

The Volatiles of Mt. Pagan, Northern Mariana Islands¹

WILLIAM C. EVANS, T. S. PRESSER, LLOYD D. WHITE, AND IVAN BARNES²

ABSTRACT: The powerful 15 May 1981 eruption and frequent subsequent activity of Mt. Pagan have led to the formation of an extensive summit fumarole field. An exhaustive search using a portable gas "sniffer" failed to detect a significant primary magmatic gas component in the fumarole field. Collected gas samples contain mostly ambient air with concentrations of CO₂ to a maximum of 5.5% of the dry gas. He, H₂, H₂S, SO₂, and CH₄ are below detection limits in all samples collected. The (H₂O)/(CO₂) ratio was 13 for one fumarole tested. The carbon isotope composition of the fumarolic CO₂ ($\delta^{13}\text{C}-\text{CO}_2 = -1.1$) shows that this gas is derived from marine carbonates. The physical location of these carbonates has not been determined. The hydrogen isotope compositions of the fumarolic water ($\delta\text{D}-\text{H}_2\text{O} = -29$ to -48) and low concentrations of HCl (approximately 500 mg/L) indicate that the fumarolic condensates are produced mostly from locally derived meteoric water. Seawater is apparently excluded from the central volcanic body. The lack of detectable primary magmatic volatiles in fumarolic emanations may reflect prior degassing of the mantle beneath Mt. Pagan.

MT. PAGAN VOLCANO, a basaltic composite cone on the northern half of Pagan Island, is one of several historically active volcanoes in the Mariana Islands active arc (Figure 1). Forming a wholly oceanic arc, the island volcanoes produce material uncontaminated by contact with continental crust (Meijer and Reagan, 1983). Karig (1971) has described the regional geologic setting and structural history of the Mariana arc system including: the active arc, the interarc basin (Mariana Trough) with axial spreading ridge, and remnant arc (South Honshu Ridge). The axial spreading ridge has been described more recently as a diffuse spreading zone of a more complex nature than midocean ridges (Karig and others, 1978). The Palau-Kyushu Ridge is apparently an older remnant arc related to the Mariana system (Karig, 1971).

The 15 May 1981 eruption was a major event in the history of Mt. Pagan which has

erupted several times since 1664. A comprehensive review of the activity of Pagan Island volcanoes and a description of the 15 May eruption have been presented by Banks and others (1984). They concluded that the volume of air-fall deposits and lava flows from the 15 May eruption may have exceeded 200 million cubic meters of magma. During the weeks following this eruption, they collected fumarolic gases which consisted chiefly of ambient air but contained significant concentrations of CO₂, H₂, CH₄, and CO. A few water supplies were also tested for chemical contamination from ashfall (Banks and others, 1984).

This paper presents results of studies conducted on Pagan Island in March, 1983. Gas, water, and rock samples were collected. Compositional and isotopic determinations were made on each sample type. A further study of potable water supplies containing bacteriological and hydrological information has been prepared by Chinn and others (1984). Other recent findings (seismic data and geologic studies) have been reported by Banks (1983) and Koyanagi and Kojima (1983).

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² U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025.

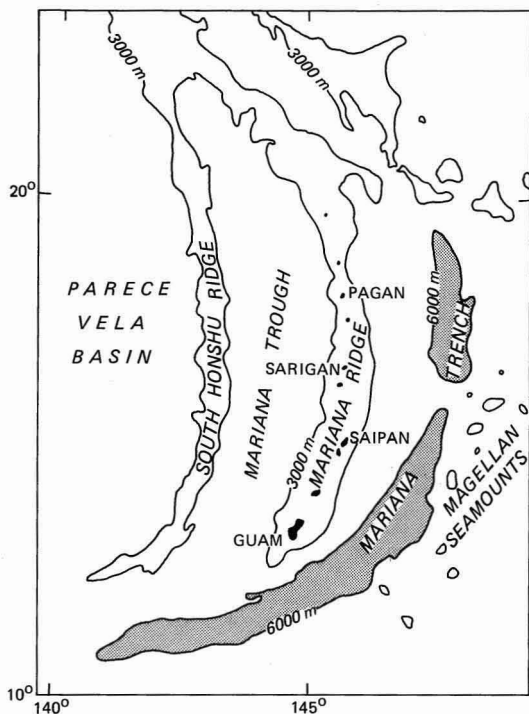


FIGURE 1. Map of Mariana region showing trench, trough, active arc, and remnant arc (after Karig 1971).

The northern half of Pagan Island and sample locations are shown in Figure 2. The dominant feature, Mt. Pagan, rises to 570 meters at the northeast rim of the summit crater. In March 1983 the summit crater was about 700 meters in diameter with a gentle inward slope toward a central vent, approximately 250 meters in diameter. The bottom of the central vent was not visible and its depth could not be determined. An additional vent on the south rim of the crater had been active during the May 1981 eruption but was buried by scoria in the summer of 1982 (Banks and others, 1984). Continuing activity of the central vent was evidenced by a minor ash eruption on 7 March 1983.

When the summit area was visited 8 March 1983, occasional explosions could be heard occurring deep inside the central vent. Seismic signals, corresponding temporally to the explosions, were being monitored at a station near Bandera village, and preliminary inter-

pretation suggested a depth of about 2 km for these events (Robert Y. Koyanagi, verbal commun.). Each of these explosions was followed within minutes by a puff of dusty smoke-like matter which rose up inside the vent and drifted skyward. As each puff or plume reached a height of 100–200 meters (depending on weather conditions) above the crater rim, its appearance changed to resemble a normal cumulus cloud. A sample (CQ15) of the densest part of one of these plumes was collected in an evacuated gas-sample tube as it exited the vent. Although this plume appeared opaque while rising inside the vent, visibility was about 250 meters inside the plume when it reached the mouth of the vent. Temperature inside the plume was 23°C. Immediately following collection of the plume sample, a sample (CQ16) of ambient air was collected at the same elevation outside of the crater and upwind of the plume.

The floor of the crater surrounding the central vent was covered with fine ash several meters thick. The absence of bombs on the crater floor suggested that strong eruptions had not occurred for a considerable time. Thousands of small fumaroles existed in virtually all parts of the crater floor. A portable gas "sniffer" (Matheson-Kitagawa Model 8014K³) used to test about 60 fumaroles in all accessible parts of the crater indicated that in every case, CO₂ concentrations were ≤5% and H₂S concentrations were <5 ppm. Some of the fumaroles tested were superheated (>98°C) but most measured temperatures were between 65 and 90°C. Four fumarole samples were collected: one (CQ19) from a small 88°C vent which gave the highest CO₂ reading (~5%) of any of the sub-boiling fumaroles tested; one (CQ20) from a 259°C fumarole on the south rim of the volcano where the sniffer indicated a high (~5%) CO₂ level; two (CQ17 and CQ18) from a crack on the east side of the crater where the high temperature (>600°C) rendered the sniffer non-functional. Though

³ "Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey."

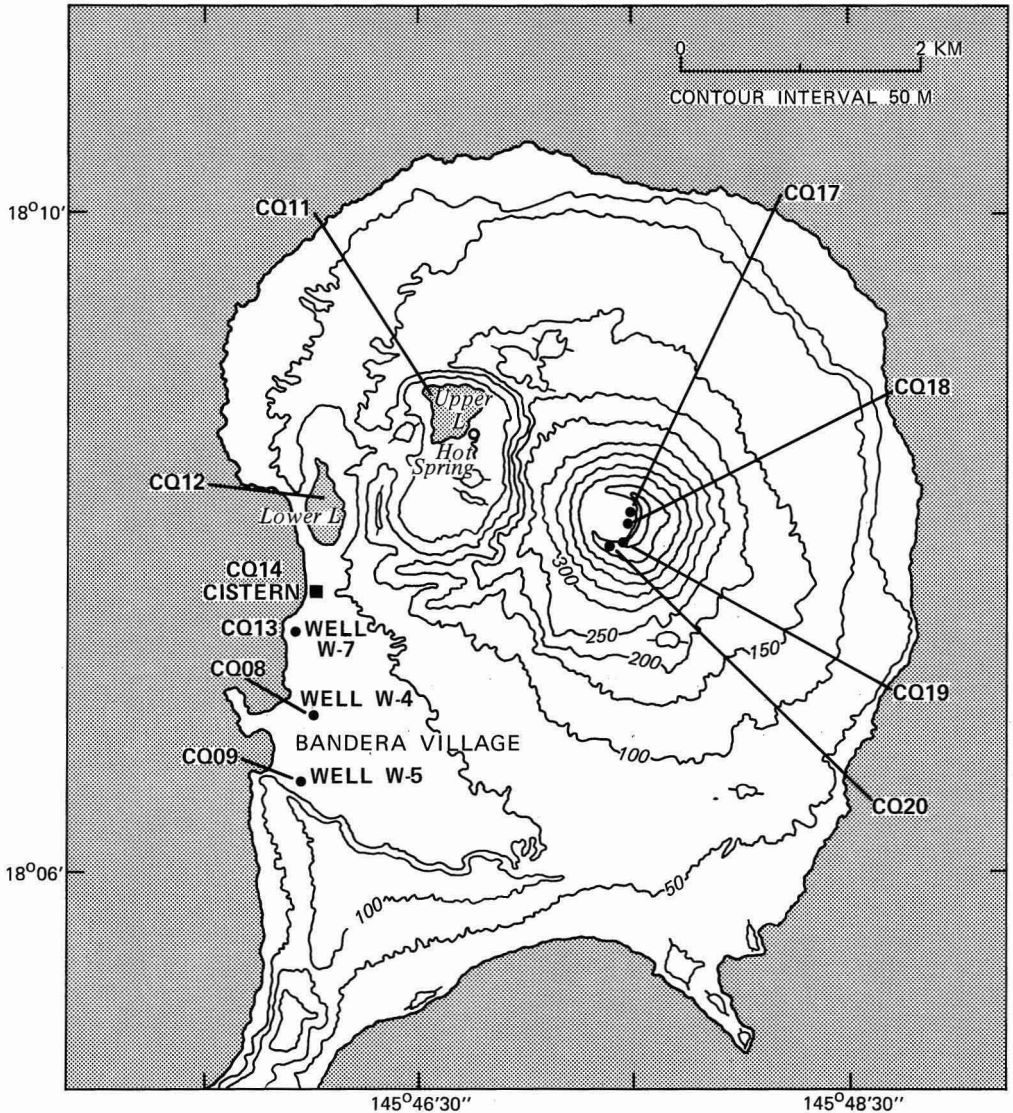


FIGURE 2. Map of Northern half of Pagan Island (after Banks et al. 1984) showing sample locations.

mineral encrustations were very sparse in the crater, some white and yellow deposits were collected from the mouth of CQ20. Samples CQ19 and CQ20 were collected from fumaroles situated in the scoria directly above the buried south-rim vent.

Most water wells sampled were open to the atmosphere and generally had pumice fragments floating on the surface. The lower lake

was at sea level and was separated from the ocean by a low sand embankment. The upper lake was approximately 10 meters above sea level. Both lakes occupy apparent maar-basins (Banks and others, 1984). Water samples were collected from three wells, one rain catchment, both upper and lower lakes, and a hot spring which discharged at the edge of the upper lake (Figure 2).

METHODS

Spring and well water samples were collected in accordance with the methods of Presser and Barnes (1974). Alkalinity and pH were determined at each site using the methods of Barnes (1964). Cations were analyzed by atomic absorption spectrophotometry, and anions were analyzed by liquid chromatography.

Plume and ambient air samples were collected by opening a ground glass stopcock on an evacuated 2-L glass bulb. Fumarole gases were collected through a cold trap which separated the condensable and non-condensable gases. The collection apparatus (Figure 3) consisted of a pyrex gas-sample tube and a pyrex dewar, joined by a 3-meter length of 1/16" O.D. 316 stainless steel tubing. The entire apparatus was evacuated and transported to the collection site. Two 15 oz. cans of liquid Freon 22— CHClF_2 (B.P. = -40.8°C) were opened and poured into the dewar. A cork and pressure-relief tube were inserted in the top of the dewar which was then lowered into the fumarole using a three finger clamp. After the dewar had warmed sufficiently to prevent condensation from forming on its outer walls, the thin bulb was broken on a rock or firm ground at the bottom of the fumarole. Gases that were condensed by liquid Freon (water vapor, HF, and HCl) froze on the inner wall of the dewar, and dry non-condensable gases flowed through the stainless steel tubing to the gas-sample tube. The immediate conversion of water vapor to ice minimized the loss from the gas phase of SO_2 which would rapidly dissolve in liquid water. Also, removal of H_2O from the remaining gases rendered them much less reactive toward the stainless steel tubing. The stopcock on the gas-sample tube was closed after the sample had been collected. The dewar was then removed from the fumarole and non-condensable gases remaining in the dewar were pumped away using a small hand-operated vacuum pump. The dewar was resealed with a small portable MicroNox torch and the Freon was poured out allowing the condensate to thaw.

The dry gases in the gas-sample tubes were

analyzed by gas chromatography, using Porapak Q and Linde Molecular Sieve 5A for all gases except SO_2 . A Teflon column packed with polyphenyl ether and phosphoric acid on Chrom T (Stevens and others, 1971) was used to determine SO_2 concentrations. The condensates were analyzed for cations by atomic absorption spectrophotometry. Anions were determined by liquid chromatography. A pH electrode was used to determine H^+ .

The CO_2 -equilibration method of Cohn and Urey (1938) and the uranium technique of Bigeleisen and others (1952) were used to analyze for oxygen and deuterium isotopes of water and condensate samples. Isotopic ratios of ^{18}O : ^{16}O , D:H, and ^{13}C : ^{12}C were determined on a modified Nier double-collecting 6-in., 60° -sector mass spectrometer (McKinney and others, 1950).

RESULTS AND DISCUSSION

The results of the water analyses are given in Table 1. The gas compositions are shown in Table 2 together with the composition of Menlo Park, California ambient air which was analyzed concurrently with the gas samples. Levels of precision and detection limits vary among the analyses based on the amount of gas used in performing the analyses and the actual analytical conditions. The values in Table 2 represent volume-percent of the total noncondensable gases. Analyses of fumarolic condensates from samples CQ19 and CQ20 are given in Table 3. Semiquantitative analyses of SO_3^{-2} showed that there had been no significant loss of SO_2 from the gas phase during sample collection. The volumes of the condensates from samples CQ17 and CQ18 (about $3\ \mu\text{L}$ each) were too small to be analyzed. The volume of condensate from CQ19 was insufficient to permit determination of oxygen isotopes or an accurate pH. Major element analyses of recent basalt and pumice from Mt. Pagan are given in Table 4. Also shown is a basalt from Sarigan Island, 160 km south of Pagan.

The dry gas compositions of the plume (CQ15) and ambient air (CQ16) samples are

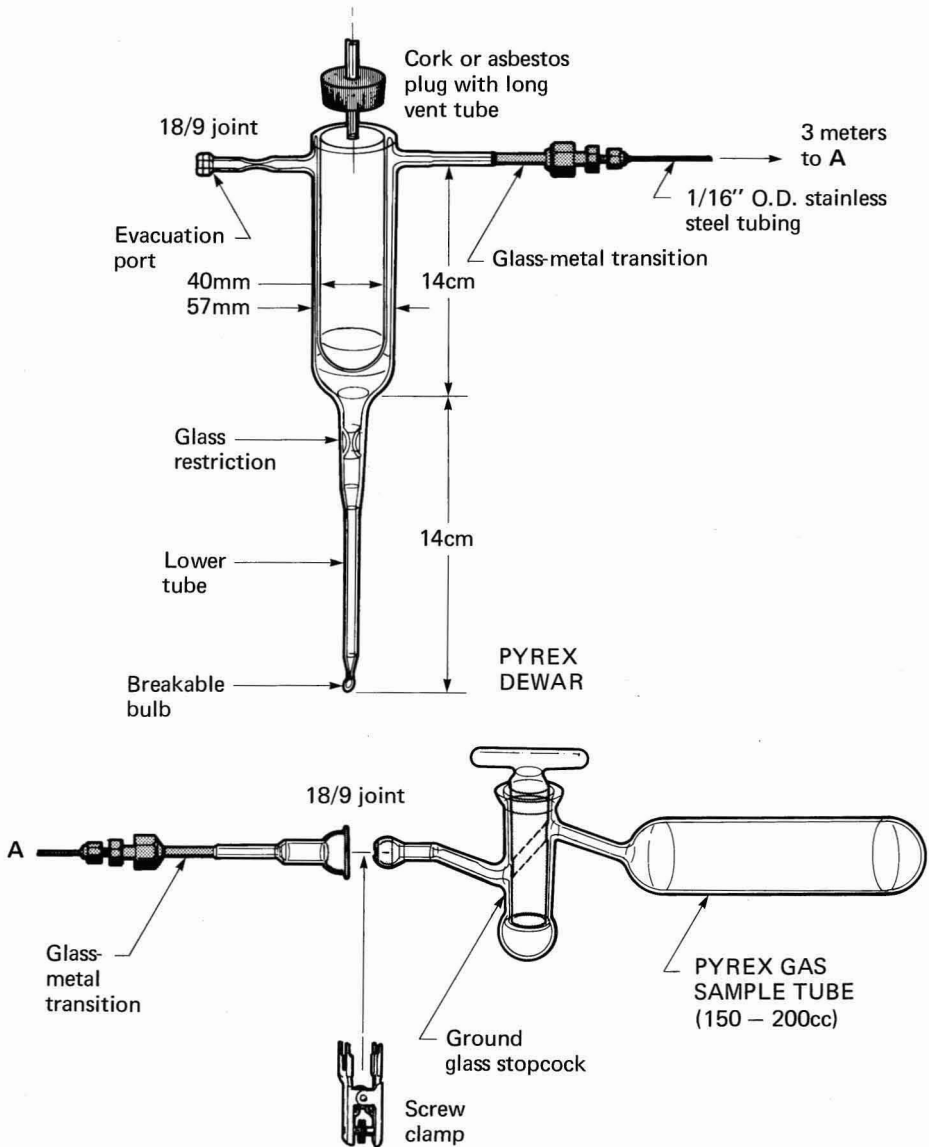


FIGURE 3. Fumarole sampling device. Gas-sample tube is attached with screw clamp and entire apparatus is evacuated. Evacuation port is heat sealed and stainless steel tubing is tightly coiled allowing transport in evacuated state to field site.

identical within experimental uncertainty (Table 1). Both samples were analyzed for quantity of water vapor and $\delta D-H_2O$ value. The ambient air (CQ16) was 2.13% H_2O (by volume) and its $\delta D-H_2O$ value was -83 . The plume sample was 2.16% H_2O (by volume) and its $\delta D-H_2O$ value was -85 . The

close similarity of the plume's $\delta D-H_2O$ value to that of ambient air and large difference from values for seawater or local groundwaters (Table 1) show that the water in the plume was contributed entirely by the ambient air mass. Apparently, the gas flux out of the central vent was insufficient to prevent

TABLE 1

COMPOSITION OF SELECTED WATER SUPPLIES OF PAGAN ISLAND, MARCH, 1983. [Concentrations are given in mg/L except for Al which is $\mu\text{g/L}$. $\delta^{13}\text{C}$ data are given in per mil (parts per thousand) relative to PDB. $\delta^{18}\text{O}$ and δD are given in per mil relative to SMOW. HCO_3 value is total alkalinity as bicarbonate. nd means not determined.]

SAMPLE NO.	CQ08	CQ09	CQ10	CQ11	CQ12	CQ13	CQ14
SAMPLE TYPE	WELL W-4	WELL W-5	HOT SPRING	UPPER LAKE	LOWER LAKE	WELL W-7	CISTERN
T°(C)	28.0	26.5	41.5	27.0	29.0	34.0	26.0
pH	7.53	7.45	7.37	8.00	8.21	7.19	7.54
Na	265	530	2100	1850	4000	1400	14
K	14	34	110	91	130	60	3.4
Mg	40	86	180	155	380	160	3.3
Ca	47	155	260	235	395	130	50
HCO_3	231	840	200	190	100	418	65
F	0.36	<0.2	1.1	1.3	2.1	1.2	2.4
Cl	420	950	3800	3300	7100	2350	51
SO_4	72	30	440	380	920	355	52
B	<1	<1	3.3	2.9	2.2	1.1	<1
SiO_2	45	69	92	77	5.2	53	8.6
Al	8	nd	3	nd	nd	7	nd
$\delta\text{D}-\text{H}_2\text{O}$	-49	-39	-18	-13	-11	-35	-17
$\delta^{18}\text{O}-\text{H}_2\text{O}$	-6.7	-5.7	-1.6	-0.9	-1.0	-5.6	-2.1
$\delta^{13}\text{C}-\text{HCO}_3$	-9.2	-7.1	+1.1	nd	nd	-2.6	nd

TABLE 2

ANALYSES OF GASES FROM MT. PAGAN VOLCANO, MARCH, 1983. [Gas compositions are exclusive of H₂O, HCl and HF. $\delta^{13}\text{C}$ data are given in per mil relative to PDB. Levels of precision and detection limits vary among the analyses based on the amount of gas used in performing each analysis and the actual analytical conditions. nd means not determined.]

SAMPLE NO.	CQ33	CQ15	CQ16	CQ17	CQ18	CQ19	CQ20
SAMPLE TYPE	MENLO PARK AMBIENT AIR	PLUME FROM CENTRAL VENT	PAGAN AMBIENT AIR-WINDWARD SIDE	FISSURE	FISSURE	FUMAROLE	FUMAROLE
T°(C)	21	23	21	619	629	88	259
COMPOSITION IN VOLUME PERCENT							
He	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
H ₂	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ar	0.94	0.94	0.95	0.94	0.94	0.89	0.89
O ₂	20.7	20.6	20.6	20.6	20.6	19.2	19.2
N ₂	78.5	78.3	78.3	78.3	78.5	75.5	74.4
CH ₄	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.002	<0.002
CO ₂	0.0340	0.0340	0.0346	0.039	0.032	5.05	5.50
C ₂ H ₆	<0.002	<0.002	<0.002	<0.002	<0.002	<0.01	<0.01
H ₂ S	<0.002	<0.002	<0.002	<0.002	<0.002	<0.01	<0.01
SO ₂	<0.0002	<0.0002	<0.0002	<0.01	<0.0002	<0.01	<0.01
CO	<0.01	nd	nd	<0.01	<0.01	nd	<0.01
total	100.2	99.9	99.9	99.9	100.1	100.6	100.0
$\delta^{13}\text{C}-\text{CO}_2$	nd	nd	nd	nd	nd	-1.1	-1.1

TABLE 3

ANALYSES OF FUMAROLIC CONDENSATES FROM MT PAGAN VOLCANO, MARCH, 1983. [Concentrations are in mg/L. $\delta^{18}\text{O}$ and D data are relative to SMOW. nd means not determined.]

SAMPLE NO. VOLUME (μL)	CQ19 78	CQ20 1350
pH	acid	1.8
Na	320	85
K	60	<10
Mg	110	22
Ca	1400	170
F ⁽¹⁾	118	11
Cl	3950	1470
SO ₄ ⁽²⁾	1800	105
Fe	55	140
Al	590	80
$\delta\text{D}-\text{H}_2\text{O}$	-48	-29
$\delta^{18}\text{O}-\text{H}_2\text{O}$	nd	0.0

¹ Mostly HF at solution pH² Mostly HSO₄ at solution pH

TABLE 4

ANALYSES OF ROCK SAMPLES, PAGAN AND SARIGAN ISLANDS. [All constituents are given in percent except Mn which is parts per million. $\delta^{18}\text{O}$ data are relative to SMOW. Major element analyses are supplied by Terry Fries, U.S.G.S. Strontium isotopes are supplied by A. C. Robinson, U.S.G.S.]

SAMPLE NO.	11B83	21B83	91B83
SAMPLE TYPE	MASSIVE FLOW SARIGAN ISLAND	PUMICE PAGAN ISLAND	AA PAGAN ISLAND
MAJOR ELEMENT ANALYSES, SEMIQUANTITATIVE			
Si	26	25	22
Al	9.0	9.3	9.0
Fe	6.8	>10	9.8
Mg	2.8	3.6	3.2
Ca	7.6	8.2	6.8
Na	2.2	3.0	2.6
K	0.58	1.0	1.0
Ti	0.46	0.76	0.75
P	0.08	0.12	0.12
Mn	1300	2000	1900
$\delta^{18}\text{O}$	6.6	6.0	6.1 ¹
⁸⁷ Sr/ ⁸⁶ Sr		0.70354	0.70347

¹ Different aa specimen than used for major element analysis.

ambient air from filling the vent. Thus the amount of magmatic gas and/or water vapor emitted during the explosions was very low. Both samples were quite unsaturated with respect to water vapor at their temperatures of

collection: 87% saturated at 21°C for the ambient sample and 78% saturated at 23°C for the plume sample. The temperature at which these samples would have been saturated is 19°C. It is clear that the plume was an ash

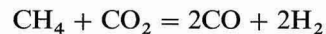
cloud (or aerosol) and not a steam cloud. Only after the plume had risen above the volcano and cooled did true condensation occur.

The dry gas in samples CQ17 and CQ18 collected from the hot fissure on the east side of the crater was entirely ambient air (Table 2). Also, the water vapor content of these two samples was roughly the same as the ambient air sample (CQ16). The dry gas from the 88°C fumarole (CQ19) contained about 5% CO₂ and 95% ambient air (Table 1). In sampling this fumarole 4,330 micromoles of water were condensed and 6,750 micromoles of dry gas (containing 341 micromoles of CO₂) were collected. The fumarole was therefore unsaturated with respect to water vapor at the collection temperature. Subsurface loss of water vapor from the ascending gas stream should not have occurred. This suggests that the $\delta D-H_2O$ value and [H₂O]/[CO₂] ratio should be representative of the gas phase at depth. When corrected for air contamination, the fumarole was 92% H₂O and 8% CO₂. The analysis (Table 1) of the 259°C fumarole (CQ20) shows that the dry gas included 5.5% CO₂. The balance of the dry gas was air. Due to sampling difficulties, the [H₂O]/[CO₂] ratio is unknown.

The $\delta^{13}C-CO_2$ value of -1.1 for both CQ19 and CQ20 is within the range expected for CO₂ from the breakdown of marine carbonates (Craig, 1953). No evidence exists for a contribution of mantle-derived CO₂ with an approximate $\delta^{13}C$ value of -7. [This value is based on the $\delta^{13}C-CO_2$ range of -4.7 to -8.1 found in mid-ocean ridge basalts (MORB) by Pineau and others (1976) and Moore and others (1977)]. Other gases commonly associated with degassing magma (H₂, H₂S, SO₂, and CO) were absent from all of the gases sampled (Table 1).

Banks and others (1984) report that gases collected 22-28 May 1981, contained mostly ambient air (which seems to be a constant problem at Mt. Pagan) with significant concentrations of CO₂, H₂, CH₄, and CO. Only traces of the sulfur gases H₂S and SO₂ were found (Banks and others, 1984). CH₄ concentrations greater than a few parts per million are seldom reported in high-temperature volcanic fumaroles and almost always indi-

cate that equilibrium between the gaseous species has not been reached (Ellis, 1957). As gas phase reactions are rapid at high temperatures, disequilibrium indicates that the CH₄ has a shallow origin and has had only brief contact with other fumarolic gases. This allowed Banks and others (1984) to conclude that the CH₄ and some of the CO and CO₂ in the 1981 samples formed from organic material buried in the new lava flows. The gases contained both CO₂ and CH₄, hence the presence of the CO and H₂ could easily be accounted for by a reaction such as:



with higher temperatures favoring the products. If the CH₄ were derived from organic material and the CO₂ from marine carbonates (as in 1983), then possibly none of the gases collected in May, 1981 had a magmatic origin.

Because vaporization of H₂O at temperatures greater than 170°C causes less than ten per mil change in δD value (Friedman and O'Neil, 1977), it is likely that for hot volcanic systems, the $\delta D-H_2O$ value of fumarolic steam will be nearly equal to the $\delta D-H_2O$ value of the subsurface water giving rise to the steam. The $\delta D-H_2O$ values of the condensate samples, CQ19 and CQ20 (Table 3), are very similar to $\delta D-H_2O$ values of the island's ground water as represented by the three well samples and the hot spring (Table 1). This similarity suggests that ground water within the volcano is the source of much of the fumarolic steam at the summit. Whereas all four ground water samples show some mixing of seawater or connate water with the locally derived meteoric water, the hot spring shows the greatest amount in terms of Cl⁻ content and $\delta D-H_2O$ (Table 1). The requirement that $\delta D-H_2O$ be similar for the fumarolic steam and parent fluid suggests that the parent ground water is intermediate in composition between the well waters and hot spring (Figure 4).

The condensates contain high concentrations of many metallic cations (Table 3). This is probably due to encrustations from the mouths of the fumaroles being sucked up by the sampling tube. Despite this problem, the excess hydrogen and chloride ions in the con-

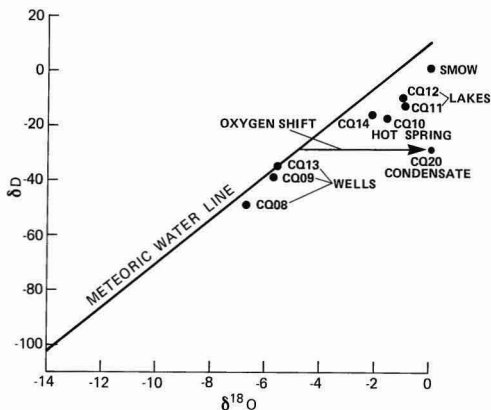
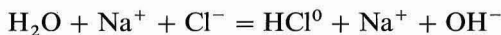


FIGURE 4. $\delta D-H_2O$ and $\delta^{18}O-H_2O$ of water samples and fumarolic condensate. Arrow shows proposed evolution of condensate from parent fluid by ^{18}O shift with no change in $\delta D-H_2O$ value.

condensates (about 500 mg/L HCl in CQ20) show that a small amount of HCl gas was present in the vapor phase. The high temperature boiling of a water containing Cl^- would convert the Cl^- to HCl^0 (Barnes, 1984) by the reaction:



Chloride ion dissolved in the groundwater can account for some of the HCl in the summit fumaroles. Small amounts of interstitial chloride-rich waters expected to be in the buried marine carbonates probably also add to the observed HCl and H_2O , though any significant contribution from a connate-type water would produce fumaroles richer in HCl than observed. The $\delta^{18}O-H_2O$ value for the condensate from CQ20 (Table 3) is shifted from the groundwater values (Table 1) as a result of reaction with the local rock at high temperatures. This situation is analogous to Mount St. Helens where the high temperature boiling of a brine at depth led to HCl-rich fumaroles with little change in $\delta D-H_2O$ and a large shift in $\delta^{18}O-H_2O$ (Evans and others, 1981).

Apparently, seawater is unable to infiltrate the volcanic edifice to any great degree. If it were, superheated fumaroles (such as CQ20) would have $\delta D-H_2O$ values close to 0 and high concentrations of HCl. Water of composition resembling either the lower or upper lake ($\delta D-H_2O$ and Cl^- values in Table 1)

can also be ruled out as a major contributor to the summit fumaroles.

The $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values of the recently erupted basalt from Mt. Pagan (Table 4) are in the same range as values published by Ito and Stern (1981) for basalts in the entire Izu-Volcano-Mariana arc system. The encrustations collected from fumarole CQ20 were found by x-ray analysis to contain gypsum and a yellow hydrate of $CaSO_4$ (Terry Keith, written commun.). Gypsum also appears as a white efflorescence on scattered ejecta on the flanks of Mt. Pagan. An occasional blue staining of rocks by the copper compound, atacamite (Terry Keith, written commun.), was found in a few localities on the flanks.

Two observations are most significant in this study. One is that no primary magmatic volatiles (mantle-derived) were detected in emanations from Mt. Pagan even though frequent eruptions occurred prior to and subsequent to the sampling. Secondly, isotopic evidence indicates that the CO_2 detected was formed from the breakdown of marine carbonates.

Mt. Pagan sharply contrasts with many other active volcanoes where the emanation of mantle-derived volatiles can easily be detected. [Well-studied examples include: Erta Ale in Ethiopia (Allard, 1980) has maintained production of primary magmatic gases for many years. Strong discharges of mantle-derived CO_2 were associated with Ukinrek Maars, Alaska (Barnes and McCoy, 1979). Continuous CO_2 (Harris and others, 1981) and SO_2 (Casadevall and others, 1981) fluxes from Mount St. Helens frequently measured thousands of tons per day for several months following the May 1980 eruption.] One explanation for this lack of mantle-derived volatiles is that Mt. Pagan may be so "porous" that magmatic gases can escape over a very large area at concentrations too low to be detected. However, no rising gas bubbles were visible in either the upper or lower lake or in the hot spring. Also, evidence for significant gas discharge on the flanks of Mt. Pagan [other than along the north-trending fissures described by Banks and others (1984)] was generally restricted to relict encrustations of

gypsum on the 1981 lava flows. These deposits were probably associated with outgassing of the actual flows. These observations, and the fact that seawater was apparently unable to gain access to the central volcanic edifice, indicate that Mt. Pagan is not necessarily extremely porous. The large quantities of air entrained in the sampled fumaroles (Table 1 and gas analyses by Banks and others, 1984) show that gases can easily diffuse through the superficial loose ash and pumice covering the volcano. In spite of this, the presence in the fumaroles of HCl and carbonate-derived CO₂ (at an elevation 550 m above the coral reef zone) shows that gases from within the volcano are channeled to the surface in some type of conduit. Such a conduit should be capable of carrying any mantle-derived gases present as well. It seems unlikely that porosity alone can explain the gases' absence from the summit fumaroles.

Banks (1983) cites extreme notching of the summit cone and erosion of vents as evidence that intense gas-jetting has occurred periodically since 15 May 1981. However, gas samples collected by Banks in the summit area one week after the 15 May 1981 eruption contained little if any primary magmatic gas. The plume sample, CQ15 (Table 2), was collected one day after a mild ash eruption but contained no detectable magmatic component. A red glow from the central vent observed the night of 7 March 1983, and the occurrence of eruptions in October and November 1983 (Norman G. Banks, verbal commun.) demonstrate the persistence of magma within the volcano. That the magma is unable to maintain any sort of flux of mantle-derived gases suggests that it contains low concentrations of these gases. This may reflect conditions in the earth's mantle beneath the volcano.

The mantle beneath Mt. Pagan is believed to be a wedge-shaped section beneath the active arc and above the subducting Pacific plate (Katsumata and Sykes, 1969). This mantle wedge may have already been involved in the formation of three successive island arcs of which only the third is currently active (Karig, 1971). The long-term production of lavas from the mantle wedge may have caused depletion of its original volatiles. Information

on mantle volatiles of the Mariana region has been obtained from studies of submarine volcanics (including vesicular glasses) dredged from the back-arc spreading zone and submarine volcanoes in the active arc, both north and south of Mt. Pagan. Poreda (1983) has shown that some submarine volcanics in the active arc and interarc basin completely lack the ³He enrichment characteristic of MORB. Water contents (0.5 to 2.5%) of rock samples from both these areas are two to ten times higher than normal MORB (Garcia and others, 1979; Poreda, 1983; Dixon and Stern, 1983). Poreda (1983) reported CO₂ contents in glasses of "low vesicularity" to be about equal to normal MORB. Garcia and others (1979) found that "vesicular" glasses contained about twice as much CO₂ as normal MORB. In addition to basalts and andesites, a highly vesicular dacitic pumice was dredged (at 899 m depth) from a seamount in the active arc (Dixon and Stern, 1983) and found to contain about 2% H₂O and 2% other volatiles (Dixon, verbal commun.). Poreda (1983) has shown that the H₂O in glasses from both the active arc and the spreading zone is enriched 30 to 50 per mil in D, and that the CO₂ is enriched 4 to 8 per mil in ¹³C, relative to the values characteristic of normal MORB. Thermal degassing experiments on submarine andesites from the active arc yielded a SO₂/CO₂ ratio of 0.025 showing that S contents of these rocks are extremely low relative to normal MORB (Garcia and others, 1979). Samples selected for analysis were judged by these authors to be "fresh," showing little sign of post-eruptive alteration. Available chemical and oxygen isotope data on the samples support this observation (Dixon and Stern, 1983; Poreda, 1983). These data show that the concentration of mantle-derived volatiles (as characterized by MORB values) in the erupted submarine lavas is low. Many of these submarine lavas were erupted at pressures high enough to prevent extensive volatile loss. It seems likely that the concentration of MORB-type volatiles in portions of the mantle supplying these lavas must be low. The concentrations of these volatiles beneath Mt. Pagan may be too small to detect in surface emanations.

The source of the volatiles actually found (abundant H_2O and isotopically "heavy" CO_2) in the submarine volcanics is uncertain. The low SO_2/CO_2 ratio and enrichment relative to MORB by 6 per mil in $^{13}C-CO_2$ for both Mt. Pagan and the submarine volcanics suggests a common method of origin. Many workers have argued that melting the subducted Pacific slab and associated sediments cannot significantly contribute to the Mariana active arc magmas. Cited as evidence are rare-earth element abundances (Dixon and Batiza, 1979), oxygen isotopic ratios (Ito and Stern, 1981), and strontium isotope ratios (Dixon and Batiza, 1979; Ito and Stern, 1981; Dixon and Stern, 1983). However, transport of volatiles from subducted material into arc magmas commonly has been suggested. Allard (1980) postulated that the shift in $\delta^{13}C-CO_2$ from a MORB value of -6 for the rift volcanoes, Erta Ale and Ardoukoba, to -3 for the island arc volcanoes, Merapi and Momotombo, results from addition of CO_2 from carbonate sediments beneath the island volcanoes. Poreda (1983) proposed that the water in the submarine volcanics of the Mariana region is supplied largely by subducted material, and that the isotopically "heavy" CO_2 may be derived in part from subducted carbonates.

The amount of carbonate in the subducting Pacific slab is unknown. A borehole in the Pacific plate just east of the Mariana Trench cored a few tens of meters of Neogene sediments (containing no carbonates) overlying impenetrable chert of Cretaceous age (Hussong and others, 1981). Seismic data indicated that the thickness of the chert is approximately 200 meters, and that 200–600 meters of other sediments lie between the chert and the igneous basement (Hussong and others, 1981). These sediments may contain carbonates (Houtz and Ludwig, 1979).

If subducted carbonates do provide the CO_2 in the submarine volcanics, they may provide the CO_2 discharging from Mt. Pagan as well. Evidence also exists to suggest a shallow intracrustal origin for the CO_2 in both instances. Corals occasionally accompany the submarine volcanics in dredge hauls in the active arc (Dixon and Stern, 1983). Calcare-

ous fossils were found in boreholes in the Mariana trough, one borehole yielding substantial nannofossil chalk as well as pillow basalts interlayered with limestone (Hussong and others, 1981). It is conceivable that CO_2 released from such sources at elevated temperatures might be incorporated into rising magmas prior to eruption on the seafloor. Similarly, burial and subsequent heating of coral reefs such as those which encircle Mt. Pagan may account for the emanation of carbonate-derived CO_2 from summit fumaroles. Shallow subsurface processes certainly affect the CO_2 production from other volcanoes. $\delta^{13}C-CO_2$ values for some volcanoes in the Aleutian arc are 2 to 5 per mil lighter than MORB (Motyka and others, 1983) showing some organic contribution to the CO_2 . They contrast with the results of Allard (1980) for island arc volcanoes previously mentioned in this report. A $\delta^{13}C-CO_2$ value of -7.5 was obtained from a submarine basalt from Loihi seamount (J. G. Moore, verbal commun.). The $\delta^{13}C-CO_2$ values for fumaroles on Kilauea volcano range from -3 to -5 (unpublished data—this laboratory). Shallow level addition of carbonate-derived CO_2 to the Kilauea fumaroles may be involved because Loihi and Kilauea share a common "hot spot" source (Klein, 1982). In the case of Mt. Pagan, it is not possible to show whether the carbonate-derived CO_2 is produced by subducted material or shallowly buried carbonates.

CONCLUSION

Hydrogen isotopes show that the water vapor in summit fumaroles on Mt. Pagan is derived from local groundwater. Low HCl contents of the fumarolic gases preclude significant infiltration of seawater into the central edifice. The complete absence of primary magmatic gases during a period of intermittent activity suggests that the mantle below the volcano is degassed of its original volatiles. The CO_2 discharging from Mt. Pagan is of marine origin but its depth of production is uncertain.

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