Valley (fig. 3). One of the samples was obtained from hydrothermally cemented fluvial deposits beneath a Recent kettle moraine located south of Gf; the other sample came from a conical mound of hydrothermally altered rock resting on a Recent lateral moraine near Gc (fig. 3). Nichols (personal commun., 1982) reported other halite deposits in the region. The association of halite deposits with these hydrothermally altered zones indicates that in the recent past alkali-chloride hot springs existed several kilometers upvalley from the presently known chloride springs in Glacier Valley. The deposits occur in an area that presently exhibits only fumarolic and low-Cl thermal-spring activity. Apparently, the Cl-rich hot-water reservoir that fed these springs has either been depleted or sealed itself, forming the current steam cap.

THERMODYNAMIC IMPLICATIONS OF SUPERHEATED FUMAROLE

A temperature of 152°C was measured in July 1982 for a superheated fumarole located near the top of fumarole field 3 (fig. 2). The measurement was made with a calibrated thermocouple accurate to ± 1°C at the point of maximum vapor flow. The location, geometry, and heat of the vent prevented insertion of the probe more than 2-3 cm down the vent orifice. Another fumarole in the immediate vicinity, with much less pressure, measured 105°C. Meltwater flowing into this vent was obviously cooling the vapor. These superheated fumaroles at the head of Glacier Valley emanate from fractured and highly altered Makushin diorite near the base of a cliff of capping Makushin volcanic flows.

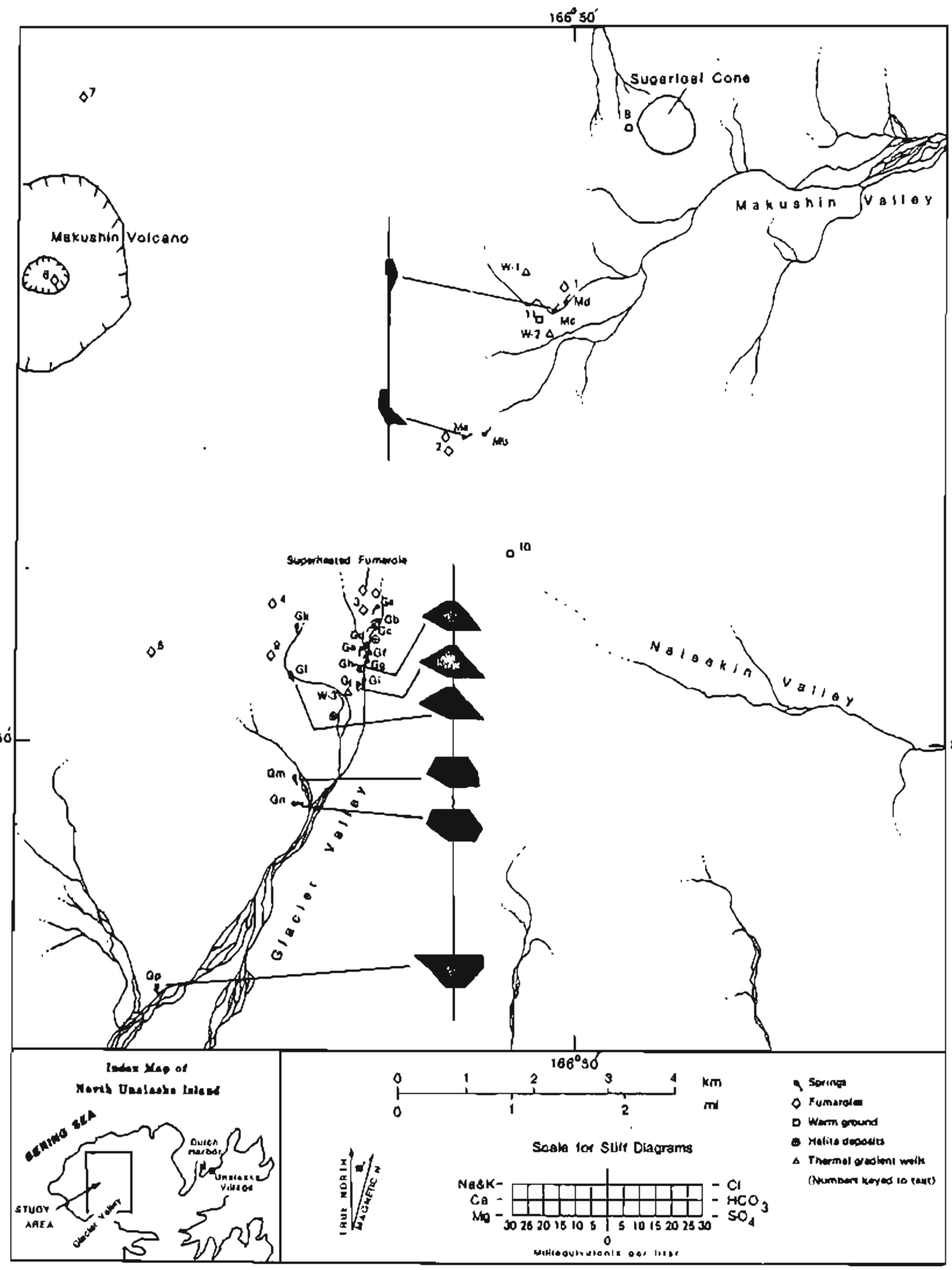

Figure 3. Stiff diagrams showing chemical composition of selected hot springs in Makushin and Glacier Valleys. The locations of two halite deposits found in association with hydrothermally concentrated rocks are also shown.

In natural geothermal systems, the limiting process for the cooling of steam is adiabatic (isoenthalpic) decompression (Muffler and others, 1982). If the steam in the superheated fumarole evolved from a saturated steam zone and ascended to the surface without further increase in enthalpy, then, from the pressure-enthalpy diagram for steam in figure 4, the exit temperature of 152°C provides a minimum estimate of 185-190°C for the parent saturated steam zone at depth. The steam from the superheated fumarole is likely to have been cooled by water, particularly near the surface; therefore the temperature of the saturated steam zone feeding the Glacier Valley fumaroles is probably higher than this minimum estimate. As a comparison, the temperature of steam decompressed adiabatically to a surface pressure of 1 bar absolute from saturated steam of maximum enthalpy (2,800 J g^{-1} at 235°C and 31 bars abs.) is 163°C.

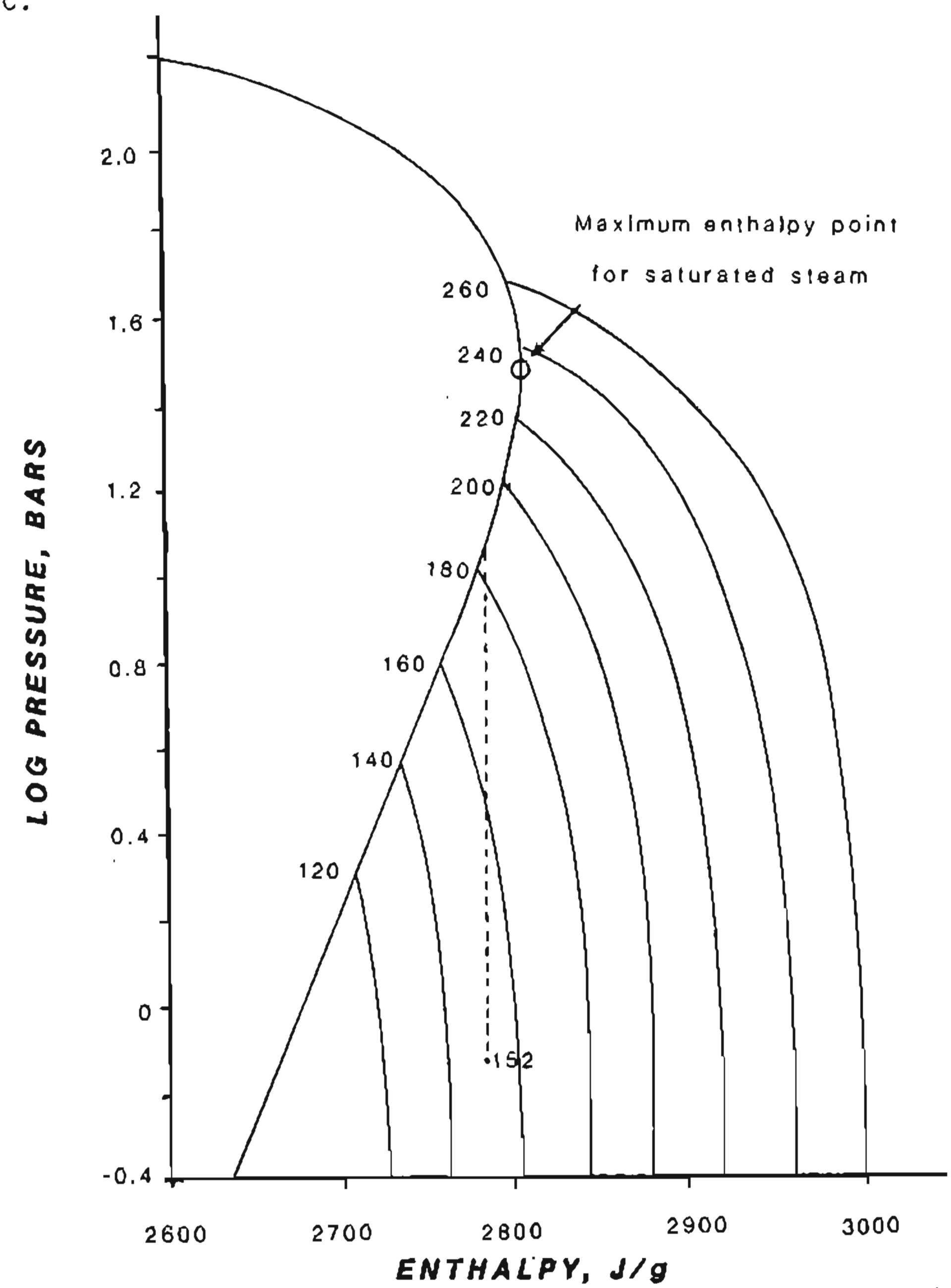

Figure 4. Enthalpy-vs-pressure diagram (from Muffler and others, 1982) showing the relationship between saturated steam and the isothermal decompression paths of superheated steam. The dashed line shows the isoenthalpic decompression path between saturated steam and the superheated fumarole at field 3.

Superheated fumaroles can also occur temporarily when saturated steam passes through wallrock that is hotter than the steam. Conduction of heat from the wallrock increases the enthalpy of the steam, creating the superheated condition. Such superheating has apparently been observed as a result of exploitation at both the Geysers and Larderello vapor-dominated geothermal fields (Isselhardt, personal commun., RGI, 1983).

High-temperature superheated fumaroles are uncommon in geothermal systems. The highest temperature ever reported for a geothermal fumarole is 159°C, measured at Big Boiler fumarole during a period of drought at the Lassen Volcano geothermal area (Muffler and others, 1982). In addition to the superheated fumarole at the head of Glacier Valley at Makushin, high-pressure fumaroles also occur on the south flank of the mountain (table 1, site 5). Although the fumaroles are at or near the boiling point, ground-water flow and observed surface-water infiltration into the vents of these fumaroles would effectively quench any superheating.

FUMAROLIC GASES

Except for site 7, fumarole-gas samples have been obtained from every major fumarole field on Makushin Volcano, including the summit. The gases were collected in two types of sampling flasks: type 1 is an evacuated 50-cc glass flask with a vacuum stopcock; type 2 is a 300-cc glass flask charged with 100 cc of 4N NaOH solution, evacuated, and closed with a vacuum stopcock. The sampling procedures are similar to those described by Giggenbach (1976) and by Nehring and others (1982).

Gas Chemistry

Chemical compositions of gas samples analyzed thus far are given in table 3. Gases from site 4 and backup samples from sites 2, 3, 5, 6, and 9 (table 1) have not yet been analyzed. The gases were analyzed in cooperation with the Stable Isotope Laboratory at the Scripps Institute of Oceanography at La Jolla, California and the U.S. Geological Survey, Menlo Park, California. Results of the 1982 analyses are still preliminary and require further verification. The chemical compositions are probably accurate to within ±5 percent of the stated value.

On the basis of the present results the following observations can be made. As with other high-temperature geothermal systems, the predominant gases at Makushin are CO_2, N_2, and H_2S. Much of the CO_2 and H_2S is probably of magmatic origin. A significant amount of H_2 is also present, particularly at site 3, where H_2 is 1 to 2 percent of the total gas composition. The relatively greater percentage of H_2 and lower H_2S found at site 3d probably reflects the loss of H_2S through rapid oxidation in shallow ground waters and surface waters. Reaction of H_2S with dissolved O_2 in these waters would result in the sulfate-rich acid spring from which the sample was obtained.

Concentrations of H_2 greater than 1 percent are commonly associated with high-temperature geothermal systems such as Lassen (Muffler and others, 1982), Yellowstone (Welhan, 1981), Mt. Hood (Nehring and others, 1982), and Cerro Prieto (Nehring and Valette-Silver, 1982). H_2 in fumarolic gases may

Table 3. Preliminary results, chemical composition of fumarole gases (mole percent).

	1a	2b	2c	3d	3e	3f	5g	6f	9i
CO_2	91.68	87.90	87.08	87.41	94.81	81.20	94.75	87.51	93.36
H_2S	2.63	2.65	5.25	1.27		10.81	0.68	5.53	2.01
H_2	0.24	0.54	0.74	1.80	1.12	1.23	0.59	0.28	0.72
CH_4	0.03	0.002	0.021	0.02	0.006	0.07	0.01	0.07	0.01
N_2	5.36	8.81	6.87	9.41	4.04	4.43	3.89	5.64	4.33
Ar	0.07	0.09	0.06	0.11	0.04	0.42	0.05	0.06	0.04
O_2	bd	bd	0.04	bd	bd		0.03		
He (ppm)	8.0	5.6	8.1	4.5	3.0	4.25	nd	17.4	nd
T (°C)	– –	98	98	78	98	152	98	96	97
Date sampled	8/13/80	8/13/80	7/14/81	7/5/81	7/5/81	7/8/82	7/13/82	7/18/82	7/14/82

[1a]Steam vent, field 1.
[2b]Steam vent near center of field 2.
[2c]Steam vent near center of field 2.
[3d]Acid spring at base of field 3.
[3e]Steam vent below superheated fumarole in field 3.
[3f]Superheated fumarole near top of field 3.
[5g]High-pressure fumarole-geyser, field 5.
[6h]Steam vent near active crater, Makushin summit.
[9i]Mudpot, fumarole field 9.

nd - not determined
bd - below detection

be derived from high-temperature interaction of water with ferrous-oxide silicates (Seward, 1974). H_2 could also be of magmatic origin; H_2 is often a significant constituent of high-temperature superheated gases that evolve from recent volcanic vents, fresh lava flows, and volcanic domes.

The relative proportions of CH_4 in gases from Makushin are very low and the H_2/CH_4 ratio is correspondingly high. The CH_4 present in the gases could be derived from thermal decomposition of organic matter entrained in meteoric waters that charge the subsurface hydrothermal system. CH_4 could also be produced from the reaction

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

(Giggenbach, 1980).

The N_2, Ar, and O_2 present in the gases are probably mostly of atmospheric origin, derived from dissolved gases in the recharge water. However, the high N_2/Ar ratio for the five samples for which an Ar analysis is available suggests some of the N_2 may have a different origin. The N_2/Ar ratio is 84 for air and 37 for air-saturated water (Mazor and Wasserberg, 1965) compared to a N_2/Ar ratio of 115 for site 2c, 101 for 3e and 98 for 2b (table 3). The excess N_2 could be of magmatic origin.

Preliminary analyses of NH_3 content of gases from two sites, 3f and 6h, indicate concentrations of about 50 ppm. The NH_3 present in the system could be produced through the reaction

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(Giggenbach, 1980). N_2 and NH_3 can also be formed from organic breakdown.

The CO_2/H_2S ratio is lowest for the superheated fumarole 3f. The ratio of CO_2/H_2S will increase with decreasing temperature in geothermal systems because H_2S is selectively removed by water-rock interactions to form pyrite and by reaction with dissolved O_2 in ground waters (Truesdell and Thompson, 1982). The gas analyses for fumarole 3f is thus likely to be the most representative of gas composition of the deep reservoir.

Stable Isotope Data

$^3He/^4He$ - In cooperation with the Stable Isotope Laboratory at the Scripps Institute of Oceanography, LaJolla, California, samples of gases obtained from fumaroles and hot springs of Makushin have been analyzed for He isotope content. Enrichments in ^3He with respect to atmospheric levels have been correlated with magmatic activity on a worldwide basis with the excess ^3He thought to be derived from the mantle (Craig and Lupton, 1981). Samples of gases for $^3He/^4He$ testing were collected from Makushin sites in 50-cc glass flasks (Corning 1720) fitted with high-vacuum stopcocks. The procedures followed for gas extraction, measurement of absolute helium amounts, mass spectrometer measurement of $^3He/^4He$ ratios, and application of He/Ne correction for air contamination are described in Lupton and Craig (1975) and Torgersen and others (1982).

Table 4 presents He isotope data thus far acquired for the Makushin sites. The R/Ra value ($^3He/^4He$ ratio, samples vs air) of 7.8 obtained for the summit vent falls within the range of values (6 to 8) obtained from other volcanic vents in the Aleutian arc and from convergent margin volcanic arc settings elsewhere in the world (Craig, Lupton, and Horibe, 1978; Poreda and others, 1981; and Poreda and Motyka, unpublished data, 1982). R/Ra values for gases from fumaroles on the flanks of Makushin are all lower than those from the summit, with the lowest values (4.5) occurring in Glacier Valley.

Table 4. Helium isotope data, Makushin Volcano fumarole fields.[a]

Location	R/Ra[b]
Summit, 6	7.8
Makushin Valley, 1	6.6
Makushin Valley, 2	4.9
Makushin Valley, 2, spring M-b	5.0
Glacier Valley, 3, GV-1	4.5
Glacier Valley, 3	4.5
Glacier Valley, 4	NA
West Flank, 5	NA
Glacier Valley, spring G-p	NA

[a]Analyzed by R. Pordea, Scripps Isotope Laboratory, LaJolla, California.
[b]R - $^3He/^4He$ ratio in sample
Ra - $^3He/^4He$ ratio in air.
NA - Not available.

Such variations in R/Ra have been found at other volcanically related geothermal systems (Craig and others, 1978; Welhan, 1981; Torgersen and others, 1982; Torgerson and Jenkins, 1982). A high value for R/Ra in gases from geothermal systems suggests a more direct connection to magmatic sources with little crustal contamination---although it may also result from leaching of young volcanic rock (Truesdell and Hulston, 1980). Lower values indicate a greater crustal influence of radiogenic ^4He.

If the summit value of R/Ra is taken to represent the $^3He/^4He$ ratio of the parent cooling magma, then the R/Ra values for sites on the flanks of the volcano represent varying degrees of mixing with a crustal ^4He component. One effective method for increasing the amount of ^4He present in the gases is by hot-water interaction with and leaching of reservoir wall rock. At Makushin the host reservoir rock appears to be a diorite pluton. Calculations by Torgersen and Jenkins (1982) indicate the R/Ra ratio in a diorite such as that at Makushin would fall to $\lesssim 0.1$ through radiogenic decay of U and Th for emplacement ages $\gtrsim 1.0$ m.y. A mixing of 40 percent crustal He and 60 percent magmatic He would produce an R/Ra value of 4.5, with 7.8 for the magmatic component and 0.1 for the crustal component.

$^{13}C/^{12}C$ and D/H - The authors' studies of $^{13}C/^{12}C$ and D/H (deuterinal hydrogen) ratios at Makushin and elsewhere in the Aleutian arc are still in their initial stages. The analyses of the stable isotopes of C and

H_2 found in geothermal gases and waters are useful in deciphering the origin of gases in the geothermal system. Fractionation of the ^{13}C isotopes between CO_2, CH_4, and HCO_3 and the D isotope between H_2O, H_2, and CH_4 has also been used to infer reservoir temperatures.

Preliminary results for sites at Makushin analyzed thus far are given in tables 5 and 6. Methods used for extracting the C gases and H_2 and analyzing them for stable isotopic composition are described in Welhan (1981), Nehring and others (1982) and Lyon and Truesdell (1982). The isotopic values are given in terms of relative differences expressed in parts per thousand (permil, or $^{o}/oo$) and defined as

$$\delta X = \left\{\frac{Rx}{Rstd}\right\}^{-1} \cdot 10^3 \qquad (1)$$

where Rx represents the isotope ratio of a sample and Rstd is the corresponding ratio in a standard. For C, the standard is the $^{13}C/^{12}C$ ratio in 'PDB' (Fritz and Fontes, 1980). For H_2 the standard is the D/H ratio in standard mean ocean water (SMOW) defined by Craig (1961).

The three $\delta^{13}C$-CO_2 analyses by Global Geochem, Inc., were done on CO_2 gas evolved from a $SrCO_3$ precipitate. The reported precision of the analysis was ±0.3 permil. The $SrCO_3$ precipitates were obtained from NaOH solutions contained in type-2 sampling flasks according to procedures described in Nehring and others (1982). The Scripps Isotope Laboratory analysis of $\delta^{13}C$-CO_2 was performed on unreacted CO_2 gas extracted from a type-1 sampling flask. The three CO_2 samples analyzed by Global Geochem are lighter by $\sim$ 2 permil than the single sample analyzed by Scripps. Additional samples from these and other sites at Makushin are being submitted to a third laboratory to determine if the differences in $\delta^{13}C$ are due to differing lab procedures or if the values in table 5 represent actual variations in isotopic composition of CO_2 at Makushin.

The $\delta^{13}C$ compositions of CO_2 from Makushin are compared in figure 5 with carbon isotope data from other geothermal areas. Although the Makushin

Table 5. Carbon isotope data, Makushin Volcano fumaroles.

Location	$\delta^{13}C$-CO_2 (PDB)	$\delta^{13}C$-CH_4 (PDB)
Summit 6[a]	NA[c]	-30.6
Makushin Valley, 2[b]	-12.22	d
Glacier Valley, 3, GV-1[a]	-10.24	(-24 to -36)[d]
Glacier Valley, 3[b]	-12.96	d
Glacier Valley, 3, spring G-d[b]	-11.75	d

[a]Analyzed by J. Welhan, Scripps Isotope Laboratory, LaJolla, California.
[b]Analyzed by Global Geochem, Canoga Park, California.
[c]Not yet available.
[d]Sample volume below detection limit of instrument.

Table 6. Hydrogen isotope data, Makushin Volcano fumaroles.

Location	$\delta D-H_2$	$\delta D-CH_4$
Summit, 6[a]	-719	-132.6
Glacier Valley, 3, GV-1[a]	-582	c
Glacier Valley, 3, Spring G-d[b]	-601	c

[a]Analyzed by M. Stallard, U.S. Geological Survey Isotope Laboratory, Menlo Park, California.
[b]Analyzed by Global Geochem., Canoga Park, California.
[c]Sample volume too small for analyses.

CO_2 appears generally lighter than most of the other geothermal areas shown, it is only slightly lighter than CO_2 analyzed from the Akutan and Atka geothermal areas in the Aleutian arc. $\delta^{13}C - CO_2$ ranges from -9 to -11 permil at Atka and is ~-10 permil at Akutan (Motyka, unpublished data, 1982). $\delta^{13}C$ of 'juvenile' or mantle-derived CO_2 is thought to range from -4 to -8 permil (Craig, 1953; Welhan, 1981). This range is based on analyses of samples obtained from midocean ridges and from carbonatites and diamonds. Subduction-related magmas, however, may become contaminated by volatiles from the downgoing slab or by incorporation of crustal material, thus changing the $\delta^{13}C-CO_2$. Analysis of $\delta^{13}C-CO_2$ from the summit of Makushin may provide an estimate for 'magmatic' $\delta^{13}C-CO_2$ at Makushin. This value in turn will allow a better evaluation of the source(s) of CO_2 in the Makushin geothermal system.

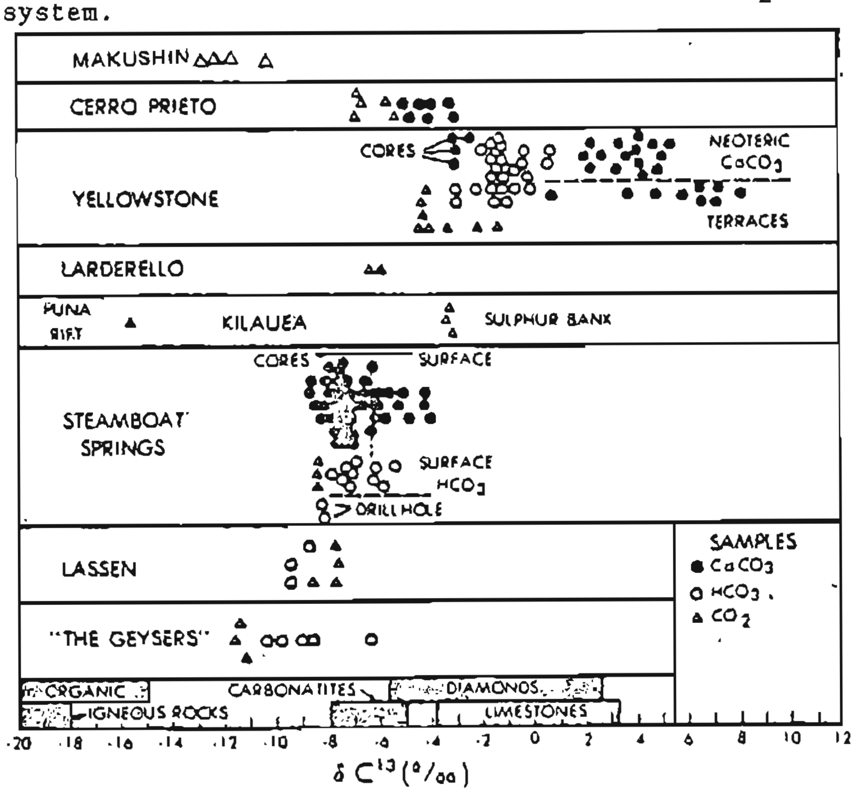

Figure 5. $\delta^{13}C$ compositions of CO_2 at Makushin compared to other geothermal areas. Diagram from Truesdell and Hulston (1980).

Except for the summit, the volume of CH_4 contained in the samples from Makushin analyzed thus far have been too low to allow determination of $\delta^{13}C-CH_4$ and $D-CH_4$. The CH_4 in the sample from site 3 (GV-1, the superheated fumarole) was barely at the detection limit for $\delta^{13}C$ and the range of values are included in table 5 only as a suggestion of what the $^{13}C-CH_4$ might be for that site. Welhan (1981) has presented evidence for CH_4 derived from a mantle source along the East-Pacific Rise. The $\delta^{13}C-CH_4$ for this abiogenic methane ranged from -15.0 to -17.6 permil. Methane from the summit and flank of Makushin is considerably lighter, which suggests it is derived from the thermogenic breakdown of organic matter or from the reaction $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$.

The δD compositions of H_2 and CH_4 from Makushin are compared in figure 6 to those for other geothermal systems and volcanic vents. Fractionation can occur between any of the hydrogen-containing gases (H_2, CH_4, H_2S, NH_3) and H_2O, but H_2O, (liquid and vapor) is usually present in such great abundance that it probably controls the D isotopic fractionation behavior of the other constituents. The fractionation of D between H_2 and H_2O is very rapid and H_2-H_2O is commonly found to be at or near isotopic equilibrium for the outlet temperature of fumarolic vents and geothermal wells. Kiyosu (1982), however, has recently reported that at several high-temperature fumarolic vents in Japan the δD in H_2-$H_2O(v)$ indicated isotopic equilibrium 100° to 200°C higher than the outlet temperatures. At the Makushin superheated fumarole, δD in H_2 and $H_2O(v)$ (table 6) appears to be nearly in equilibrium for the measured orifice temperatures as discussed below. The equilibrium temperature for D in H_2 and $H_2O(v)$ for the summit fumarole sampled is considerably below the outlet temperature. The steam in this vent may be of local meltwater origin and may not have come to equilibrium.

The single $\delta D-CH_4$ value available for Makushin, obtained from the summit, is heavier in D than most other reported sites. Experimental data for D in the system CH_4-H_2O are still lacking and the significance of the Makushin summit $\delta D-CH_4$ is not yet apparent.

Geothermometry

D'Amore and Panichi (1980) have proposed a gas geothermometer for estimating reservoir temperatures that is based on the proportions of CO_2, H_2S, H_2, and CH_4 measured at a geothermal vent. The geothermometer temperature is calculated by using an empirical relationship derived from examining the composition of 42 gas samples and measured reservoir temperatures from a variety of explored geothermal areas. The uncertainty of the calculated vs observed temperatures is ±13 percent. Only 14 of the samples used to derive the relationship were from natural manifestations; the rest were from geothermal wells. However, Muffler and others (1982), found reasonable agreement between temperatures predicted by Na-K, Na-K-Ca, and sulfate-water oxygen isotope geothermometers for Growler-Morgan Hot Spring waters and the gas geothermometer of D'Amore and Panichi for gases from fumaroles and hot springs in Lassen Volcano National Park and vicinity.

The results of applying the gas geothermometer to the Makushin area are given in table 7. The deep temperature estimates range from 230° to 297°C.

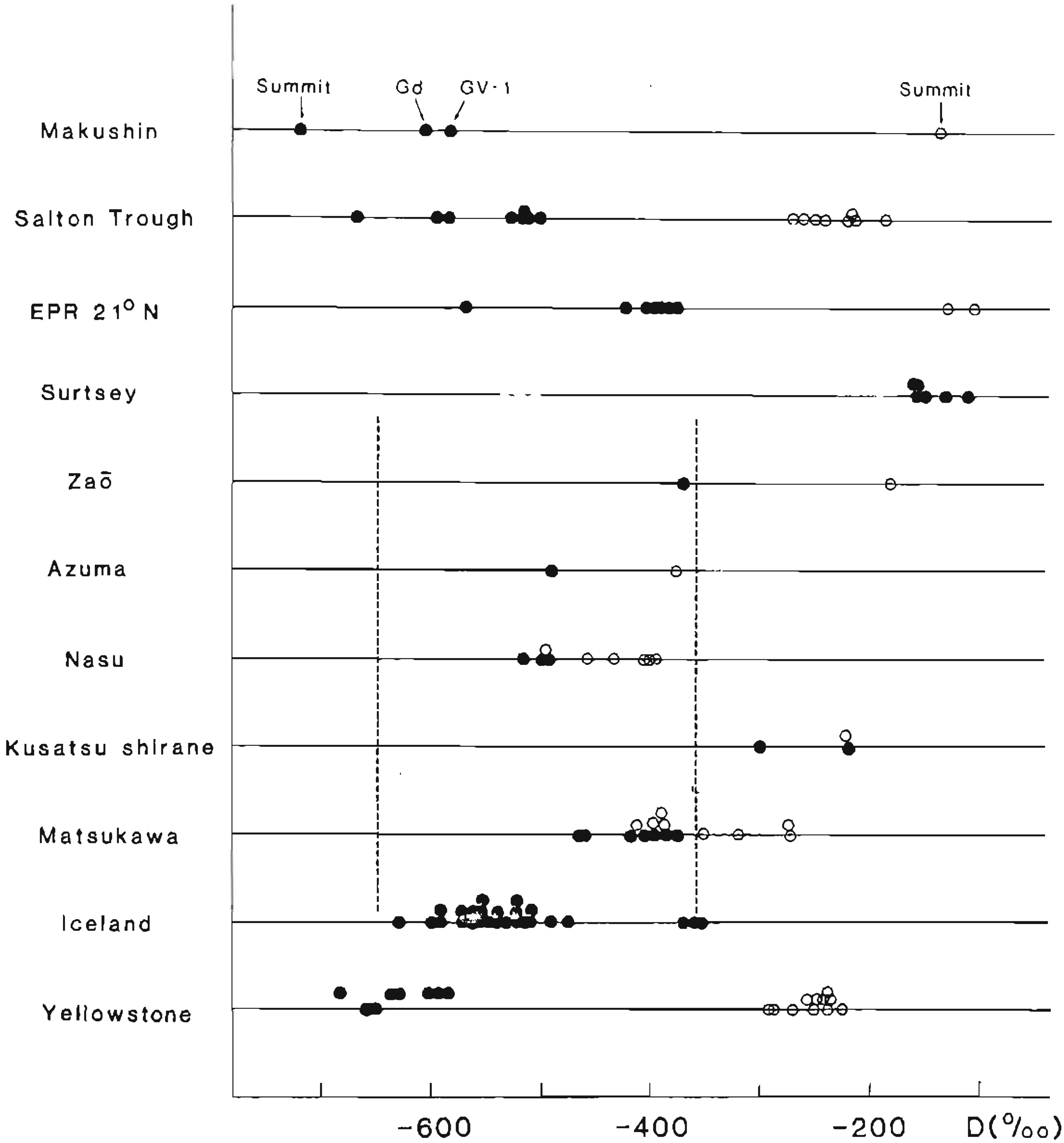

Figure 6. δD compositions of H_2 and CH_4 at Makushin compared to other geothermal areas and volcanic vents. Data for Japanese areas, Iceland, and Yellowstone from Kiyosu (1982); data for Salton Trough and EPR 21°N from Welhan (1981).

Table 7. Geothermometer of D'Amore and Panichi (1980) applied to Makushin fumaroles and thermal spring gases (all temperatures in °C).

	Temperature (C°)
Makushin Valley	
Fumarole in field 1	230
Fumaroles in field 2	
2b	238
2c	279
Glacier Valley	
Fumarole field 3	
Acid spring	285
Superheated fumarole	297
Summit	
Fumarole near active crater	239

The temperature estimates overlap within the limits of calculation uncertainty. Because the gas constituents used in the geothermometer can be affected by near-surface water-rock reactions, the gas geothermometer is best applied to fumaroles and springs that have high gas-flow rates and to gases that are not in contact with a large, low-temperature water table (D'Amore and Panichi, 1980). On the basis of these criteria, the superheated fumarole geothermometer temperature of 297°C would then be the most dependable estimate for the deep reservoir. Two of the other analyses (2C and 3 - acid spring) also give temperatures greater than 275°C.

Fractionation of the ^{13}C isotope between CO_2 and CH_4 has been used as a geothermometer based on the assumption the gases are in isotopic equilibrium through the exchange reaction:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

Craig's (1953) calculations of the temperature dependence of ^{13}C fractionation between CO_2 and CH_4 were subsequently modified by Bottinga (1969). However, geothermometric temperatures calculated with Bottinga's fractionation curve were found to be significantly higher than observed system temperatures, which casts doubt on the validity of the geothermometer (Truesdell and Hulston, 1980). Gunter and Musgrave (1971) suggested that isotopic equilibrium is not established, and investigations by Des Marais and others (1981) indicated that methane in geothermal systems is formed by the thermal decomposition of organic matter, not by the reaction of H_2 with CO_2.

Others suggested the isotopic temperatures are real but occur in deeper parts of the system (Panichi and others, 1977; Hulston, 1977). This hypothesis was reinforced by the discovery of higher temperatures (>300°C) in deep research drill holes at Lardello and at Broadlands (Truesdell and Hulston, 1980). However, application of this geothermometer remains controversial, particularly for temperatures below 400°C, where experimental and theoretical investigations indicate ^{13}C equilibration requires residence times on the order of tens of thousands of years (Sackett and Chung, 1979; Giggenbach, 1982).

Available ^{13}C analyses of coexisting CO_2 and CH_4 in geothermal gases, as well as some analyses of low-temperature gases with indicated isotopic temperatures, are shown in figure 7. Makushin data is also plotted for comparison. Using a $\delta^{13}C$ value of -31 for CH_4 and -10.2 for CO_2 gives an isotope equilibration temperature of ~360°C for Makushin.

The δD values of coexisting H_2 and H_2O have also been used as geothermometers based on the assumption that the gases are in isotopic equilibrium through the reaction

$$H_2O + HD \rightleftharpoons HDO + H_2$$

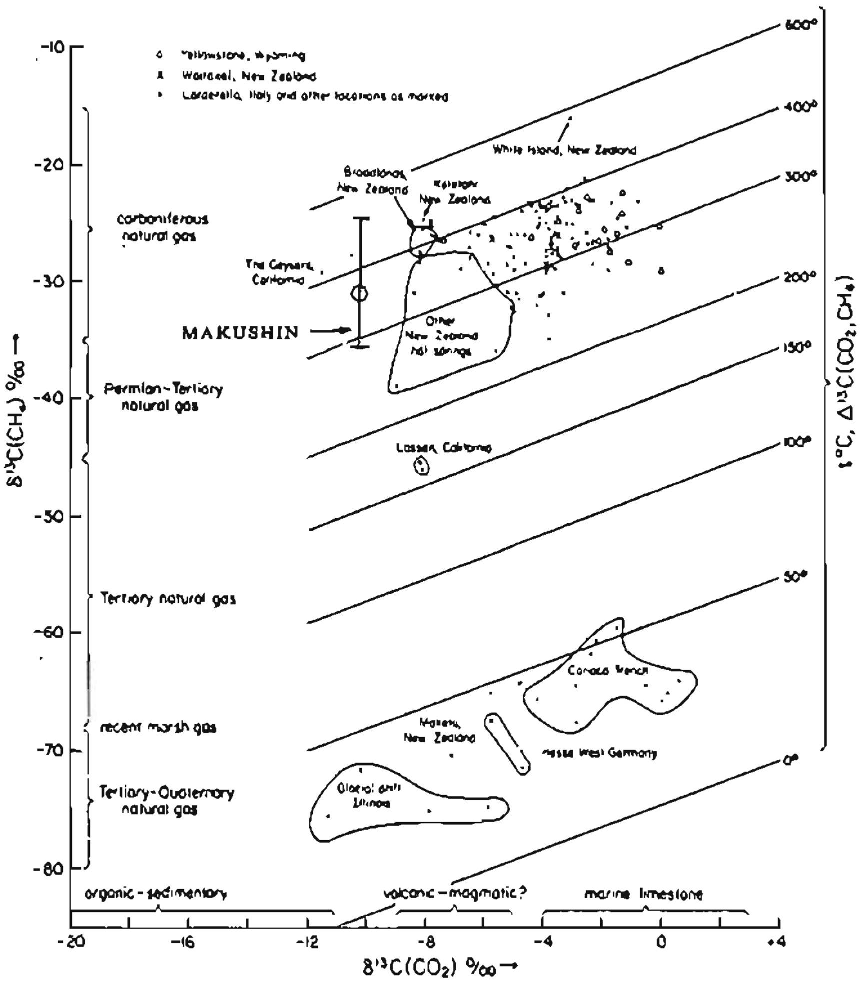

Figure 7. Carbon isotope compositions of coexisting CH_4 and CO_2 from volcanic, geothermal, and sedimentary sources. Diagram from Truesdell and Hulston (1980); fractionation-temperature data from Bottinga (1969).

As discussed above, isotopic fractionation of D occurs rapidly and application of the δD, $H_2 - H_2O$ geothermometer to geothermal systems has shown variable degrees of reequilibration between the reservoir and the sampling point (Truesdell and Hulston, 1980). The fractionation factor, α, over the range 273-473°K can be expressed as:

$$\ln \alpha = -0.2735 + 499.2/T + 2280/T^2 \qquad (2)$$

where T is the absolute temperature and

$$\alpha = \frac{1000 + D\ (H_2)}{1000 + D\ (H_2O)} \qquad (3)$$

(Richet and others, 1977; Rolson and others, 1976). Applying these equations to the superheated fumarole of Makushin gives an equilibration temperature of 157°C, which is slightly above the measured outlet temperature indicating the D has reequilibrated during ascent of the gases.

The deep temperature estimates of 280-300°C given by the D'Amore-Panichi geothermometer are significantly higher than the minimum estimate provided by thermodynamic considerations of the superheated fumarole (~190°C) and the highest temperature encountered in the thermal gradient wells drilled during the summer of 1982 (195°C, W-2, see below; P. Parmentier, RGI, personal commun., 1982). The temperatures are also well above the 235-240°C normally found in deep vapor-dominated reservoirs. Because of the uncertainties of the geothermometry calculations and the preliminary nature of the gas analysis data, particularly for the superheated fumarole, any discussion on the significance of the gas geothermometry must be speculative: a) the gases may be equilibrating in a vapor-dominated reservoir and the geothermometry has overestimated the temperature of equilibration; b) the gases may be equilibrating in a hot-water reservoir of 280°-300°C that underlies a vapor-dominated reservoir at ~235°-240°C; c) the gases may be equilibrating in a hot-water reservoir at 280°-300°C in which boiling and steam separation occurs at temperatures $\geq$190°C; d) the deep system is 'dry' (i.e., no liquid water) at temperatures ~280°-300°C. In the case d) surface waters infiltrating the fractured dioritic pluton would react with and be vaporized by superheated gases and hot dry rock; from the standpoint of development of geothermal energy, this possibility is by far the least desirable.

THERMAL WATERS

Locations, descriptions, and physical characteristics of thermal springs identified in the Makushin area are summarized in table 2 and figure 2.

Water Chemistry

Fifteen thermal springs and five cold waters located in Glacier and Makushin Valleys were sampled and analyzed for major and minor chemical constituents. The results of these analyses are given in tables 8-11. For most of the sites, sampling procedures followed those described in Presser and Barnes (1974). Bicarbonate and pH were determined in the field by using methods described by Barnes (1964). For several sites (analyses 1, 3, 7, 11, and 19) lack of time prevented following rigorous field sampling procedures

Table 8. Water chemistry, Makushin Valley thermal springs (M-a through M-d). Units are mg/l unless otherwise noted.

	1. M-a	2. M-b	3. M-c	4. M-c	5. M-d
SiO_2	155	140	88	105	88
Fe	2.5	0.1	0.1	0.1	0.1
Ca	65	69	23	34	23
Mg	13	12	5.5	6.1	8.0
Na	54	28	24	32	14
K	9.0	5.6	3.2	4.3	3.4
Li	0.02	0.01	0.01	0.01	0.01
Sr	0.3	0.3	0.1	0.1	0.1
HCO_3	nd	191	nd	201	116
SO_4	344	155	25	15	21
Cl	5	5	7.8	7.9	5
F	1.0	0.12	0.13	1.0	0.11
B	0.5	0.5	0.5	0.5	0.5
TDS[a] (calc)	-	510	-	303	217
pH, field	6	5.5	5.28	6.8	5.32
T (°C)	84	87	58	35	67
Date sampled	7/17/82	8/13/80	7/4/81	7/18/82	8/13/80

[a]Total dissolved solids.

and analyses were performed on unfiltered, untreated waters. All samples were analyzed at the DGGS Geothermal Fluids Laboratory. Descriptions of the analytical methods used and their precisions are found in Motyka and others (1981). Deviation from anion-cation balances are 5 percent for the majority of the samples for which a field determination of bicarbonate was performed. The balance for one cold-water sample (analysis 6) exceeded 25 percent and is probably attributable to the very low concentration of dissolved solids in the sample.

The percentage of cation and anion contents of the thermal waters and cold waters is plotted on trilateral diagrams in figure 8. These 'piper' diagrams are useful for classifying and grouping water types and determining similarities, relationships, and trends in water chemistry. The bicarbonate percentages plotted for analyses 1, 3, 7, 11, and 19 were determined by calculating the amount of bicarbonate needed to balance anions with cations.

General Features

Most of the thermal springs are near-neutral in pH although acid springs also occur, usually near fumarolic vents. All the near-neutral pH thermal springs sampled in Glacier and Makushin Valleys have significant concentrations of HCO_3 and SO_4 and all except Gn, Gm, and Gp are very low in Cl (<10ppm). The HCO_3 and SO_4 contents of thermal waters in Makushin Valley and upper Glacier Valley are probably derived from oxidation and reaction of ascending H_2S and CO_2 gases with ground waters.

Makushin Valley:

1. Hot Spring M-a
2. Hot Spring M-b
3. Hot Spring M-c, 1981
4. Hot Spring M-c, 1982
5. Hot Spring M-d
6. Cold Spring, camp

Driftwood Valley:

7. Cold Stream

Glacier Valley:

8. Hot Spring G-d1
9. Hot Spring G-d2
10. Hot Spring G-d3
11. Hot Spring G-e
12. Hot Spring G-f
13. Hot Spring G-h
14. Hot Spring G-j
15. Hot Spring G-l
16. Hot Spring G-m
17. Hot Spring G-n
18. Hot Spring G-p
19. Cold Stream at G-d
20. Cold Spring at G-j
21. Cold Stream at G-l

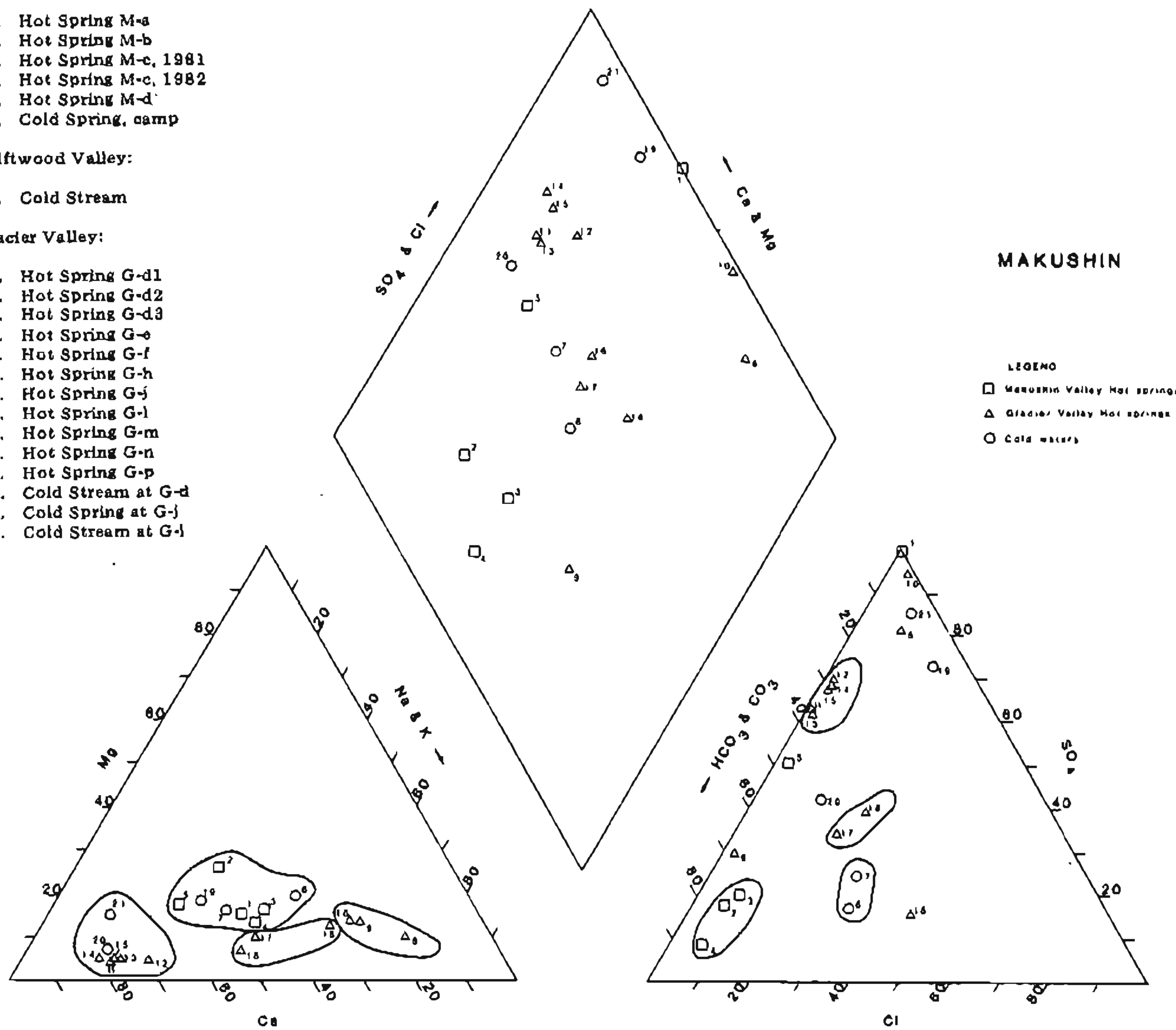

Figure 8. Diagrams showing percentage of cation and anion compositions of thermal springs and locally derived meteoric waters at Makushin. Numbers keyed to tables 8-11.

Table 9. Water chemistry, Makushin and Driftwood Valley cold streams and Springs. Units are mg/l unless otherwise noted.

	6. Cold spring at W-2	7. Cold stream, Driftwood Valley
SiO_2	13	4.5
Fe	0.1	0.1
Ca	1.8	2.6
Mg	0.6	0.5
Na	2.6	2.0
K	0.2	0.1
Li	0.01	0.01
Sr	0.1	0.1
HCO_3	11	nd
SO_4	2.8	3.1
Cl	3.7	2.6
F	1.0	0.1
B	0.5	0.5
TDS[a] (calc)	30	-
pH field	6.6	nd
T (°C)	6.4	3.8
Date sampled	7/19/82	7/1/81

[a]Total dissolved solids.

Cations in the thermal waters are primarily Ca and Na, with Ca usually predominating. Thermal springs in the upper Glacier Valley are particularly rich in Ca and several springs are depositing $CaCO_3$ at the surface. Mg and K are present in subordinate amounts. The cations in the thermal waters probably originate from the interaction of warm waters with the diorite host rock. CO_2-rich waters at elevated temperatures can readily leach calcic feldspars in the diorite to produce clay minerals, bicarbonate, and Ca and alkali ions (Truesdell, 1976; D. Hawkins, U. of Alaska, personal commun.),

$$CO_2 + H_2O + (Ca, Na, K) \text{ silicate} = HCO_3 + Ca+, Na+, K+ + SiO_2(aq) + \text{clay minerals}$$

The concentration of Mg in the springs is particularly significant because it indicates that water-rock reactions have occurred at relatively low temperatures. With increasing temperatures Mg is usually removed in the production of chlorite through alteration reactions.

All the thermal springs have significant concentrations of SiO_2, usually $\geq$100 ppm. The high SiO_2 may reflect equilibration of waters with quartz or chalcedony, or possible leaching of SiO_2 from silicates in the country rock by CO_2-rich waters (D. Hawkins, personal commun., 1982). Numerous Mg-rich low-temperature soda springs saturated with respect to amorphous SiO_2 occur in California. The SiO_2 in these waters is thought to be derived from the low-temperature interaction of CO_2-rich waters with serpentinite (Barnes and others, 1981).

Table 10. Water chemistry, Glacier Valley thermal springs. Analyses of waters collected in 1982 are preliminary. Units are mg/l unless otherwise noted.

	8. G-d1	9. G-d2	10. G-d3	11. G-e	12. G-f	13. G-h	14. G-j	15. G-l	16. G-m	17. G-n	18. G-p
SiO_2	94	125	120	138	142	145	120	135	113	119	104
Fe	0.1	0.1	nd	0.0	0.2	0.4	0.7	0.5	1.7	1.9	2.1
Ca	12	32	25	258	208	243	275	262	203	179	159
Mg	4.0	11	8.0	9.6	7.8	11	11	10	15	23	38
Na	52	87	62	61	81	64	53	63	176	176	299
K	4.8	5.7	5.2	3.3	4.8	3.8	3.4	4.5	19	19	31
Li	0.01	0.01	0.01	0.04	0.03	0.03	0.03	0.03	0.48	0.40	0.86
Sr	0.1	0.3	0.2	1.1	1.1	1.2	1.4	1.2	1.1	1.0	1.4
HCO_3	18.5	288	3	nd	256	358	332	325	463	563	590
SO_4	129	95	218	491	476	472	581	542	363	321	178
Cl	10	5	6.1	2.3	7.5	5.8	6.6	6.6	164	142	382
F	0.14	0.28	0.1	0.26	0.24	1.0	1.0	1.0	1.0	1.0	1.0
B	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	4.2	4	9.9
Br	nd	nd	nd	nd	nd	nd	nd	nd	0.1	0.1	Tr
TDS[a] (calc)	305	503	448	-	1182	1122	1214	1185	1286	1258	1485
pH, field	6.4	6.5	4.3	nd	6.4	6.0	6.1	6.0	5.9	5.8	6.3
T(°C)	97	82	78	68	79	60.5	41.5	62.5	39	27	40
Date sampled	8/11/80	8/11/80	7/15/81	7/5/81	7/5/81	7/11/82	7/10/82	7/13/82	7/20/82	7/20/82	7/20/82

[a]Total dissolved solids.

Table 11. Water chemistry, Glacier Valley cold streams and springs. Units are mg/l unless otherwise noted.

	19. Cold stream at G-d	20. Cold spring at G-j	21. Cold stream at G-1
SiO_2	20	9	28
Fe	0.1	0.1	0.4
Ca	8.9	20	52
Mg	1.9	1.1	6.6
Na	4.7	4.1	8.5
K	0.8	0.3	1.4
Li	0.01	0.01	0.01
Sr	0.1	0.1	0.1
HCO_3	nd	38	13
SO_4	29	27	148
Cl	5.6	5.9	12
F	0.1	1.0	1.0
B	0.5	0.5	0.5
TDS[a] (calc)	-	86	262
pH, field	nd	6.6	6.5
T (°C)	5	15.5	5
Date sampled	7/15/82	7/15/82	7/13/82

[a]Total dissolved solids.

The thermal springs of Makushin appear to fall into several distinctive groups on the basis of chemistry and location. These divisions are discernible on the cation piper diagram (fig. 8) as a) Makushin Valley; b) upper Glacier Valley, springs Gd; c) upper Glacier Valley, springs Ge-Gl; and d) lower Glacier Valley, springs Gm-Gp.

Makushin Valley

The four thermal springs sampled in Makushin Valley have lower concentrations of dissolved solids, lower pH, and generally lower flow rates compared to most of the springs found in Glacier Valley. Cation concentrations in the Makushin Valley thermal waters occur in roughly similar proportions with the ratios of Ca:Na ranging from 1 to 2.5. The cation proportions in fact are very similar to three of the cold waters sampled in the Makushin area. These cold waters, two of which are streams (analyses 7 and 19; tables 9 and 11) and one of which was a snow-melt spring, had very low concentrations of dissolved solids. Anion proportions in the Makushin thermal springs are similar to each other but differ from the cold waters.

Thermal springs in Makushin Valley are much fewer than in Glacier Valley and usually occur in close association with fumarolic activity. Rock cores obtained from thermal-gradient holes show much less fracturing at shallow levels in Makushin Valley than in Glacier Valley. The opportunity for circulation of ground waters and formation of thermal springs would thus be more limited in Makushin Valley. Also, the upper part of Makushin Valley has been inundated with a Recent debris flow, which may have buried and masked thermal springs at lower elevations.

The similarity in cation proportions to local cold waters, the low Cl and high HCO_3-SO_4 concentrations, and the proximity to active fumaroles all indicate that the Makushin Valley thermal springs originate as local meteoric waters that circulate along fractures and are subsequently heated by condensing steam and hot gases. The relatively low concentration of dissolved solids in the thermal waters suggests shallow circulation and rapid flow of the waters through the country rock.

Upper Glacier Valley, Gd

The three springs sampled at site Gd are within 100 m of each other but show marked variations in TDS, HCO_3, and SO_4. The springs are located at the base of fumarole field 3 and the variations are probably a function of the degree of interaction of the waters with fumarolic gases and the depth from which the individual spring waters ascend. The springs at Gd are similar in their cation concentration and are distinguished from other springs further down Glacier Valley by their much lower Ca/Na ratios. The low concentration of Ca at Gd suggests that depths of circulation at Gd are shallower than elsewhere in Glacier Valley. As at Makushin Valley, the springs at Gd probably originate from the near-surface mixing and interaction of ground waters with steam and hot gases.

Upper Glacier Valley, Ge-Gl

Six groups of thermal springs (Ge-Gj) occur in a canyon located near the head of Glacier Valley, below fumarole field 3 (table 2; fig. 2). The springs cover a distance of about 1/2 km and emanate from colluvium and glacial till at the base of the canyon walls and along stream channels. Local bedrock is highly fractured Makushin pluton. Each spring group consists of several vents. Discharge averages about 50 lpm per group; temperatures range from 40° to 80°C.

Hot springs also occur in a western tributary valley to Glacier Valley (Gk and Gl) below fumarole fields 4 and 9. Site Gl consists of numerous spring vents covering a distance of 100 m along a stream channel. Total flow is about 350 lpm and temperatures range from 50°to 63°C.

The hot springs sampled have very similar chemical compositions (table 10). The total dissolved solids (TDS) is over twice the amount found at Gd and in Makushin Valley. Most of the increased TDS is due to higher concentrations of Ca, HCO_3, and SO_4. All the spring groups sampled are saturated in Ca and HCO_3 and are depositing calcite at the surface. One spring at Gd has constructed a multihued calcite cone about 1 m in diameter.

The thermal-springs waters plot in a tight group on both the cation and anion diagrams (fig. 8), which indicates that the waters have a similar origin or perhaps are derived from a common parent reservoir. The thermal-spring waters are also similar in cation proportions to two cold-spring waters sampled in the immediate vicinity (analyses 20 and 21). Waters from these cold springs, which are much higher in TDS than the other cold waters sampled, are apparently circulating along fractures in the diorite but at much shallower levels than the thermal springs.

Thermal-gradient well W-3, drilled near Gj, intersected a zone of rapidly increasing temperatures and artesian flow at a depth of about 60-70 m (Parmentier and Isselhardt, RGI, personal commun., 1982). The volume and temperature of flow increased with continued drilling. The increases were probably caused by entry of thermal waters under hydrostatic pressure into the well along fractures in the diorite. Temperatures 10 days after well completion measured 45°C at 70 m; bottomhole temperature at 460 m below the surface (150 m below sea level) was 78°C. A reversal in thermal gradient near the bottom of W-3 indicates thermal-water entry is primarily from the upslope direction. Samples of the artesian-well waters were not obtained by the drillers or well loggers and the chemical composition of the waters is unknown. Judging from the proximity of the well to upper Glacier Valley thermal springs and the similarity in temperatures measured in the well to those measured at the springs, the well waters are likely to be the same as the waters feeding the springs.

The low Cl content, high HCO_3 and SO_4, the association with fumarole fields, the cation composition, and the similarity in cation proportions to local cold ground waters are evidence that the thermal-spring waters originate as meteoric waters that circulate through the fractured diorite and interact with steam and gases rising from a vapor-dominated zone. Observations from well W-3 indicate the thermal waters that feed the springs flow down the hydrologic gradient and are probably in part derived from the fumarolic areas upslope from the springs. On the basis of drilling evidence, thermal waters appear to flow to at least 150 m below sea level in upper Glacier Valley.

Lower Glacier Valley, Cl-springs

Three Cl-rich thermal springs are found in the lower portions of Glacier Valley (fig. 2). Two of the springs, Gm and Gn, occur at and near the mouth of a western tributary valley at an elevation of about 75 m; spring Gp lies north of the mouth of Pakushin Valley at an elevation of about 200 m. The thermal springs Gp emanate near the major fault in Pakushin Valley, whereas the springs at Gm and Gn are close to the projection of a fault mapped on the east side of the valley. Spring Gm is located near the contact between the Makushin pluton and the overlying Unalaska Formation. Exposures of diorite downvalley of Gm are reported by Henning and Reeder (1983). Bedrock exposed above Gp and Gn is Unalaska Formation and is presumed to underlie the alluvium from which these springs emerge. All three springs have low discharge (< 20 lpm) and moderate temperatures (30°-40°C).

The chemical compositions of Gm and Gn are similar (table 10) and the two springs plot closely together on both cation and anion diagrams (fig. 8), indicating the two spring waters are derived from the same source. Compared to Gm and Gn, waters from Gp are depleted in Ca and SO_4 but are enriched in all other constituents. When compared to the thermal springs in upper Glacier Valley, there appears to be a downvalley trend of depletion of Ca and SO_4 accompanied by an enrichment in nearly all other constituents (fig. 3). Depletion of Ca and SO_4 suggests anhydrite is being deposited beneath the lower part of Glacier Valley. The concentrations of Mg, Na, and K at Gp are uniformly 65 percent greater than at Gn. The similarities in ratios between the waters of Mg:Na, Mg:K, and the conservative elements Cl:B suggests the thermal waters at Gp are genetically related to those at Gm and Gn or perhaps originate through similar chemical processes. All three spring waters have high concentrations of HCO_3 and SO_4, which probably reflects extensive reactions with CO_2 and H_2S.

The concentrations of HCO_3 and SO_4 strongly suggest that at least a portion of the lower Glacier Valley thermal-spring waters are related to thermal waters at the head of Glacier Valley. Evidence from well W-3 indicates that lateral flow of Cl-poor, HCO_3-SO_4 rich waters at the head of the valley extends to depths of 150 m below sea level. If these thermal waters continue to flow downvalley under a hydrologic gradient, HCO_3-SO_4 rich waters could underlie much of Glacier Valley. Concentrations of various constituents could have increased simply through longer contact with reservoir rocks during downvalley flow. Several high-temperature experimental studies have shown that appreciable concentrations of constituents normally found in geothermal waters can be brought into solution by interaction with fresh rocks, provided the reaction times are long enough (Henley and Ellis, 1983). However, temperatures are probably not high enough nor residence times long enough in lower Glacier Valley to account for all of the increased concentration of constituents in this manner.

Increases in some of the constituents could have occurred during passage of the thermal waters through rocks of the Unalaska Formation in the lower part of the valley. Although parts of the Unalaska Formation are reported to have been deposited in a submarine environment (Drewes and others, 1961), it is not known if such deposits occur in the Glacier Valley area. Another potential source of Cl and other constituents found in the lower Glacier Valley springs is through seawater contamination of HCO_3-SO_4 thermal waters. A dilution of 50:1 would produce the Cl concentration observed at Gp and account for 25 ppm of Mg plus the increases in many of the other constituents that are found in the HCO_3-SO_4 waters in upper Glacier Valley.

An alternative explanation for the origin of the lower Glacier Valley thermal spring waters is that they are derived by mixing of a Cl-rich hot-water component from a deep reservoir with waters from a shallower reservoir containing the HCO_3-SO_4 waters. Halite deposits found in upper Glacier Valley suggests a Cl-hot water reservoir underlies the area but has become depleted or sealed from the surface in the recent past. Stratification of HCO_3-SO_4 waters over Cl-rich reservoirs has been documented at various convergent-margin volcanic geothermal systems, for example, Hakone Volcano, Japan (Oki and Hirano, 1970) and the Kamahung System, Indonesia (Kartokusumo and others, 1975). To account for the greater concentration of constituents at Gp vs Gm and Gn, differing proportions of mixing between the component waters must be invoked. The Cl and B concentrations indicate the deep-water fraction should be twice as much at Gp than at Gm and Gn. However, such linear mixing is not reflected in the temperatures of the springs nor in their SiO_2 concentrations if the deep Cl waters are presumed to be higher in temperature and richer in SiO_2 than waters in the intermediate reservoir. In fact, SiO_2 concentrations appear to decrease not increase, downvalley and are lower than SiO_2 concentrations in the upper Glacier Valley. Because Mg is rapidly removed from high-temperature waters through alteration reactions, the deep hot-water component would be presumed to have little or no Mg. The concentration of Mg at Gp, however, is 65 percent greater than at Gm and Gn rather than less, as would be expected from a simple mixing model. Determining the origin of the spring waters is further complicated by possible near-surface mixing with cold ground waters. All three springs lie in marshy areas and at the base of steep slopes.

The model most consistent with the geochemical evidence is that waters at springs Gpm, Gn, and Gp originate primarily as HCO_3-SO_4 thermal waters that flow beneath the valley under a hydrologic gradient from regions on the flanks of Makushin Volcano and perhaps Pakushin Cone. The downvalley decrease in SiO_2 suggests the waters cool upon descent or are diluted with colder waters. However, temperatures in the reservoir must be high enough for deposition of $CaSO_4$ to occur. Increases in other constituents, including Mg and Cl, could be accounted for by seawater contamination or perhaps by passage of the waters through the Unalaska Formation. However, the possibility that Cl and particularly B are derived from a deep hot-water reservoir cannot be dismissed.

Geothermometry

Results of applying SiO_2 and cation geothermometers to representative thermal waters at Makushin are given in table 12. However, the geothermometers are of questionable value because of the ambiguities associated with the origins of the chemical constituents in these waters. Quartz does occur in the Makushin pluton and both secondary quartz and chalcedony have been identified in fractures in rock cores from the thermal-gradient wells. The SiO_2 geothermometer could therefore reflect equilibration with either of these SiO_2 phases. However, as noted before, the SiO_2 present in the waters could have also been introduced by dissolution of feldspars by CO_2-rich waters or by acidleaching and dissolution of country rock.

A similarly ambiguous situation occurs with the cation geothermometers. The Na/K geothermometers predict high temperatures, whereas, the calcium-corrected (4/3) cation thermometer based on Fournier and Truesdell's (1973) criteria, gives temperatures lower than the outlet temperatures for Gf and Gh and well below the SiO_2 predicted temperatures for Mc, Gf, and Gh. Residence time of the thermal waters may have been too short for cation equilibration to occur.

Ambiguities also occur at the Cl-springs. The quartz conductive geothermometer gives temperatures of 144°C for Gm and 139°C for Gp. The (1/3) Na-K-Ca for Gp gives a temperature of 175°C, but application of an Mg correction suggested by Fournier and Potter (1978) drops the predicted cation temperature to 70°C. Use of the Mg correction, however, depends on whether the Mg is introduced through mixing or whether it is a property of the deep thermal water itself, a situation that is not yet clearly resolvable at Gp. Following the criteria of Fournier and Truesdell (1973), the 4/3 Na-K-Ca geothermometer would apply to spring Gm, which gives a temperature of 76°C. However, Fournier (1981) has pointed out that if a particular water is suspected of having undergone substantial mixing with a cold-water component, the choice of the (4/3) temperature would be erroneous and the (1/3) temperature is more likely to apply. Mixing with cold waters would also dilute the SiO_2 concentration of the hot-water component, and thus the reservoir temperature could be substantially greater than indicated by the quartz geothermometers.

Table 12. Silica and cation geothermometers applied to Makushin thermal springs. Temperatures in °C.

Spring	Surface temp	Quartz conductive	Chal-cedony	Amor-phous	Na-K	Na-K-Ca, 4/3	Na-K-Ca, 1/3	Na-K-Ca-Mg, corrected
Mc	34	140	114	19	244	50	162	-
Gf	79	158	134	36	176	29	125	-
Gh	61	159	135	37	176	20	121	-
Gm	39	144	119	24	225	76	166	-
Gp	40	139	112	18	221	104	175	70

The downvalley depletion of Ca and SO_4 suggests temperatures in the underlying reservoir are high enough to cause deposition of anhydrite. The SO_4 concentrations at Gn and Gp are consistent with anhydrite solubility temperatures of 120°C and 145°C, respectively (Holland and Malinin, 1979). However, if the Mg present in these waters is derived from the reservoir and not from mixing with a cold-water component, the Mg concentrations suggest reservoir temperatures decrease downvalley and are 100°C. Similarly, the downvalley decrease in SiO_2 suggests SiO_2 is reequilibrating to cooler reservoir temperatures.

The ambiguities, discordance, and contradictory interpretations afforded by the geothermometers underscore the need to treat the thermal-water geothermometers with caution. The lack of outflow from the deep Cl reservoir and the near-surface origin of dissolved constituants of the hot-spring waters is strongly supported by the inconsistant geothermometer indications.

Stable Isotope Analysis of Waters

Samples of thermal waters, steam condensates, and locally derived meteoric waters (LDMW) obtained from Makushin have been analyzed for ratios of $^{18}O/^{16}O$ and D/H (table 13; fig. 9). Stable-isotope analyses of geothermal waters have proved useful for identifying the sources of waters in the geothermal system, for estimating mixing with nonthermal waters, and for estimating the degree of water-rock interaction within the reservoir. A review of the application of water-isotope studies for geothermal systems is contained in Truesdell and Hulston (1980). The isotopic values in table 13 are given in terms of relative differences, as defined by equation (1), with respect to standard mean ocean water (SMOW) defined by Craig (1961). All $\delta^{18}O$ and δD analyses were performed by Dr. R. Harmon either at the Scottish Universities Reactor Centre, Glasgow, Scotland (1980 and 1981 analyses) or at the Stable Isotope Laboratory at Southern Methodist University, Houston, Texas (1982 analyses). The reported precisions are 1.0 permil for δD and 0.2 permil for $\delta^{18}O$.

The isotopic compositions of meteoric waters were found by Craig (1961) to lie close to a line described by $\delta D = 8\ \delta^{18}O + 10$. Craig's (1961) meteoric water line and the Adak precipitation line are plotted on figure 9

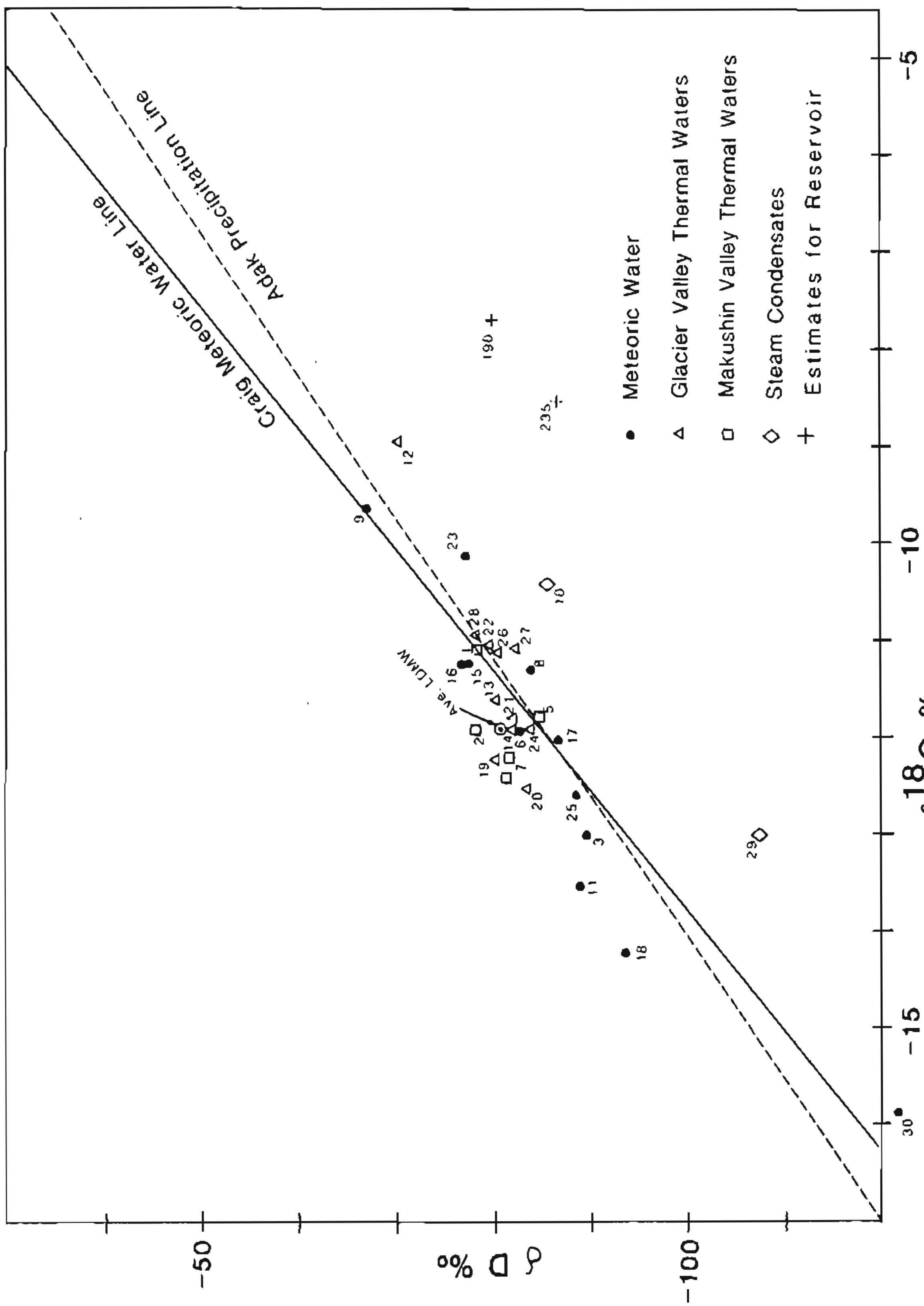

Figure 9. Diagram of stable isotope composition of Makushin waters. Values are relative to SMOW. Numbers keyed to table 13. Craig's (1961) meteoric water line and the Adak precipitation line (discussed in text) are included for comparison.

Table 13. Stable isotope data, Makushin thermal springs, steam condensates, and locally derived meteoric waters. All values reported relative to SMOW.[a]

Location	Type	$\delta^{18}O$ (permil)	δD (permil)	Year of analysis
Makushin Valley				
1. M-a	SO_4-HCO_3 hot spring	-11.05	-77	1982
2. M-b	SO_4-HCO_3 hot spring	-11.9	-78	1980
3. M-b	Cold stream	-13.0	-89	1980
4. M-c	SO_4-HCO_3 hot spring	-12.4	-81	1981
5. M-c	SO_4-HCO_3 hot spring	-11.7	-84	1982
6. M-c	Cold stream	-11.9	-82	1981
7. M-d	SO_4-HCO_3 hot spring	-12.1	-81	1980
8. M-d	Cold stream	-11.3	-83	1980
9. M-Camp	Cold spring	-9.65	-67	1982
Glacier Valley				
10. Fumarole 3	Steam condensate	-10.4	-85	1982
11. Fumarole 3	Cold stream	-13.5	-88.5	1982
12. G-d1	Acid hot spring	-8.9	-70	1980
13. G-d2	SO_4-HCO_3 hot spring	-11.6	-80	1980
14. G-d3	SO_4-HCO_3 hot spring	-11.9	-83	1981
15. G-d	Cold spring	-11.1	-77	1980
16. G-d	Snow run-off	-11.2	-76	1980
17. G-d	Cold stream	-12.0	-86.5	1980
18. G-d	Cold stream	-14.2	-93	1981
19. G-e	SO_4-HCO_3 hot spring	-12.2	-80	1981
20. G-f	SO_4-HCO_3 hot spring	-12.5	-83	1981
21. G-h	SO_4-HCO_4 hot spring	-11.7	-82	1982
22. G-j	SO_4-HCO_4 hot spring	-11.0	-79	1982
23. G-k	Cold spring	-10.	-76.5	1982
24. G-1	SO_4-HCO_3 hot spring	-11.9	-83	1982
25. G-1	Cold stream	-12.6	-88	1982
26. G-m	Cl - hot spring	-11.1	-80	1982
27. G-n	Cl - hot spring	-11.05	-82	1982
28. G-p	Cl - hot spring	-10.9	-78	1982
Summit				
29. Fumarole 6	Stream condensate	-13.0	-107	1982
30. Fumarole 6	Snow melt	-15.9	-121	1982

[a]Standard mean ocean water.

for comparison. Adak, located in the Aleutian chain about 600 km west of Unalaska, is the only station in the Aleutians for which stable isotopes of precipitation have been analyzed. The Adak line was derived by a linear-regression analysis of 57 data points. The coefficient of determination for the line is 0.95. The data were obtained from the International Atomic Energy

Agency, Vienna, Austria. Analyses of stable isotopes were performed on total precipitation collected monthly at 4 m above sea level. Precipitation on Adak for which $\delta^{18}O$ and δD data are available fell during the years 1962-1966 and 1973. Reported values from Adak for $\delta^{18}O$ and δD range from $\delta^{18}O = 14.8$ and $\delta D = 111$ to $\delta^{18}O = -4$, $\delta D = -28$. This wide range partially reflects seasonal variations, but is probably also due to the difference in isotopic composition of precipitation derived from colder Bering Sea waters vs warmer North Pacific waters.

The Adak precipitation line deviates from Craig's meteoric water line in that it has a slightly shallower slope and a negative δD intercept for $\delta^{18}O = 0$. The Makushin area is affected by the same weather systems as Adak and the precipitation line for Makushin is likely to be similar to that for Adak. However, many of the locally derived meteoric waters (LDMW) at Makushin tend to fall slightly to the left of the precipitation lines, with $\delta^{18}O$ values 0.2 to 1.0 permil lighter than the precipitation trend. The LDMW data show considerable scatter, but tend to parallel the meteoric water lines.

The isotopic compositions of most deep geothermal waters have been related to those of local meteoric waters, but in general the compositions do not lie on the meteoric water line (Truesdell and Hulston, 1980). Although δD compositions are similar to meteoric waters, $\delta^{18}O$ compositions are generally shifted toward high values. These shifts, typically about 3 to 5 permil for high-temperature systems, are caused by $\delta^{18}O$ exchange between hot rocks and deeply circulating meteoric waters. A comparable shift in δD does not occur because rock minerals contain little H. The magnitude of the $\delta^{18}O$ shift depends on the original $\delta^{18}O$ values for both water and rock, the rock type, temperature, water/rock ratio, and duration of contact. Truesdell and Hulston (1980) reported that some systems in igneous rocks with an original $\delta^{18}O \simeq +5$ permil, maximum temperatures below 150°C, and moderate water/rock ratios showed little or no isotopic shift.

The thermal springs at Makushin plot closely together and fall within the range of LDMW compositions (fig. 9). The sole spring that falls out of this range, point 12, is an acid spring whose isotopic composition probably reflects nonequilibrium surface evaporation such as seen at acid springs elsewhere (Craig, 1963). Most of the Makushin thermal springs show no apparent $\delta^{18}O$ shift and appear compositionally identical to the average of the LDMW values. The Cl springs appear slightly shifted in $\delta^{18}O$ with respect to the average value but still fall within the range of scatter of LDMW points.

The lack of any $\delta^{18}O$ shift in the HCO_3-SO_4 thermal spring waters could be attributed to one or a combination of the following possibilities: a) the water-rock contact time was too short, b) water temperatures were too low for significant isotopic exchange to occur, and c) the $\delta^{18}O$ composition of the host diorite is in equilibrium with the LDMW. Although most igneous rocks have whole-rock $\delta^{18}O$ values of +4 to +9 permil, compositions can be lowered through previous exchange with meteoric waters (Taylor, 1974, 1977; Truesdell and Hulston, 1980). Perfit and Lawrence (1979) reported $\delta^{18}O$ whole-rock compositions ranging from -4.1 to +7.0 permil for the neighboring Captains Bay pluton. The $\delta^{18}O$ depleted samples were found to correlate with zones of hydrothermal alteration. No $\delta^{18}O$ analyses of the Makushin diorite have yet been made, but values similar to Captains Bay pluton could probably be expected.

In comparison to the thermal springs, the fumarole condensates show a positive $\delta^{18}O$ shift of 1.5 permil with respect to the meteoric water line. If, as discussed above, the superheated steam from field 3 is derived directly by adiabatic expansion of steam rising from the deep reservoir, the isotopic composition of the superheated steam provides an estimate of the isotopic composition of the reservoir waters. Using fractionation data from Truesdell and others (1977) and assuming the steam was in equilibrium with and separated from liquid water at temperatures of either 190°C (minimum estimate) or 235°C (temperature of maximum enthalpy saturated steam) yields deep-reservoir-water isotope compositions of δD = -80 to -87 permil and $\delta^{18}O$ = -7.7 to -8.6 permil, respectively. The range of δD lies within the range of LDMW; the $\delta^{18}O$ is shifted by ~+3.5 permil with respect to the meteoric water line.

Thus the isotopic evidence is consistent with the following model for the origin of the HCO_3-SO_4 springs. Local meteoric waters at higher elevations infiltrate the host diorite, and circulate to shallow or intermediate depths, where they encounter and are heated by superheated steam to temperatures ≤150°C. These waters then ascend to the surface under a hydrostatic pressure head and emerge as HCO_3-SO_4 thermal springs. Data from well W-3 indicate circulation in Glacier Valley can occur to depths of 430 m.

The Cl springs Gm, Gn, Gp appear slightly shifted in $\delta^{18}O$ with respect to the average LDMW values but still fall within the range of scatter. If the spring waters are a result of mixing of cold, shallow ground waters with a deep, Cl-rich hot-water component, from balance calculations the hot-water fraction would have to be less than 20 percent to produce the isotopic compositions at Gm, Gn, and Gp. This calculation is based on an assumed value of $\delta^{18}O$ = -11.9 permil (the average LDMW value) for the cold-water component and $\delta^{18}O$ = -8.0 permil for the deep-thermal-water component. However, the lack of any linear trend between the Cl concentration and $\delta^{18}O$ for these spring waters argues against such mixing. The isotopic shift that would result from seawater contamination of 2 percent or less would be undetectable within the limits of scatter of the LDMW values.

THERMAL-GRADIENT WELLS

Three thermal-gradient wells were drilled by Republic Geothermal, Inc. (RGI) at Makushin during the summer of 1982. The purpose of the wells was to obtain information about the shallow thermal regime and to help locate an optimum site for a deep exploratory well. The wells were core drilled, 2 in. dia, to depths of approximately 460 m (1,500 ft), then cased and filled with water for subsequent temperature logging. No fluids were sampled from any of the three wells. Detailed discussions on choosing the well sites, drilling procedures, temperature and lithologic logs, and so forth, can be found in RGI's preliminary report (in preparation) on the results of the 1982 Makushin Geothermal Drilling Program. The results of the drilling program are briefly discussed here because of their obvious bearing on understanding the Makushin geothermal system and the origin of the geothermal fluids. The following discussion is based primarily on personal communication with C. Isseherdt, P. Parmentier, and S. Matlick of RGI (1982) and on well logs and temperature profiles provided to the authors by RGI. Generalized temperature profiles from temperature logs of the three wells are shown in figure 10.

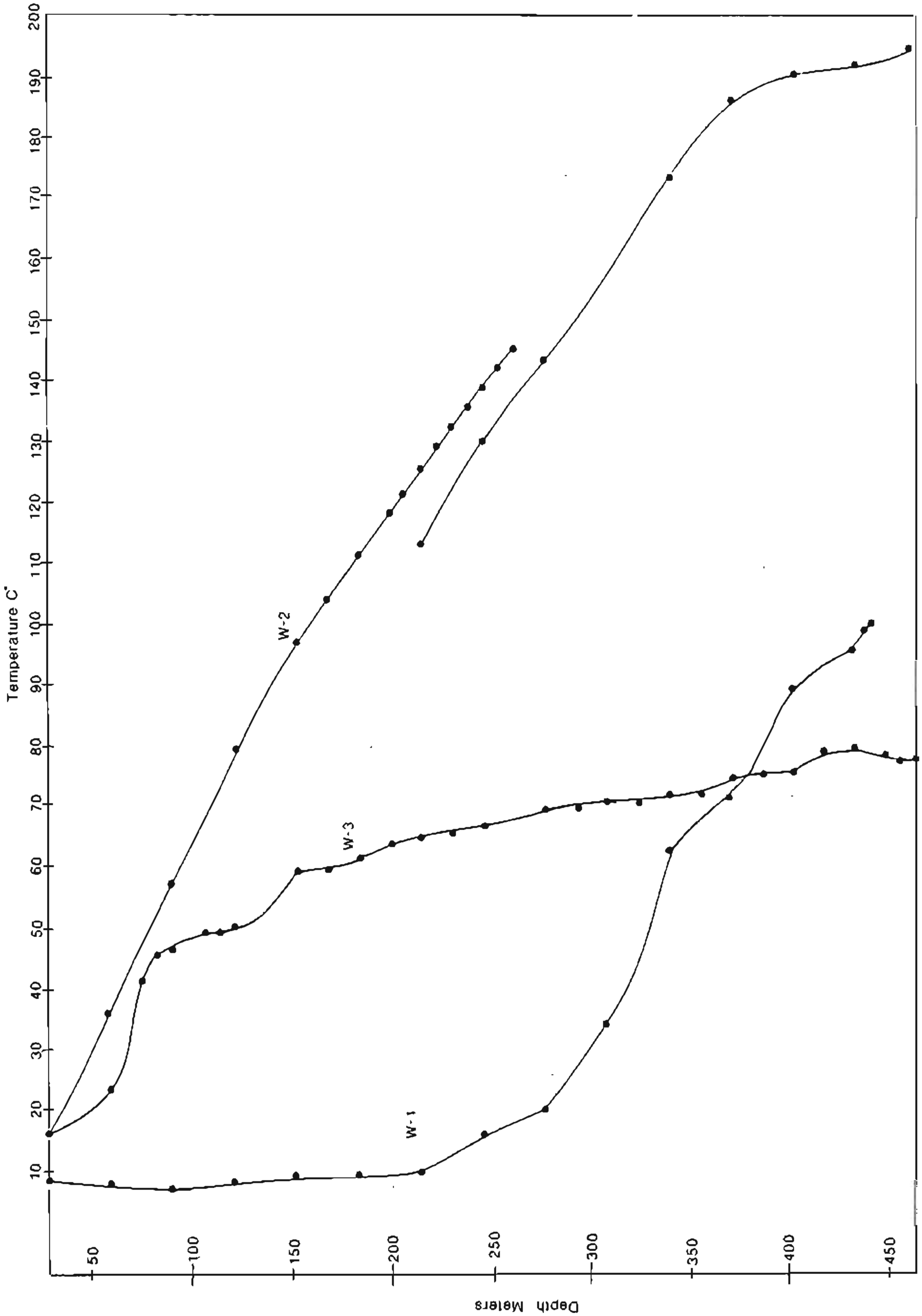

Figure 10. Temperature profiles for thermal-gradient wells in the Makushin geothermal resource area. Temperature logs are from September 18, 1982 for W-1; September 15, 1982, upper curve, and September 18, 1982, lower curve for W-2; and September 18, 1982 for W-3. Data provided by RGI.

Well W-1 was drilled at an elevation of approximately 550 m (1,800 ft) about 2 km west of Sugarloaf Cone, near 'Fox Canyon.' The bottom of the well reached 438 m (1,435 ft), 113 m (370 ft) above sea level. The well penetrated 275 m (900 ft) of Makushin basaltic and andesitic lava flows before encountering a series of cinder beds, lahars, and debris flows. The volcanic rocks extended down 372 m (1,220 ft) before Makushin diorite was finally reached. An andesitic dike, thought to be related to the Makushin volcanic rocks, intersects the diorite in the well at a depth of 420 m (1,380 ft). The well was completed July 14, 1982; the temperature log shown in figure 10 was obtained September 18, 1982.

The temperature profile is essentially isothermal down to 215 m (700 ft), which reflects the influence of vertical convection of cold ground waters through the lava flows. Temperatures steepen rapidly in the lower part of the well, with temperature gradients measuring 70°C/100 m between 275 and 335 m (900-1,100 ft) and 36.5°C/100 m between 335 and 438 m (1,100-1,435 ft). Bottom-hole temperature measured 100°C.

The volcanic section of the hole shows little or no alteration. The diorite at the bottom of the well is reported to be highly fractured and highly altered with occurrences of native sulfur, pyrite, epidote, quartz, anhydrite and chlorite, and kaolinite and other clays. Isselhardt (personal commun.,1982) reports evidence for two separate episodes of hydrothermal deposition within the fractures.

Well W-1 has shown that the Makushin geothermal prospect and Makushin diorite both extend northeastward of upper Makushin Valley for at least 0.5 km. Fractured Makushin diorite appears to be the host reservoir rock at W-1. Well W-1 also illustrates the effectiveness of volcanic flows in masking underlying geothermal systems.

Well site W-2 is located in upper Makushin Valley at an elevation of about 365 m (1,200 ft), approximately 2 km NE of fumarole field 2 and 0.5 km SW of fumarole field 1. After penetrating a 10-m-thick surface layer of volcanic ash, the well was drilled through Makushin diorite to a depth of 457 m (1,500 ft), 91 m (300 ft) below sea level. The upper two-thirds of the section is fairly fresh diorite with minor fracturing and minor amounts of chlorite, pyrite, silica, epidote, and occasional kaolinite or zeolites either disseminated or localized in small concentrated vugs or veins. Calcite becomes more prevalent below 275 m (900 ft). A zone of moderate chloritization with considerable veining and fracturing occurs at 350 to 375 m (1,150-1,230 ft). Secondary minerals of this altered zone are clays, quartz, anhydrite, pyrite, and epidote.

The well was completed on August 8, 1982; the temperature logs shown in figure 10 were measured on September 15 (upper curve) and September 18, 1982 (lower curve). Temperatures in the lower part of the well exceeded the range of the measuring device used on September 15, 1982. Consequently, the hole was logged with a different instrument on September 18, 1982. The offset between the two curves at overlapping measurement depths is thought to be due to differences in the measuring instruments rather than a temperature drop within the hole between the time of measurements. Bottom-hole temperature measured 195°C.

The temperature increases rapidly between 30 and 365 m (100 to 1,200 ft) at a rate of 44°C/100 m. The linearity of the temperature profile indicates the thermal regime above 365 m (1,200 ft) is dominated by conduction. The gradient drops rapidly but remains positive below 365 m (1,200 ft). This depth coincided with loss of circulation of drilling fluid reported by the drillers and a marked increase in fractures reported in the well log. These coincidences indicate that thermal fluids are convecting along fractures below 365 m (1,200 ft). The bottom-hole temperature is consistent with the minimum estimated reservoir temperature obtained from the superheated fumarole but lower than the gas geothermometry of table 7. Well W-2 lies along the strike of the Glacier Valley lineament. The high temperatures encountered at the bottom of W-2 and the occurrence of fumaroles, hot ground, and thermal springs in the immediate vicinity suggest the heat source is directly below the area.

The third well, W-3, was drilled in upper Glacier Valley at approximately 305 m (1,000 ft) elevation, on a terrace adjacent to thermal spring Gj. Fumarole fields 3, 4, and 9 indicated the existence of a high-temperature reservoir at the heads of Glacier Valley. Site W-3 was chosen in part to try to delineate the lateral extent and influence of this high-temperature resource and also to provide information regarding subsurface hydrology and the nature and origin of the upper Glacier Valley spring systems.

After penetrating a 10-m-thick surface layer of glacial till, the drillers encountered the Makushin pluton, which extended to the bottom of the well, 457 m (1,500 ft) below the surface, 152 m (500 ft) below sea level. Nearly the entire section of diorite has localized zones of alteration associated with fractures and veins. One highly altered and fractured zone occurs at 60 to 115 m (200-380 ft). Another altered zone, possibly representing a recemented fault zone, occurs at 260 to 265 m (845-865 ft). Alteration minerals throughout include kaolinite and clays, pyrite, calcite, quartz, chlorite, and epidote.

The well loggers reported encountering artesian flow at a depth of 60 to 70 m (200-230 ft), with flow increasing in volume and temperature as drilling progressed. Final wellhead flow rate was 600 lpm with a head pressure of 6 m.

Well W-3 was completed on September 8, 1982; the temperature profile in figure 10 was obtained on September 18, 1982. Temperatures in the hole increased markedly (approximately 10°C) with respect to measurements made 3 days previously, which indicated the well had not attained equilibrium by September 18, 1982.

An abrupt increase in temperature occurs between 60 and 75 m (200-250 ft), the zone at which artesian flow begins. Another but smaller increase in gradient occurs at 120 to 150 m (400-500 ft). The profile fluctuates slightly in the lower section of the well with the thermal gradient becoming negative near the bottom. Bottom-hole temperatures measured 77.5°C; the maximum temperature, measured at 425 m (1,400 ft), was 80°C. Equilibrium temperatures are likely to be higher throughout much of the well.

The well appears to have penetrated through the zone of circulation of cold meteoric waters at a depth of 60 to 70 m (200-230 ft). The changes in temperature gradient below 70 m and the apparent reversal in gradient near the bottom of the well indicate lateral flow of thermal waters occurs between 70 and 430 m (230-1,410 ft). This thermal zone is probably caused by meteoric waters heated in the areas of fumarolic activity and flowing down vertical fractures under a hydrologic gradient.

Suites of rock samples taken from cores from each of the wells were analyzed for selected trace and minor elements (R.W. Bamford, written commun. to RGI, 1982). On the basis of investigations of explored geothermal systems, Bamford and others (1980) found that depletions or enrichments of certain key elements relative to background samples provide signatures that are indicative of the type and degree of thermal fluid-rock interactions; these characteristics can also frequently distinguish between past and ongoing hydrothermal activity. Bamford (written commun. to RGI, 1982) found a single type of geochemical anomaly---characterized by spatially associated Li-F-As-S (±Hg) enrichments---in rocks from all three wells. These enrichments indicate that hydrothermal rock alteration occurred under intermediate pH or alkaline water-dominated geothermal conditions. On the basis of this enrichment-depletion signature and on other evidence, he tentatively identified hot-water entries at 200°C between 360 and 430 m (1,180-1,410 ft) in well W-2. However, Bamford (verbal communication, 1983), indicated that the technique and the broad interval used for sampling the Makushin cores ($\sim$30 m) would not be capable of distinguishing vapor-dominated fluid flow if the vapor-dominated system had evolved in the recent past. This is partially because acid-leaching overprinting takes time to develop.

MODEL OF GEOTHERMAL SYSTEM

New geologic, geochemical, and isotopic data combined with results from thermal gradient wells have now provided sufficient detail to allow speculating on a model of the Makushin geothermal system. The summit collapse caldera indicates that a shallow magma chamber exists beneath Makushin volcano. Age of caldera formation is unknown, but is thought to be late Pleistocene or Recent. The cooling magma could provide the heat source for driving the Makushin hydrothermal system.

Fumarolic activity, zones of warm ground, and low-Cl HCO_3-SO_4 thermal springs occur in an arcuate band along the southern and eastern flanks of the volcano. This distribution is roughly concentric with the form of the volcano and of the summit caldera, which suggests that the fumarolic gases and steam are derived in part from a core region beneath the Makushin central vent of volcanic activity.

The young volcanoes to the northeast (Sugarloaf Cone, Table Mountain, and Wide Bay Cone) and to the southwest (Pakushin Cone) of Makushin argue either for an elongate magma body that extends from Makushin Volcano along the NE-SW trend or for separate heat sources that underlie the northeastern and southwestern areas. The alignment of Cl-rich thermal springs; low-Cl, HCO_3-SO_4 thermal springs; fumaroles; and zones of heated ground indicate the hydrothermal system also underlies the northeast-trending 'Glacier Valley' lineament. Major structural features in the region in addition to this lineament include several northwest-trending faults and a northeast-trending gravity low that passes through Makushin Volcano (Reeder and others, 1982). The Cl springs and some of the fumarole fields occur at the intersection of the faults with the lineament. The grabenlike tensional faulting in Glacier Valley is probably related to the intense compressional stress exerted by plate convergence. The lack of surficial thermal activity on the western flank of the volcano may be due to the great thickness of volcanic deposits that are suggested by gravity data. The impermeable volcanic flow could be effectively masking any underlying hydrothermal system.

The host reservoir rock for the geothermal system appears to be the fractured Makushin granodiorite pluton. Much of the thermal activity at the surface coincides with the exposure of the pluton at the heads of Makushin and Glacier Valleys. This zone is at the intersection of several features: a) the lineament trending down Glacier Valley and Driftwood Valley, b) the arcuate zone of fumarolic and thermal spring activity on the flanks of Makushin Volcano, c) the alignment of satellitic volcanic vents, and d) exposure of glacier-eroded diorite. Makushin volcanic flows and units in the Unalaska Formation may serve as effective cap rocks elsewhere. Volcanic flows may also be helping to direct fluid flow outward from the core region to the periphery of the volcano, where the diorite is exposed.

On the basis of thermodynamic considerations of the superheated fumarole and of the temperature log from well W-2, deep reservoir temperatures must exceed 190°C. Gas geothermometry suggests reservoir temperatures of 235°-300°C.

Gas composition in the deep reservoir is most apt to resemble that of the superheated fumarole (table 3). The $^3He/^4He$ compositions of fumarole and hot-spring gases indicate a magmatic influence on the geothermal system.

Variations in $^3He/^4He$ compositions may reflect varying degrees of hot-water leaching of radiogenic ^4He from reservoir wall rock. Isotopic composition of the CO_2 suggests that much of the CO_2 is derived from the cooling magma. H_2S is also probably largely derived from the magma. Other gases present primarily originate from water-gas and water-rock reactions or from gases dissolved in the charging meteoric waters. Isotopic composition of waters in the deep reservoir is estimated to be $\delta^{18}O \sim -8$ permil and $\delta D \sim -80$ to -86 permil. The range of δD is similar to that of the LDMW samples from Glacier and Makushin Valleys, but is much heavier than that of snow melt from the summit of Makushin. Meteoric waters charging the deep system appear to originate at lower elevations on the flanks of the volcano or perhaps are a mixture of valley waters with waters from higher elevations. The $\delta^{18}O$ is shifted + 3.5 permil with respect to LDMW.

Thermal springs in upper Makushin and Glacier Valleys, rich in HCO_3, SO_4, and Ca, originate from the circulation of meteoric waters along fractures in the Makushin pluton. The waters are heated by ascending steam and hot gases and by conduction from wall rock. Low Cl concentrations indicate isolation from any deep hot-water system. If the SiO_2 in the waters is assumed to be in equilibrium with quartz or chalcedony, temperatures at the base of circulation would range from 100° to 150°C. Isotopic evidence indicates that the charging waters in both areas are of local origin. Results from well W-3 indicate that circulation of thermal waters in upper Glacier Valley extends to a depth of 430 m, about 150 m below sea level. Lower concentrations of dissolved solids in thermal waters suggests shallower circulation of meteoric waters or a higher pH in upper Makushin Valley. Fracturing and alteration of the host Makushin pluton are more intense and more pervasive in upper Glacier Valley than in Makushin Valley, which probably accounts for the greater number of thermal springs found in Glacier Valley. The high temperatures encountered in well W-2 indicate the heat sources for springs and fumaroles in Makushin Valley lie beneath the immediate area. Well W-3 penetrated beyond the zone of meteoric water circulation at 60 to 70 m (200-230 ft); thermal springs in upper Glacier Valley are apparently heated by lateral flow of waters that pass through the zones of fumarolic activity above the spring sites.

The explanation most consistent with the geochemical and isotopic data for the origins of the Mg-rich Cl-springs in lower Glacier Valley, coupled with evidence from well W-3, is that the thermal waters originate on the flanks of Makushin Volcano. SiO_2-rich HCO_3-SO_4 waters such as those that feed the springs in upper Glacier Valley flow downward beneath the valley under a hydrologic gradient before emerging as springs along fault-induced conduits in lower Glacier Valley. Increases in Mg, Cl, and several other constituents can be accounted for by seawater contamination or perhaps by passage of the waters through the Unalaska Formation. However, the possibility that the salinity of the waters is due to mixing of a hot-water component from a deep Cl-rich reservoir cannot be dismissed.

The extent of surface thermal activity provides a minimum estimate of the size of the subsurface system (fig. 2). Fumarolic activity implies the existence of at least a discontinuous vapor-dominated zone, the bottom of which must extend at least down to 365 m (1,200 ft), the lowest fumarole in fields 3 and 1. Fumarolic activity, acid springs, and HCO_3-SO_4 rich thermal waters that are low in Cl are commonly associated with vapor-dominated systems (White and others, 1971). Vapor-dominated systems have been identified or are thought to exist at several convergent-margin volcanoes (Oki and Hirano, 1970; Mahon and others, 1980; Muffler and others, 1982). However, such surface manifestations of thermal activity can also be produced by a hot-water system boiling at depth. The steam and gases that evolve from the hot-water reservoir form a shallow vapor-dominated zone and give rise to fumaroles and acid-sulfate springs, similar to the surficial expressions of deep vapor-dominated systems.

The occurrence of fractures, the temporary loss of circulation of drilling fluid, the decrease in thermal gradient, and geochemical evidence suggest that thermal fluids are flowing along fractures near the bottom portion of well W-2. The zone occurs at a depth of 0 to 100 m below sea level in the upper part of Makushin Valley. The geochemical signature suggests the hydrothermal alteration in the zone developed primarily under neutral to alkaline pH water-dominated geothermal conditions---despite the presence of a recently evolved vapor-dominated flow in the zone.

Hydrothermal activity appears to have been more widespread in the recent past. Several mounds and areas of hydrothermally altered glacial till and fluvial sediments can be found in Glacier Valley. The clay-size fractions from at least two of these sites are rich in halite, indicative of alkali-chloride thermal-spring activity. Both sites occur in a region that presently displays only low-Cl thermal-spring activity. The halite deposits that are in association with hydrothermal alteration on or within Recent moraines are further evidence of the existence of a hot-water system at Makushin; however, it is apparently a system that is either depleting rapidly or is self-sealing.

The preceding observations support a model for the geothermal system in which meteoric waters on the flanks of Makushin Volcano infiltrate a deep hot-water reservoir. The waters are heated by a cooling magma, possibly one that is related to the recent caldera-forming eruption, to temperatures of 250°-300°C. Geothermal waters boil at 190°-235°C to form a discontinuous vapor-dominated zone at higher elevations, steam and gases from which feed the numerous fumaroles on the southern and eastern flanks of the volcano. Part of the steam heats meteoric waters that circulate from shallow to moderate depths along fractures in the host diorite before emerging as HCO_3-SO_4 thermal springs. Subsurface downvalley flow of some thermal waters either passes through marine sediments or is contaminated by seawater to produce Cl-rich thermal springs in lower Glacier Valley. The distribution of fumaroles and springs suggests that the main hydrothermal system extends outwards from beneath the volcano to the southern and eastern flanks and perhaps along the lineament at the heads of upper Glacier and Makushin Valleys. The host reservoir rock appears to be the Makushin pluton, which is exposed at the heads of Glacier, Nateekin, and Makushin Valleys.

POTENTIAL DRILLING SITES

Geologically, the optimum site for a future deep exploratory test well would be at or near fumarole fields 2 or 3, where the existence of a high-temperature resource is evident from the intensity of thermal activity. However, the lack of a road necessitates use of a helicopter-transportable drill-rig. Logistically, however, the steepness of the terrain and high elevation make these sites impractical for helicopter landings and for the set-up and operation of a drill-rig capable of well depths of 4,000 ft.

Republic Geothermal, Inc. has recommended siting the deep exploratory well near thermal gradient well W-2. The site is located near regions of fumarolic and thermal spring activity and lies along the Glacier Valley lineament. Temperatures and evidence for convection at the bottom of W-2 suggest a high-temperature resource capped by unfractured diorite. The site is accessible and has a broad, flat area for both a camp and a drilling platform. RGI has proposed angling the well toward a thermal area upstream from fumarole 1 to enhance the potential of intersecting a developable high-temperature reservoir.

On considering the geologic field evidence, the logistical accessibility, the anticipated size of the drillrig required, and the evidence from well W-2, the authors are compelled to concur with RGI's choice for the site of the first deep exploratory well at Makushin.

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