Magmatic gas efflux at the Ukinrek Maars, Alaska

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ABSTRACT: Diffuse efflux of CO_2 was suspected at plant-kill areas near the Ukinrek Maars a decade ago, but its magnitude and corresponding significance to the magmatic volatile budget was not evaluated. We document a diffuse efflux of 44 t d^{-1} of CO_2 from areas of vegetation damage and kill, while prominent gas vents near The Gas Rocks 3-km away release only ~0.5 t d^{-1} of CO_2. The diffuse efflux of CO_2 near the maars apparently increased with time, while discharges of gas and hot water at The Gas Rocks declined. Gases from all sites are compositionally similar, suggesting that the Ukinrek basalt is the common source. We discuss magmatic degassing and local toxicity hazards in light of the new efflux data.

1 INTRODUCTION

The Ukinrek Maars formed in early 1977, erupting through a low ridge of glacial till and pyroclastic deposits from Mt. Peulik, the nearest stratovolcano of the Aleutian arc (Fig. 1). The erupted alkalic olivine basalt is a fairly primitive mantle melt showing little contamination during transport and is thought to be unrelated to the compositionally different Ugashik-Mt. Peulik magma system (Kienle et al. 1980, Miller 2004). The maars are described as rear-arc features by Hildreth et al. (2004) and are located near the Bruin Bay Fault, a major structural boundary that could serve as a pathway for rising mantle melts. Carbon dioxide with mantle-like $\delta^{13}C$ values is emitted from gas vents a few km north along the fault at The Gas Rocks, a small cluster of late Pleistocene dacite domes (Hildreth et al. 2007).

The main gas vent at The Gas Rocks occurs just offshore in Becharof Lake and is strong enough to lift the water surface several cm in a 1-m diameter circle. Smaller gas vents cover a large area at the edge of the lake. The discharge was described as vigorous when gas was first sampled in 1974, but some form of venting has likely occurred here since prior to 1917 (Miller 2004). Increased gas discharge was observed during investigations that followed maar formation. Gassy, saline hot springs (T = 52.8°C) as well as a mud volcano were found onshore at The Gas Rocks in August of 1977 (Barnes & McCoy 1979). Subsequent investigations (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).

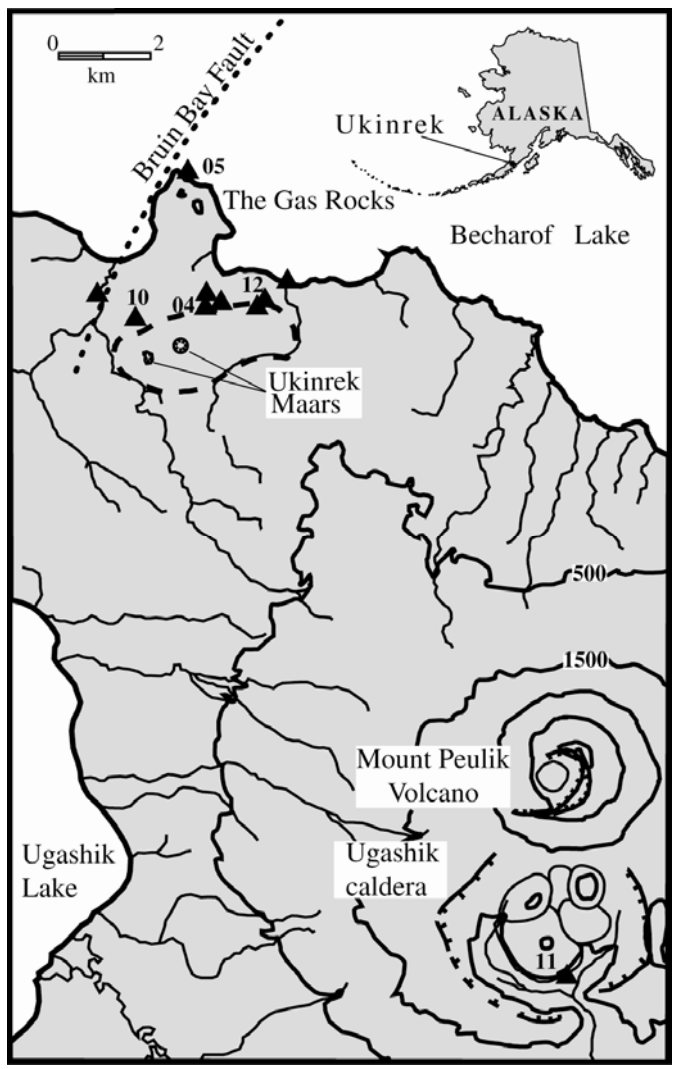

Figure 1. Study area showing samples collected in 2004 (triangles). Numbers correspond to selected samples shown in Tables 1 and 2. Dashed line around maars is outline of low ridge. Contour interval is 1000 feet (adapted from Miller 2004).

The rapid appearance of hot springs and increased venting of gas followed by a two-decade decline in temperature and output would seem to be a logical response to the eruption. The basalt was an immediate source of heat and gas, while the dike that could feed such a small eruption (0.01 km^3 dense-rock equivalent) would probably not contain enough magma to support a long-lived hydrothermal system. Some important questions remain. Why had the most obvious gas and water discharges occurred 3 km away from the maars and at the site of an apparently long-lived CO_2 vent? Was that CO_2 vent a precursory signal or a feature related to the older dacite domes at The Gas Rocks?

Previous studies have examined the chemistry of the gases and waters. Our fieldwork in June 2004 was designed to provide additional perspective on the above questions by measuring gas discharge rates. Although the offshore venting at The Gas Rocks appeared to be the main player, we also studied small bubbling seeps and areas of vegetation kill on the ridge hosting the Ukinrek Maars. The seeps had been sampled during an expedition in 1995 by Symonds et al. (1997), who urged a follow-up study of diffuse emissions in the plant-damage zones.

2 METHODS

Gas discharge from the main offshore vent at The Gas Rocks was estimated by timing the rate of water displacement in an inverted container of known volume. Because the mouth of the container was much smaller than the area of the gas vent, total output was calculated from the ratio of the two areas. Diffuse CO_2 flux from areas of dead or unhealthy vegetation was measured using the accumulation chamber procedure described by Bergfeld et al. (2006). Lacking sufficient time to establish regular grids, we made measurements at 148 randomly chosen sites, 20 of which were re-measured on a subsequent day to evaluate uncertainties. All significant zones of apparent vegetation damage, covering a combined area of ~50,000 m^2, were visited. Total diffuse CO_2 efflux for each area was calculated as the average flux for the area times its size.

Samples of water, gas bubbles, and soil gas were collected and analyzed using published methods (Evans et al. 2002). Selected sites are described in Tables 1 and 2.

3 RESULTS

Three gas discharge measurements at the main Gas Rocks vent agreed within 20% and gave a total output of 2.37 L s^{-1}, or 0.39 t d^{-1} of CO_2. The vent is an upflow of both gas and water, which possibly makes the gas discharge appear more voluminous than what we measured. From this discharge measurement and a visual comparison to the other, numerous but much smaller, gas vents in Becharof Lake, we estimate the total offshore CO_2 gas output at 0.5 t d^{-1} with probably a factor of 2 uncertainty. No onshore discharge of gas was evident here in 2004, either in the form of bubbling springs or plant-damage zones.

Plant damage and high diffuse CO_2 flux on the Ukinrek-Maars ridge was found in 4 areas, a large area of mixed plant kill and unhealthy grass on the northeastern flank (27 t d^{-1}), a cluster of sharply delimited plant-kill zones high on the ridge (9.5 t d^{-1}), and 2 clusters of kill zones at the northern base of the ridge where seeps of bubbling water emerged (6.8 t d^{-1}). All 4 areas contained sites where the CO_2 flux was several thousand g m^{-2} d^{-1}, and flux values were generally so high that no correction for background biogenic soil respiration was made.

The possibility of some anomalous CO_2 flux from areas that show no visible plant damage means that the 44 t d^{-1} we documented is a minimum estimate for the diffuse efflux. The CO_2 gas discharge from the bubbling seeps is certainly insignificant compared to the diffuse efflux, but the amount that leaves the ridge in solution needs further investigation. Dissolved inorganic carbon in the two streams bounding the ridge on the east and west showed ^{14}C depletions (0.906 and 0.475, respectively, as fraction Modern Carbon). 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 may instead be magmatic.

Representative water and gas chemistries are shown in Tables 1 and 2. Water and gas compositions from seeps on the Ukinrek Maars ridge and from the main vent at The Gas Rocks are similar to previously reported analyses except that no warm, saline springs were found. Dilute seep VH04 may be slightly warm, and seep VH10 shows slight elevations in Na and Cl. A saline brine still discharges along with the gas at the main Gas Rocks vent but is greatly diluted by lake water in the surface sample we collected (VH05) as shown by its low SiO_2. A dilution factor of at least 20-100 is indicated by comparison with SiO_2 concentrations in the seeps and springs in Table 1; larger factors if the lake water contains >0.1 mg/L SiO_2.

As found by Symonds et al. (1997) the gases (Table 2) contain CO_2 and He with isotopic ratios close to those of the mantle, minor amounts of hydrocarbons, and in some cases (e.g. VH04 and VH12), a component of non-atmospheric N_2 recognizable by N_2/Ar ratios >83.6 (the air value). Very low ^{14}C values show that recent organic matter does not contribute significant amounts of CO_2, and this would seem to rule out thermal breakdown of buried vegetation as the source of hydrocarbons and non-atmospheric N_2.

4 DISCUSSION

4.1 *Efflux implications*

The compositional similarity between the gases bubbling out at Ukinrek Maars and The Gas Rocks was noted by previous workers. We extend this comparison to the diffuse gas emission by showing the similarity in composition of soil gas (VH12) from a plant damage area near the maars. There is thus a large emission of mantle-derived gas in close spatial association with the maars. The gas venting at The Gas Rocks is only a tiny fraction of the total.

We propose that The Gas Rocks area is a discharge point for groundwater that flows beneath Ukinrek, driven by hydraulic head from Mt. Peulik and possibly guided by the Bruin Bay fault. As the maar basalts erupted through the Jurassic Naknek Formation, brine within those sedimentary rocks was heated, charged with gas, and forced upward. While pools of brine briefly appeared in the new maar craters (Barnes & 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 dropped. Onset of diffuse gas emission along the maar ridge presumably reflects the opening of near-surface pathways but also indicates 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.

Vegetation surrounding the maars was killed by the eruptions, but Symonds et al. (1997) recognized that areas of new kill had developed after re-vegetation. The die-off had started some years prior to their visit in 1995 but was apparently still expanding as shown by dying and freshly damaged plants. We found no evidence for recent expansion of plant-damage areas in 2004, suggesting that CO_2 efflux might have stabilized. A stable efflux of 44 t d^{-1} for the ten years prior to our visit would total 1.6×10^5 tonnes of CO_2. The volume of magma required to source this CO_2, assuming complete degassing of a mantle melt that begins ascent with a CO_2 content of ~0.65 wt.-%, is ~10^7 m^3, comparable to the amount actually erupted (Kienle et al. 1980). Thus the diffuse efflux is a significant component in the volatile budget of this small basaltic system.

Airborne plume measurements were made at Ukinrek by Stith et al. (1978) on 9 April 1977, the final day of the maar-forming eruptive activity. These measurements constrain 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 ≤100 t d^{-1} for reasonable C/S ratios in eruptive gas. At the magma eruption rate averaged over the entire eruptive period, a CO_2 emission rate of ~4000 t d^{-1} would be expected if basalt with 0.65 wt.-% CO_2 released all of its gas at eruption. Although gas emission rates may have been much higher during brief explosive episodes, the large disparity between actual and expected CO_2 emission rates during the eruptive period indicates that gas had largely separated from the rising magma at depth. A separated gas phase might begin reaching the surface many years before the magma and still, as our results may show, support an increase in efflux many years after eruption ends.

4.2 *Geochemistry implications*

The saline water of the now-defunct hot spring at The Gas Rocks (CQ135 in Table 1) was identified by Barnes & McCoy (1979) as a sedimentary brine based on chemistry and highly anomalous δD and $\delta^{18}O$ values. Symonds et al. (1997) concurred but noted that the brine might be either connate water or

Table 1. Water chemistry at selected sites. Concentrations in mg/L; isotopic ratios in ‰ (SMOW).

Sample	VH04	VH10	VH05	CQ135	VH11
T °C	16.5	7.8	8.6	52.8	21.7
Li	0.004	0.010	0.048	44	2.4
Na	7.6	37	23	17700	809
K	1.5	3.8	1.1	410	45
Mg	5.1	13	3.0	460	47
Ca	13	60	10	1500	96
F	0.03	0.22	0.04	0.13	0.2
Cl	4.2	47	42	32000	1440
Br	0.003	0.16	0.11	92	3.9
SO_4	11	73	6.8	140	1.0
HCO_3	68	179	27	1240	535
SiO_2	45	24	1.1	120	104
B	<0.02	<0.2	0.39	360	35
δD	-88	-84	-77	-38	-84
$\delta^{18}O$	-12.0	-10.9	-10.2	+0.42	-10.7

VH04 and VH10 are seeps on the Ukinrek ridge; VH05 is Lake Becharof surface water at the main gas vent; CQ135 is an Aug 1977 sample from the hot spring at The Gas Rocks (Barnes and McCoy, 1979); VH11 is a previously unsampled warm spring on the floor of the Ugashik caldera.

Table 2. Gas chemistry at selected sites. Concentrations in vol-%; $\delta^{13}C$ in ‰ (PDB); ^{14}C in fraction Modern Carbon; R_C/R_A is the air-corrected $^3He/^4He$ ratio.

Sample	VH04	VH12	VH05	CQ135	VH11
He	0.0143	0.0048	0.0044	<0.02	0.0003
H_2	0.0001	<0.0002	<0.0002	<0.01	0.0004
Ar	0.0146	0.0706	0.0378	<0.02	0.0122
O_2	0.0683	1.44	0.792	0.02	0.0329
N_2	3.63	6.82	2.55	0.54	0.545
CH_4	1.26	0.189	0.0541	0.04	1.52
CO_2	95.0	91.5	96.6	98.4	97.8
C_2H_6	0.0035	0.0017	<0.0002	<0.05	0.0614
$\delta^{13}C$-CO_2	-6.13	-6.29	-5.60	-6.36	-5.94
^{14}C-CO_2	0.0013	0.0006	0.0031		0.0057
R_C/R_A	5.9	--	7.2	--	2.7
$CO_2/^3He$	1×10^9	--	2×10^9	--	9×10^{10}
N_2/Ar	249	96	68	--	45

Gases from sites in Table 1 except VH12 is soil gas (70 cm depth) from an area of plant damage on the Ukinrek ridge.

modern seawater with SO_4/Cl and Mg/Ca lowered due to heating and precipitation of anhydrite and magnesium oxysulfate. However, CQ135 is enriched in Ca/Na relative to seawater. A highly diluted but compositionally similar fluid (Na-Ca-Cl water with high B) issues 20 km SE of The Gas Rocks at 450 m above sea level on the floor of the Ugashik caldera. Discovery of this spring (VH11) suggests that the Naknek Formation, exposed nearby in the caldera wall, is indeed a source of connate water.

The extremely low SO_4 in VH11 clearly reflects sulfate reduction, a process that could also account for the low SO_4/Cl in the brine at The Gas Rocks (CQ135). Sulfate reduction by organic matter produces carbonate alkalinity, and since brines trapped for long periods in sedimentary rocks gradually increase in Ca/Na though water-rock interaction, eventually calcite precipitation occurs. Through this process, organic matter in the Naknek Formation breaks down to produce hydrocarbon gases and N_2, but little CO_2. This could explain why CH_4 and N_2 do not correlate with lighter $\delta^{13}C$-CO_2 values in the suite of gas samples from Ukinrek and The Gas Rocks, a question raised by Symonds et al. (1997).

If the CO_2 in the gas discharges is entirely magmatic, and differential solution in near-surface water does not separate the CO_2 and He, then the $CO_2/^3He$ ratios will reflect the magmatic source. The relatively small range (~3×) in He concentration in the three gas samples from Ukinrek and The Gas Rocks (Table 2) indicates only minor near-surface fractionation and suggests that the Ukinrek basalt has a $CO_2/^3He$ ratio in the MORB range ($1\text{-}3 \times 10^9$). Most arc volcanoes have higher $CO_2/^3He$, although in Alaska, MORB-like $CO_2/^3He$ ratios have also been reported for Augustine Volcano and Mount Griggs (Symonds et al. 2003). The much higher $CO_2/^3He$ ratio (9×10^{10}) in VH11 is probably the most striking difference between gas at the Ugashik-Mount Peulik system and the Ukinrek Maars.

5 CONCLUSIONS

Although the offshore gas venting at The Gas Rocks is visibly impressive, the diffuse CO_2 discharge near the Ukinrek Maars is ~100 times greater. 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 separates from the basalt at great depth and rises to the surface independently, some arriving many years before the basalt, some arriving afterward. The pre-1977 gas venting at The Gas Rocks would indeed be precursory in this scenario, even if not particularly useful in a "predictive" sense. The possibility that gas discharge may pre-date the eruption of magma by years to decades carries important implications for geochemical monitoring at volcanoes.

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). Symonds et al. (1997) suggested that camping here could be hazardous if CO_2 flux was sufficiently high. In fact, sites where 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 tenting. The CO_2 fluxes and total efflux at Ukinrek are similar to the ranges reported for the Horseshoe Lake tree-kill (Lewicki et al. 2007), a popular area at Mammoth Mountain California that has been closed to camping because of safety concerns.

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