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Diffuse gas emissions at the Ukinrek Maars, Alaska: Implications for magmatic degassing and volcanic monitoring

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ABSTRACT

Diffuse CO_2 efflux near the Ukinrek Maars, two small volcanic craters that formed in 1977 in a remote part of the Alaska Peninsula, was investigated using accumulation chamber measurements. High CO_2 efflux, in many places exceeding 1000 g m^{-2} d^{-1}, was found in conspicuous zones of plant damage or kill that cover 30,000–50,000 m^2 in area. Total diffuse CO_2 emission was estimated at 21–44 t d^{-1}. Gas vents 3-km away at The Gas Rocks produce 0.5 t d^{-1} of CO_2 that probably derives from the Ukinrek Maars basalt based on similar $\delta^{13}C$ values ($\sim$−6‰), $^3He/^4He$ ratios (5.9–7.2 R_A), and $CO_2/^3He$ ratios (1–2 × 10^9) in the two areas. A lower $^3He/^4He$ ratio (2.7 R_A) and much higher $CO_2/^3He$ ratio (9 × 10^{10}) in gas from the nearest arc-front volcanic center (Mount Peulik/Ugashik) provide a useful comparison. The large diffuse CO_2 emission at Ukinrek has important implications for magmatic degassing, subsurface gas transport, and local toxicity hazards. Gas–water–rock interactions play a major role in the location, magnitude and chemistry of the emissions.

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1. Introduction

Maar volcanism is commonly characterized by short-lived, isolated eruptions of basaltic magma, producing craters that rarely reactivate (Ollier, 1967; Lorenz, 2007). However, emissions of gas associated with maar volcanoes can be surprisingly large and long-lived. Examples include the Lake Nyos maar in Cameroon, where CO_2 seepage into bottom waters creates hazardous conditions at least 400 a after maar formation (Lockwood and Rubin, 1989), and the Eifel Maars in Germany, where CO_2 vents through a lake in an 11-ka-old maar (Aeschbach-Hertig et al., 1996).

The Ukinrek Maars formed on the Alaska Peninsula during 11 days of eruptions in 1977. The eruptions were followed by hot spring discharge and increased gas venting 3-km away at The Gas Rocks, where prominent CO_2 vents just offshore in Becharof Lake long pre-date maar formation. A few bubbling seeps have formed near the maars, but the visible gas output is trivial compared to the impressive gas vents at The Gas Rocks. One goal of the authors' June 2004 visit was to investigate areas of vegetation damage and kill near the maars where diffuse efflux of CO_2 through the root zone was suspected. This paper focuses mainly on gas emission rates, whether they might be high enough to create a hazard for visiting campers, and what they might tell us about the linkage between the gas emissions at the two locations. For example, could the long-lived gas discharge at The Gas Rocks have been a precursor to eruption of the Ukinrek Maars? Samples of gas and water were collected at several locations. Analytical results were generally similar to those published and discussed in detail by previous investigators (Barnes and McCoy, 1979; Motyka et al., 1993; Symonds et al., 1997), but some new interpretations of the data are offered herein.

2. Background

The Aleutian-Arc on this part of the Alaska Peninsula consists of a very narrow line of major volcanoes plus a few eruptive features, classified as "rear-arc" by Hildreth et al. (2004), located distinctly behind the line (Fig. 1). Mount Griggs is the only major rear-arc volcano. Among the otherwise small vent clusters and isolated vents of the rear-arc, the only Holocene features are the Ukinrek Maars. Other eruptive features near the Ukinrek Maars include two glacially eroded basaltic cones and The Gas Rocks (Fig. 2), a small cluster of dacite domes recently dated with $^{40}Ar/^{39}Ar$ methods at 24 ± 3 ka (Hildreth et al., 2007). This local grouping of rear-arc volcanism may be related to the intersection of a buried cross-arc structural discontinuity with the regionally important Bruin Bay Fault, which divides crystalline basement on the NW from the sedimentary Naknek Formation on the SE side (Kienle et al., 1980; Miller, 2004; Hildreth et al., 2007).

The Ukinrek Maars erupted through a low ridge (herein called "Ukinrek ridge") composed of glacial till and pyroclastic deposits

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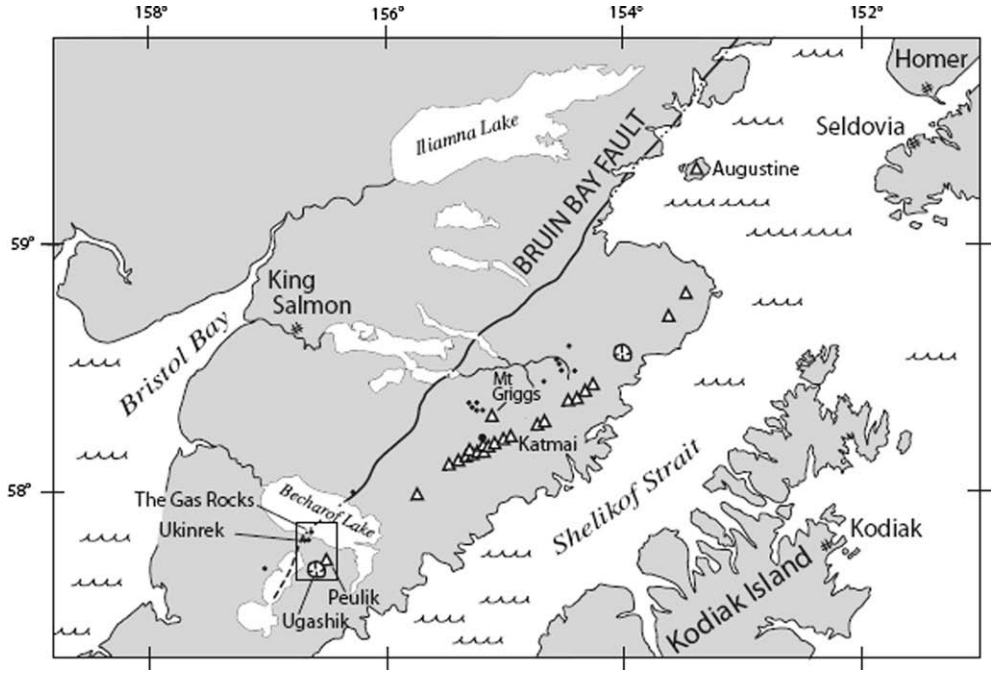

Fig. 1. Regional map of the upper Alaska Peninsula showing stratovolcanoes as triangles, calderas as hachered circles, and smaller "rear-arc" features as dots (adapted from Hildreth et al., 2004). Study area in rectangular inset.

from Mount Peulik, the nearest arc-front stratovolcano, located near the rim of the Ugashik caldera (Miller, 2004). The eruption sequence that produced first the 170-m diameter west maar, and then the 300-m diameter east maar, began on 30 March and ended on 9 April, 1977 (Kienle et al., 1980). The total amount of erupted juvenile material was estimated at 1.5–5.7 $\times$ 10^6 m^3 as dense-rock equivalent (Kienle et al., 1980; Self et al., 1980). The magma is a fairly primitive alkaline olivine basalt that is geochemically unrelated to the magmas of the Mount Peulik/Ugashik system (Miller, 2004; Kienle et al., 1980; Hildreth et al., 2007).

Water began pooling in the craters soon after the eruption. CO_2-rich gas bubbled up through hot (81 °C) saline water at the bottom of the western maar in late-August 1977 (Barnes and McCoy, 1979), and in July 1979 both craters contained lakes with trains of gas bubbles visible from shore (Kienle et al., 1980). The lake filling the larger eastern maar gradually covered a lava dome and remained warm for some years. Apart from this apparently direct release of heat and gas from magma in or just beneath the craters, no hot springs or gas vents formed in the immediate area around the craters. Instead, these types of features appeared at The Gas Rocks (Fig. 2).

The Gas Rocks are named for the vents of CO_2-rich gas ~100-m offshore in Becharof Lake. The name first appears on a 1924 map (Smith and Baker, 1924) following the earliest geologic studies in the area, although the gas vents were probably the "hot springs" reported by hunters visiting the area a decade earlier (Waring, 1917; Miller, 2004). The gas vents are not hot, but the roiling water prevents local freezing of the lake surface in winter. The most vigorous gas vent was first sampled in 1974, 3 a before the Ukinrek Maars eruptions (Blasko, 1976). Investigations that followed the eruptions documented new areas of gas emission and discharges of hot water onshore at The Gas Rocks. Gassy, saline hot springs (52.8 °C) as well as a mud volcano were found at the lake's edge in August of 1977 (Barnes and McCoy, 1979). Gas output from onshore features at that time was strong enough to temporarily asphyxiate one investigator (Symonds et al., 1997). The onshore activity gradually died away; investigations in subsequent years (Motyka et al., 1993; Symonds et al., 1997) reported declines in the number and maximum temperature of springs (39 °C in 1981 and 16.3 °C in 1995).

Gas emissions were unknown on the Ukinrek ridge prior to maar formation. Bubbling seeps were discovered near the base of the ridge in 1994 (Ort et al., 2000). These and other newly discovered seeps along the ridge were sampled in 1995 by Symonds et al. (1997), who also recognized that areas of dead and dying vegetation might signal a diffuse efflux of CO_2 gas from the soil and called for the follow-up study described here.

In 2004, plant mortality or damage was found in 4 zones (A–D in Fig. 3) on the Ukinrek ridge. Zone A is a large area of mixed plant-kill and unhealthy grass on the northeastern flank, Zone B is a cluster of sharply delimited plant-kill zones high on the ridge, and Zones C and D are clusters of kill zones at the northern base of the ridge where seeps of bubbling water emerge.

3. Sample locations and methods

Diffuse CO_2 flux was measured using the accumulation chamber procedure, where an inverted chamber is placed on the ground, and the rate of CO_2 buildup within the chamber is monitored by an infrared gas sensor (Bergfeld et al., 2006; Chiodini et al., 1998). Flux measurements would ideally be made at regularly spaced points on a grid that completely covered the area of anomalous efflux and adjacent background on all sides; however, time constraints precluded this approach at Ukinrek. Therefore measurements were made at 131 randomly chosen sites in and near the four plant damage zones, as shown in Fig. 3, enabling the acquisition of some data from all major areas of damage. Locations were determined by a handheld Global Positioning System (GPS) with an uncertainty of ±6 m.

The boundaries between healthy and dead vegetation/bare soil at Zones B–D were very sharp (Fig. 4a) and corresponded to the dividing line between low and high fluxes, respectively, as verified in several places by chamber measurements. At Zone A, bare soil graded into healthy vegetation through a broad region of un-

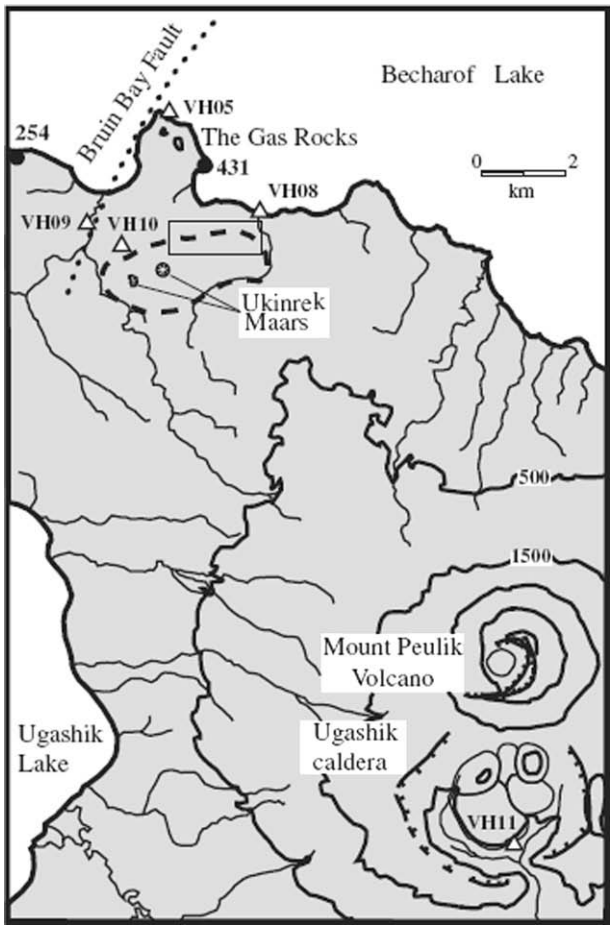

Fig. 2. Map of the study area showing locations of the Ukinrek maars, The Gas Rocks, two eroded basaltic cones (254 and 431 of Hildreth et al., 2007), Mount Peulik, and Ugashik caldera. The dashed line around the maars is the approximate outline of "Ukinrek ridge". Triangles denote sample locations: offshore gas vent (VH05), streams (VH08 and VH09), and springs (VH10 and VH11). Rectangular inset shown in Fig. 3. Contour interval is 1000 feet (305 m; map adapted from Miller, 2004).

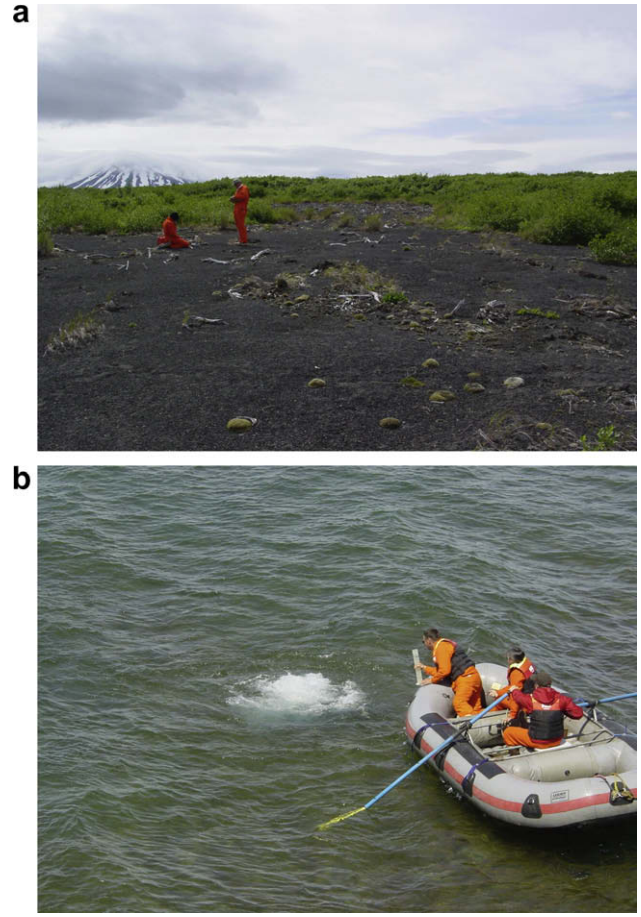

Fig. 4. (a) Plant damage Zone B showing bare ground and dead plants surrounded by healthy grasses and shrubs. Mount Peulik in background; (b) main gas vent at The Gas Rocks.

healthy, discolored grasses. Although most flux measurements in Zone A were made in areas of bare soil or obvious plant distress, a few measurements extended out into low-flux areas to help establish the zone boundaries. Removal of grass and moss prior to flux measurement disturbed the soil surface at 12 Zone A sites, and 11 of these were re-measured on the following day to assess the effect of soil disturbance on the flux.

An attempt was made to compute total CO_2 emissions and uncertainties using stochastic simulations of the flux data (see, e.g., Cardellini et al., 2003). Except for Zone B, the modeled variograms indicated relatively poor spatial correlation between measurement sites, precluding the use of this technique. The total diffuse emission from each zone was therefore calculated as the

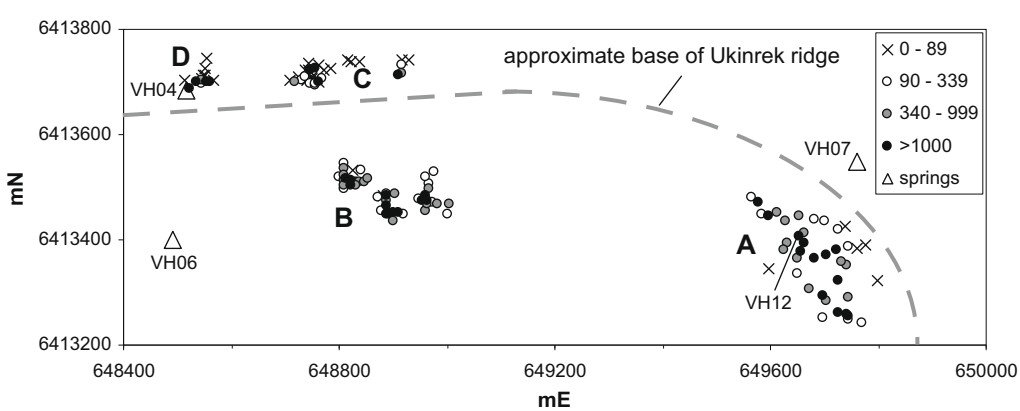

Fig. 3. Detailed plan view of NE edge of Ukinrek ridge (inset in Fig. 2), showing plant damage zones A–D and CO_2 flux measurement sites (Datum: NAD 1927 AK). Flux designators (g m^2d^{-1}) separated by quartiles. Some low-flux sites are in healthy vegetation peripheral to the damage zone. Location of soil gas sample VH12 is shown, and triangles denote sampled springs and seeps (VH04, VH06, and VH07).

Table 1
Water chemistry for sampled features at the Ukinrek Maars, The Gas Rocks, and Ugashik caldera.

Sample[a]	VH04	VH06	VH07	VH10	VH08	VH09	VH05	CQ135	VH11
Date	6/19/04	6/22/04	6/22/04	6/22/04	6/22/04	6/22/04	6/21/04	8/25/77	6/22/04
Type	Ukinrek ridge springs				Ukinrek ridge streams		Lake	Hot spr.	Ugashik
T (°C)	16.5	10.3	6.2	7.8	14.1	14.4	8.6	52.8	21.7
pH	5.26	5.24	5.92	7.26	7.78	7.47	5.44	5.9	5.71
Major elements (mg/L)									
Na	7.6	8.2	15.2	37	5.6	7.3	22.8	17700	809
K	1.5	1.9	4.7	3.8	0.6	1.0	1.1	450	45
Ca	13.1	14.5	70	60	6.3	12.6	10.1	1500	96
Mg	5.1	4.4	22	13	2.2	5.5	3.0	460	47
SiO_2	45	38	54	24	22	23	1.1	120	104
B	<0.02	<0.02	<0.2	<0.2	<0.02	0.04	0.39	360	35
Fe	1.02	0.27	0.14	0.13	0.35	0.21	0.20	na	34
HCO_3[b]	68	79	356	179	34	72	27	1240	535
F	0.03	0.03	0.01	0.22	0.05	0.05	0.04	0.13	0.2
Cl	4.2	4.8	3.9	47	3.7	5.7	42	32,000	1440
SO_4	10.6	9.7	2.3	73	2.3	1.4	6.8	140	1.0
Br	0.003	0.05	0.012	0.158	0.002	0.005	0.11	92	3.9
NO_3–N	0.02	0.54	0.05	0.82	0.11	0.02	<0.01	na	<0.2
Trace elements (μg/L)									
Li	4.3	4.1	8.3	10	2.2	5.8	48	44,000	2400
Mn	70	137	750	0.4	22	53	13	na	1700
Zn	4.9	5.6	5.7	5.2	1.1	1.2	2.9	na	21
Al	42	62	14	9.8	22	11	2.5	na	440
Pb	0.05	0.02	0.11	0.08	<0.01	0.01	0.05	na	1.3
Mo	<0.01	0.06	<0.1	0.50	0.22	0.19	0.09	na	<1
V	<0.08	0.48	<0.8	<0.8	2.3	2.2	0.16	na	<8
Ba	10	14	13	20	2.1	2.8	6.0	na	187
Sr	60	52	260	170	25	53	132	na	2770
As	0.4	0.4	0.8	0.3	0.98	0.62	37	na	111
Rb	2.0	1.5	5.2	2.8	1.2	3.0	2.7	2.1	165
Cs	0.06	0.04	<0.04	0.11	0.02	0.15	1.6	3.6	58
U	<0.01	<0.01	2.5	0.54	<0.01	0.05	<0.01	na	<0.01
Isotopes[c]									
δD	−87.5	−90.5	−88.5	−84.4	−87.2	−87.3	−77.2	−37.9	−83.9
$\delta^{18}O$	−12.03	−12.29	−11.98	−10.91	−11.90	−11.83	−10.23	+0.42	−10.74
$\delta^{13}C$-DIC	na	na	na	−13.7	−8.6	−2.4	na	na	−3.7
^{14}C-DIC	na	na	na	0.935	0.906	0.475	na	na	0.006

("na" means not available).

[a] VH04: (648517 mE, 6413865 mN) bubbling seep in vegetation-kill Zone D, site A-1 of Symonds et al. (1997); VH06: (648491 mE, 6413401 mN) bubbling spring in canyon on N side of Ukinrek ridge, site UK-1 of Symonds et al. (1997); VH07 (649762 mE, 6413547 mN) spring at NE base of Ukinrek ridge; VH10: (646930 mE, 6413178 mN) seep near west maar; VH08: (650279 mE, 6414016 mN) mouth of stream flowing around E end of maar ridge; VH09: (646140 mE, 6413694 mN) mouth of stream flowing around W end of maar ridge; VH05: (647091 mE, 6416416 mN) lake surface water inside upwelling gas vent at The Gas Rocks, site GR-1C of Symonds et al. (1997); VH11: (656490 mE, 6398552 mN) warm spring near stream outflow from Ugashik caldera. CQ135 is published (Barnes and McCoy, 1979) analysis of onshore hot spring at The Gas Rocks in Aug 1977. (Datum for all locations – NAD 1927 AK).

[b] HCO_3 is alkalinity as bicarbonate.

[c] δD and $\delta^{18}O$ were analyzed at USGS Reston VA and are in ‰ relative to V-SMOW. $\delta^{13}C$ was analyzed at USGS Menlo Park CA and is in ‰ relative to PDB. ^{14}C was analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory and is in fraction Modern.

mean flux for the zone multiplied by its area. To investigate bias in the sampling scheme, the means were calculated from both actual and declustered flux data using the "declus" module of the GSLIB statistics program (Deutsch and Journel, 1998). Because the zone boundaries could not be accurately surveyed, the GPS site locations were plotted, and the areas of the zones were computed by drawing simple polygonal shapes around the measurement points. Areas were also estimated based on closed curves that minimally encompassed the outermost measurement points in each zone.

The main gas vent at The Gas Rocks is strong enough to lift the surface of Becharof Lake several cm in a 1-m diameter circle (Fig. 4b). Two smaller gas vents occur nearby, and single trains of rising bubbles cover a large area at the edge of the lake. Gas discharge from the main offshore vent was estimated by timing the rate of water displacement in an inverted graduated cylinder held from an anchored raft. Because the mouth of the cylinder was much smaller than the area of the gas vent, total discharge was calculated from the ratio of the two areas.

Samples of water were collected from four springs (VH04, VH06, VH07 and VH10) on the Ukinrek ridge, from streams (VH08 and VH09) that bound the ridge on the east and west, and from the main gas vent (VH05) at The Gas Rocks (Figs. 2 and 3). Some of these features had been sampled by previous investigators. A gassy warm spring (VH11) inside the Ugashik caldera 20-km SE of The Gas Rocks was also sampled. Gas samples were collected from features that showed visible bubbling. Soil gas (VH12) was collected in plant damage Zone A through a stainless steel tube driven 70 cm into the ground. Gas and water samples were collected and analyzed using published methods (Evans et al., 2002). Sites are described in footnotes to Tables 1 and 2.

4. Results

Water chemistry results from the Ukinrek ridge and The Gas Rocks (Table 1) are generally very similar to those of previous investigators (e.g., Symonds et al., 1997). Although no springs (or gas vents) were found onshore at The Gas Rocks, saline water still discharges along with the gas at the main offshore gas vent. The sample collected at the surface (VH05) is mostly lake water, as shown by its low SiO_2 concentration. If the undiluted vent water

Table 2
Analyses of bubbling gases at the Ukinrek Maars, The Gas Rocks, and Ugashik caldera.

Sample[a]	VH04	VH06	VH12	VH05	USBM	CQ134	CQ135	VH11
Date	6/19/04	6/22/04	6/21/04	6/21/04	6/74	8/25/77	8/25/77	6/22/04
Type	Bubbling springs		Soil gas	Gas vent in Becharof Lake			Hot spring	Ugashik
Composition (vol-%)								
He	0.0143	0.0074	0.0048	0.0044	Trace	<0.02	<0.02	0.0003
H_2	0.0001	<0.0002	<0.0002	<0.0002	0.0	<0.01	<0.01	0.0004
Ar	0.015	0.009	0.071	0.038	0.2	0.03	<0.02	0.012
O_2	0.068	0.065	1.44	0.792	3.0	0.59	0.02	0.033
N_2	3.63	1.83	6.82	2.55	12.3	2.52	0.54	0.545
CH_4	1.26	0.450	0.189	0.054	0.1	0.08	0.04	1.52
CO_2	95.0	97.6	91.5	96.6	84.5	97.1	98.4	97.8
C_2H_6	0.0035	0.0019	0.0017	<0.0002	0.0	<0.05	<0.05	0.061
H_2S	<0.0005	<0.0005	<0.0005	<0.0005	0.0	na	na	<0.0005
CO	<0.001	<0.001	<0.001	<0.001	na	<0.02	<0.02	<0.001
C_3H_8	<0.0005	<0.0005	<0.0005	<0.0005	Trace	na	na	0.0013
N_2/Ar	249	198	96	68	62	84	na	45
Isotopes[b]								
$\delta^{13}C$-CO_2	−6.13	−6.16	−6.29	−5.60	na	na	−6.36	−5.94
^{14}C–CO_2	0.0013	0.0021	0.0006	0.0031	na	na	na	na
$^3He/^4He$	5.9	na	na	7.2	na	na	na	2.7
$CO_2/^3He$	1×10^9	na	na	2×10^9	na	na	na	9×10^{10}

("na" means not available).
[a] VH12: (649655 mE, 6413405 mN) soil gas from 70 cm depth in vegetation-kill Zone A; see Table 1 for other sites. USBM is published (Blasko, 1976) analysis of the main vent at The Gas Rocks 3a prior to formation of the Ukinrek Maars; CQ134 is published (Barnes and McCoy, 1979) analysis of main vent 5 months after formation of the Ukinrek Maars.
[b] $\delta^{13}C$ was analyzed at USGS Menlo Park CA and is in ‰ relative to PDB. ^{14}C was analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory and is in fraction Modern. $^3He/^4He$ ratios were measured at USGS Denver CO and are corrected for air contamination (based on measured He/Ne ratios) and expressed in units of R/R_A, where R is the $^3He/^4He$ ratio in the sample and R_A is the $^3He/^4He$ ratio in air.

has a SiO_2 concentration comparable to the seeps and springs in Table 1, a dilution factor of at least 20 is indicated; larger factors are possible, especially if the surrounding lake water contains >0.1 mg/L SiO_2. Thus the Cl concentration in undiluted vent water might exceed 1000 mg/L.

The warm spring at Ugashik (VH11) is located where the creek that drains the caldera has cut through its southern rim. Although this creek was named Hot Springs Creek as early as 1923 (Capps, 1923), no descriptions of thermal springs have been published, and only dilute cold springs were found in 1973 (Miller, 2004). Gassy, sulphurous cold springs (<10 °C) were seen during a reconnaissance visit in 1980 (Roman Motyka (ADGGS), pers. comm., 2007). The location of VH11 in an abandoned channel of Hot Springs Creek suggests that it may have been underwater and not visible during the 1973 and 1980 investigations, and implies that springs of similar or even warmer temperatures were on the stream banks decades earlier when the creek was named.

As found by Symonds et al. (1997) the bubbling gases at Ukinrek ridge and The Gas Rocks (Table 2) contain CO_2 and He with isotopic ratios close to those of mantle-derived gases, minor amounts of hydrocarbons, and in some cases, a component of non-atmospheric N_2 recognizable by N_2/Ar ratios >83.6 (the air value). Very low ^{14}C activities show that recent organic matter does not contribute significant amounts of CO_2, and this would seem to rule out thermal breakdown of vegetation buried by the maar deposits as the source of hydrocarbons and non-atmospheric N_2.

Results of the diffuse flux measurements, summarized in Table 3, show that the mean fluxes for the four plant damage zones (689–1190 g m^{-2} d^{-1}) are so high that any potential contribution from biogenic soil respiration is an insignificant part of the calculated CO_2 emissions for each zone. The 11 "disturbed" sites in Zone A showed an 11% drop in flux one day after soil disturbance compared to initial values, with eight sites showing flux decrease and three sites showing flux increase. Thus, plant removal may have temporarily increased flux values slightly, but this effect appears to be a very small source of error in the estimate of Zone A emissions based on 40 sites. Using the mean fluxes and polygonal shapes to represent all four zones results in a combined CO_2 emission of 44 t d^{-1} from a total area of ~50,000 m^2.

Table 3
Summary of diffuse CO_2 flux data from plant damage zones on the Ukinrek ridge. Emissions are in metric tonnes per day (t d^{-1}).

Zone	A	B	C	D
Polygonal area (m^2)	33,100	7980	8770	956
Minimum area (m^2)	21,800	6120	3050	300
# of sites	40	46	32	13
Min. flux (g m^{-2} d^{-1})	21	19	0	0
Max. flux (g m^{-2} d^{-1})	3980	8050	11,700	3430
Mean flux (g m^{-2} d^{-1})	828	1190	689	803
Dcl. mean (g m^{-2} d^{-1})	679	815	473	679
CO_2 emission (t d^{-1})[a]	27.4	9.5	6.0	0.8
CO_2 emission (t d^{-1})[b]	22.5	8.3	4.2	0.6
CO_2 emission (t d^{-1})[c]	14.8	5.0	1.4	0.2
CO_2 emission (t d^{-1})[d]	nc	8.5 ± 4.5	nc	nc

("nc" means not calculated).
[a] Using actual mean fluxes and polygonal areas.
[b] Using declustered "Dcl." mean fluxes and polygonal areas.
[c] Using declustered mean fluxes and minimum areas.
[d] Using stochastic simulation (see Cardellini et al., 2003) and minimum area.

Mean fluxes calculated from the declustered data are 15–32% lower than the simple mean fluxes, suggesting that the "random" distribution of measurement sites was biased toward high-flux locations. Restricting zone sizes to the exact areas covered by the measurements; i.e., using closed curves around outermost points, reduces the total area of emissions to ~31,000 m^2. Because the measurement sites did not extend to the edge of the damage zones in all cases, this could be considered the minimum area estimate. Combining these minimum areas with the declustered mean fluxes yields a minimum estimate for total diffuse CO_2 emissions of 21 t d^{-1}, about half as large as the initial estimate. Conversely, the possibility of some anomalous CO_2 flux from areas that show no apparent plant damage means that the total could be larger.

Reproducibility of diffuse emission estimates with regular grid spacing is likely no better than 20% (Lewicki et al., 2005). Temporal (day-to-day) changes of up to ±50% in diffuse emissions have been observed elsewhere, usually linked to major meteorological changes (Lewicki et al., 2007; Rogie et al., 2001). The authors' visit to Ukinrek occurred during stable weather conditions, but was a one-time survey that does not address temporal variability. Given this fact and the emission comparisons presented above, the uncertainty in the estimate of total emissions is certainly no better than ±50%. A ~50% uncertainty is also indicated by stochastic simulation of Zone B flux (Table 3).

The CO_2 gas discharge from the bubbling seeps and springs on the Ukinrek ridge is certainly insignificant compared to the diffuse emission, but the dissolved inorganic C (DIC) in groundwaters may represent a considerable efflux of magmatic CO_2. While springs VH04 and VH06 contain magmatic DIC, as shown by the C isotopes of the evolved CO_2 (Table 2), the high ^{14}C content of the DIC in VH10 (Table 1) shows a biogenic predominance, probably from soil respiration. A complete isotopic study of all springs and seeps at the Ukinrek ridge was impractical, but it was assumed that much of the spring discharge and groundwater flow from the ridge eventually fed into the two streams bounding the ridge on the east and west. Samples collected near mouths of both streams showed ^{14}C depletions in DIC relative to Modern Carbon (Table 1). Based on visual estimates of stream flow and the calculation method of James et al. (1999), the two streams carry ~3 t d^{-1} of CO_2 (mostly in the form of HCO_3^- that cannot be attributed to shallow biogenic production, and probably reflects addition of magmatic C from the Ukinrek ridge. Additional stream samples collected upstream from the ridge would be needed to confirm this hypothesis.

The main gas vent at The Gas Rocks has received much attention because of its impressive appearance, but probably the upflow of both gas and water makes the gas discharge appear more voluminous. The three gas discharge measurements with the inverted cylinder agreed within 20% and gave a total output of 2.4 L s^{-1}, or 0.39 t d^{-1} of CO_2. From this discharge measurement and a visual comparison to the other, numerous but much smaller, gas vents in Becharof Lake, the total offshore CO_2 gas output is estimated to be 0.5 t d^{-1} with probably a factor of 2 uncertainty.

5. Discussion

5.1. Gas source

The small size and Pleistocene age of The Gas Rocks dacite domes would normally argue against a residual magmatic gas source related to those features. However, lithic fragments resembling the mineralogy of the dacites were found in a 2–2.7 ka ash layer exposed north of Becharof Lake and tentatively attributed by Fierstein (2007) to a hydrothermal explosion through the dome complex. Intrusive activity beneath The Gas Rocks may therefore have continued into Holocene time. Still, the high $^3He/^4He$ ratio of 7.2 R_A (Table 2) and a similar value of 6.9 R_A in 1981 (Motyka et al., 1993) in the main gas vent (VH05) require a magmatic source young enough to be unaffected by radiogenic ^4He addition. These ratios are as high as any value reported for the Ukinrek ridge features (Table 2; Symonds et al., 1997). The recently intruded basalt associated with the maar eruptions is the most obvious source for both Ukinrek and The Gas Rocks gases.

The compositional similarity between the gases at both areas, as noted by previous workers (e.g., Symonds et al., 1997), supports the assumption that the gas emissions at The Gas Rocks derive from the Ukinrek basalt, as does the appearance of onshore gas vents and hot springs immediately after the maar eruptions. Despite strong evidence for connecting emissions at both areas to a common source, the nature of the linkage between the two areas has not been elucidated.

5.2. Implications of the gas emission rates

The estimated total CO_2 emission at The Gas Rocks is two orders of magnitude smaller than the diffuse CO_2 emission from the Ukinrek ridge, and is even smaller than the magmatic fraction of the DIC flux in the streams flowing past the ridge. Comparison of these relative emission rates suggests that the linkage between the two areas may be a shallow hydrologic one. It is proposed that The Gas Rocks area is a discharge point for groundwater that flows beneath the Ukinrek area, driven by hydraulic head from Mount Peulik and possibly guided by the Bruin Bay Fault. When the maar basalts erupted through the underlying Naknek Formation, interstitial brine within those Jurassic sediments was heated, charged with gas, and forced upward. While pools of brine briefly appeared in the new maar craters (Barnes and McCoy, 1979), most was carried northward in the regional groundwater flow system. Vertical fractures in the dacite outcrops at The Gas Rocks provided the ultimate escape path for both hot brines and gas. As the heat supply dwindled in the decade following eruption, brine discharge and spring temperatures dropped. Regional groundwater flow continues to dissolve a small fraction of the CO_2 upflow beneath the Ukinrek area and transport it to The Gas Rocks, where depressurization during discharge allows vigorous bubbling.

Vegetation surrounding the maars was killed by the eruptions, and Symonds et al. (1997) recognized that areas of plant damage and kill observed in 1995 had developed after re-vegetation. The diffuse CO_2 emission associated with the kill was apparently still increasing in 1995 as shown by dying and freshly damaged plants. This delayed onset of diffuse gas emission along the Ukinrek ridge is interesting and presumably reflects a belated increase in gas upflow after eruption, rather than the decline that might be anticipated as un-erupted magma in the conduit progressively crystallizes.

In 2004, elevated CO_2 flux was detected in all areas of plant damage but there was no evidence for recent expansion of those areas. These observations suggest that the diffuse CO_2 emission might have stabilized after 1995. A stable emission of 21–44 t d^{-1} for the 10a prior to the 2004 visit would total ~10^5 tonnes of CO_2. The volume of magma required to source this quantity of CO_2, assuming complete degassing of a mantle melt that begins ascent with a CO_2 content of ~0.65 wt.-% (see e.g., Gerlach and Taylor, 1990), is 5.7×10^6 m^3, at least as great as the amount actually erupted (Kienle et al., 1980; Self et al., 1980). Thus the diffuse efflux is a significant component in the volatile budget of this small basaltic system.

Airborne measurement of gases in eruptive plumes was a new technique in 1977, but Stith et al. (1978) flew gas sensors through the plume at Ukinrek on 9 April, the final day of the maar-forming eruptions. Their results constrain the emission rates of SO_2 (1–2 t d^{-1}) and H_2S (0.3 t d^{-1}). The CO_2 emission rate was not measured but would probably be $\leqslant$20 t d^{-1} given the range in C/S ratios observed in high-temperature or eruptive basaltic gas (e.g., Gerlach, 1983; Allard et al., 2005; McGee et al., 2008). Although gas emission rates may have been much higher during brief explosive episodes, that the likely CO_2 emission rate during eruption was less than present-day diffuse emissions offers some evidence for eruption of gas-depleted magma.

Rising basaltic magma can reach CO_2 saturation at depths of 30–60 km (Gerlach and Taylor, 1990). If a gas phase physically separates from magma at great depth, some gas might begin reaching the surface years to decades before the magma, while some gas could be temporarily trapped in strata that the magma penetrates, escaping years later in pulses as permeable pathways form. Such a

scenario could account for the low S emission rates measured in the eruptive plume, and is essentially required to explain the delayed onset of the large diffuse CO_2 efflux. Linking the pre-eruption gas emissions at The Gas Rocks to the Ukinrek basalt is more speculative given only the one pre-eruption gas analysis from 1974 that lacks critical He and C isotope data, but the gas emission rates seem compatible with such a linkage. At steady emission rates comparable to those measured in the offshore vents, the amount of CO_2 produced in 60 a at The Gas Rocks would be smaller than the diffuse CO_2 emission during one year at Ukinrek ridge.

5.3. Ugashik comparisons

Some aspects of water and gas geochemistry at The Gas Rocks and Ukinrek areas can be better evaluated through comparison with the newly sampled warm spring in the Ugashik caldera (VH11). The saline water of the now-defunct hot spring at The Gas Rocks (CQ135 in Table 1) was identified by Barnes and McCoy (1979) as a fossil sedimentary brine based on its chemistry; e.g., seawater Na/Cl and Br/Cl ratios and highly anomalous δD and δ^{18}O values. Symonds et al., (1997) generally concurred but suggested possible involvement of more modern seawater. Although The Gas Rocks is almost 50 km from the sea, Becharof Lake surface is only a few meters above sea level. VH11 is compositionally like CQ135 (e.g., Na-Cl dominated with high B) and appears to be a similar brine that is greatly diluted by meteoric water (Fig. 5). VH11 issues at an elevation of 450 m, so a component of modern seawater can be ruled out, but it discharges from stream cobbles adjacent to an exposure of the Naknek Formation at the base of the Ugashik caldera wall (Miller, 2004). The Naknek Formation thus appears to be a regional source of fossil brine, supporting the idea that the hot spring at The Gas Rocks (CQ135) was associated with expulsion of old interstitial brine by magmatic heating.

Symonds et al. (1997) noted the low SO_4/Cl and Mg/Ca ratios in CQ135 relative to initial seawater of any age, and attributed this shift to precipitation of anhydrite and Mg oxysulfate at 300 °C. However, CQ135 has a higher Ca/Na ratio than seawater (Fig. 6), so another explanation for the ionic ratios must be found. VH11 also shows low SO_4/Cl, low Mg/Ca, and high Ca/Na relative to seawater. General water–rock interaction processes, not intense local heating, must control ionic ratios in both these waters.

The extremely low SO_4 in VH11 is clear evidence of SO_4 reduction in the Naknek Formation, and this process probably also accounts for the low SO_4/Cl in CQ135. Sulfate reduction by organic matter produces carbonate alkalinity, but Ca/Na ratios in interstitial brines frequently increase through water–rock interaction (e.g., Connolly et al., 1990), so the DIC concentration is kept low by calcite precipitation. The brine could thus be a significant source of hydrocarbon gases while not releasing much CO_2. This may explain why the CH_4 concentration does not correlate with lighter δ^{13}C–CO_2 values in the gases (Table 2), another question raised by Symonds et al. (1997). VH11, with the highest CH_4, shows a typical magmatic δ^{13}C–CO_2 value. Its low N_2/Ar ratio reflects the great dilution by meteoric water (as is true for VH05), so it sheds no light on whether the excess N_2 at Ukinrek is magmatic or derived from the Naknek Formation.

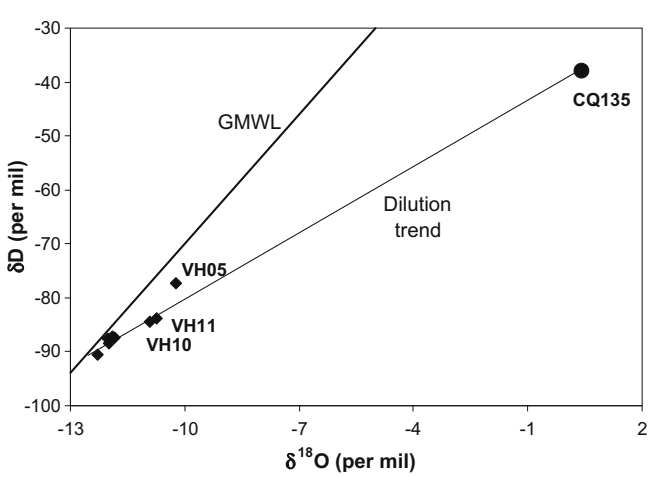

Fig. 5. Isotopic composition of water samples in Table 1 and Global Meteoric Water Line (GMWL) of Craig (1961). Spring VH11 at Ugashik caldera is likely a mixture of brine, similar to CQ135, greatly diluted by local meteoric water. Isotope shifts in seep VH10 and lake surface water VH05 probably reflect evaporative fractionation.

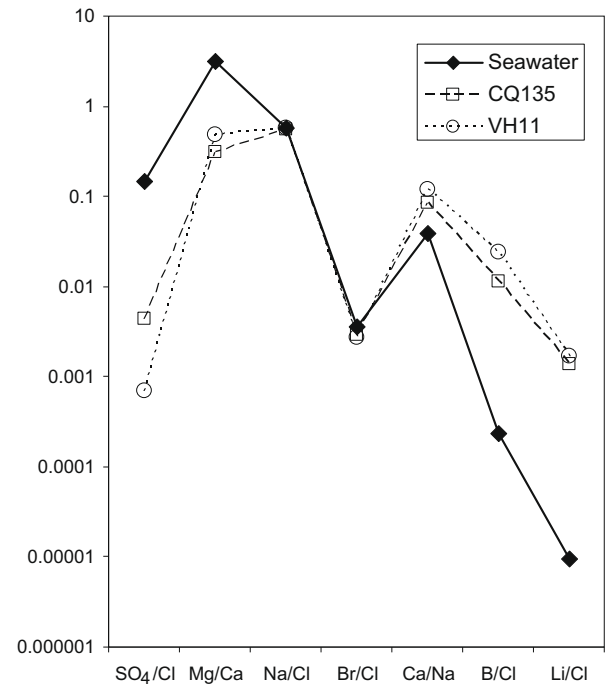

Fig. 6. Selected ratios (weight basis) for 1977 hot brine at The Gas Rocks (CQ135), warm spring in Ugashik caldera (VH11), and seawater.

High He concentrations and ^{3}He/^{4}He ratios in the gases at Ukinrek and The Gas Rocks contrast clearly with lower values at Ugashik (Table 2). If the CO_2 in the gas discharges is entirely magmatic, and differential solution in near-surface water does not fractionate the CO_2 and He, then the $CO_2/^3$He ratios will reflect the magmatic source. The relatively small range (~3×) in He concentration in the gas samples from Ukinrek and The Gas Rocks indicates only minor near-surface fractionation and suggests that the Ukinrek basalt has a $CO_2/^3$He ratio in the range of 1–2 × 10^9, the same as in mid-ocean ridge basalt (MORB). Most arc volcanoes have higher $CO_2/^3$He ratios (Sano and Marty, 1995; Fischer and Marty, 2005), although in Alaska, MORB-like $CO_2/^3$He ratios have also been reported for Augustine Volcano and Mount Griggs (Symonds et al., 2003). The much higher $CO_2/^3$He ratio (9 × 10^{10}) in VH11 is probably the most striking difference between gas at the Mount Peulik/Ugashik system and the Ukinrek Maars.

5.4. Gas emissions and volcanic hazards

Gas emissions from volcanoes are studied in part to discern signals that might be precursory to eruption, such as increased SO_2 in plume emissions (Symonds et al., 1994). Changes in discharge rates and chemistry of gases in springs, fumaroles, or diffuse emissions have been linked to unrest at some volcanoes; examples include

Mammoth Mountain (Sorey et al., 1998) in the USA and the Phlegrean Fields (Chiodini et al., 2003) and Stromboli (Carapezza et al., 2004) in Italy. However, gas emissions at long-lived volcanoes can be derived from a new intrusion, older co-located intrusions, or disruption of a hydrothermal system, which complicates the interpretation.

The Ukinrek Maars – a tiny, isolated "volcano" apparently resulting from a single intrusion of primitive basalt – should offer no such complexity. Yet even here, major aspects of the gas emission history are difficult to interpret, such as the reason for the delayed onset of the large diffuse CO_2 emission reported in this work. Magma-induced inflation of nearby Mount Peulik was detected in 1996 by Interferometric Synthetic Aperture Radar (InSAR), and an unusually intense earthquake swarm occurred beneath Becharof Lake in 1998 (Lu et al., 2002), but the diffuse emission began before 1995, so the onset is clearly unrelated to these events. Similarly, a 60-a period of gas venting prior to nearby eruption, while precursory, would be uninterpretable in a predictive sense. The long and somewhat puzzling history of gas emissions related to these maars highlights the difficulties of interpreting gas emissions at long-lived volcanoes, beneath which repeated intrusions of magma occur.

Gas emissions can pose a direct hazard due to toxicity, and human fatalities have occurred elsewhere in areas of high CO_2 flux (e.g., Hill, 2000). Only one suspicious fatality was found during the 2004 survey of the plant damage zones at Ukinrek – a dead bird in Zone C, but scavenging by animals may have removed other evidence. The Ukinrek area is very remote, but bare ground in the plant-kill areas might appeal to the few tent-campers that visit (mostly hunters and fishermen). Sites where CO_2 flux exceeds 1000 g m^{-2} d^{-1} occur in all of the areas of plant damage, and thus those areas should all be considered unsafe for camping. The CO_2 fluxes and total emission at Ukinrek are similar to the ranges recently reported for the Horseshoe Lake tree-kill area (Lewicki et al., 2007), a popular recreation area at Mammoth Mountain USA that has been closed to camping because of safety concerns.

6. Conclusions

High CO_2 efflux was detected in all areas of plant damage and kill near the Ukinrek Maars. Diffuse emissions are sufficiently strong to cause concern for the safety of visitors who might camp in these areas. The estimate of the total diffuse CO_2 emission from all areas of plant damage is 21–44 t d^{-1}, and even allowing a 50% uncertainty in the estimate, the diffuse emission at Ukinrek exceeds the CO_2 output from the visibly impressive gas vents at The Gas Rocks by more than an order of magnitude. The gas venting there may simply mark the terminus of a groundwater flow path beneath Ukinrek.

If the above scenario is correct, then the timing of gas-efflux changes and hot water discharges are best explained by assuming that all of the CO_2 at Ukinrek and The Gas Rocks begins to separate from the basalt at great depth and rises to the surface independently, some arriving before and some after the basalt. Historical evidence suggests that the gas vents in Becharof Lake became active at least 6 decades prior to maar formation, and thus, nearly a century of gas emission is apparently linked to an 11-day eruption of a small quantity of basalt. The pre-1977 gas venting at The Gas Rocks would indeed be precursory in this scenario, even if not interpretable in a "predictive" sense. The possibility that gas discharge may pre-date the eruption of magma by 6 decades carries obvious implications for geochemical monitoring at volcanoes, where precursory signals are usually sought on much shorter timescales.

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