HYDROTHERMAL ACTIVITY AND CARBON-DIOXIDE DISCHARGE AT SHRUB AND UPPER KLAWASI MUD VOLCANOES, WRANGELL MOUNTAINS, ALASKA

By Michael L. Sorey, Cindy Werner, Robert G. McGimsey,
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HYDROTHERMAL ACTIVITY AND CARBON-DIOXIDE DISCHARGE AT SHRUB AND UPPER KLAWASI MUD VOLCANOES, WRANGELL MOUNTAINS, ALASKA

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ABSTRACT

Shrub mud volcano, one of three mud volcanoes of the Klawasi group in the Copper River Basin, Alaska, has been discharging warm mud and water and CO_2–rich gas since 1996. A field visit to Shrub in June 1999 found the general level of hot-spring discharge to be similar, but somewhat more widespread, than in the previous two years. Evidence of recent animal and vegetation deaths from CO_2 exposure were confined to localized areas around various gas and fluid vents. Maximum fluid temperatures in each of three main discharge areas, ranging from 48-54°C, were equal to or higher than those measured in the two previous years; such temperatures are significantly higher than those observed intermittently over the past 30 years. At Upper Klawasi mud volcano, measured temperatures of 23-26°C and estimated rates of gas and water discharge in the summit crater lake were also similar to those observed in the previous two years. Gas discharging at Shrub and Upper Klawasi is composed of over 98% CO_2 and minor amounts of meteoric gases (N_2, O_2, Ar) and gases partly of deeper origin (CH_4 and He). The rate of CO_2 discharge from spring vents and pools at Shrub is estimated to be ~10 metric tonnes per day. This discharge, together with measured concentrations of bicarbonate, suggest that a total CO_2 upflow from depth of 20-40 metric tonnes per day at Shrub.

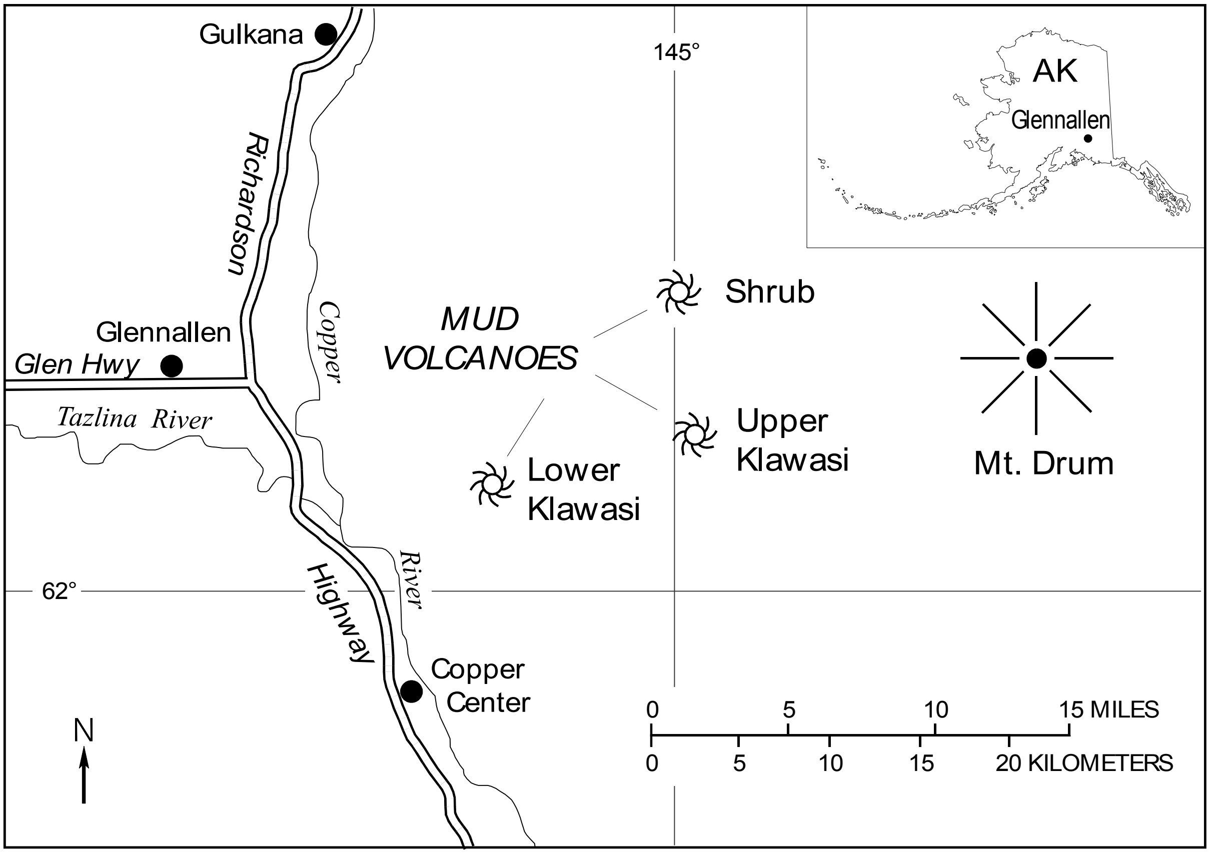
Measurements were made of diffuse degassing rates from soil at one ~300 m^2 area near the summit of Shrub that included vegetation kill suggestive of high CO_2 concentrations in the root zone. Most of measured gas flow rates in this area were significantly higher than background values, and a CO_2 concentration of 26 percent was measured at a depth of 10 cm where the gas flow rate was highest. Although additional measurements of diffuse gas flow were made elsewhere at Shrub, no other areas of vegetation kill related to diffuse degassing and high soil-gas CO_2 concentrations could be seen from the air.

Chemical and isotopic compositions of the gas and water discharging at Shrub and Upper Klawasi indicate derivation from a com-bination of mantle (magmatic) and crustal (marine sedimentary rock) sources and suggest a common fluid reservoir at depth. In particular, both the total dissolved carbon and values of ^{13}C in CO_2 are similar for fluids and gas sampled at each area, and do not appear to have changed with the onset of increased spring temperatures and fluid discharge at Shrub. This suggests that the underlying cause of the recent changes in discharge rate and temperature at Shrub is not an increase in the rate of input of magmatic heat and volatiles, but rather increases in the permeability of the upflow conduits that connect the gas-rich reservoir to the surface.

INTRODUCTION

Shrub mud volcano is situated in the Copper River Basin some 27 km east of Glennallen, Alaska (figs. 1 and 2). The first known description of Shrub and its activity was presented by Nichols and Yehle (1961), who visited the volcano in 1955 and 1956. At that time, a vegetation-free basin containing numerous small, gassy spring-fed pools was located in the area now occupied by the active vents in the Main Vent Area (fig. 2). Gas and water samples were collected from a mineral spring near the summit of Shrub in July 1973 by Ivan Barnes (U.S. Geological Survey), whose unpublished field notes list a vent temperature of 18°C. A brief examination of Shrub in August 1991 revealed no spring activity, nor any indication of recent activity (Richter and others, 1998a). In the spring of 1997, however, Shrub was observed to be vigorously venting potentially dangerous CO_2–rich gas and warm saline mud. This thermal discharge may have begun on a smaller scale in 1996, according to reports from a helicopter pilot who observed active mud springs low on the north flank of the cone (fig. 2) and possible activity on the summit area (Richter and others, 1998a).

Since June 1997, the U.S. Geological Survey (USGS) and the National Park Service have monitored the activity at Shrub and nearby Upper Klawasi mud volcano. Site investigations were conducted on June 21 and 30, 1997 and August 31, 1998, and an aerial inspection was made on December 2, 1997. During the visit on June 30, 1997, gas samples were collected from a vent near the summit of Shrub (Richter and others, 1998a,b). Video surveys of spring activity at Shrub and Upper Klawasi were made in June 1997 and July 1998.



Base from U.S. Geological Survey Gulkans A-3 quadrangle, Alaska; mud deposits from U.S. Bureau of Land Management aerial photography taken August 14, 1988

Figure 1. Index map of the Glennallen, Alaska region showing locations of Shrub, Upper Klawasi, and Lower Klawasi mud volcanoes and Mt. Drum (from Richter and others, 1998a).

One particularly striking feature was the appearance of narrow bands of alder and birch browned to heights of as much as 2 m above the ground surface, extending downhill toward the northwest from a vent area on the north flank of the Shrub (fig. 2). On June 21, 1997, this vent area consisted of a ~5 m-diameter pit filled with bubbling mud; Richter and others (1998a) speculated that the bands of browned vegetation may have been caused by significant amounts of CO_2–rich gas pouring out of the pit into rivers of gas.

Video surveys were initially used to map the extent of mudflows that occurred over the 1996-1998 period (Richter and others, 1997a,b). Subsequent mapping (fig. 2) represents revisions based on aerial photo-graphs taken in August, 1998. Most of the 1996-1997 mud flows originated from violently discharging vents located just below the summit. During visits in the summer of 1998 and 1999, mud and gas were quietly discharging from bubbling mud pools at these same vent areas. Total mud production since 1996 is estimated at 500,000 m^3 (Richter and others, 1998b).

Shrub is one of three large mud volcanoes in the Copper River Basin that are collectively referred to as the Klawasi group. Each mud volcano is elevated some 50-100 m above the surrounding terrain and constructed entirely of erupted material derived from the underlying glacio-lacustrine deposits (fig. 2). The mud volcanoes occur approximately 20 km west of Mt. Drum, a large Pleistocene volcano that was last active about 240,000 years ago, and about 60 km northwest of Mt. Wrangell, an active shield volcano (Richter and others, 1994).

Shrub was virtually inactive prior to 1997. Minor activity was observed in the mid-1950's; Nichols and Yehle (1961) report the occurrence of small, gassy pools in a basin some 30 feet below the summit in July 1956, and list a temperature of 12°C for these features. A water sample was obtained from a summit "mineral spring" in July 1973, but this feature was reported dry during a visit in August 1981 (Motyka and others, 1989).

The other two mud volcanoes in this group, Upper and Lower Klawasi, have been active throughout at least the past 40 years and have yielded temperature and chemical data on the mud and gas discharges (Nichols and Yehle, 1961; Grantz and others, 1962; Reitsema, 1979; and Motyka and others, 1989). These investigations showed that Upper and Lower Klawasi periodically erupt mud at temperatures of 20-25°C and mixed with Ca-poor, Na-HCO$_3$ -rich saline water and CO$_2$–rich gas. The chemistry and gas composition of water discharged at Shrub is similar to that at the other Klawasi vents, but since 1996 has occurred at higher temperatures (40-54°C). Motyka and others (1989) suggest that the warm saline water is connate in origin and that the CO$_2$ derives from degassing of deep-seated magma and contact decarbonization of underlying Mesozoic limestone beds. At least one of the oil and gas exploration wells drilled near the town of Glennallen encountered fluid pressures in excess of hydrostatic at depths of 1,700 m during drilling through the Mesozoic sequence (Reitsema, 1979). Bottom-hole temperatures in this and other deep exploration wells in the region range from 49-59°C (Motyka and others, 1989), similar to present-day vent temperatures at Shrub.

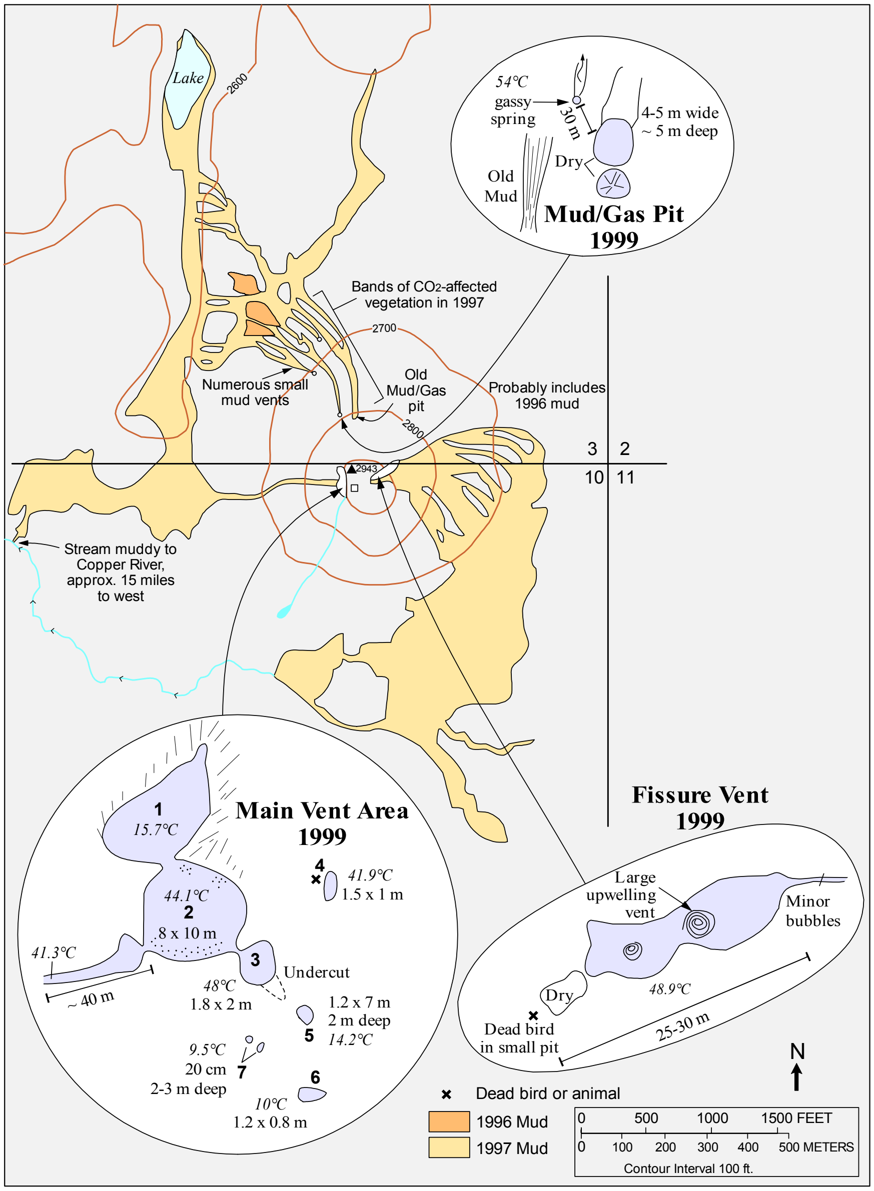


Figure 2. Map of Shrub mud volcano showing vent locations and temperatures on June 23, 1999, extent of mud deposits in August (from Richter and others, 1998b), and inset sketches of vent areas (not to scale). Approximate location of the area of diffuse gas flow measurements shown in figure 7 is denoted by an open rectangle between the Main Vent and Fissure Vent area.

1999 ACTIVITY

Shrub Mud Volcano

Shrub mud volcano was visited on June 23 and 24, 1999, at which time the general level of activity (mud, water, and gas discharge) was observed to be less intense, but more widespread than during visits the previous two years. Several new thermal and nonthermal spring vents were noted near the summit. Measured vent temperatures around the summit and north flank were slightly higher than in previous years. Each of the discharging pools and streams appeared to carry significant mud loads, and although there was no active mud fountaining or erupting, mud from recent eruptions was splattered against trees around several vents (fig. 3).

The map in fig. 2 is identical to that in Richter and others (1998b), except for the addition of inserts depicting details of each of the three main discharge areas on or near the summit - Main Vent Area (MVA) on the west side, Fissure Vent Area (FVA) on the east side, and Mud/Gas Pit Area (MGPA) on the north side below the summit region. Particularly noteworthy changes in activity at Shrub between 1999 and previous years include:

1. The appearance of several cold, degassing pools at the MVA (vents #5, #6, and #7).
2. The disappearance of gas/mud/water discharge from the collapse pit at the MGPA.
3. The appearance of a new gassy hot spring 30 m downhill from the collapse pit at MGPA with a temperature (54°C) that was 5-7°C hotter than in any of the MGPA and FVA vents visited in 1997 and 1998.

Figure 3. Vent #42, a 44°C gassy pool in the Main Vent Area at Shrub mud volcano (see Figure 2 for location). Photo shows mud spattered on the branches of adjacent trees from previous eruptions in this vent.

We found carcasses of dead birds and snowshoe hares on the inner slopes of several degassing pits (for example vents #4 and #5 at MVA) and a few small holes, or point sources, with cold CO_2 gas venting through the soil. At one location between MVA and FVA, such a vent was surrounded by a ~300 m^2 area of soil with anomalously high diffuse gas flow rates (up to 5,600 $g/d/m^2$) and a spring seep discharging water at 13°C. In 1997, this same area contained several small (1-2 cm diameter) holes audibly venting CO_2, and in 1998 vegetation kill and mud seeps accompanied water and gas discharge from a small vent in the same area.

A few diffuse gas flow measurements made at the MGPA were all anomalously high (~400 $g/d/m^2$), including those made at a site ~30 m southwest of MGPA where there was a stand of alders with dead or wilting leaves, most prevalent on the lower branches. These conditions appeared to extend over a small isolated area, unlike the elongated zones of browned vegetation observed in 1997 farther down the north flank. A possible explanation for the leaf kill observed in 1999 is that elevated CO_2 concentrations in the root zone affected oxygen and nutrient uptake by the tree roots.

Upper Klawasi Mud Volcano

During our visit on June 24, 1999, the general level of activity at Upper Klawasi mud volcano was similar to that during visits the previous two years. Measured temperatures in the summit pool at Upper Klawasi ranged from 23-26°C. Temperatures of 29-31°C in this pool had been measured prior to, and during visits in 1998, and Motyka and others (1989) report temperatures of 13-19°C for pool samples collected in the 1980's. Gas discharge occurs primarily from vents that produce a general upwelling near the center of the 30-40 m

Figure 4. Summit crater area on Upper Klawasi mud volcano, showing formation of a roil created by periodic upwelling of warm (23°C), CO_2-charged water.

diameter pool; upwelling was observed to occur every 20-25 minutes during our visit on June 24, 1999. The size of the roil created by this upwelling grew with time during each cycle to cover approximately half of the total area of the pool (fig. 4). Surrounding the roil was a 10-m-wide zone of dark, floating organic fluid.

An old rim, ~10 m from the edge of the current pool, rises about 5 m above the pool level. A dozen or so mature spruce trees were dead around the edge of the pool (inside this older rim) and in the outflow zone from the pool. Fresh deposits of gray mud filled much of the outflow channel. Measurements of diffuse degassing through the soil both inside and outside the old crater rim showed no evidence of anomalous discharge rates.

MEASUREMENT TECHNIQUES

Gas and Water Sampling

Gas samples were collected from thermal pools at MVA (vent #3, fig. 5), FVA (the upwelling vent noted in fig. 2), and the 54°C spring in the MGPA. Each sample was collected using a funnel placed over a bubbling vent and connected by tygon tubing to an evacuated glass sample bottle. After purging air from the sampling line using either a hand pump or mouth suction, the outlet of the sample bottle was closed and the inlet opened. Gas composition and carbon isotopic values (^{13}C) were determined at the USGS laboratories in Menlo Park, California, using methods described by Evans and others (1981).

Water samples were collected from the same vents noted above, and from the cold degassing vent at MVA (vent # 6, fig. 2). Bulk water samples were filtered by hand in the field, but because of vigorous degassing in the spring vents, pH values were not determined in the field. Instead, values of pH, specific conductance, alkalinity, dissolved inorganic carbon (DIC), and CO_2 concentration ([CO_2]) were determined in the laboratory, along with anion concentrations in each water sample. We then corrected the measured CO_2 and DIC concentrations for the effects of gas loss by computing pH values expected for CO_2 saturation at the measured vent temperatures and elevations (~3,000 ft above sea level). In previously published geochemical studies, only laboratory pH values are reported.

Figure 5. Vent #3, a 48°C gassy pool adjacent to a much larger pool (vent #2) in the Main Vent Area at Shrub mud volcano (see figure 2 for location). Photo shows the filling of the larger pool with smoke from a smoke bomb set off in vent #3 in order to visualize the overland flow of CO2.

Vent Degassing

The rate of degassing from vent #6 at MVA was measured with equipment consisting of a large cylinder of flexible plastic fitted at the top with a smaller cylinder into which a hot-wire anemometer was inserted for gas-velocity measurements (fig. 6). The degassing rate at this site required that the exit area of the top cylinder be reduced in order to increase gas exit velocity. This was

Figure 6. Equipment used to measure the rate of degassing from cold-temperature vent #6 (see figure 2 for location). Gas flowed upward through the plastic cylinder and exited through a smaller-diameter neck at the top, where its velocity and temperature were measured. The mass flow rate per unit surface area was 0.46 t/d/m2.

accomplished with duct tape. The gas discharge (volumetric) was then computed as the product of the velocity and exit area. Assuming that most of the gas is CO_2, the mass discharge was determined from the density of CO_2 at the vent temperature. Although this equipment could not be used directly at the thermal vents because the approach conditions were too dangerous, we were able to extrapolate the results from vent #6 to the other gassy pools using ratios of the pool areas to that of vent #6.

Diffuse Gas Flux from Soils

Measurements of diffuse gas flow rate from the soil were made with an accumulation chamber placed on the soil and connected by a gas-pumping system to an infrared CO_2 analyzer. This equipment is portable and has been extensively used at other volcanic areas to map the distribution and magnitude of diffuse gas flow (see, for example, Sorey and others, 1999). We made individual measurements of diffuse flow at some 10 sites around Shrub and a more detailed grid of 24 measurements in the region between MVA and FVA (location of the grid given by the open square near the summit in fig. 2). Rates of diffuse gas flow are measured in units of grams per day per square meter (g/d/m^2), whereas total flux over a discharge area is specified in metric tonnes per day (t/d).

At the grid-measurement area, we also measured the concentration of CO_2 in soil gas at a depth of 10 cm. For this, we inserted a perforated steel probe and connected it with tygon tubing to an infrared meter with an internal pump. This same meter was used to check for dangerous gas concentrations in various depressions both before and after entering. No such concentrations where found.

RESULTS AND DISCUSSION

Gas and Water Compositions

Results of chemical and isotopic analyses of water and gas samples are listed in tables 1 and 2. Gas compositions are reported in volumetric percent of dry gas normalized to 100%. Samples from MVA, FVA, MGPA, and Upper Klawasi contain over 98% CO_2 and minor amounts of N_2, O_2, Ar, and He. Methane contents were quite low (<0.02%) in all but the samples from Main Vent Area (0.47%) and the Fissure Vent Area (0.08%). The gas compositions are virtually the same as those determined for a vent sampled at the FVA in 1997 (Richter and others, 1998a).

Waters from the thermal vents at Shrub and the summit vent at Upper Klawasi are saline, containing high concentrations of chloride and bicarbonate and moderate concentrations of sulfate (table 2). This is also true for water issuing from the cold degassing pool at Shrub, although lower anion concentrations suggest dilution with fresher water (table 2). Cation concentrations were not measured on the 1999 samples. Analyses of previous samples from Upper Klawasi and Shrub show high ratios of Na/Ca relative to seawater (Motyka and others, 1989). These characteristics have been interpreted as resulting from addition of magmatic CO_2 to connate waters in marine sedimentary formations, causing water-rock reactions with limestones and silicates and calcite pre-cipitation (Motyka and others, 1989).

Table 1. Chemical analysis of gas collected in June 1999 from bubbling vents at Shrub and Upper Klawasi mud volcanoes

[MGPA, Mud/Gas Pit area (54°C spring in figure 2); FVA, Fissure Vent area (large upwelling vent in figure 2); MVA, Main Vent area (feature #3 in figure 2); values in normalized volume percent]

Gas Component	MGPA	FVA	MVA	Upper Klawasi[1]
He	0.0002	0.0007	0.0012	<0.0002
H_2	<0.0002	<0.0002	<0.0002	<0.0002
Ar	0.0022	0.0040	0.0021	0.0253
O_2	0.0873	0.0896	0.0643	0.5020
N_2	0.1762	0.4561	0.5699	1.7792
CH_4	<0.0002	0.0804	0.4681	0.0020
CO_2	99.7341	99.3686	98.8938	97.6916
C_2H_6	<0.0002	0.0005	0.0006	<0.0002
H_2S	<0.0005	<0.0005	<0.0005	<0.0005
CO	<0.001	<0.001	<0.001	<0.001
C_3H_8	<0.0005	<0.0005	<0.0005	<0.0005
C_4H_{10}	<0.0005	<0.0005	<0.0005	<0.0005

[1] Sample taken from bubbling vent near northern shoreline of a muddy, water-filled summit crater.

Table 2. Laboratory values of chemical analyses for water samples collected in June 1999 and July 1973 at Shrub and Upper Klawasi mud volcanoes

[Concentrations expressed in mg/L; MVA, Main Vent area (feature #3 in figure 2); FVA, Fissure Vent area (large upwelling vent in figure 2); MGPA, Mud/Gas Pit area (54C spring in figure 2); Shrub cold spring, feature #6 in figure 2, --, no data]

Site	Temp[1] (°C)	pH	Alkalinity	CO_2	DIC[3]	Cl	SO_4	Br
Shrub MVA	20	7.73	7,442	220	1,520	11,100	340	27
Shrub FVA	20	7.79	9,644	264	1,970	10,200	460	24
Shrub MGPA	20	7.67	9,644	352	1,990	10,000	470	24
Shrub cold spring	20	6.83	7,716	1,960	2,050	8,880	260	22
Upper Klawasi[2]	20	7.52	8,857	480	1,872	11,300	500	28
Shrub spring[4]	18	7.20	10,000	1,040	2,240	10,000	460	--

[1] All temperatures are lab measurements except for a field value listed for Shrub Spring.

[2] Upper Klawasi sample taken from bubbling vent near northern shoreline of a muddy, water-filled summit crater.

[3] Dissolved inorganic carbon, in mg/L = (alkalinity/61 + CO_2/44) x 12.

[4] Sample from mineral spring near summit collected July 9, 1973 by Ivan Barnes and analyzed by the U.S. Geological Survey, Menlo Park, California.

Table 3. Chemical analyses for water samples collected in June 1999 and July 1973 at Shrub and Upper Klawasi mud volcanoes, with parameters corrected for field conditions, assuming pH values for CO_2 saturation at 0.9 atmospheres (i.e. for an elevation of 3,000 feet above sea level)

[Concentrations expressed in mg/L; MVA, Main Vent area (feature #3 in Figure 2); FVA, Fissure Vent area (large upwelling vent in figure 2); MGPA, Mud/Gas Pit area (54°C spring in figure 2); Shrub cold spring, feature #6 in figure 2]

Site	T (°C)	pH	Alkalinity (mg/L)	CO_2 (mg/L)	DIC (mg/L)
Shrub MVA	48	7.2	7,440	818	1,690
Shrub FVA	49	7.22	9,640	818	2,120
Shrub MGPA	54	7.23	9,640	800	2,110
Shrub cold spring	6	6.82	7,720	2,490	2,200
Upper Klawasi	23	7.01	8,860	1,430	2,140
Shrub spring[1]	18	7.02	10,000	1,670	2,420

[1] Sample collected from mineral spring near summit in July 1973 by Ivan Barnes (U.S. Geological Survey).

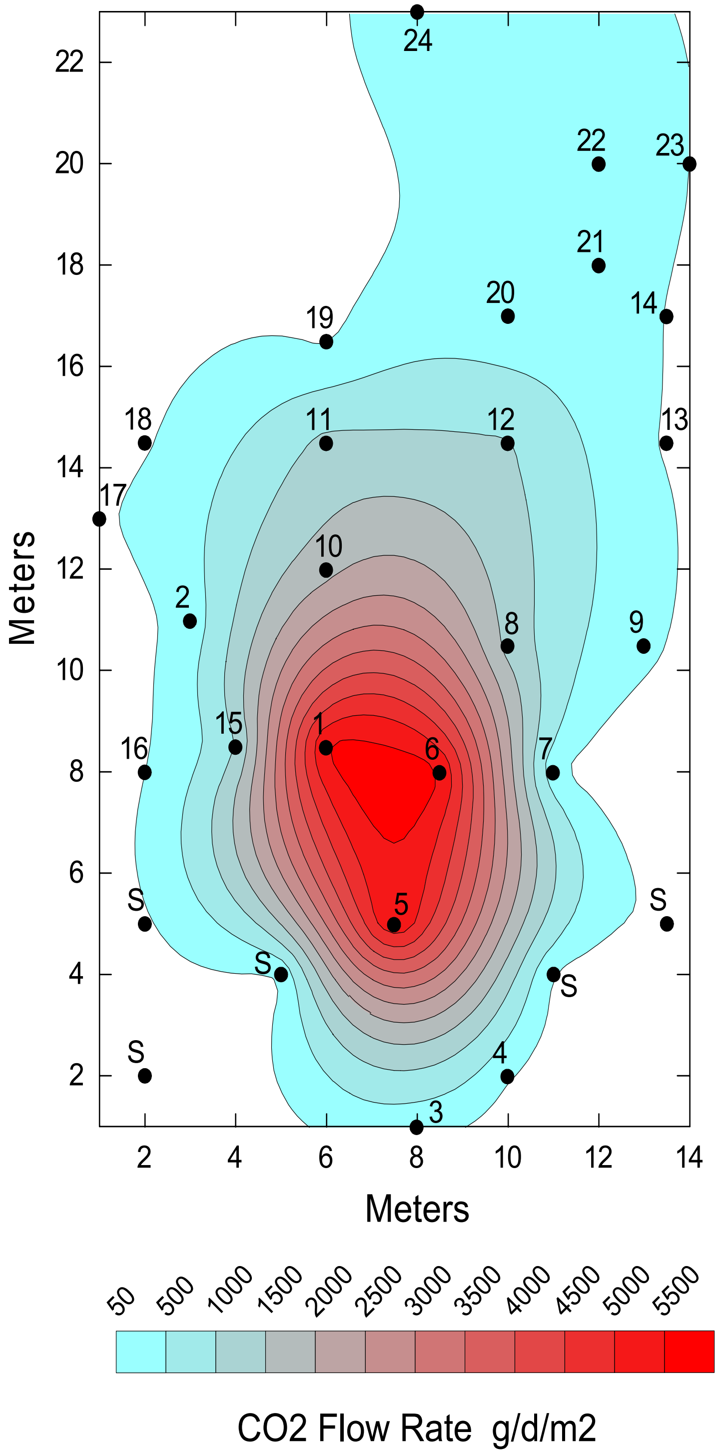
The computed pH values for field conditions are significantly lower than those measured in the laboratory for all but the cold vent at MVA (table 3). For the thermal vents, these differences reflect the fact that pH increases as gas is lost during and after sampling. The lower pH and higher gas concentration under field conditions also results in higher (computed) values of total inorganic carbon, although the effect on DIC concentrations is less than on CO_2 con-centrations because most of the DIC exists as bicarbonate. For the cold vent at MVA, the computed field pH is virtually the same as the laboratory value, so that measured and computed CO_2 and DIC concentrations are much closer. In this case, the effect of correcting for the difference in temperature between field (6°C) and laboratory conditions (20°C) is to offset the effect of gas loss during and after sampling, because raising the temperature also raises gas pressure and lowers the pH required for gas saturation.

Comparison of the computed results for different vents shows that DIC values are remarkably similar for each feature sampled at Shrub and Upper Klawasi. The cooler vents ("Shrub cold spring" and "Shrub spring"), however, carry significantly more CO_2 than the hotter vents because of the inverse relation between CO_2 saturation and temperature. For vent #6 at MVA, the concentration of dissolved CO2, in mg/L, exceeds the corresponding concentration of DIC. This, of course, would not be the case if both quantities were expressed in units of moles/L.

Motyka and others (1989) report a laboratory pH value of 7.2 and an alkalinity of 10,000 mg/L for a July 1973 sample from the Shrub "mineral spring" (table 2). A vent temperature of 18°C was measured (unpublished field notes by Ivan Barnes), but was not reported by Motyka and others (1989). Comparison of the chemistry of this sample with that of present-day thermal waters shows that they are basically the same water. In terms of our computed parameters such as field pH and dissolved CO2 concentration, the colder temperature "mineral spring" sampled in 1973 would have held more gas at a lower pH, and hence would have held a slightly greater amount of total dissolved carbon than our 1999 thermal spring samples. This suggests that higher vent temperatures at present result in more gas loss as the fluid approaches the land surface.

Carbon isotopic values, expressed as 13C for CO2, range from –4.7 to –5.5‰ for gas sampled in 1999 at Shrub and Upper Klawasi. For comparison, Richter and others (1998a) obtained a value of –4.64 for gas sampled from a vent in the FVA in 1997, while Motyka and others (1989) list values of –4.3 to –4.8‰ for gas sampled at Upper Klawasi and Shrub (1973-1985). These data indicate a narrow range in 13C for gases from each mud volcano and show that values for our 1999 samples are similar to those determined in previous years.

Motyka and others (1989) also list 13C values of –6.5 to –6.7‰ for fumarolic gas sampled from the North Crater of the Mt. Wrangell summit caldera, some 60 km to the northeast of the Klawasi group mud volcanoes. Citing corresponding values of 3He/4He for this vent of 5.3 and



Site #	Co$_2$ Flow (g/d/m^2)
1	5,600
2	230
3	188
4	100
5	5,500
6	5,600
7	133
8	1,360
9	172
10	1,845
11	1,140
12	1,035
13	10
14	44
15	906
16	43
17	18
18	10
19	10
20	200
21	177
22	234
23	50
24	161
S	0
S	0
S	0
S	0
S	0

Figure 5. Results of measurements of diffuse carbon dioxide flow from soils near the summit of Shrub mud volcano made on June 24, 1999. See figure 2 for the approximate location of the measurement grid. A commercially available grid-based contouring program was used to contour the data and to compute a total gas flux of 0.23 t/d. Five synthetic values of gas flow (labeled S) were added in order to better constrain the contours to the southeast and southwest.

6.0 Ra, these authors argue that the Mt. Wrangell gas represents the probable composition of mantle volatiles in this region. Lower helium isotopic ratios (2.1-4.1 Ra), including a value of 3.54 for Shrub (Richter and others, 1998a) and heavier 13C values in the gases from the Klawasi group mud volcanoes (Motyka and others, 1989) suggest an additional component from crustal sources and/or carbon-isotope fractionation associated with the formation of bicarbonate and precipitation of calcite.

Vent Gas Discharge

The total CO2 discharged from spring waters at the summit of Shrub mud volcano is the sum of CO2 dissolved in the spring-fed outflow streams and CO2 bubbles discharging directly from the vents. One way to compute the total CO2 discharge is to multiply an average value of CO2 concentrations dissolved in the vents (field conditions) by the total flow rate of streams draining these vents. From table 3 we would use concentrations of 820 and 2500 mg/L, respectively, for gas content under field conditions at the hot and cold-water vents. Then, for visual estimates of a total hot-water flow of 50 L/s and a total cold-water flow of 10 L/s, we compute a gas discharge of ~7 t/d.

An alternative approach is to compute the rate of gas loss occurring directly at the pools and spring vents, using our measured degassing rate at the cold vent #6 at the MVA and measurements and estimates of the areas of bubbling pools. At vent #6, we measured a degassing rate of 0.46 t/d from an upwelling roil over a collector area of 0.8 m2 (fig. 6), yielding a unit area rate of 0.58 t/d/m2. At the thermal pools, gas is lost both from upwelling roils and numerous point sources of bubbles. For this calculation we assume that (1) the average rate of degassing from the thermal pools is equal to that measured at the cold pool and (2) the total area of degassing pool surfaces is 10-20 m2. This yields a range of 6-12 t/d for the total rate of CO2 degassing from vents, a result which is comparable to the ~7 t/d derived from estimates of stream flow rates.

We are also interested in estimating the discharge of total inorganic carbon (DIC), effectively represented by the sum of the discharges of CO2 and bicarbonate phases. Note that computations involving sums of concentrations of different carbon species are done using molar concentrations and then converted to units of mg/L using the appropriate molecular weight (12 g/mole for carbon, 44 g/mole for CO2 and 61 g/mole for HCO3). At the land surface, we measure an average DIC value of 2,100 mg/L; multiplying this concentration by the total fluid upflow rate noted in the previous paragraph (60 L/s) yields a discharge of 10 t/d of total carbon.

Deeper into the fluid upflow system, the fractions of dissolved CO2 and bicarbonate vary with pH and hence with depth, while the total DIC remains constant, except for possible loss of dissolved carbon from calcite precipitation. For example, at the surface where pH = 7.2, CO2 makes up only 10 percent of the DIC, whereas at depths where the pH value is as low as perhaps 5.5, the total dissolved carbon is distributed as 90 percent CO2 and only 10 percent HCO3. Thus, at depths where pH is below 5.5, essentially all of the DIC is derived from dissolved CO2. Under such conditions, the total carbon flux of 10 t/d derived in the last paragraph would be associated with a CO2 flux of 40 t/d. Thus, all the DIC reaching the surface at Shrub could be supplied by this rate of magmatic degassing of CO2.

If, instead, DIC is supplied by a combination of magmatic degassing and reactions between this gas and carbonate-rich reservoir rocks, it is possible that enough carbon could be liberated to double the DIC flux in fluids flowing upward from the reservoir. Under this condition, a magmatic CO2 degassing rate of 20 t/d is sufficient. Again, however, these computations of a range of 20-40 t/d for the magmatic CO2 flux rate do not take into account the likelihood that some carbon is lost to calcite precipitation and travertine formation at or near the land surface.

To place gas flux of 20-40 t/d in some context, we can compare with values deter-mined for Mammoth Mountain, California, where diffuse CO2 discharge through soils has resulted in extensive tree kills over some 0.4 km2 (100 acres) of pine forest. Measurementsat Mammoth show that diffuse discharge, although variable between the different tree-kill areas, averages about 50 t/d at each area and totals some 300 t/d. An additional CO2 flux of ~50 t/d leaves the mountain dissolved in the ground-water system (Sorey and others, 1999).

Diffuse Gas Discharge

Measurements of diffuse degassing at ~10 isolated sites on Shrub mud volcano yielded values that were each less than 10 g/d/m2, except in the area of vegetation kill between the MVA and FVA and in the general vicinity of the MGPA. At MGPA, values of 400-430 g/d/m2 were found on the banks of both active and inactive vents and in a small growth of alders, located ~30 m southwest of the 54°C hot spring, where there was evidence of recent leaf kill.

At the vegetation-kill area near the summit, gas-flow measurements were made over a grid of 24 sites covering a 14x22 m area, or ~300 m2 (fig. 7). This area included a 13°C spring seep (next to grid point #1) with travertine deposits and mud lining the outflow channel, suggesting higher flow rates in the past. Diffuse gas flow rates near 5,600 g/d/m2 were measured at points 1, 5, and 6; elsewhere within the grid, flow rates ranged from 10 to 5,600 g/d/m2. A CO2 concentration of 26 percent at 10 cm depth was found at point #6. As seen at Mammoth Mountain, such high gas concentrations can cause vegetation kill as a result of oxygen deprivation and nutrient uptake inhibition within the root zone (Sorey and others, 1998).

A commercially available contouring program was used to analyze the measured gas flow data at this grid area on Shrub. An initial run made using only the 24 measured points yielded a total flux of 0.29 t/d. To compensate for the sparseness of the data in the southeastern and southwestern corners of the area, five "synthetic" grid points with low flow rate values were added. This yielded the contour map shown in fig. 7, from which a total flux of 0.23 t/d was determined. The area inside the 50 g/d/m2 contour is 195 m2, and the average flow rate here is 1,200 g/d/m2. Although this total flux is rather low compared to gas discharge from the springs, the measured rates of diffuse degassing in this area are sufficiently high to require more than just a shallow, biogenic source. A likely possibility is near-surface gas loss from the conduits channeling water toward the surface. A more complete flux survey on Shrub might delineate other areas of anomalous flow, but it seems that such areas will be found only in close proximity to the gassy springs.

CONCLUSIONS

Visual observations suggest that total rates of discharge of water, mud, and gas from the summit region and northern flank of Shrub mud volcano have not changed significantly over the 1997-1999 period. There does appear to have been a general expansion of each of the areas of discharge, as the surficial conduit system has more fully developed, and flow rates of some vents have declined. The chemical characteristics of hot water and gas sampled in 1999 were similar to published results from previous years, as were the carbon-isotopic compositions. Continuous, high flow-rate discharge of hot water and gas discharge from the summit region over this 3-year period is unique compared to activity observed intermittently over the past 30 years.

Several new features (both thermal and nonthermal) developed between July 1998 and June 1999, including a 54°C gassy hot spring on the north flank of the volcano and several small thermal and nonthermal features at the Main Vent Area. The hot spring in the Mud/Gas Pit Area occurs some 30 m downhill and to the east of the large collapse pit from which gas and mud discharge were observed in previous years. At the Main Vent Area, the salinity and dissolved carbon content of water from the cold pool are similar, but slightly diluted, compared to those in water in the nearby hot pools. The origin of this cold, CO_2–charged water is uncertain. It could be derived from the same source as the hot saline fluid at Shrub, but reaches the surface along a longer, more tortuous path or is cooled by passage through near-surface permafrost layers. In the future, gas samples should be collected from any cold pools or springs for comparison with gas from the thermal vents to delineate whether different gas sources are involved for the thermal and nonthermal features.

Carbon and helium isotopic compositions of the gas discharging at Shrub and Upper Klawasi mud volcano suggest derivation from a combination of magmatic and crustal sources. The high salinity and dissolved carbon content of these spring waters also suggest inputs of magmatic volatiles to fluids in sedimentary rock aquifers. The uniformity in fluid and gas compositions between vents at Shrub and Upper Klawasi, both now and in the past, along with similar vent temperatures at these two volcanoes in the decades prior to the 1990s, suggest similar sources at depth.

The relatively high-temperature discharge conditions occurring at Shrub since 1996 seem to require either (1) increases in heat and volatile inputs at depth or (2) an increase in the rate of fluid upflow. In the first case, an increase in heat input in the form of magmatic steam should be accompanied by additional inputs of magmatic CO_2 and He. However, observed values of DIC, ^{13}C, and/or $^{3}He/^{4}He$ for recent samples are within the ranges of values determined for previous gas and fluid samples from all three Klawasi Group mud volcanoes. In the second case, an increase in the rate of fluid upflow did accompany the onset of thermal activity at Shrub in 1996. Greater flow rates would tend to lessen the temperature drop between the source reservoir and the surface, for the same rate of conductive heat loss from the flow conduits. We note also that present-day vent temperatures at Shrub are similar to bottom-hole temperatures in ex-plorations wells completed in the Mesozoic basements rock beneath the Copper River Basin. Thus, the higher vent temperatures measured over the past few years are most likely a result of more rapid rates larger volumes of fluid upflow from the deep source reservoir. Such increases in upflow would require corresponding increases in the permeability of fault-controlled upflow conduits.

We estimate the present rate of CO_2 discharge from springs and pools at Shrub to be ~10 t/d, and suggest that this discharge, along with the discharge of dissolved bicarbonate, requires inputs of roughly 20-40 t/d of magmatic CO_2 at depth. These rates are comparable to CO_2 fluxes measured at Mammoth Mountain, California, both as diffuse flux at individual tree-kill areas and dissolved in the shallow ground-water system. Anomalous diffuse gas discharge at Shrub has been observed in areas immediately adjacent to some of the thermal features and from a more extensive area of normal-temperature soil located between the Main Vent Area and the Fissure Vent Area. Total CO_2 flux from the latter area is ~0.23 t/d, and high CO_2 concentrations in the root zone there have caused some vegetation kill. Gas flow from dry vents that settles in localized depressions in the soil surface is probably responsible for the demise of small birds and animals.

Although the potential for sudden, large-volume releases of CO_2 from vents at the summit and on the northern flank of Shrub clearly exists, no evidence was found of the occurrence of such events in 1998 or 1999, and no lethal atmospheric concentrations of CO_2 were found. Such events likely occurred prior to June 1997, when extensive browning of vegetation along narrow bands on the north flank were observed during field investigations.

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REFERENCES

Evans, W.C., Banks, N.G., and White, L.D., 1981, Analyses of gas samples from the summit crater, in The 1980 Eruptions of Mount St. Helens, Washington, edited by P.W. Lipman and D.R. Mullineaux: U.S. Geological Survey Professional Paper 1250, p. 227-232.

Grantz, A., White, D.C., Whitehead, H.C., and Tagg, A.A., 1962, Saline Springs, Copper River Lowland, Alaska: American Association of Petroleum Geologists Bulletin, v. 46, p. 1890-2002.

Motyka, R.J., Poreda, R.J., and Jeffrey, W.A., 1989, Geochemistry, isotopic compo-sition, and origin of fluids emanating from mud volcanoes in the Copper River basin,Alaska: Geochemica et Cosmochimica Acta, v. 53, p. 29-41.

Nichols, D.R., and Yehle, L.A., 1961, Mud volcanoes in the Copper River Basin, Alaska, in Geology of the Arctic, edited by G.O. Raasch: International Symposium on Arctic Geology, 1st Calgary, 1960, Proceedings, v. 2, p. 1063-1087.

Reitsema, R.H., 1979, Gases of mud volcanoes in the Copper River Basin, Alaska: Geochemica et Cosmochimica Acta, v. 43, p. 183-187.

Richter, D.H., Moll-Stalcup, E.J., Miller, T.P., Lanphere, M.A., Dalrymple, G.B., and Smith, R.L., 1994, Eruptive history and petrology of Mount Drum volcano, Wrangell Mountains, Alaska: Bulletin of Volcanology, v. 56, p. 29-46.

Richter, D.H., Symonds, R.B., Rosenkrans, D.S., McGimsey, R.G., Evans, W.C., and Poreda, R.J, 1998a, Report on the 1997 activity of Shrub mud volcano, Wrangell-St. Elias National Park and Preserve, south-central Alaska: U.S. Geological Survey Open-file Report 98-128, 13 pp.

Richter, D., McGimsey, R., and Rosenkrans, D., 1998b: Addendum to U.S. Geological Survey Open-file Report 98-128, 3 pp.

Sorey, M., Evans, B., Kennedy, M., Rogie, J., and Cook, A., 1999, Magmatic gas emissions from Mammoth Mountain: California Geology, v.52, no.5, p. 4-16

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