U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

# INVESTIGATIONS OF GAS SEEPS AND SPRINGS IN THE VICINITY OF THE GAS ROCKS, SOUTH SHORE BECHAROF LAKE, ALASKA

by

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**Open-File Report 97-127**

**1997**

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## ABSTRACT

In August 1995, we investigated gas seeps and springs in the vicinity of The Gas Rocks and Ukinrek Maars on the southern shore of Becharof Lake, Alaska. At The Gas Rocks, a site of intense $CO_2$-degassing since at least 1974, $CO_2$-rich gases discharge into the lake from three large vents and hundreds of small seeps. An onshore saline spring also discharges into the lake. No evidence exists for additional degassing saline springs that existed in 1981. Along the ridge that hosts the Ukinrek Maars, weak or diffuse $CO_2$ degassing occurs from at least four sites, all characterized by dead and dying vegetation. Vegetation was apparently killed both during the 1977 eruption and sometime between 1977 and 1995, but the dying vegetation experienced trauma in 1995.

Gas samples were collected at five sites at The Gas Rocks and the Ukinrek Maars ridge to determine bulk gas composition, $\delta^{13}C$ in $CO_2$, and rare-gas isotopes. The samples contain 89.5 - 99.5 % $CO_2$, 0.5 - 10.5% air and air-saturated-water gases ($N_2$, $O_2$, Ar), and, for the Ukinrek Maars ridge samples, 0.3 - 2.1% $CH_4$ and $N_2$ probably derived from heating of the sedimentary rocks beneath the maars. These results suggest that the sub-water-table gases are nearly 100% $CO_2$, except for minor amounts of thermogenic $CH_4$ and $N_2$ in the Ukinrek Maars samples. Data for $\delta^{13}C$ in $CO_2$ and $^3He/^4He$ suggest that $CO_2$ and He in these gases ultimately come from a mantle source.

Water samples were collected at most gas-sampling sites, The Gas Rocks spring, the east Ukinrek Maar lake, and from a background site on Becharof Lake. Samples were analyzed to determine concentrations of major and selected trace elements, $\delta D$ and $\delta^{18}O$ in $H_2O$, and $\delta^{13}C$ in dissolved inorganic carbon (DIC). The water samples collected at sites of gas discharge in Becharof Lake and along Ukinrek Maars ridge are dilute waters, except that they contain major amounts (300 - 1900 mg/L) of DIC (mostly as $H_2CO_3$) from dissolution of the discharged $CO_2$. But the saline waters discharging from The Gas Rocks spring contain a NaCl-brine component, which has decreased along with temperature since the spring was first sampled in 1977. Additional saline springs may exist offshore from The Gas Rocks peninsula. Similar to sedimentary brines, The Gas Rocks brine probably derives from seawater or meteoric waters that have reacted with the underlying marine sedimentary rocks. All the saline springs discharge $CO_2$-rich gas, which probably plays a role in transporting the brine to the surface.

The main gas hazards to visitors in the vicinity of The Gas Rocks and the Ukinrek Maars are tent camping and digging snow pits near the areas of gas discharge, including the areas of dead and dying vegetation along the Ukinrek Maars ridge. Such enclosures may concentrate $CO_2$ to lethal levels. The potential for open-air $CO_2$ asphyxiation at The Gas Rocks and Ukinrek Maars has decreased since a visitor experienced asphyxia at The Gas Rocks in 1977. Apparently the $CO_2$ flux at The Gas Rocks has decreased since 1977 as indicated by the reduction in the number of onshore springs (or vents) and their visible degassing rate. This decrease may reflect progressive outgassing of the $CO_2$ source. However, the potential for open-air $CO_2$ asphyxiation could potentially change at any time should mantle $CO_2$ input increase.

Areas of dead and dying vegetation on the Ukinrek Maars ridge are the main impact of the $CO_2$ emissions on the local onshore and aquatic ecosystems. In addition, just offshore from The Gas Rocks, subaqueous $CO_2$ and saline-water discharges produce elevated DIC, Cl, Na, $SO_4$, $SiO_2$, and $H^+$ concentrations in lake waters. More work is needed to discern the soil-gas $CO_2$ concentrations in the plant-kill zones, the areal extent and flux of the diffuse $CO_2$ emissions, and the spatial extent of the geochemical anomalies in Becharof Lake.

## INTRODUCTION

The Gas Rocks are located on the southern shore of Becharof Lake on the Alaska Peninsula (Fig. 1). They are part of a series of Quaternary volcanic plugs that

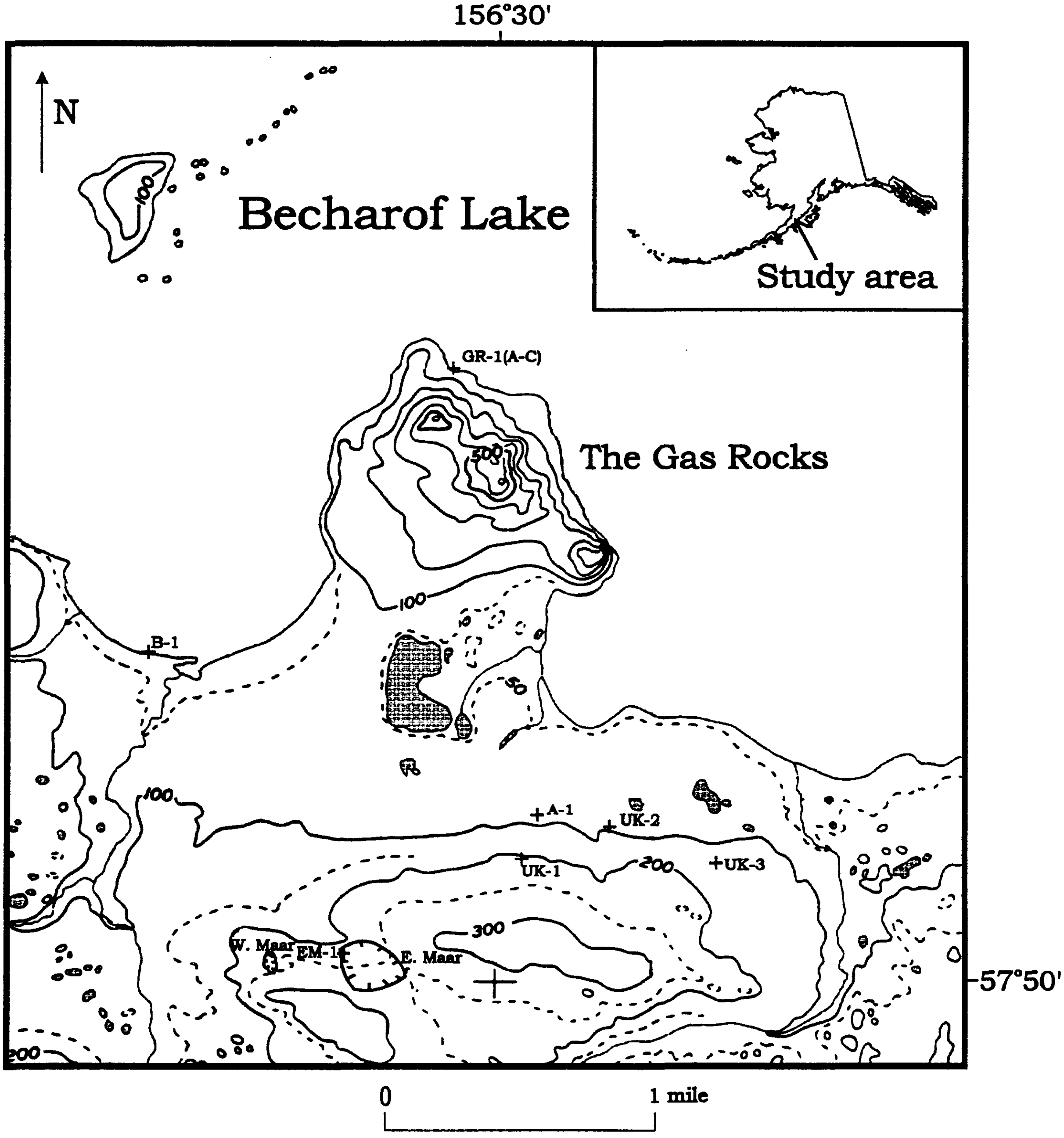

**Figure 1.** Location map showing sites investigated in the vicinity of The Gas Rocks and Ukinrek Maars. Base is from U.S. Geological Survey, Ugashik D2 quadrangle. Contour interval is 100 feet; dashed lines represent interpolated 50 foot contours. Approximate locations of the East and West Ukinrek Maars are shown for reference. Inset shows location of study area.

lie along the Bruin Bay fault. Mesozoic marine sedimentary rocks underlie the area (Burk, 1965; Detterman et al., 1987).

The Gas Rocks area has been known as a site of vigorous $CO_2$ degassing since at least 1974, when it was first investigated by US Bureau of Mines scientists (Bureau of Mines, 1976). About two miles south of The Gas Rocks are the Ukinrek Maars, two monogenetic craters that formed during their March-April 1977 eruption (Kienle et al., 1980; Self et al., 1980). In July 1977, R. L. Smith visited The Gas Rocks area and reported a new onshore spring and much higher gas discharges than before Ukinrek Maars erupted (Barnes and McCoy, 1979). In early August 1977, Tom Miller (personal communication, 1995) visited The Gas Rocks area and noted three vigorous offshore gas vents, several degassing onshore springs (saline and up to 55°C), and a fuming onshore mud volcano. The mud volcano apparently erupted about one month prior to Miller's visit because vegetation defoliated by hot erupted mud was just leafing out during Miller's visit. During his investigations near one of the springs, he was asphyxiated temporarily by a $CO_2$-rich gas pocket while kneeling over the vent. In late August, Barnes and McCoy (1979) sampled offshore gases and the hottest onshore spring (52.8°C) in the vicinity of The Gas Rocks; they also sampled gases and waters from a bubbling pool (80.9°C) in the West Ukinrek Maar. Their work shows that the 1977 gases emanating from The Gas Rocks area contained up to 98% $CO_2$ and that the $CO_2$ apparently derived from the mantle as indicated by $\delta^{13}C$ data (Table 1). Obviously, the primitive olivine basalt erupted from the Ukinrek Maars also came from the mantle.

The pool in the West Ukinrek Maar and the hottest Gas Rocks spring were resampled in 1980 and 1981, respectively (Motyka et al., 1993). At the time of these visits, there were still several onshore

**Table 1.** Chemical compositions of gas samples collected in 1977 from The Gas Rocks and Ukinrek Maars areas. Samples collected in evacuated bottles and analyzed by gas chromatography. Data from Barnes and McCoy (1979).

| Field numbers: | CQ135GM77 | CQ134GM77 | CQ133GM77 |
|---|---|---|---|
| Map site: | GR-1A | GR-1C | |
| Location: | onshore spring at The Gas Rocks | Becharof Lake near largest gas vent | Pool, West Ukinrek Maar |
| Date: | August 25, 1977 | August 25, 1977 | August 24, 1977 |
| **Site temperature** | | | |
| T°C | 52.8 | 9.3 | 80.9 |
| **Chemical Species of Dry Gas (mol%)[†]** | | | |
| $CO_2$ | 98.40 | 97.08 | 77.48 |
| $N_2$ | 0.54 | 2.52 | 15.14 |
| $O_2$ | 0.02 | 0.59 | 3.19 |
| Ar | <0.02 | 0.03 | 0.34 |
| $CH_4$ | 0.04 | 0.08 | 1.88 |
| $C_2H_6$ | <0.05 | <0.05 | 0.23 |
| **Selected ratios** | | | |
| $N_2/Ar$ | >27 | 84 | 45 |
| $N_2/(O_2+Ar)$ | >13.5 | 4.1 | 4.3 |
| **Carbon Isotope Composition** | | | |
| $\delta^{13}C$ | -6.36 | --- | --- |

[†] Species below detection in all samples include He (<0.02), $H_2$ (<0.01), and CO (<0.02).

**Figure 2.** Photograph of the two largest gas vents off The Gas Rocks Peninsula. The largest vent, about 1 meter in diameter, is site GR-1C.

springs at The Gas Rocks, but the mud volcano had apparently washed away. Also, the pool in the West Ukinrek Maar and the hottest Gas Rocks spring had cooled to 16°C and 39°C, respectively. However, The Gas Rocks gases remained $CO_2$-rich (99.99% $CO_2$) and $\delta^{13}C$ and $^3He/^4He$ data indicated that both $CO_2$ and He derived from the mantle.

Degassing on the ridge that hosts the Ukinrek Maars was investigated partially in 1994 by Tina Neal and Michael Ort (personal communication, 1995). They discovered a bubbling spring (site A-1) at the base of the ridge. They also collected water samples from the lake (15-16°C) in the East Ukinrek Maar.

In August 1995, with partial funding from the U.S. Fish and Wildlife Service (USFWS), Becharof National Wildlife Refuge, we investigated gas seeps and springs in the vicinity of The Gas Rocks and Ukinrek Maars. This is the first comprehensive investigation of degassing at The Gas Rocks since 1981. The purposes of our work at The Gas Rocks and Ukinrek Maars are to (1) investigate the gas seeps and springs, (2) sample the gases and spring waters to determine their present compositions and origins, (3) make a preliminary evaluation of the potential hazards of degassing to visitors, and (4) initiate study of the impact of degassing on the local aquatic and onshore environments.

**Figure 3**. Photograph showing collection of bulk-gas samples. Site is an offshore seep (site GR-1B) just off The Gas Rocks Peninsula. The pool to the left of the samplers is the onshore spring (site GR-1A).

## FIELD OBSERVATIONS AND SAMPLING

We investigated gas seeps and springs in the vicinity of The Gas Rocks and along the ridge that hosts the Ukinrek Maars (Fig. 1; Table 2). At The Gas Rocks, visible degassing occurs offshore of The Gas Rocks peninsula; minute amounts of gas also vent through the onshore spring. We lack evidence (e.g., dead vegetation, bubbling in pools) for additional onshore degassing in the vicinity of The Gas Rocks, but diffuse onshore degassing would be detected best by soil-gas studies (e.g., Farrar et al., 1995; Gerlach et al., 1996). Offshore, gases discharge from three large vents that disrupt lake-surface areas in circular upwellings up to one meter in diameter (Fig. 2) and from hundreds of smaller vents that discharge single-bubble-width streams of gas. The onshore spring (16°C) fills a small (0.5 meter wide) pool and contains reddish brown deposits of iron oxyhydroxide (Fig. 3). Since the visits by Motyka et al. (1993) in 1981, the number of onshore springs has decreased from several to one and the hottest spring has cooled by 23°C.

At The Gas Rocks, we collected gas samples to determine bulk-gas composition from one of the smaller vents (site GR-1B; Fig. 3) and from the largest vent (site GR-1C; Fig 2). Samples were collected following the procedures of Fahlquist and Janik (1992). A 15-cm funnel was held beneath the water surface over the bub

**Table 2.** 1995 sites investigated in the vicinity of The Gas Rocks and Ukinrek Maars. Figure 1 shows site locations.

| Site | Site description | latitude longitude | T(°C) | Sampling and measurements accomplished |
|---|---|---|---|---|
| GR-1A | onshore spring at The Gas Rocks | N57° 52.00'<br>W156° 30.18' | 16.3 | 5-9 |
| GR-1B | small offshore gas seep at The Gas Rocks; near onshore spring | N57° 52.00'<br>W156° 30.18' | 10.1 | 1-3 |
| GR-1C | Largest gas vent at The Gas Rocks | N57° 52.00'<br>W156° 30.18' | 10.1 | 1,5-9 |
| A-1 | spring on same ridge as the Ukinrek Maars; gas bubbling into pool; dead vegetation observed | N57° 50.53'<br>W156° 29.82' | 10.2 | 1, 4-9 |
| UK-1 | spring-fed steam on the same ridge as the Ukinrek Maars; gas bubbling into stream; dead vegetation observed | N57° 50.39'<br>W156° 29.87' | 7.5 | 1-9 |
| UK-2 | 8-inch diameter pool (no outlet) on same ridge as the Ukinrek Maars; gas bubbling into pool; dead vegetation observed | N57° 50.50'<br>W156° 29.45' | 12.3 | 1, 4-9 |
| UK-3 | site of dead vegetation along the same ridge as the Ukinrek Maars; no spring observed | N57° 50.36'<br>W156° 28.72' | --- | none |
| EM-1 | Lake in East Ukinrek Maar; no degassing observed in lake | N57° 50.10'<br>W156° 30.84' | 12.0 | 4-9 |
| B-1 | Becharof Lake near camp | N57° 51.10'<br>W156° 32.07' | 9.5 | 4-9 |

1. gas sample for chemical analysis, 2. gas sample for $\delta^{13}C$ in $CO_2$ analysis, 3. gas sample for rare-gas isotope analysis, 4. field conductivity, 5. laboratory conductivity and pH, 6. water sample for anion analysis, 7. water sample for cation analysis, 8. water sample for $\delta D$ and $\delta^{18}O$ analysis, 9. water sample for $\delta^{13}C$ in DIC analysis.

bling vent. This funnel was attached to a short-length of Tygon tubing that led to an evacuated double-port sampling bottle partly filled with a known volume of 4N NaOH solution. After purging air from the sampling line with a hand pump attached to the outlet port, we clamped the outlet and opened the bottle's inlet valve. Regulation of the valve prevented water from entering the sampling line. Occasional shutting of the valve and shaking the bottle facilitated $CO_2$ gas dissolution. Gas was collected until the flow rate ceased or precipitates (probably $Na_2CO_3$) formed, usually

**Figure 4**. Photograph of the site UK-2 along the ridge that hosts the Ukinrek Maars. Note dead vegetation around the pools of water, some of which are bubbling (see Fig. 5). The Gas Rocks are in the background.

within 3-8 minutes. At site GR-1B, we also filled two evacuated flasks (without NaOH solution) for analysis of $\delta^{13}C$ in $CO_2$ and rare-gas isotopes. The rare-gas isotope flasks were made of Corning-1720 glass and fitted with high-vacuum stopcocks to prevent leakage of He.

Oxygen concentration was below the analytical detection of our $O_2$ meter (< 3 volume percent) in gases discharged from the offshore seeps (Fig. 3). These measurements were verified by the total gas analyses (below).

We also collected water samples from the onshore spring (site GR-1A; Fig. 3) and from the lake at site GR-1C. At each site, we collected four samples. One sample was collected into a 250-ml polyethylene bottle for analysis of anions, alkalinity excluded. Another sample was filtered (with 0.45 µm filters), acidified (to a pH of 2), and stored in a 250-ml polyethylene bottle for cation analysis. A third sample was collected into a 60-ml glass bottle with a Polyseal closure for analysis of δD and $\delta^{18}O$ in water. A fourth sample was collected in a 250-ml glass bottle with a Polyseal closure for analysis of alkalinity and $\delta^{13}C$ in DIC. Equipment failure prevented field measurements of conductivity at The Gas Rocks sites and pH at all sites investigated so these parameters were determined in the laboratory (conductivity, pH of near-neutral waters) or by thermochemical techniques (pH of acidic samples; see below).

**Figure 5**. View of bubbling pool sampled at site UK-2.

In addition, we investigated three gas seeps (sites A-1, UK-1,2; Fig. 4) on the ridge that hosts the Ukinrek Maars. All three seeps vent through spring-fed water (Fig. 5). At these sites, we measured field conductivity, collected bulk-gas-composition samples, and obtained water samples for analyses of anions, cations, $\delta^{13}C$ in DIC, and $\delta D$ and $\delta^{18}O$ in water. At site UK-1, we also filled two evacuated flasks to analyze $\delta^{13}C$ in $CO_2$ and rare-gas isotopes. Field evidence for high $CO_2$ concentrations in these seep gases include below-detection readings on our $O_2$ meter at all three sites and formation of precipitates in the gas collection bottles at two sites. Moreover, at site UK-1, the gas extinguished a match (not tested at other sites) and Beatrice Ritchie experienced a sharp pepper-like burning when the sampling tube discharged a small amount of gas in front of her nose. All three sampling sites (A-1; UK-1,2) and at least one other area (site UK-3) along the ridge exhibit vegetation that has been killed recently (e.g., dying alders and grass) and vegetation that has been dead for some time (Figs. 4 and 6). Also, some alders lost their leaves earlier in the season, and were just budding again in mid-August. At some sites, there are apparently two ages of dead vegetation including large logs that probably represent trees killed during the 1977 eruption and several-cm-diameter twigs that appear too fresh to have died in 1977. Examination of 1983 infrared photos of the Ukinrek area

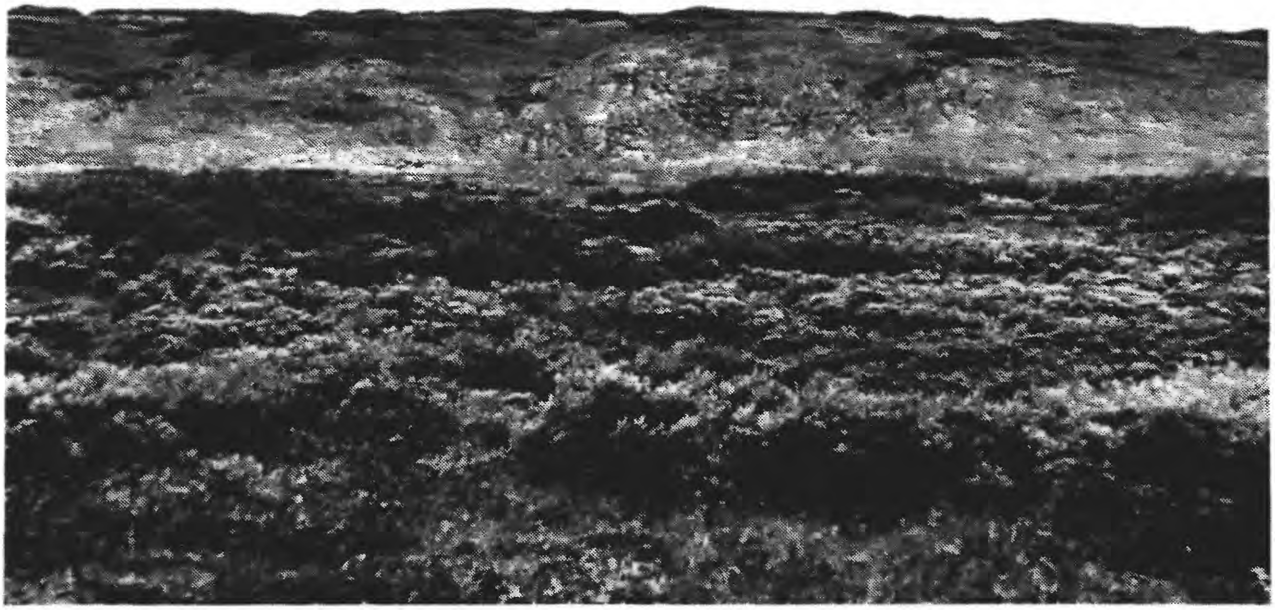

**Figure 6**. Photograph of an area of dead vegetation along the ridge that hosts the Ukinrek Maars.

shows that many of the dead-vegetation areas existed in 1983, which is consistent with the vegetation dying during the 1977 eruption. Thus, we conclude that one set of vegetation was killed in 1977, a second set was killed some years after 1977, and a third set suffered trauma in 1995. We speculate that $CO_2$ is killing the vegetation as has been observed recently at Mammoth Mountain, CA (Farrar et al., 1995). These areas of dead vegetation suggest that there are significant emissions of diffuse $CO_2$ in The Gas Rocks-Ukinrek Maars area. A soil gas survey is highly recommended as a future investigation for this area (see below).

Finally, we measured conductivity and collected water samples from the lake in the East Maar (site EM-1; Fig. 7) and, for background information, a sample of Becharof Lake (site B-1). Again, samples were collected for analyses of anions, cations, $\delta^{13}C$ in DIC, and $\delta D$ and $\delta^{18}O$ in water.

On 4 March 1996 Bill Smoke, the U.S. Fish and Wildlife Service pilot, flew over the area to check for visible thermal anomalies. He noted that the lakes in both the East and West Ukinrek Maars were frozen and, although the area had little snow cover, he saw no sign of any thermal anomalies at any of the above sites.

## ANALYTICAL METHODS

### Gases

The bulk-gas samples were analyzed by Thermochem in Santa Rosa, CA, for $CO_2$, $H_2O$, $N_2$, $O_2$, $CH_4$, Ar, total S ($SO_2$ +

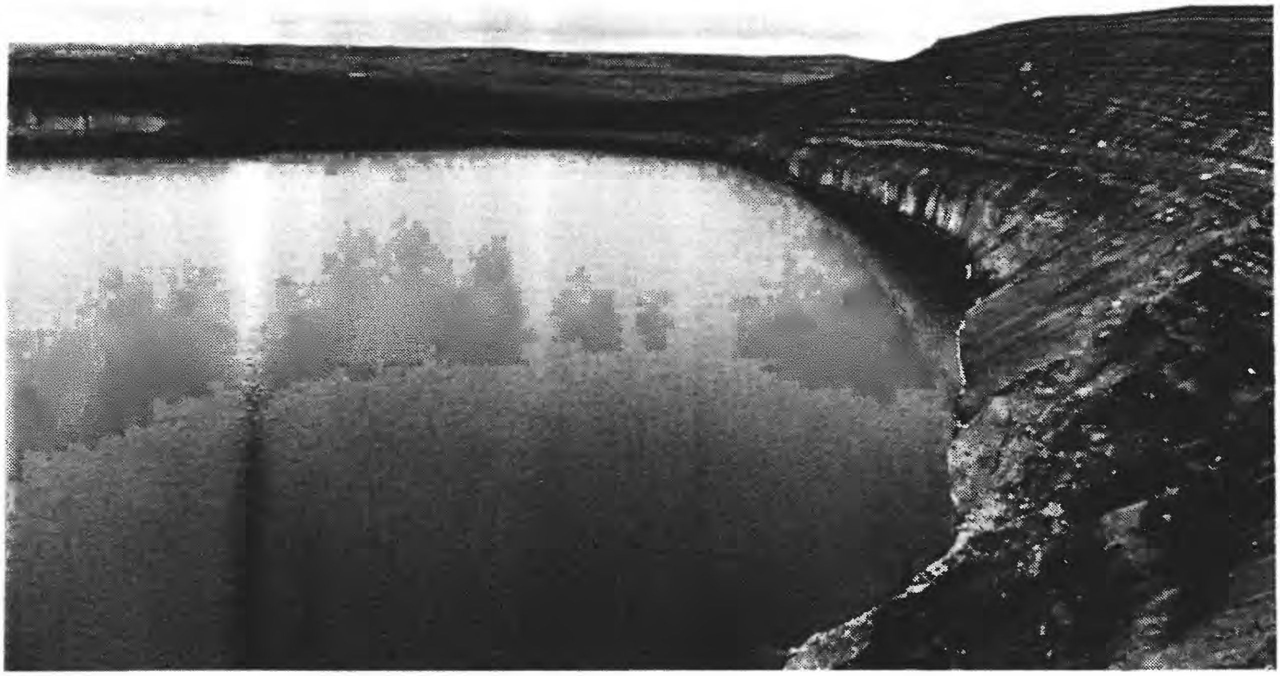

**Figure 7**. View of East Ukinrek Maar looking west. Sampling site EM-1 is located on the lake shore below the low point in the crater rim.

$H_2S$), $H_2$, HCl, HF, and $NH_3$. Before collection, bottles were partly filled with a known volume of 4 N NaOH solution, evacuated to <0.026 bar, and weighed. After collection, the sample bottles were reweighed, and their head space volumes and pressures were measured. Gas chromatography was used to determine the composition of the nearly insoluble (in NaOH solution) headspace gases ($N_2$, $O_2$, $CH_4$, Ar, $H_2$). The composition of the gases dissolved in the NaOH solution ($CO_2$, total S, HCl, HF, $NH_3$) was determined by acidification followed by gas chromatography ($CO_2$), oxidation of all sulfur species to $SO_4^{2-}$ followed by ion chromatography ($SO_4^{2-}$), ion chromatography ($Cl^-$, $F^-$), and, for $NH_3$, by a flow injection analysis where the $NH_3$ diffused across a teflon membrane and the separated stream was passed through a conductivity detector. The amount of $H_2O$ in each sample was determined by subtracting the cumulative weights of non-$H_2O$ species from the total weight gained by the sample bottles during collection.

The helium isotope samples were analyzed by Robert Poreda using methods described elsewhere (Poreda et al., 1992; Poreda and Farley, 1992). The gases in the flasks were extracted on a high vacuum line constructed of stainless steel and Corning-1724 glass. After removal of $H_2O$ vapor and $CO_2$ at - 90°C and -195°C, respectively, the non-condensable gases (He, Ne, Ar, $N_2$, $CH_4$) were concentrated using a Toepler pump in series with a Hg-diffusion pump. The amount of non-condensable gas was measured using a calibrated gas splitter fitted with a capacitance manometer. Gas ratios ($N_2$, Ar, $CH_4$) were analyzed on a Dycor Quadrupole mass spectrometer fitted with a variable leak valve. The results are combined with the capacitance manometer measurement to obtain gas concentrations. Prior to isotope analyses, $N_2$ and $O_2$ were removed by reaction with Zr-Al alloy (SAES-ST707) and Ar and Ne were adsorbed on activated charcoal at 77 K and at 40 K, respectively. Helium isotope ratios and concentrations were then analyzed on a VG 5400 Rare Gas Mass Spectrometer fitted with a Faraday cup and a Johnston electron multiplier. The Mass Spectrometer was also used to measure concentrations of argon, neon, and krypton isotopes. The 2$\sigma$ errors in the $^3He/^4He$ ratios are ±0.3% for the reported helium isotope value.

William Evans purified the carbon isotope samples using liquid nitrogen traps on a high-vacuum line. A Finnigan MAT 251 was used to determine $\delta^{13}C$ in $CO_2$.

### Waters

The anion samples were analyzed by Chemical and Mineralogical Services (CMS) in Salt Lake City, UT, for $Cl^-$, $SO_4^{2-}$, $F^-$, and conductivity. $Cl^-$ and $SO_4^{2-}$ were analyzed using colorimetric methods, and $F^-$ was determined using an ion selective electrode. The pH was also determined by CMS in anion samples from sites B-1 (Becharof Lake) and EM-1 (east Ukinrek Maar ), but degassing of $CO_2$ from the other anion samples prevented accurate determination of the pre-degassing pH. The cation samples were analyzed by CMS for major cations using atomic absorption spectrophotometry; they also analyzed selected samples for trace elements using inductively coupled plasma mass spectroscopy.

Cathy Janik analyzed the carbon isotope samples for alkalinity and prepared these samples to determine $\delta^{13}C$ in DIC. Prior to opening the bottles, the samples were refrigerated to redissolve any degassed $CO_2$. Then, 10 mL of saturated solution of $NH_4OH$ and $SrCl_2$ was added to each sample through a 0.45 µm-pore filter membrane. A precipitate consisting mostly of $SrCO_3$ and $SrSO_4$ was formed. The purity of the precipitate was determined by reacting an aliquot of the precipitate with phosphoric acid in an evacuated flask and measuring manometrically the volume of liberated $CO_2$. The $CO_2$ was then transferred in a vessel to Carol Kendall's laboratory (U.S. Geological Survey, Menlo Park, CA) for mass spectrometric $\delta^{13}C$ analysis using a Finnigan MAT 251. By knowing the mass of precipitate and its purity for each sample, we calculated the alkalinity prior to degassing. Using the methods of Reed and Spycher (1984), we were then able to calculate the pre-degassing pH of the degassed samples.

The water isotope samples were submitted to Tyler Coplen's laboratory (U.S. Geological Survey, Reston, VA) to determine $\delta D$ and $\delta^{18}O$ in water.

## RESULTS

### Chemical and Isotopic Compositions of Gases

#### Bulk composition

Table 3 lists the chemical analyses of the bulk-gas samples collected in 1995 from The Gas Rocks and Ukinrek Maars areas. For each sample, we report the composition of the dry gas and $X_g$, which is the mole fraction of dry gas to dry gas + $H_2O$ in the bulk sample. The $X_g$ values have large uncertainties because of the associated errors of calculating the apparent $H_2O$ concentrations from small differences (< 0.9 g) between the weight gains of the samples and the weights of non-$H_2O$ species. Reported dry-gas species include $CO_2$, $N_2$, $O_2$, Ar, $CH_4$, total S, HCl, HF, $H_2$, and $NH_3$.

The dry gas compositions contain 89.5 - 99.5% $CO_2$, 1.0 - 7.9% $N_2$, 0.2 - 2.5% $O_2$, 0.008 - 0.11% Ar, and, for the Ukinrek-Maars-ridge samples, 0.3 - 2.1% $CH_4$. Total S, HCl, HF, $H_2$, and $NH_3$ are below detection in all samples. The compositions of the 1995 samples from The Gas Rocks sites GR-1B and GR-1C (Table 3) are very similar to the 1977 samples

**Table 3.** Chemical compositions of gases in The Gas Rocks and Ukinrek Maars areas.

| Field numbers: | 950803-1 | 950803-(3-4) | 950803-9 | 950804-1 | 950805-1 | 950807-(6-7) |
|---|---|---|---|---|---|---|
| Map site: | GR-1B | GR-1B | GR-1C | A-1 | UK-2 | UK-1 |
| Location: | small offshore gas seep at The Gas Rocks | small offshore gas seep at The Gas Rocks | Becharof Lake near largest gas vent | spring on Ukinrek Maars Ridge | bubbling pool on Ukinrek Maars Ridge | spring-fed stream on Ukinrek Maars ridge |
| Date: | August 3, 1995 | August 3, 1995 | August 3, 1995 | August 4, 1995 | August 5, 1995 | August 7, 1995 |
| Site temperature and Xg | | | | | | |
| T°C | 10.1 | 10.1 | 10.1 | 10.2 | 12.3 | 7.5 |
| Xg | 0.68 | 0.72 | 0.66 | 0.57 | 0.59 | 0.60 |
| Chemical Species of Dry Gas (mol%) | | | | | | |
| $CO_2$ | 98.5 | 99.5 | 89.5 | 90.5 | 94.9 | 95.9 |
| $N_2$ | 0.992 | 0.356 | 7.86 | 6.58 | 3.67 | 2.91 |
| $O_2$ | 0.534 | 0.171 | 2.50 | 0.719 | 0.785 | 0.901 |
| Ar | 0.0235 | 0.00782 | 0.110 | 0.0492 | 0.0421 | 0.044 |
| $CH_4$ | $<1.1x10^{-3}$ | $<7.3x10^{-4}$ | $<4.0x10^{-3}$ | 2.12 | 0.598 | 0.265 |
| $S_{Total}$ | <0.054 | <0.028 | <0.053 | <0.074 | <0.087 | <0.086 |
| HCl | <0.044 | <0.023 | <0.044 | <0.064 | <0.069 | <0.070 |
| HF | <0.021 | <0.011 | <0.021 | <0.030 | <0.032 | <0.033 |
| $H_2$ | $<2.7x10^{-3}$ | $<1.7x10^{-3}$ | $<9.6x10^{-3}$ | $<3.7x10^{-3}$ | $<4.4x10^{-3}$ | $<4.6x0^{-3}$ |
| $NH_3$ | $<1.6x10^{-3}$ | $<8.5x10^{-4}$ | $<1.6x10^{-3}$ | $<2.3x10^{-3}$ | $<2.5x10^{-3}$ | $<2.4x10^{-3}$ |
| Selected ratios | | | | | | |
| $N_2/Ar$ | 42 | 46 | 71 | 134 | 87 | 66 |
| $N_2/(O_2+Ar)$ | 1.8 | 2.0 | 3.0 | 8.6 | 4.4 | 3.1 |
| Carbon Isotope Composition | | | | | | |
| $\delta^{13}C$ | --- | -6.50 | --- | --- | --- | -6.38 |

Xg is mol fraction of total dry gas in total dry gas + $H_2O$; $S_{Total}$ = $H_2S$ + $SO_2$ + any other sulfur species.

from The Gas Rocks (Table 1). This suggests that there has been little change in discharged gas composition from The Gas Rocks area over this 18-year timespan. However, the flux of $CO_2$ from The Gas Rocks area has apparently decreased since 1977 as indicated by post-1977 aerial observations by Tom Miller (personal communication, 1996) and the decrease in the number of onshore springs and their degassing rate.

Ratios of $N_2/Ar$ versus $N_2/(O_2+Ar)$ show that most of the 1995 gas samples lie on a mixing line between air-saturated water (ASW) and air (Fig. 8). This indicates that $N_2$, $O_2$, and Ar in most samples derive from ASW and air, both of which are meteoric in origin. But the trend towards $N_2/Ar$ ratios greater than air in UK-2, UK-1 (in the He isotope sample; Table 4), and especially A-1 indicates that the samples collected on the Ukinrek Maars ridge contain some non-atmospheric $N_2$. These same samples also contain minor amounts (0.3 - 2%) of $CH_4$. After accounting for the near-surface $N_2$, $O_2$, and Ar in the samples, we infer that the gases emanating from below the water table in The Gas Rocks and Ukinrek Maars area are virtually 100% $CO_2$, except for the small amounts of non-atmospheric $N_2$ and $CH_4$ in the Ukinrek Maars samples.

To explain the non-atmospheric $N_2$ and $CH_4$ in the Ukinrek Maars ridge samples we consider four possible sources:

(1) Rotting of vegetation in the swampy ground around the vents. This seems an unlikely source for the excess $N_2$ and $CH_4$ because there is only a thin layer (<1 meter) of organic debris in the swampy ground around the Ukinrek Maars ridge seeps. Also, swamp gases should contain some $H_2S$, but $H_2S$ is below detection (<0.09%) in the Ukinrek Maars samples (Table 3).

(2) They are magmatic along with the $CO_2$. As indicated below the $CO_2$ probably comes from a mantle-derived magma. However, the magma may also contain volatiles derived from the subducted slab. Thermal decomposition of subducted organic material is commonly invoked to explain the

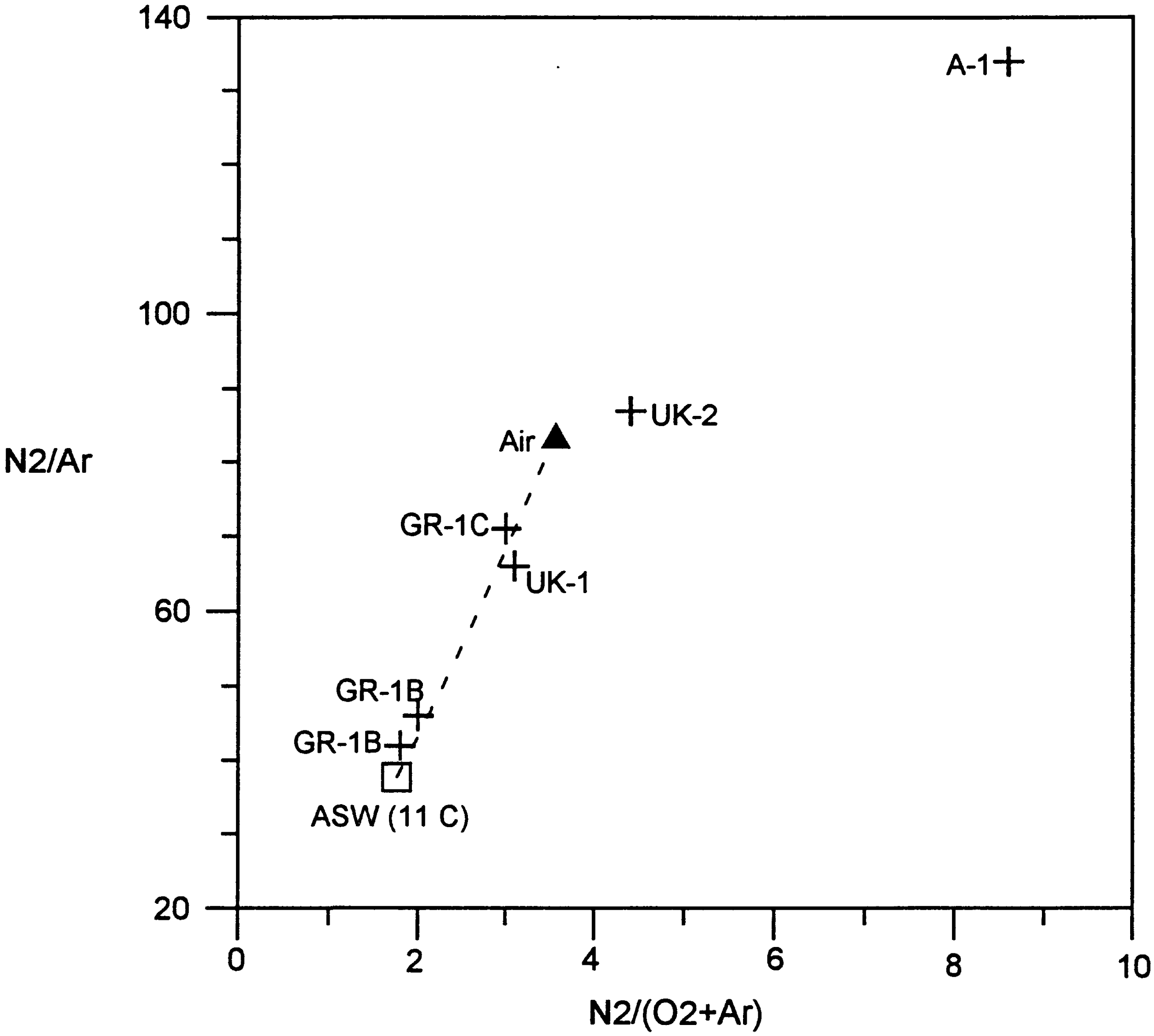

**Figure 8**. Plot of $N_2/Ar$ versus $N_2/(O_2 + Ar)$ for the bulk gas samples from The Gas Rocks and Ukinrek Maars. All data from Table 3.

elevated $N_2$ (e.g., $N_2/Ar > 84$) in gases from convergent plate volcanoes (Matsuo et al., 1978; Giggenbach and Gougel, 1989). However, the subducted slab is an implausible source for the elevated $CH_4$ in the Ukinrek Maars gases because magmatic gases from convergent-plate volcanoes generally do not contain much $CH_4$ (Symonds et al., 1994). It is possible that magmatic $CO_2$ reacts with $H_2O$ to produce $CH_4$ in the following reaction:

$$CO_2 + 2H_2O = CH_4 + 2O_2, \qquad (1)$$

which is driven to the right at low temperature (<200°C), moderate pressure (≥ 100 bars), and under reducing conditions. But such $CH_4$-producing reactions are generally much slower than the timeframe of volcanic degassing (Giggenbach, 1987). Another pitfall of the idea that $N_2$ and $CH_4$ are magmatic is that, assuming that The Gas Rocks and Ukinrek Maars gases come from the same magmatic source, this idea fails to account for the much lower concentrations of $N_2$ and $CH_4$ in The Gas Rocks gases.

**Table 4.** Dry-gas and rare-gas compositions of rare-gas isotope samples from The Gas Rocks and Ukinrek Maars areas.

| Field number: | Poreda and Craig (1989); Motyka et al. (1993) | 950803-2 | 950807-8 |
|---|---|---|---|
| Map site: | GR-1A | GR-1B | UK-1 |
| Location: | The Gas Rocks spring | small offshore gas seep at The Gas Rocks | spring-fed steam on Ukinrek Maar ridge |
| Date: | July 21, 1981 | August 3, 1995 | August 7, 1995 |
| T°C | 39 | 10.1 | 7.5 |
| | | Bulk composition (mol%) | |
| $CO_2 + H_2S$† | 99.99 | 99.96 | 99.78 |
| $N_2$ | 0.0114 | 0.034 | 0.187 |
| $CH_4$ | 0.00045 | 0.00053 | 0.0282 |
| $O_2$ | 0.0026 | 0.00053 | 0.00055 |
| | | Rare gases (ppbv) | |
| $^{40}Ar$ | 2600 | 11200 | 18400 |
| $^{4}He$ | 1000 | 72 | 11990 |
| $^{36}Ar$ | --- | 36.9 | 51.9 |
| Ne | --- | 8.1 | 6.7 |
| $^{84}Kr$ | --- | 2.48 | 1.02 |
| | | Rare gas ratios | |
| $^{3}He/^{4}He$ $(R/R_A)$ | 6.91 | 6.42 | 6.55 |
| $\frac{He/Ne}{(He/Ne)_A}$ | 114 | 31 | 6224 |
| $^{3}He/^{4}He$ $(R_C/R_A)$ | 6.95 | 6.61 | 6.55 |
| $Ne/^{36}Ar$ | --- | 0.22 | 0.13 |
| $N_2/Ar$ | 44 | 30 | 101 |
| $N_2/(O_2+Ar)$ | 4.0 | 21 | 78 |
| He/Ne | --- | 9 | 1792 |
| $^{40}Ar/^{36}Ar$ | --- | 304 | 355 |
| $^{4}He/^{40}Ar$ | --- | 0.21 | 3.84 |

†Represents the portion of the anydrous gas ($CO_2 + H_2S$) that was condensed at -195°C during the analysis. Mostly consists of $CO_2 + H_2S$.

(3) They come from a subsurface hydrocarbon reservoir. We consider this possible because sedimentary gases in the vicinity of Becharof Lake contain minor amounts (5-20%) of $N_2$ and $CH_4$ along with 70-80% $CO_2$ (Bureau of Mines, 1976).

(4) Thermal breakdown of organic residue in the sedimentary sequence beneath the Ukinrek Maars. Magma emplaced most likely before or during the 1977 eruption could heat the surrounding sedimentary rocks. Thermal decomposition of these sedimentary rocks would probably produce a gas dominated by $H_2O$, $CO_2$, $CH_4$, and $N_2$, the latter demonstrated experimentally by Matsuo et al. (1978). Heating of sedimentary rocks might also produce $NH_3$, but this is probably scrubbed by groundwater en route to the surface. Assuming that $H_2O$ is also scrubbed by groundwater, mixing of a small fraction of the resulting $CO_2$-$CH_4$-$N_2$ gases with magmatic-meteoric gases (e.g. similar to those discharged from The Gas Rocks) can explain the composition of the Ukinrek Maars gases. We prefer this explanation because it links $CO_2$, $N_2$, and $CH_4$ to the underlying magma and its thermally heated country rock. One potential pitfall, however, is that mixing between magmatic and sedimentary-derived $CO_2$ is not substantiated by the $\delta^{13}C$ in $CO_2$ or $\delta^{13}C$ in DIC data for the Ukinrek Maars sites with the exception of the $\delta^{13}C$ in DIC

for the UK-1 site (see below). However, this is a potential problem with the other proposed sedimentary sources of $N_2$ and $CH_4$, all of which should produce isotopically light $CO_2$ (e.g., $\delta^{13}C < -20$).

### Carbon isotopes

Table 3 also reports the $\delta^{13}C$ values for $CO_2$ in the carbon isotope samples collected from sites GR-1B (-6.50) and UK-1 (-6.38). These values are virtually identical with the 1977 results (-6.36; Table 1) indicating that the source of the $CO_2$ emissions at The Gas Rocks and Ukinrek Maars has not changed over this 18-year period. Potential sources for this $CO_2$ include thermal decomposition of limestone or organic material from underlying sedimentary rocks, the atmosphere, or the mantle (or mantle-derived magma). Thermal breakdown of limestone or organic material seems implausible because $\delta^{13}C$ values for nearby limestone (+3.86°/₀₀; Barnes and McCoy, 1979) or for biogenic material ($\delta^{13}C$ = -24 to -34°/₀₀ for most terrestrial plants; Smith and Epstein, 1971) are much higher and lower, respectively, than the observed $\delta^{13}C$ values. The observed $\delta^{13}C$ values are identical to the -6 to -7 °/₀₀ values for atmospheric $CO_2$ (Anderson and Arthur, 1983), but the atmosphere seems an unlikely source because it requires provoking a mechanism to concentrate $CO_2$ from ~0.0360% in the atmosphere to over 99% in the discharged gases. Instead, we concur with Barnes and McCoy (1979) that $CO_2$ from The Gas Rocks and Ukinrek Maars derives from the mantle because observed $\delta^{13}C$ values are within the range (-5 to -8) for mantle-derived $CO_2$ (Allard, 1983; Taylor, 1986). Furthermore, a mantle source is consistent with the geochemical arguments for mantle-derived magmas erupted from the Ukinrek Maars (Kienle et al., 1980).

### Rare-gas isotopes

Analytical results for the rare-gas isotope samples are reported in Table 4. For each sample, we report the bulk composition ($CO_2 + H_2S$, $N_2$, $CH_4$, $O_2$), the concentrations of rare-gas isotopes ($^{40}Ar$, $^{4}He$, $^{36}Ar$, Ne, $^{84}Kr$), and selected rare-gas ratios ($^{3}He/^{4}He$, $Ne/^{36}Ar$, $N_2/Ar$, He/Ne, $^{40}Ar/^{36}Ar$, $^{4}He/^{40}Ar$). All $^{3}He/^{4}He$ ratios are reported as $R/R_A$ values where R is the ratio in the sample and $R_A$ is the atmospheric ratio, using air helium as the absolute standard. We also report $^{3}He/^{4}He$ ratios corrected for atmospheric contamination ($R_C/R_A$ values), using the equation after Craig et al. (1978a,b):

$$R_C = \frac{RN - R_A N_A}{N - N_A}, \qquad (2)$$

where R is $^{3}He/^{4}He$, N is He/Ne, and subscript "A" denotes atmospheric ratios.

The $^{3}He/^{4}He$ ($R_C/R_A$) values for the 1995 samples collected from The Gas Rocks (site GR-1B; 6.61) and the Ukinrek Maars ridge (site UK-1; 6.55) are virtually identical, indicating that the He in gas discharges from both sites comes from a similar source. Assuming that the mantle has a $^{3}He/^{4}He$ ratio of 8 and the crust, rich in radiogenic $^{4}He$, has a ratio of 0.02 (e.g., Poreda and Craig, 1989), the 1995 samples contain 82-83% mantle He. Table 4 shows that the 1981 sample from The Gas Rocks (site GR-1A) has a slightly higher $^{3}He/^{4}He$ of 6.95, implying an 87% mantle He component. The 4-5% decrease in mantle He at The Gas Rocks between 1981 and 1995 implies that the $^{3}He$ flux from the source magma has decreased since 1981.

## Chemical and Isotopic Compositions of Waters

### Bulk composition

Analyses of the water samples collected in 1995 from The Gas Rocks and Ukinrek Maars area are reported in Table 5. Data are given for the site temperature, calculated (or laboratory determined) pH (see above), conductivity, major and minor anions and cations, $\delta D$ and $\delta^{18}O$ in $H_2O$, and $\delta^{13}C$ in DIC. Table 6 reports trace element analyses of samples collected from The Gas Rocks spring (site GR-1A) and the East Ukinrek Maar Lake (site EM-1). For comparison, Table 7 reports previous (1977, 1980, 1981, 1994) chemical and isotopic analyses of waters from several sites

**Table 5** - Chemical and isotopic compositions of waters in The Gas Rocks and Ukinrek Maars areas.

| Field numbers†: | 950803-(5-8) | 950803-(10-13) | 950804-(2-6) | 950807-(1-5) | 950805-(2-5) | 950807-(9-13) | 950808-(1-4) |
|---|---|---|---|---|---|---|---|
| Map site: | GR-1A | GR-1C | A-1 | UK-1 | UK-2 | EM-1 | B-1 |
| Location: | The Gas Rocks spring | Becharof Lake near largest gas vent | spring on Ukinrek Maars Ridge | spring-fed stream on Ukinrek Maars Ridge | bubbling pool on Ukinrek Maars Ridge | Lake, east Ukinrek Maar | Becharof Lake |
| Date: | August 3, 1995 | August 3, 1995 | August 4, 1995 | August 7, 1995 | August 5, 1995 | August 7, 1995 | August 8, 1995 |
| | | | | Conditions | | | |
| T (°C) | 16.3 | 10.1 | 10.2 | 7.5 | 12.3 | 12.5 | 9.5 |
| pH‡ | 5.22 | 5.58 | 5.29 | 5.72 | 5.72 | 7.45⁺ | 6.45⁺ |
| field cond. (µS) | ND | ND | 255 | 144 | 560 | 791 | 106 |
| lab cond. (µS) | 7320 | 215 | 211 | 132 | 528 | 715 | 95 |
| | | | | Chemical Species (mg/l) | | | |
| Na | 650 | 40 | 3.2 | 5.7 | 12 | 39 | 3.5 |
| K | 49 | 1.7 | 2.3 | 1.7 | 3.8 | 3.2 | 0.9 |
| Li | 2.9 | 0.08 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 |
| Ca | 400 | 11 | 25 | 12 | 63 | 82 | 9.6 |
| Mg | 203 | 4.3 | 9.6 | 3.6 | 28 | 19 | 2.3 |
| Fe | 48 | 0.14 | 0.87 | 0.12 | 0.08 | 0.06 | 0.05 |
| Mn | 3.3 | 0.05 | 0.36 | 0.11 | 0.09 | 0.03 | 0.06 |
| Al | 0.3 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Cl | 2300 | 55 | <5 | <5 | <5 | 88 | 22 |
| $SO_4$ | 18 | 15 | 11 | 10 | <10 | 75 | <10 |
| DIC• | 1880 | 320 | 1420 | 295 | 1730 | 135 | 24 |
| $NH_4$ (as N) | 2.6 | ND | 0.15 | 0.05 | <0.05 | <0.05 | <0.05 |
| $SiO_2$ | 120 | 12 | 64 | 40 | 48 | 34 | 1.3 |
| B | 23 | 1 | 0.3 | 0.2 | 0.3 | 0.8 | 0.2 |
| | | | | hydrogen and oxygen isotope composition (°/₀₀ relative to SMOW) | | | |
| δD | -80.7 | -81.1 | -91.6 | -91.8 | -83.6 | -82.4 | ND |
| $\delta^{18}O$ | -10.79 | -10.69 | -12.19 | -12.36 | -11.14 | -10.82 | ND |
| | | | | carbon isotope composition of DIC (°/₀₀ relative to PDB) | | | |
| $\delta^{13}C$ | -3.6 | -6.9 | -6.7 | -8.0 | -5.1 | -9.2 | -3.2 |

†Several sub-samples were collected from each site to complete the requisite analyses.

‡pH determined numerically at the collection temperature using program CHILLER (Reed, 1982)

⁺pH determined by electrode in the laboratory at 20°C

•dissolved inorganic carbon (DIC) reported as $HCO_3$

ND =not determined

Species below detection in all samples include $H_2S$ (< 0.01) and F (< 0.2).

**Table 6.** Trace element analyses of waters from The Gas Rocks and Ukinrek Maars areas.

| Field number: | 950803-7 | 950807-10 |
|---|---|---|
| Map site: | GR-1A | EM-1 |
| Location: | The Gas Rocks spring | East Ukinrek Maar lake |
| Date: | August 3, 1995 | August 7, 1995 |
| | Element (µg/l) | |
| V | 3 | 15 |
| Cr | 9 | 4 |
| Co | 35 | <1 |
| Ni | 32 | 4 |
| Cu | 30 | 2 |
| Zn | 70 | 5 |
| As | 2876 | 62 |
| Se | <5 | 13 |
| Br | 19050 | 929 |
| Rb | 215 | 5 |
| Sr | 9376 | 270 |
| Zr | 2 | 2 |
| Mo | 2 | 2 |
| Cd | 2 | <1 |
| Te | <1 | 1 |
| I | 293 | 27 |
| Cs | 42 | <1 |
| Ba | 414 | 25 |
| Ce | 3 | <1 |
| Sm | 1 | <1 |
| Hf | 2 | 3 |
| W | 1 | <1 |
| Au | 1 | 1 |
| Tl | 1 | <1 |
| Pb | 1 | <1 |
| Bi | <1 | 1 |

Elements below detection in all samples include Ti (<1), Ag (<1), Sn (<1), Sb (<1), La (<1), Pr (<1), Nd (<1), Eu (<1), Gd (<1), Dy (<1), Er (<1), Yb (<1), Re (<1), and Hg (<1).

in The Gas Rocks and Ukinrek Maars area.

The waters in the vicinity of The Gas Rocks and Ukinrek Maars can be classified as gas-fed waters, waters containing a brine component, and dilute meteoric waters (Fig. 9). The gas-fed waters are dominated by DIC (mostly $H_2CO_3$ but reported as $HCO_3$ in Fig. 9 and Tables 5, 7) obtained from the $CO_2$-rich gases that discharge through them. These include waters collected in the proximity of the gas vents in Becharof Lake and waters from the cold gas seeps on Ukinrek Maars ridge. In contrast, waters from The Gas Rocks spring and the West Ukinrek Maar pool contain a major NaCl brine component. Other constituents in this brine include (in decreasing abundance in the GR-1A sample) DIC, Ca, Mg, K, B, $SO_4$, $SiO_2$, Fe, Br, Li, Sr, As, $NH_4$, Ba, and I (Tables 5-7).

Although not all the gas seeps discharge saline waters, the saline springs always discharge gas. It seems likely that the acending $CO_2$-rich gas plays a role in transporting the saline waters to the surface. Model equilibrium calculations show that the 1995 GR-1A sample is close to saturation with respect to $CO_2$ gas. Although some past samples (Table 7) of saline waters from The Gas Rocks area are undersaturated with respect to $CO_2$, we think it likely that this probably reflects improper determination of DIC rather than true undersaturation of $CO_2$. Therefore, we suggest that gas rising through the subsurface brine reservoir saturates the brine with gas, which decreases its density and enables the brine to ascend to the surface.

The most saline water sample was collected in 1977 from The Gas Rocks spring. This sample has similar salinities and elemental ratios to sedimentary formation waters (e.g., oil-field brines; Fig. 10; White et al., 1963). But compared to seawater, the 1977 sample has 1.5 times the salinity, lower Mg/Ca and $SO_4$/Cl ratios, and higher Li/Na, I/Cl, and B/Cl ratios (Fig. 10). However, simple heating of seawater to 300°C lowers Mg/Ca and $SO_4$/Cl due to precipitation of anhydrite ($CaSO_4$) and magnesium oxysulfate (Bischoff and Seyfried, 1978). So the brine could represent concentrated seawater that has reacted with underlying sedimentary rocks at some elevated temperature, assuming that this process could also account for the elevated salinity, Li/Na, I/Cl, and B/Cl of the brine. The brine also could have formed by reaction of meteoric water with the underlying sedimentary rocks (see below). Regardless of the ultimate source of the water, the above observations support the conclusions of Barnes and McCoy (1979) that the brine equilibrated with the underlying Mesozoic marine sedimentary rocks.

Between 1977 and 1995, the temperature and brine component in the hottest Gas Rocks spring have decreased dramatically (Tables 5,7) along with the num

**Table 7.** Chemical and isotopic compositions of waters collected in 1977, 1980, 1981, and 1994 from The Gas Rocks and Ukinrek Maars areas.

| Reference: | Barnes and McCoy (1979) | Motyka et al. (1993) | Barnes and McCoy (1979) | Barnes and McCoy (1979) | Motyka et al. (1993) | C. Neal and M. Thompson (pers. comm. 1996) | Barnes and McCoy (1979) |
|---|---|---|---|---|---|---|---|
| Map site: | GR-1A | GR-1A | GR-1C | --- | --- | EM-1 | --- |
| Location: | Gas Rocks spring | Gas Rocks spring | Becharof Lake near largest gas vent | Pool, west Ukinrek Maar | Pool, west Ukinrek Maar | Lake, east Ukinrek Maar | Becharof Lake |
| Date: | August 25, 1977 | August 17, 1981 | August 25, 1977 | August 24, 1977 | August 24, 1980 | August 6, 1994 | April 20, 1977 |
| | | | Conditions | | | | |
| T (°C) | 52.8 | 39 | 9.3 | 80.9 | 16 | 14.7 | ND |
| field pH | 5.9 | 5.7 | 4.4 | 6.3 | 9.0 | 6.9$^{\dagger}$ | 6.9$^{\dagger}$ |
| | | | Chemical Species (mg/l) | | | | |
| Na | 17700 | 13900 | 7.1 | 3600 | 190 | 39 | 4.9 |
| K | 450 | 410 | 0.5 | 400 | 11 | 4.6 | 0.47 |
| Li | 44 | 42 | <0.01 | 2.5 | 0.01 | 0.012 | ND |
| Ca | 1500 | 1430 | 7.2 | 380 | 30 | 91 | 6.2 |
| Mg | 460 | 420 | 1.6 | 7.6 | 6.9 | 15 | 1.2 |
| Fe | ND | 19 | ND | 0.13 | 0.07 | 0.13 | ND |
| Al | ND | ND | ND | ND | ND | ND | ND |
| Cl | 32000 | 26100 | 10 | 6300 | 210 | 103 | 6 |
| F | 0.13 | 0.1 | <0.1 | 0.72 | 0.6 | 0.54 | <0.1 |
| $SO_4$ | 140 | 134 | 13 | 370 | 100 | 96 | 6 |
| $H_2S$ | 1.7 | ND | <0.1 | 1.2 | ND | ND | ND |
| field $HCO_3$ | 1240 | 72 | 19 | 28 | 199 | 124$^{\dagger}$ | 16$^{\dagger}$ |
| $NH_4$ (as N) | 13 | ND | <0.05 | 13 | ND | ND | <0.1 |
| $SiO_2$ | 120 | 110 | 2 | 275 | 29 | 22 | 1 |
| B | 360 | 3.4 | <0.1 | 33 | 1.8 | 0.13 | 0.1 |
| | | | Trace elements (µg/l) | | | | |
| Br | 92000 | ND | ND | ND | ND | ND | ND |
| Rb | 2100 | ND | <20 | 550 | ND | ND | ND |
| Sr | ND | 87000 | ND | ND | 0.10 | ND | ND |
| I | 5000 | 2600 | ND | 1000 | ND | ND | ND |
| Cs | 3600 | ND | <100 | 100 | ND | ND | ND |
| | | | hydrogen and oxygen isotope composition (°/₀₀ relative to SMOW) | | | | |
| δD | -37.9 | -41 | -79.5 | -87.6 | -53 | ND | ND |
| $\delta^{18}O$ | +0.42 | -2.6 | -10.5 | -6.31 | -5.9 | ND | ND |

ND =not determined

$^{\dagger}$measured in lab at 20°C

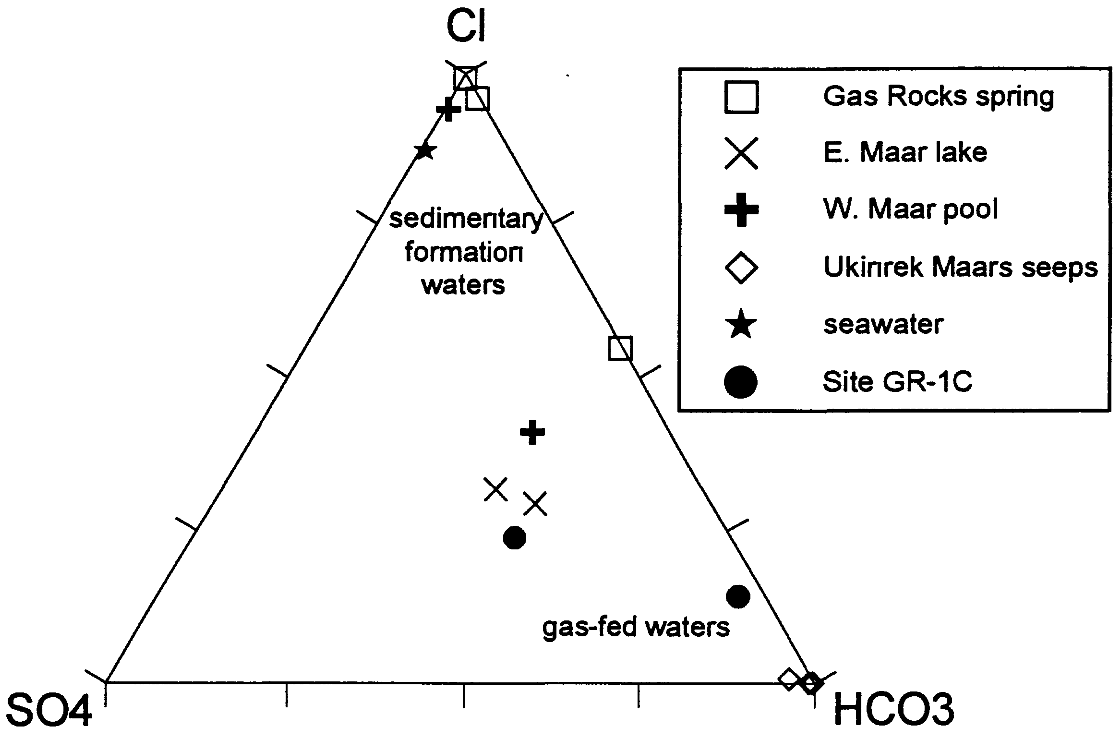

**Figure 9.** Ternary diagram of Cl, $SO_4$, and $HCO_3$ for selected waters from The Gas Rocks and Ukinrek Maars area. Data from Tables 5 and 7.

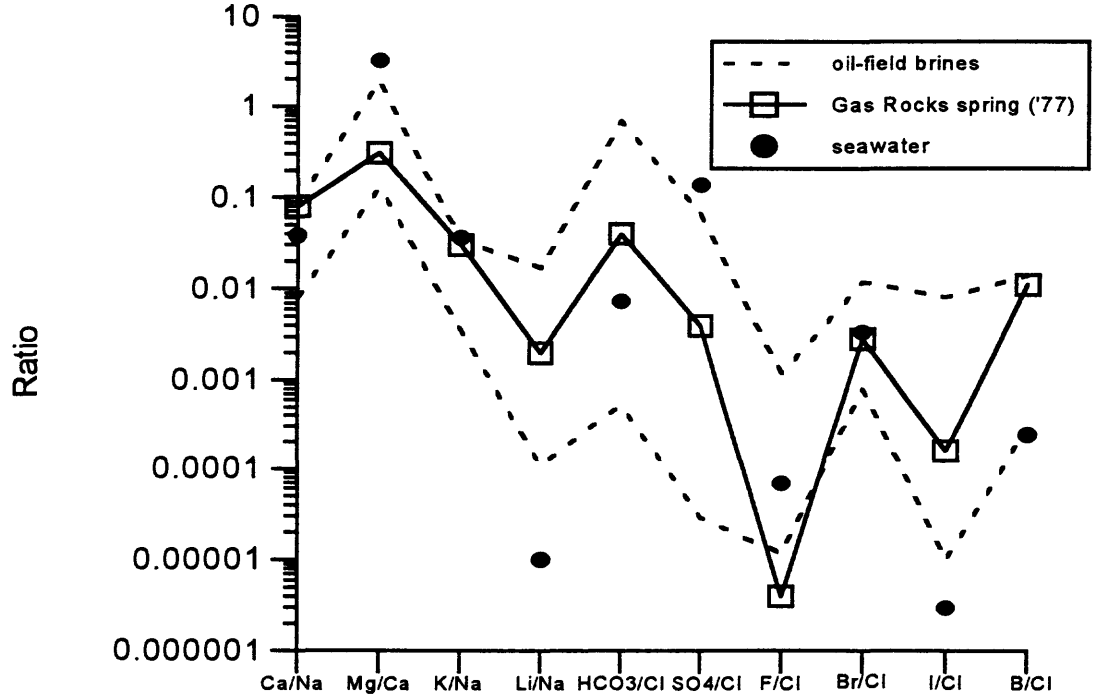

**Figure 10.** Plot showing selected elemental ratios for the 1977 Gas Rock spring waters (Table 7). For comparison, we plot seawater and the range of oil-field brines from White et al. (1963).

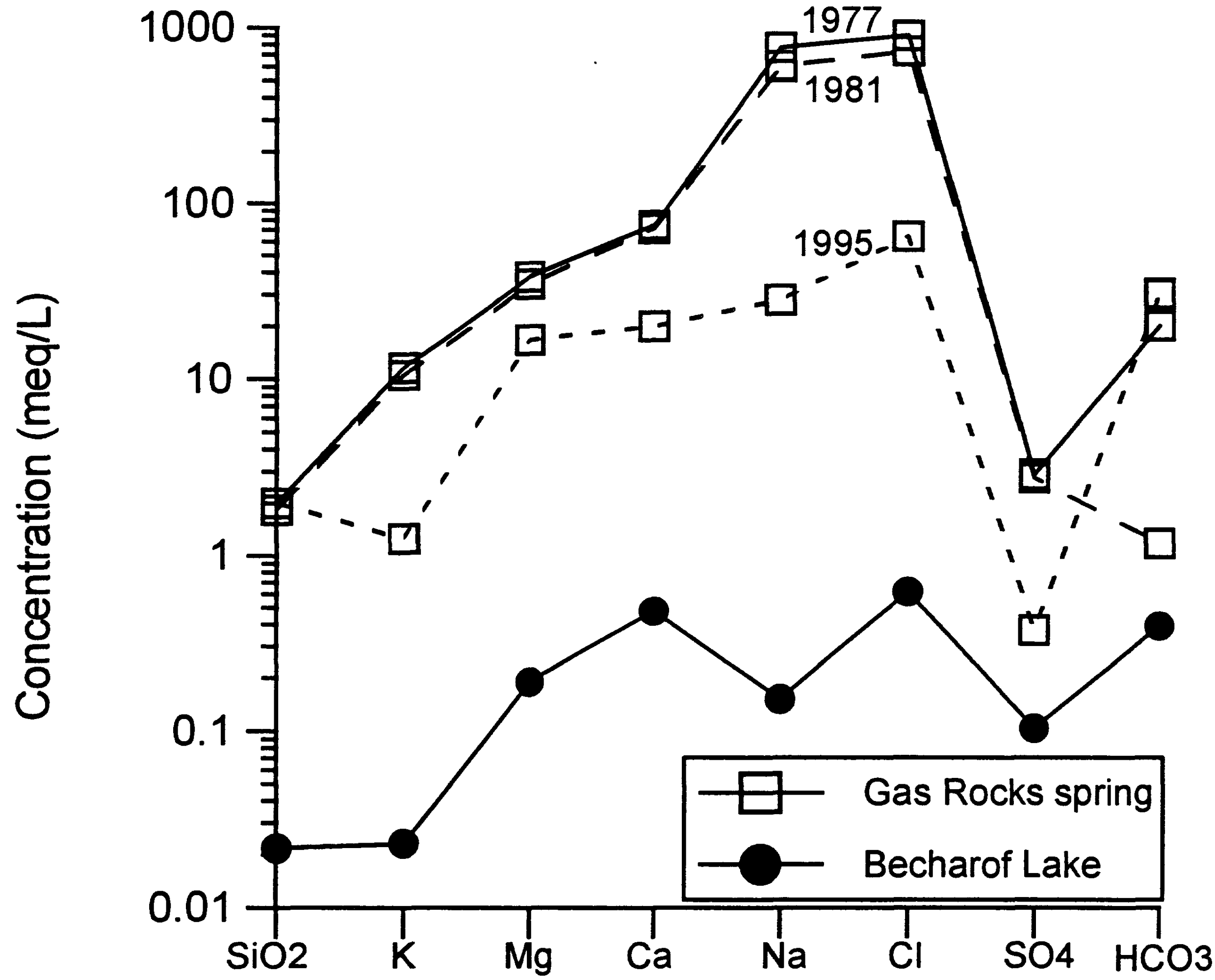

**Figure 11.** Modified Schoeller plot of major constituent concentrations for The Gas Rocks spring waters in 1977, 1981, and 1995. For comparison, we plot the 1995 water sample from Becharof Lake (Table 5). All ionic species are in meq/L and $SiO_2$ is in mmol/L.

ber of onshore springs. Figure 11 shows the decreasing concentrations of the major components (Cl, Na, Ca, Mg, K, $SO_4$) in the brine over this timespan. These decreases reflect dilution of the brine by meteoric water. We suggest that the declining gas flux at The Gas Rocks has caused a corresponding decrease in the rate that the brine ascends to the surface.

**Hydrogen and oxygen isotopes**

Figure 12 shows the $\delta D$ and $\delta^{18}O$ compositions of water samples from The Gas Rocks and Ukinrek Maars area. The samples from the 1995 cold gas seeps, the 1995 Gas Rocks spring, and the 1995 East Maar lake are dominated by local meteoric waters. In contrast, the 1977 and 1981 samples from the hottest Gas Rocks spring are greatly enriched in deuterium and $^{18}O$ relative to local meteoric water, which reflects the isotopic signature of the large brine component in these samples. The 1977 Gas Rocks sample displays the highest enrichments in deuterium and $^{18}O$, and the largest "chemical" brine component (Table 7). The 1980 sample from the West Maar pool is also enriched in deuterium and $^{18}O$, but this may reflect evaporative enrichment rather than a brine signature because this dilute sample has a low Cl concentration (210 ppm; Table 7). Finally,

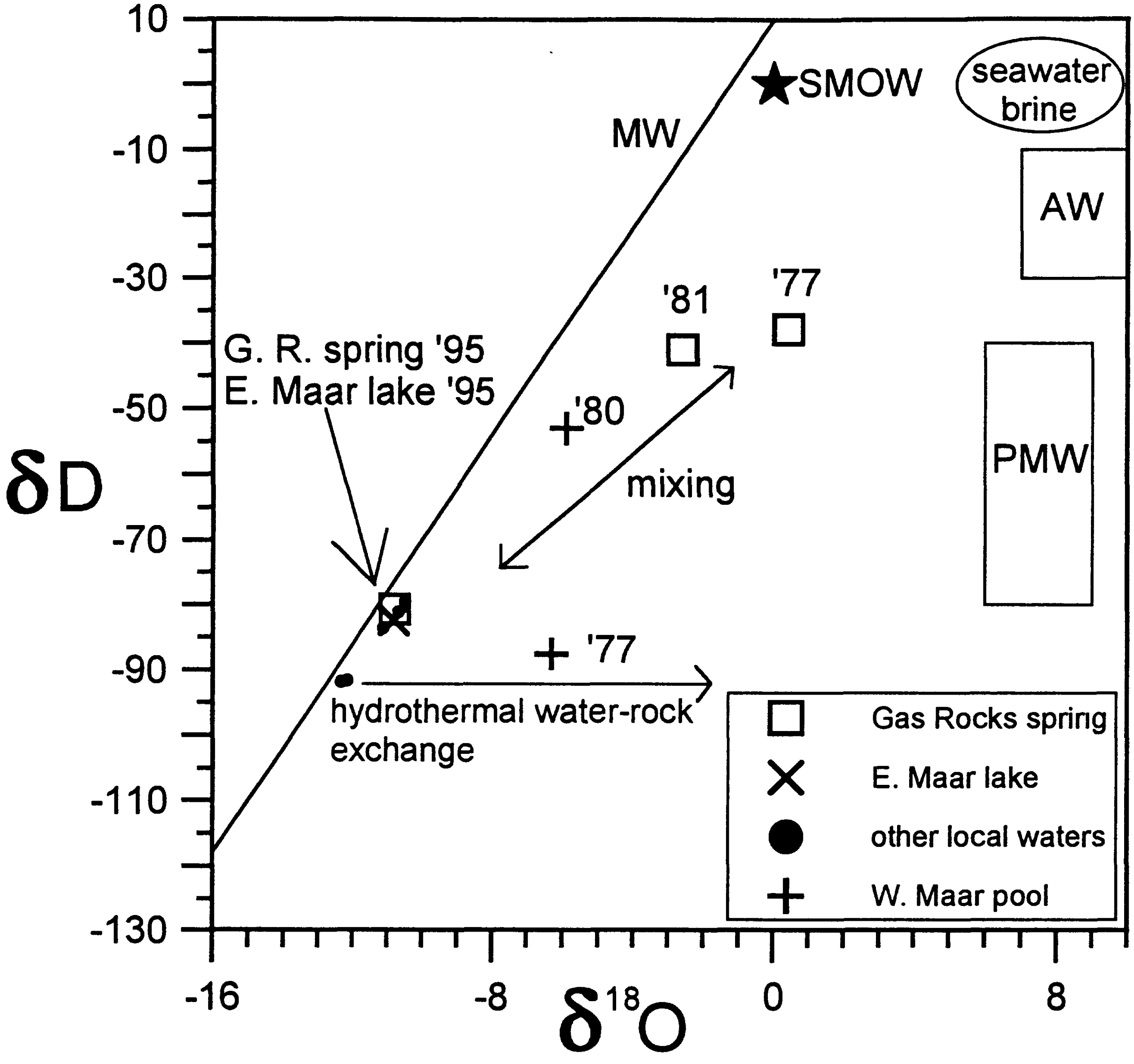

**Figure 12.** Plot of δD versus $\delta^{18}O$ for waters collected in the vicinity of The Gas Rocks and Ukinrek Maars. All data are from Tables 5 and 7 in °/₀₀ relative to Standard Mean Ocean Water (SMOW; Craig, 1961a). Shown for reference are SMOW, the meteoric water line (MW) of Craig (1961b), the field of primary magmatic water (PMW; Sheppard et al., 1969), and the field for andesitic water (AW; Giggenbach, 1992) that represents high-temperature volcanic gases from convergent-plate volcanic gases. The vectors indicate the δD-$\delta^{18}O$ trends expected for hydrothermal water-rock exchange and for mixing of the 1977 Gas Rocks spring waters with local meteoric waters.

the 1977 sample from the West Maar pool is enriched in $^{18}O$, probably due to hydrothermal water-rock exchange. Significant hydrothermal water-rock interactions in the 1977 West Maar pool are also supported by the pool's large amount of dissolved silica (275 ppm; Table 7). Clearly the 81°C temperature of the pool in 1977 enhanced water-rock interactions.

Relative to local meteoric waters, the 1977 waters from the hottest Gas Rocks spring are enriched by 40-50°/₀₀ in deuterium and 10-12°/₀₀ in $^{18}O$. Such enrichments are fairly typical for sedimentary brines (e.g., oil-field brines from the Alberta, Gulf Coast, Illinois, and Michigan basins and oil-field waters from California; Clayton et al., 1966; White et al., 1973). To account for the δD and $\delta^{18}O$ enrichment in The Gas Rocks brine, we consider two explanations: (1) The brine is a mixture of a more saline, $^{18}O$-enriched seawater brine and local meteoric waters. Relative to the 1977 brine, standard seawater (Craig, 1961a) is less saline (see above), is enriched in deuterium by 38°/₀₀, and has similar $\delta^{18}O$ values (Fig. 12). However, reaction of seawater with the underlying sedimentary rocks could produce an $^{18}O$-enriched seawater brine (Fig. 12) that could mix with local meteoric waters to produce the 1977 brine. Potential sources for the seawater include modern seawater from the Pacific (25-30 miles away) or connate seawater; the latter source suggested by Hitchon and Friedman (1969) to explain the origin of oil-field brines in western Canada. (2) The brine is meteoric water that has reacted with clays and calcite in the underlying sedimentary rocks to produce the observed enrichments in δD and $\delta^{18}O$. Isotope exchange reactions with hydrous minerals (clays, gypsum) and calcite have been suggested as a mechanism to produce the observed δD and $\delta^{18}O$ enrichments in several oil-field brines (Clayton et al., 1966).

Unfortunately, we lack sufficient data to distinguish between the above explanations for the origin of The Gas Rocks brine. Nonetheless, the observed isotopic (Fig. 12) and chemical trends in the 1977-1995 Gas Rocks spring waters are clearly produced by mixing of local meteoric water with a brine component.

### Carbon isotopes

The $\delta^{13}C$ values for DIC in the 1995 water samples range from -3.2 to -9.2°/₀₀ (Table 5). Potential sources for DIC in these waters include (1) $CO_2$ from the discharged gases ($\delta^{13}C$ = -6.4 to -6.5°/₀₀; Tables 1,3), (2) biogenic $CO_2$ ($\delta^{13}C$ = -24 to -34°/₀₀ for most terrestrial plants; Smith and Epstein, 1971), and (3) atmospheric $CO_2$ ($\delta^{13}C$ = -6 to -7°/₀₀; Anderson and Arthur, 1983). The nearly equal molar proportions of Ca plus Mg to DIC in waters from sites GR-1A, EM-1, and B-1 suggest that dissolution of carbonate minerals from underlying sedimentary rocks ($\delta^{13}C$ for nearby limestone is +3.86°/₀₀; Barnes and McCoy, 1979) is another potential source of DIC in these samples. In addition to the source of carbon, the $\delta^{13}C$ in DIC values are affected by fractionation between the source and the aqueous carbonate species. The main aqueous carbonate species in The Gas Rocks and Ukinrek Maars waters should be $H_2CO_3$ at pH < 6.4 and $HCO_3$ at pH = 6.4 - 10.3 (Drever, 1981).

To discern the origin of DIC in the 1995 water samples, we predicted their hypothetical $\delta^{13}C$ in DIC values for the potential sources (above) using the estimated $\delta^{13}C$ values for each source (above), the calculated relative abundances of $H_2CO_3$ and $HCO_3$, and the appropriate temperature-dependent fractionation factors for $H_2CO_{3(aq)}$-$CO_{2(g)}$, $HCO_{3(aq)}$-$CO_{2(aq)}$, $H_2CO_{3(aq)}$-$CaCO_3$, and $HCO_{3(aq)}$-$CaCO_3$ modified from Deines et al. (1974). The equilibrium distribution of $H_2CO_3$ and $HCO_3$ was determined using program CHILLER (Reed, 1982) for the temperature, pH, and composition of the water samples (Table 5). We used the ambient collection temperature for all calculations, except to model the dissolution of carbonates in the GR-1A sample, we used the Na-K-Ca equilibrium temperature (162°C; Fournier and Truesdell, 1973).

The predicted $\delta^{13}C$ in DIC values for the potential sources of DIC in the 1995 water samples are shown in Table 8. For sites GR-1C, A-1, and UK-2, there is close agreement between the observed $\delta^{13}C$ in DIC values and those predicted for a dis charged-gas origin, suggesting that DIC in these waters comes mostly from mantle-derived $CO_2$. The observed $\delta^{13}C$ in DIC for these samples could also be explained by an atmospheric source, but this seems very unlikely due to the large absolute

**Table 8.** Predicted $\delta^{13}C$ in DIC values for potential sources of DIC in water samples from The Gas Rocks and Ukinrek Maars area (see text). For comparison, we report the observed $\delta^{13}C$ in DIC values from Table 5.

| Site | Observed $\delta^{13}C$ in DIC (°/₀₀) | Predicted $\delta^{13}C$ in DIC (°/₀₀ relative to PDB) for hypothetical sources | | | |
|---|---|---|---|---|---|
| | | discharged gases ($\delta^{13}C$ = -6.4 - -6.5 °/₀₀) | local carbonates ($\delta^{13}C$ = +3.86 °/₀₀) | biogenic $CO_2$ ($\delta^{13}C$ = -24 - -34 °/₀₀) | atmospheric $CO_2$ ($\delta^{13}C$ = -6 - -7°/₀₀) |
| GR-1A | -3.6 | -6.4 - -6.5 | +0.5† | -24 - -36 | -6.0 - -7.0 |
| GR-1C | -6.9 | -5.7 - -5.8 | NA | -23 - -35 | -5.3 - -6.3 |
| A-1 | -6.7 | -6.4 - 6.5 | NA | -24 - -36 | -6.0 - -7.0 |
| UK-1 | -8.0 | -5.2 - -5.3 | NA | -23 - -35 | -4.8 - -5.8 |
| UK-2 | -5.1 | -5.2 - -5.3 | NA | -23 - -35 | -4.8 - -5.8 |
| EM-1 | -9.2 | +1.8 - +1.7 | +1.0 | -16 - -28 | +2.2 - +1.2 |
| B-1 | -3.2 | -1.5 - -1.6 | -2.6 | -19 - -31 | -1.1 - -2.1 |

†estimated at the equilibrium temperature of 162°C (see text); NA = not applicable.

concentrations of DIC in these waters (Table 5). The waters from sites UK-1 and EM-1 have lower-than-mantle $\delta^{13}C$ in DIC values, implying that DIC in these waters may be mixtures of mantle and biogenic components. In contrast, the heavier-than-mantle $\delta^{13}C$ value for the GR-1A sample suggests that DIC in this sample is a mixture of DIC from the mantle and DIC from a brine endmember. The $\delta^{13}C$ in DIC values for ambient Becharof Lake water (site B-1) is consistent with admixtures of a heavier source (mantle, carbonates, atmosphere) with lighter biogenic $CO_2$. Given the low concentration of DIC (24 mg/L) in the B-1 water, consistent with an atmospheric source, we favor the atmosphere as the source of the heavier DIC. If air supplies the heavy DIC, then only a small fraction (5-10%) of biogenic DIC is required to account for the observed DIC for the B-1 sample.

## GAS HAZARDS IMPLICATIONS

This study shows that $CO_2$-rich gases continue to discharge near The Gas Rocks, although the current $CO_2$ flux appears lower than just after the maars erupted in 1977. $CO_2$-rich gases also discharge from at least four Ukinrek-Maars-ridge sites (Table 2), all of which display newly killed and dying vegetation indicating recent increases in soil-gas $CO_2$ concentrations. The continued release of $CO_2$ at The Gas Rocks and the elevated $CO_2$ discharge along the Ukinrek Maars ridge raise concerns about $CO_2$ hazards to potential visitors.

$CO_2$ concentrations of ≥ 30% cause rapid unconsciousness and, if sustained for several minutes, death in humans (Stupfel and Le Guern, 1989). However, when $CO_2$ is discharged into the atmosphere, it normally dissipates rapidly. Therefore, the main hazard to humans generally occurs when $CO_2$, which is heavier than air, concentrates in depressions, snow, or manmade structures. During field study, none of the sites at The Gas Rocks or Ukinrek Maars presented direct asphyxiation hazards as tested by measuring the $O_2$ concentrations in ambient air around the vents. We developed no symptoms of asphyxia during field study, nor did we observe any dead animals, which are sometimes seen at sites of lethal $CO_2$ discharge (e.g., "Valley of Death" in Indonesia, Loudon, 1832; Hekla volcano in Iceland, Thorarinson, 1950). This mostly reflects the open-air geometry of these sites, but the lower post-1977 $CO_2$ flux at The Gas Rocks also helps minimize asphyxiation hazards as experienced by Tom Miller in 1977. Thus, our preliminary observations suggest that manmade enclosures near the gas seeps might be the main gas hazard in the vicinity of The Gas Rocks and Ukinrek Maars. In particular, we recommend against tent camping and digging snow pits near the areas of gas discharge, including sites of dead vegetation on the Ukinrek Maars ridge, because tents and snow pits can concentrate $CO_2$. We also recommend that visitors exercise caution around all gas seeps because we do not know how static the degassing is, and the flux could change at any time as indicated by the evidence of recent vegetation damage and mortality in the areas of $CO_2$ discharge.

## IMPACT ON LOCAL ECOSYSTEMS

This study shows that $CO_2$-rich gases and saline water discharges continue to be anomalous geochemical inputs into the aquatic and onshore ecosystems in the vicinity of The Gas Rocks and Ukinrek Maars. The $CO_2$-rich gases discharge from offshore seeps in the vicinity of The Gas Rocks and from several seeps along the Ukinrek Maars ridge. There are also diffuse $CO_2$ emissions along the Ukinrek Maars ridge as indicated by the areas of dead and dying vegetation. These vegetation-kill areas are the most obvious impact of the $CO_2$ emissions on the local ecosystems. We expect that soil gases in these vegetation-kill zones contain high (>20-30%) $CO_2$ concentrations based on soil-gas sampling by Farrar et al. (1995) in the tree-kill areas at Mammoth Mountain, CA. We encourage soil-gas studies at Ukinrek Maars ridge to help define the exact $CO_2$ concentrations in the kill zones, as well as the areal extent and flux of the diffuse $CO_2$ emissions. A complete soil-gas survey using the LI-COR $CO_2$ analyzer and the methods of Gerlach et al. (1996) would be an ideal way to conduct such a study.

A less obvious impact of the gas discharges is the elevated DIC content of lake water in the vicinity of The Gas Rocks. Compared to the background Becharof Lake water sample (site B-1), the 1995 water sample collected near the largest gas vent (site GR-1C) contains 13-times more DIC and has a 0.9-unit-lower pH (Table 5). Clearly some of the discharged $CO_2$ dissolves in and acidifies lake water in and around The Gas Rocks. However, we do not know the extent of the elevated DIC and $H^+$ contents in lake waters. To help assess the overall impact of the $CO_2$ emissions on the aquatic ecosystem, we suggest a water-composition survey to help define the spatial extent of the DIC anomaly.

The extent of the saline-water discharges and their impact on the Becharof Lake ecosystems needs further study. Saline waters discharge into Becharof Lake from The Gas Rocks spring. As discussed above, the major to trace constituents in the saline Gas Rocks spring water presently include (in decreasing abundance) Cl, DIC, Na, Ca, Mg, $SiO_2$, K, Fe, B, Br, $SO_4$, Sr, Li, As, $NH_4$, Ba, I, and Rb (Tables 5 and 6). The impact of these saline-water discharges on the Becharof Lake ecosystem depends on their flux into the lake. During time of field study, The Gas Rocks spring (site GR-1A) discharged a seemingly insignificant amount of saline water (< 1 liter/minute). However, additional saline springs may exist on the lake floor along the Bruin Bay fault zone that extends across the lake (Detterman et al., 1987). For instance, subsurface springs probably exist near the largest gas vent (site GR-1C) because the water sample collected from this site contains anomalous concentrations (≥2 times those of the background B-1 sample) of several brine components including Cl, Na, $SO_4$, and $SiO_2$ (Table 5). Again, a detailed water-composition survey could help define the spatial extent of the saline-water discharges.

## CONCLUSIONS

This 1995 study confirms that $CO_2$-rich gases continue to discharge from three large vents and hundreds of smaller seeps in the vicinity of The Gas Rocks, as they have since at least 1974. $CO_2$ also discharges from three seeps along the Ukinrek Maars ridge. In addition, $CO_2$ degasses diffusely along the ridge as indicated by areas of dead and dying vegetation at all three seeps and at least one other ridge site. The discharged gases from The Gas Rocks and Ukinrek Maars ridge contain nearly 100% $CO_2$, excluding minor amounts of air and ASW gases ($N_2$, $O_2$, Ar) in all samples and thermogenic $CH_4$ and $N_2$ in the Ukinrek Maars ridge gases. The $\delta^{13}C$

and $^3He/^4He$ isotopic data suggest that $CO_2$ and He in these gases derive from a mantle source

The main gas hazards to visitors in the vicinity of The Gas Rocks and Ukinrek Maars are tent camping and digging snow pits near the areas of gas discharge, including the areas of dead and dying vegetation along the Ukinrek Maars ridge. Such enclosures may concentrate $CO_2$ to lethal levels. The potential for open-air $CO_2$ asphyxiation at The Gas Rocks and Ukinrek Maars has decreased since Tom Miller experienced asphyxia at The Gas Rocks in 1977. Apparently, the $CO_2$ flux at The Gas Rocks has declined since 1977 probably due to outgassing of the $CO_2$ source. However, the potential for open-air $CO_2$ asphyxiation could potentially change at any time should mantle $CO_2$ input increase.

Besides the $CO_2$ seeps, saline waters discharge from an onshore spring on The Gas Rocks peninsula. This spring also discharges $CO_2$-rich gas, which helps transport the brine to the surface. The waters derive their salinity from a NaCl-brine component. Additional saline waters may discharge offshore from The Gas Rocks peninsula, perhaps along the Bruin Bay fault zone. The temperature and brine component of the spring have decreased significantly since first measured in 1977, probably due to the corresponding decrease in the gas flux in The Gas Rocks area. The brine is similar to sedimentary brines and apparently comes from the underlying marine Mesozoic sedimentary rocks. The brine probably originates from seawater or meteoric waters that reacted with the underlying marine sedimentary rocks.

The main effect of the $CO_2$ gas emissions on the onshore and aquatic ecosystems are the vegetation-kill zones on the Ukinrek Maars ridge. These zones indicate areas of diffuse $CO_2$ emissions with soil-gas $CO_2$ concentrations probably exceeding 20-30%. We propose a soil-gas survey to help define (1) the exact $CO_2$ concentrations in the kill zones and (2) the areal extent and flux of the diffuse $CO_2$ emissions. In the vicinity of The Gas Rocks, subaqueous $CO_2$-gas and saline-water discharges produce elevated DIC, Cl, Na, $SO_4$, $SiO_2$, and $H^+$ concentrations. We suggest a lake-water-composition survey to help define the spatial extent of these geochemical anomalies.

## ACKNOWLEDGMENTS

This project grew in part out of AVO's invited participation in a USFWS-sponsored meeting of the Bristol Bay/Kodiak Ecosystem TEAM. This work was viewed as part of a baseline inventory of the Becharof Lake Ecosystem under the leadership of USFWS in King Salmon. Funding for this project was provided by the USGS Volcano Hazards Program, the USFWS Becharof Lake Ecosystem Project, the USFWS King Salmon Fishery Resources Office, and Northern Arizona University. Ron Hood, Bill Smoke, and others at the USFWS helped make our field work successful and safe. Tina Neal played an instrumental role in soliciting funds from USFWS, coordinating logistics, and reviewing an earlier version of this work. An additional review by Jake Lowenstern helped clarify discussions on the potential origins of the gases and brines.

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