



Scrubbing Masks Magmatic Degassing During Repose at Cascade-Range and Aleutian-Arc Volcanoes

By Robert B. Symonds¹, Cathy J. Janik², William C. Evans², Beatrice E. Ritchie³,
Dale Counce⁴, Robert J. Poreda⁵, and Mark Iven¹

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¹U.S. Geological Survey, Cascades Volcano Observatory, 5400 MacArthur Blvd., Vancouver,
WA 98661

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

³Department of Geology, Portland State University, P.O. Box 751, Portland, OR 97207

⁴Los Alamos National Laboratory, Los Alamos, NM 87545

⁵Department of Earth and Environmental Science, 227 Hutchison Hall, University of Rochester,
Rochester, NY 14627

ABSTRACT

Between 1992 and 1998, we sampled gas discharges from $\leq 173^\circ\text{C}$ fumaroles and springs at 12 quiescent but potentially restless volcanoes in the Cascade Range and Aleutian Arc (CRAA) including Mount Shasta, Mount Hood, Mount St. Helens, Mount Rainier, Mount Baker, Augustine Volcano, Mount Griggs, Trident, Mount Mageik, Aniakchak Crater, Akutan, and Makushin. For each site, we collected and analyzed samples to characterize the chemical (H_2O , CO_2 , H_2S , N_2 , CH_4 , H_2 , HCl , HF , NH_3 , Ar , O_2 , He) and isotopic ($\delta^{13}\text{C}$ of CO_2 , $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$ of CH_4 , $\delta^{15}\text{N}$, and δD and $\delta^{18}\text{O}$ of water) compositions of the gas discharges, and to create baseline data for comparison during future unrest. The chemical and isotopic data show that these gases contain a magmatic component that is heavily modified from scrubbing by deep hydrothermal ($150^\circ - 350^\circ\text{C}$) water (primary scrubbing) and shallow meteoric water (secondary scrubbing). The impact of scrubbing is most pronounced in gas discharges from bubbling springs; gases from boiling-point fumaroles and superheated vents show progressively less impact from scrubbing. The most effective strategies for detecting gas precursors to future CRAA eruptions are to measure periodically the emission rates of CO_2 and SO_2 , which have low and high respective solubilities in water, and to monitor continuously CO_2 concentrations in soils around volcanic vents. Timely resampling of fumaroles can augment the geochemical surveillance program by watching for chemical changes associated with drying of fumarolic pathways (all CRAA sites), increases in gas geothermometry temperatures (Mount Mageik, Trident, Mount Baker, Mount Shasta), changes in $\delta^{13}\text{C}$ of CO_2 affiliated with magma movement (all CRAA site), and increases in $^3\text{He}/^4\text{He}$ coupled with intrusion of new magma (Mount Rainier, Augustine Volcano, Makushin, Mount Shasta). Repose magmatic degassing may discharge substantial amounts of S and Cl into the edifices of Mount Baker and several other CRAA volcanoes that is trapped by primary and secondary scrubbing. The consequent acidic fluids produce ongoing alteration in the 0.2- to 3-km-deep hydrothermal systems and in fields of boiling-point fumaroles near the surface. Such alteration may influence edifice stability and contribute to the formation of more-hazardous cohesive debris flows. In particular, we recommend further investigation of the volume, extent, and hazards of hydrothermal alteration at Mount Baker. Other potential hazards associated with the CRAA volcano hydrothermal systems include hydrothermal eruptions and, for deeper systems intruded by magma, deep-seated edifice collapse.

INTRODUCTION

The Cascade Range, related to subduction of the Juan de Fuca plate beneath the North American plate, forms a 1200-km-long arc that extends from British Columbia to northern California. The much longer Aleutian Arc in Alaska extends 2500 km from Hayes volcano in the east to Buldir in the west and results from subduction of the Pacific plate beneath the North American plate. The U.S. Geological Survey (USGS) is charged with providing timely warnings of future volcanic activity at over 60 potentially restless volcanoes in the Cascade Range and Aleutian Arc (CRAA). In 1992, as part of the USGS's overall geophysical and geochemical monitoring effort, we began sampling the gas discharges from 12 quiescent but potentially restless CRAA volcanoes (Figure 1) to characterize the compositions and origins of these gases, and to create baseline data for comparison during future unrest.

Our data show that these $\leq 173^\circ\text{C}$ discharges are dominated by meteoric water, CO_2 , and H_2S . In contrast, high-temperature ($>500^\circ\text{C}$) magmatic gases (HTMG) from convergent-plate volcanoes contain magmatic water and substantial CO_2 , SO_2 , and HCl (Giggenbach, 1992; Symonds and others, 1994; Giggenbach, 1996). Despite the apparent differences between the CRAA gases and HTMG, here we use thermochemical modeling (Symonds and others, 2001), evidence for subsurface heat, and a large body of chemical and isotopic data to demonstrate that these hydrothermal gases are mostly scrubbed HTMG (i.e., HTMG that reacted with large but variable amounts of liquid consisting mostly of meteoric water).

Scrubbing encompasses all processes that reduce emissions during reactions between HTMG, water, and sometimes rock, including dissolution into the aqueous phase (e.g., hydrolysis) and formation of precipitates (e.g., sulfur, sulfides, fluorides, sulfates) from gas-water or gas-water-rock reactions (Symonds and others, 2001). The concept of scrubbing, developed to explain low SO_2 emissions before and between the 1992 eruptions of Crater Peak at Mount Spurr (Doukas and Gerlach, 1995), builds on a large body of previous work. Economic geologists and geothermalists have long supported the idea that hydrothermal systems absorb HTMG, producing acidic fluids that promote hydrothermal alteration and mineralization (Holland, 1965; Burham, 1979; Brimhall and Ghiorso, 1983; Armannsson and others, 1982; Hedenquist and Lowenstern, 1994). In particular, hydrolysis of SO_2 produces $\text{SO}_4^{2-}(\text{aq})$, $\text{H}_2\text{S}(\text{aq})$, elemental sulfur, and $\text{H}^+(\text{aq})$, although $\text{H}_2\text{S}(\text{aq})$ can be consumed by reacting with $\text{Fe}^{2+}(\text{aq})$ to form pyrite (Holland, 1965; Armannsson and others, 1982). Recently, volcanologists have even shown that selective absorption of the more water-soluble species in HTMG (e.g., SO_2 and HCl) can produce some of the chemical variation in $>200^\circ\text{C}$ volcanic gases (Giggenbach, 1996; Giggenbach and others, 1990; Fischer and others, 1996; Fischer and others, 1997).

However, by linking hydrolysis and precipitation processes under one umbrella, scrubbing provides a fundamentally new way of thinking of low-temperature volcanic-hydrothermal gases as part of the continuum of reaction products between HTMG and water. New thermochemical modeling (Symonds and others, 2001) shows that scrubbing reactions with water cause $\text{H}_2\text{O-CO}_2\text{-SO}_2\text{-HCl}$ -dominated HTMG to evolve to $\text{H}_2\text{O-CO}_2\text{-H}_2\text{S}$ -dominated gases (with meteoric-magmatic water and magmatic C and S). These modifications are the result of hydrolysis and sulfur precipitation reactions that consume most of the SO_2 and HCl , produce small amounts of H_2S , and have little effect on CO_2 (Doukas and Gerlach, 1995; Symonds and others, 2001). Scrubbing in concert with significant water-rock reaction removes all species except CO_2 (Symonds and others, 2001). By demonstrating that the CRAA gases are scrubbed HTMG and therefore part of the continuum of reaction products between HTMG and water helps provide insight on potential gas precursors during future unrest and on hydrothermal hazards at CRAA volcanoes.

SAMPLING AND ANALYTICAL METHODS

During 1992-8, R. Symonds and B. Ritchie made two to six site visits to each volcano, except for Akutan and Makushin (only sampled in 1995), to sample the hottest or most vigorous summit or flank fumaroles. In some cases, only springs effervescing CO_2 (soda springs) or bubbling acidic pools are available to sample. The gas-sampling sites (from southeast to northwest in Figure 1) include Mount Shasta (bubbling acidic hot pool near summit), Mount Hood (3 boiling-point fumaroles at Crater Rock and Devils Kitchen near summit), Mount St. Helens (boiling-point fumarole on September 1984 lobe of lava dome), Mount Rainier (2 cold

soda springs at Longmire near base of southern flank), Mount Baker (3 superheated fumaroles in Sherman Crater), Augustine Volcano (boiling-point fumarole on 1986 dome), Mount Griggs (2 boiling-point summit fumaroles and 3 superheated flank fumaroles), Trident (boiling-point fumaroles on southeastern flank of pre-1963 edifice), Mount Mageik (4 superheated fumaroles in summit crater), Aniakchak Crater (cold soda spring on southwestern shore of Surprise Lake in caldera), Akutan (3 summit and 1 flank boiling-point fumaroles, and one hot soda spring at the base), and Makushin (boiling-point flank fumaroles in Glacier and Makushin Valleys).

At each site, they collected several gas subsamples for later analysis for bulk-gas composition, C isotopes, noble-gas isotopes, and, occasionally, δD and $\delta^{18}O$ of water. To sample fumaroles, a Ti tube was inserted into the vent and attached to a dewared tube that minimizes condensation; this apparatus was connected to the sampling bottle with a short piece of silicone rubber (Symonds and others, 1994). Bubbling-springs and pools were sampled using a funnel attached to a short piece of Tygon tubing (Fahlquist and Janik, 1992). Utmost care was taken in all sampling to avoid air contamination.

Between 1992 and 1998, 113 bulk-gas subsamples were collected in evacuated bottles partly filled with 4N NaOH solution (Fahlquist and Janik, 1992). Analytical work was performed by M. Iven in 1992, M. Thompson in 1993-4, the Thermochem Company in 1995, and C. Janik and D. Counce in 1996-8. In general, these subsamples were analyzed by gas chromatography (H_2 , CH_4 , N_2 , O_2 , Ar, He), ion chromatography (total S, HCl, HF), titration or manometric methods (CO_2), selective-ion electrode (NH_3), and gravimetric methods (H_2O) (Fahlquist and Janik, 1992; Trujillo and others, 1987). Total S is reported as H_2S based on the dominance of H_2S and the absence of SO_2 in concomitant dry gas analyses (see below). C. Janik and D. White also analyzed the 1996 samples for $\delta^{34}S$ of total S; analytical precision on the $\delta^{34}S$ values is ± 0.2 per mil.

To quality-assure the analytical results from the five different laboratories, we compared (1) analyses of duplicate bulk-gas subsamples collected simultaneously from the same vent, (2) dry-gas analyses of bulk-gas subsamples with dry-gas analyses from C-isotope and noble-gas subsamples (see below) collected concurrently from the same vent, and (3) analyses of bulk-gas subsamples collected from the same vent but on different dates to check for unreasonable changes in analyzed gas composition. Our evaluation shows that the bulk-gas analyses for the 1992 and 1996-8 samples display excellent agreement with the concurrent dry-gas analyses, although septum leaks produced small amounts of air contamination in some bulk-gas samples. Sampling and analytical precision on duplicate samples is generally better than $\pm 0.1\%$ for H_2O , $\pm 5\%$ for CO_2 and H_2S , $\pm 10\%$ for H_2 and CH_4 , $\pm 50\%$ for HCl, and $\pm 30\%$ for all other species. Higher precision values for N_2 , O_2 , Ar, and He reflect small but variable amounts of air contamination in duplicate samples. The high precision values for HCl probably indicate variable amounts of condensation in the sampling apparatus or scrubbing in the vent, which is more serious for samples from boiling-point fumaroles; HCl precision is generally better than $\pm 10\%$ for samples from $>110^\circ C$ superheated vents. The 1995 bulk-gas analyses are also of decent quality, although they bear high detection limits for HCl and have similar air-contamination problems. Unfortunately, the 1993-4 bulk-gas analyses suffer from several analytical errors and will not be considered further in this study.

Between 1994 and 1998, 37 C-isotope subsamples were collected in evacuated bottles. W. Evans analyzed these subsamples using mass spectrometry for $\delta^{13}C$ of CO_2 , $\delta^{13}C$ of CH_4 , and $\delta^{15}N$ of N_2 , and gas chromatography for dry-gas composition (CO_2 , H_2S , H_2 , CH_4 , N_2 , O_2 , Ar, He, C_2H_6 , CO, SO_2). Most samples have less than 0.5% air contamination. Analytical precision is

± 0.1 per mil for $\delta^{13}\text{C}$ of CO_2 , ± 0.5 per mil for $\delta^{13}\text{C}$ of CH_4 , and ± 0.2 per mil for $\delta^{15}\text{N}$ of N_2 . During the same period, 31 noble-gas subsamples were collected in leak-resistant bottles made of Corning-1720 glass and fitted with vacuum stopcocks. R. Poreda analyzed these subsamples for dry-gas composition ($\text{CO}_2 + \text{H}_2\text{S}$, CH_4 , H_2 , N_2 , O_2 , Ar, Ne, He, Kr), $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$, and several other noble-gas isotope ratios using mass spectrometry and other methods (Poreda and others, 1992). Analyses of the noble-gas subsamples are virtually free of artificial air contamination; any air in these samples is from the exhaled gas. Analytical precision is $\pm 3\%$ for concentrations of gas species, $\pm 0.3\%$ for $^3\text{He}/^4\text{He}$ ratios, and $\pm 0.2\%$ for $^{40}\text{Ar}/^{36}\text{Ar}$.

A few gas condensates were collected from superheated fumaroles at Mounts Baker, Griggs, and Mageik, and from a boiling-point fumarole at Makushin. These samples were analyzed by M. Huebner and L. White for δD and $\delta^{18}\text{O}$ of water. Analytical precision is ± 1.5 per mil for δD and ± 0.05 per mil for $\delta^{18}\text{O}$.

RESULTS

After careful evaluation, we have 80 high-quality bulk-gas analyses from 1992 and 1995-8 together with dry-gas analyses from concomitant noble-gas and C-isotope subsamples, 31 analyses of $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ from 1994-8, 37 analyses for $\delta^{13}\text{C}$ of CO_2 from 1994-8, and several analyses for $\delta^{13}\text{C}$ of CH_4 , $\delta^{15}\text{N}$ of N_2 , and δD and $\delta^{18}\text{O}$ of water. While broadly similar to related studies (Nehring and others, 1981; Poreda and Craig, 1989; Sheppard and others, 1992; Motyka and others, 1993), our analyses benefit from minimal sampling-induced air contamination, excellent quality assurance, and much better control on sulfur speciation. We also report the first published bulk-gas analyses from Aniakchak Crater, Mount Baker, Mount Shasta, and Trident, and the first C and He isotopic data for several sites.

We only present a subset of our chemical and isotopic data to support the scrubbing hypothesis. Additional isotopic data are published elsewhere (Symonds and others, 2003). Representative bulk-gas analyses for gas discharges from each volcano are reported in Table 1. Fumarole gas compositions reported as mol% in total gas; spring gas compositions reported as mol% in dry gas. Gases from boiling-point and superheated fumaroles are generally dominated by H_2O , CO_2 , and H_2S , but also contain lesser but variable amounts of N_2 , CH_4 , H_2 , HCl, HF, NH_3 , Ar, O_2 , and He. Dry-gas analyses of C-isotope subsamples collected at all sites demonstrate that H_2S is the dominant sulfur gas species and that SO_2 is below the 500 ppm detection limit (Symonds and Evans, unpublished results). In contrast, analyses of 1998 fumarole samples from Mount St. Helens (not shown) only contain detectable amounts of H_2O , CO_2 , and air. Likewise, CO_2 and meteoric components (N_2 , O_2 , Ar; mostly from air-saturated water) dominate samples from springs at Akutan, Aniakchak Crater, and Mount Rainier.

Table 1 also reports the $^3\text{He}/^4\text{He}$ isotope ratios and $\delta^{13}\text{C}$ of CO_2 values for the noble-gas and C-isotope subsamples, respectively, collected at the same time as the reported bulk-gas subsamples. All $^3\text{He}/^4\text{He}$ ratios are reported as R_C/R_A values where R_C is the ratio in the subsample, after correction for atmospheric contamination (Poreda and Craig, 1989), and R_A is the atmospheric ratio, using air helium as the absolute standard. The $\delta^{13}\text{C}$ of CO_2 data are reported as per mil values (‰) relative to PDB.

DISCUSSION

Evidence for scrubbing

Our samples of 25° to 173°C CRAA discharges differ significantly from HTMG. First, they are dominated by meteoric rather than magmatic water, as shown by a plot of $\delta^{18}\text{O}$ and δD values for condensed water from several CRAA superheated and boiling-point fumaroles (Figure 2). The isotopic shifts are in the general direction of andesitic (e.g., magmatic) water (Giggenbach, 1992), and suggest that superheated vents at Mount Mageik, for example, could contain up to ~35% andesitic water. However, some of the shift in $\delta^{18}\text{O}$ is probably due to hydrothermal water-rock exchange, as is likely the case for the boiling-point fumaroles on Mount Griggs. An additional complication is that all the condensates probably represent steam that separated from waters that are more isotopically enriched in $\delta^{18}\text{O}$ and possibly δD . So a precise computation of the amount of andesitic water in each feature cannot be made. Nonetheless, the data suggest that boiling-point vents contain mostly meteoric water and even superheated vents, which are meteoric-andesitic water mixtures, contain at least ~65% meteoric water.

Second, the CRAA gases have much more water relative to anhydrous species than do HTMG. Third, they lack detectable SO_2 , the third most abundant species in HTMG. Fourth, they possess mixtures of meteoric and magmatic Ar. $^{40}\text{Ar}/^{36}\text{Ar}$ values for most studied sites are <350 indicating a strong meteoric Ar component ($^{40}\text{Ar}/^{36}\text{Ar} = 295.5$ for air and air-saturated water); $^{40}\text{Ar}/^{36}\text{Ar}$ values between 350 and 550 for some or all samples from Trident, Mount Baker, Mount Hood, Mount Griggs, and Mount Shasta indicate a radiogenic Ar component in these gases from magmatic or crustal sources (Symonds and others, 2003).

Fifth, in contrast to HTMG, the CRAA gases have larger amounts of N_2 , CH_4 , and NH_3 . N_2 is a relatively minor species in air-free HTMG (Symonds and others, 1994; Giggenbach, 1996), but more abundant in the CRAA gases. N_2/Ar ratios in our leak-resistant noble-gas subsamples are between values for air-saturated water (38.4) and air (83.6) at Augustine Volcano, Aniakchak Crater, Mount St. Helens, and Mount Rainier indicating meteoric sources of N_2 at these sites (Symonds and others, 2003). Elevated N_2/Ar ratios between 117 (Makushin) and 1350 (Mount Shasta) point to excess N_2 at the other sites (Symonds and others, 2003); preliminary $\delta^{15}\text{N}$ values between +1‰ and +5‰ (relative to air) suggest a sedimentary source for the excess N_2 (Symonds and others, 2003). We think this sedimentary N_2 comes from thermogenic breakdown of subvolcanic sedimentary rocks (Symonds and others, 2003) in contrast to most studies that favor subducted sedimentary material as the source of sedimentary N_2 in convergent-plate volcanic gases (e.g., Matsuo and others, 1978). CH_4 and NH_3 are trivial species in HTMG (Symonds and others, 1994; Giggenbach, 1996), but are common in hydrothermal gases where they generally come from reactions between subvolcanic hydrothermal fluids and sedimentary rocks. A sedimentary origin for CH_4 is supported by the $\delta^{13}\text{C}$ of CH_4 data for Mount Shasta (-28‰ to -29‰ relative to PDB), Trident (-30‰), and Akutan (-40‰), which are much lighter than the -15‰ to -20‰ range for mantle CH_4 (Welhan, 1981), although somewhat heavier $\delta^{13}\text{C}$ of CH_4 values for Mount Baker (-22‰ to -23‰) may indicate mixing of magmatic and sedimentary C in CH_4 at this site (Symonds and others, 2003).

Despite their dissimilarities with HTMG, the CRAA gases have significant magmatic components of He, CO_2 , and S. The $^3\text{He}/^4\text{He}$ ratios of the CRAA gases range from 2.76 to 8.11 R_C/R_A , but exceed 7 R_C/R_A at eight volcanoes (Table 1). Convergent-plate mantle He is $8 \pm 1 R/R_A$ and crustal He is 0.02 R/R_A (Poreda and Craig, 1989). Using a simple mixing model

between mantle and crustal He, all of the CRAA discharges, including the cold springs, contain $\geq 91\%$ mantle or magmatic He, except for summit sites venting degassed magma (Mount Shasta, 74% mantle He; Augustine Volcano, 54% mantle He), or flank vents several km from the central conduit (Makushin, 60% mantle He; Mount Rainier, 35% mantle He). The $\delta^{13}\text{C}$ of CO_2 data for the CRAA gases range from -5.43‰ to -12.95‰ (Table 1), extending from typical mantle (e.g., magmatic) values of -5‰ to -8‰ (Allard, 1983) towards organic carbon, generally $< -20\text{‰}$. These results suggest that CO_2 comes from a mixture of mantle (e.g., magmatic) and organic sedimentary sources. At time of writing, we have $\delta^{34}\text{S}$ of total S for the 1996 bulk-gas samples from Mount Hood ($+4.7\text{‰}$ to $+5.3\text{‰}$ relative to CDT), Mount Shasta ($+3.8\text{‰}$), Makushin ($+1.0\text{‰}$ to $+1.1\text{‰}$), Akutan (-0.1‰ to -4.7‰), and Mount Baker (-7.3‰ to -9.8‰) (Symonds and Janik, unpublished results). The $\delta^{34}\text{S}$ values are within the reported range of volcanic sulfur gases and consistent with magmatic sulfur gases modified by scrubbing; the overall range in $\delta^{34}\text{S}$ values from $+5.3\text{‰}$ to -9.8‰ may reflect differences in the $\text{SO}_2/\text{H}_2\text{S}$ ratio in the magmatic gas and variable influence from several scrubbing reactions, especially hydrolysis of SO_2 to form SO_4^{2-} or HSO_4^{2-} (Rollison, 1993; Ohmoto and Rye, 1979).

The above observations suggest that the CRAA discharges are chiefly scrubbed HTMG based on the following evidence: (i) The fumarolic gases (Table 1) are mostly mixtures of meteoric and andesitic water with minor amounts of magmatic-organic C and magmatic S discharged primarily as CO_2 and H_2S , generally consistent with predictions for the reaction between HTMG and large but variable amounts of meteoric water (Symonds and others, 2001). The CO_2 -rich cold-spring discharges in Table 1 probably represent HTMG scrubbed at very low gas/water ratios in concert with water-rock reaction. (ii) Vent temperatures between 80° and 173°C (Table 1) are evidence for significant subvolcanic heat sources at all studied sites except Aniakchak Crater and Mount Rainier (Longmire Springs), but Rainier also has summit fumaroles up to 81°C indicating a heat source (Frank, 1995). Heat flow studies of the thermal areas at one site, Mount Hood, suggest that the heat source is deep-seated (Friedman and others, 1982). (iii) An empirical gas geothermometer (D'Amore and Panichi, 1980) applied to bulk-gas analyses from Akutan, Makushin, Mount Baker, Mount Griggs, Mount Hood, Mount Mageik, Mount Shasta, and Trident yields hydrothermal reservoir temperatures between 150° and 350°C (Figure 3). If these hydrothermal systems are heated by magma, such temperatures suggest that magma exists at depths of 3-10 km. (iv) The CRAA discharges contain significant magmatic components of He and CO_2 .

Nature of scrubbing

Scrubbing apparently occurs at both shallow and deep levels in CRAA volcanoes. The distribution of CRAA gases on a ternary diagram of CO_2 , total S, and HCl provides evidence for shallow scrubbing (Figure 4). The CRAA gases extend in an L-shaped pattern from the CO_2 apex of the diagram towards the HCl apex where HTMG plot. This trend is consistent with the predicted results (Symonds and others, 2001) for scrubbing of HTMG by various amounts of water (Figure 4). Samples from cold soda springs at Aniakchak and Mount Rainier, and the hot soda spring at Akutan are affected most by scrubbing and imply scrubbing conditions that include very low gas/water ratios with simultaneous water-rock reaction. These are followed consecutively by samples from the hot acidic pool at Mount Shasta and boiling-point fumaroles at Mount Griggs, Akutan, Makushin, Trident, and Mount Hood; these low-temperature samples are consistent with scrubbing at 0.1 MPa and gas/water weight ratios from 0.008 to 0.2. In

contrast, samples from superheated vents from Mounts Baker, Griggs, and Mageik show progressively less impact from scrubbing; these hotter samples imply scrubbing conditions ranging from 0.1 MPa and gas/water ratios of 0.04 (Mount Baker) to 1-2 MPa and gas water ratios of up to 1.5 (Mount Mageik).

Scrubbing conditions vary significantly from vent to vent at many CRAA volcanoes (Figure 4). As pointed out above, there are obvious variations in scrubbing conditions between springs and boiling-point fumaroles at Akutan, and boiling-point and superheated fumaroles at Mount Griggs. In addition, samples from different boiling-point fumaroles at Akutan and Mount Hood exhibit a range of S/CO₂ ratios, probably indicating variable degrees of scrubbing by shallow meteoric water; the sample with the high S/CO₂ ratio from Mount Hood may also contain extra sulfur from volatilization of near-vent sulfur deposits. Samples from different superheated fumaroles at Mounts Baker, Griggs, and Mageik also show wide variation in CO₂-S-HCl composition that may reflect variable degrees of scrubbing by shallow meteoric water. Interestingly, at Mount Mageik, as vent temperature increases from 101.6°C (one data point) to 130.1°C (one data point) to 149.8°C (one data point) to 167° - 173°C (cluster of data), the implied gas/water ratio also shows stepwise increases with an overall gain from ~0.3 to ~1.5. At the same time, the implied reservoir temperatures for all Mageik samples form a tight cluster between 301° and 316°C (Figure 3). These results imply that a similar reservoir gas feeds all the Mageik fumaroles and that variable amounts of scrubbing by shallow groundwater modify the deep gas to produce the observed variations in HCl concentrations (Figure 4) and vent temperatures.

Similar L-shaped patterns to those in Figure 4 have been documented for gases from White Island, Ngauruhoe, Nevado del Ruiz, and Galeras (Giggenbach, 1996; Giggenbach and others, 1990; Fischer and others, 1996; Fischer and others, 1997). However, these studies generally distinguish between magmatic gases (C/S < 10, S/Cl < 100) and hydrothermal gases (C/S > 10, S/Cl > 100) in the lower and upper arms of the "L", respectively, as though they come from separate reservoirs, and chemical variation along the "L" is attributed to absorption of HCl into hydrothermal waters and mixing of magmatic and hydrothermal gases. In contrast, the scrubbing hypothesis accounts for the entire range of magmatic and hydrothermal gases as part of the continuum of reaction products between HTMG and water in a single magmatic-hydrothermal system.

The CRAA gases also exhibit signatures of scrubbing within deeper hydrothermal systems. Gas geothermometry (Figure 3) implies higher temperatures than those obtained during low-pressure scrubbing. Also, many CRAA volcanoes have superheated fumaroles (Makushin, Mount Mageik, Mount Baker, Mount Griggs), flank hot springs (Akutan, Makushin, Mount Baker, Mount St. Helens), or summit crater lakes that are hot and acidic (Mount Mageik), which are common surface manifestations of subvolcanic hydrothermal systems; summit or flank boiling-point fumaroles indicate either subvolcanic hydrothermal systems or HTMG interacting with near-surface water. Finally, significant amounts of CH₄ and NH₃ in most CRAA gases (Table 1) point to hydrothermal fluids reacting with subvolcanic sedimentary rocks (see above). Therefore, we envision a several-stage process whereby magmatic gases are scrubbed in deeper hydrothermal systems (primary scrubbing) that boil to give rise to hydrothermal gases that often undergo additional though incomplete (disequilibrium) scrubbing as the gases react with near-surface meteoric water (secondary scrubbing).

Conceptual model for origin of CRAA discharges

Many processes affect the compositions of gas discharges from CRAA volcanoes during their current state of repose (Figure 5). Degassing magma is the ultimate source of many species in the CRAA gases. Depths to magma are probably within 3 to 10 km of the summits of CRAA volcanoes based on three factors: (i) Seismic and petrologic constraints on several CRAA volcanoes (Pallister and others, 1992; Power and others, 1994; Power and others, 1995). (ii) We estimate the depths of the CRAA hydrothermal systems at ≤ 3 km (Figure 3). Given these shallow depths and the $>300^\circ\text{C}$ gas-geothermometry temperatures at Mount Mageik, Makushin, Trident, and Mount Hood (Figure 3), this implies magma at 3-5 km depth for these systems. (iii) The $^3\text{He}/^4\text{He}$ isotope ratios of $>7.2 R_C/R_A$ values at Akutan, Mount Mageik, Mount Hood, Mount Baker, Trident, Mount Griggs, and Aniakchak Crater imply proximal magma.

This shallow magma degasses HTMG (H_2O , CO_2 , SO_2 , H_2 , H_2S , HCl , HF , CO , Ar , He) (Symonds and others, 1994; Giggenbach, 1996) that are scrubbed by descending meteoric waters in a hydrothermal system to typically produce gases with $\geq 98\%$ H_2O , $\leq 2\%$ CO_2 and H_2S , and trace amounts of H_2 , HCl , HF , Ar , and He . This is the zone of primary scrubbing. Other potentially significant sources for some minor species include anoxic meteoric water as another source of Ar and crustal sedimentary rocks reacting with hydrothermal fluids to produce N_2 , CH_4 , and NH_3 . The resulting gas mixture may be scrubbed again (secondary scrubbing) in the zone of saturation prior to discharge from boiling-point to superheated fumaroles in CRAA volcanoes. Secondary scrubbing may be somewhat variable producing vent-to-vent variations in S/CO_2 ratios and HCl concentrations. A significant amount of the magmatic S , Cl , and F dissolve in hydrothermal or meteoric water, and magmatic S also precipitates as native sulfur. Additional sulfur loss comes from reaction of the hydrothermal fluids with the surrounding wall rocks and precipitation of sulfides and sulfates. These hydrothermal water-rock reactions weaken the edifice by altering competent volcanic rock. A significant portion of the hydrothermal fluid may discharge through the groundwater system. Neutral groundwaters may dissolve CO_2 and other gases at higher pressures within the edifice and discharge them when the waters surface at springs.

Potential precursors

In addition to seismic and geodetic monitoring, gas studies can play an important role in assessing volcanic activity at CRAA volcanoes. Prior to future eruptions at CRAA volcanoes, we expect intrusion of new magma or movement of older magma to shallower levels. What gas geochemical precursors might best indicate such changes? We think that airborne monitoring of CO_2 and SO_2 emission rates and continuous monitoring of CO_2 concentrations in soil are the best gas-monitoring methods available at time of writing. The strong evidence for scrubbing at multiple CRAA volcanoes bolsters the proposal (Symonds and others, 2001) of simultaneously monitoring the emission rates of CO_2 and SO_2 to help forecast future eruptions at these wet volcanoes. Movement of magma from a deep reservoir to shallow levels within the edifice would most certainly be accompanied by increased degassing. CO_2 is the most likely candidate for early detection in CRAA volcanoes where scrubbing might be widespread, whereas the onset of SO_2 emissions requires establishing dry magma-to-atmosphere pathways (Doukas and Gerlach, 1995; Symonds and others, 2001). The most practical methods for determining CO_2 and SO_2 emission rates in the snow- and ice-clad CRAA volcanoes are airborne LICOR and

Correlation Spectroscopy, respectively (Gerlach and others, 1997). Continuous monitoring of CO₂ concentrations in soils in relatively snow-poor thermal areas might also be effective (McGee and others, 2000).

However, gas sampling can augment other monitoring methods by providing complete chemical and isotopic compositional information on the gas discharges. For gas sampling, the most promising precursors might indicate the evolution of these hydrothermal discharges towards HTMG. If this evolution occurs, we expect the following precursors using predictions from thermochemical modeling (Symonds and others, 2001) and results from other volcanoes (Giggenbach, 1996; Giggenbach and others, 1990; Fischer and others, 1996; Fischer and others, 1997). Initially, as fumarolic pathways begin to dry out, we expect the gases to have increasing proportions of HCl relative to CO₂ and total S as they become more magmatic, following the predicted trends in Figure 4. If pathway drying proceeds further so that HTMG vents to the surface, then we also expect significant increases in vent temperatures and concentrations of SO₂ and HCl. CO₂ concentrations and several gas ratios might also increase as pathways dry out, but such changes require a case-by-case interpretation (Symonds and others, 2001).

Complete drying of fumarolic pathways seems most promising for superheated vents at Mounts Mageik, Griggs, and possibly Baker, which show the least influence from scrubbing. However, most CRAA volcanoes discharge highly scrubbed gases from boiling-point fumaroles and bubbling springs; these vents might not dry out sufficiently to show significant chemical or temperature gas precursors before the next eruption. For example, large amounts of water from snowmelt or groundwater prevented drying of magma-to-atmosphere pathways before recent eruptions at Mount St. Helens (1980) and Crater Peak of Mount Spurr (1992) (Doukas and Gerlach, 1995; Symonds and others, 2001).

Another promising precursor at some CRAA volcanoes might be increases in gas geothermometry temperatures. Intrusion of new magma or movement of older magma to shallower levels might heat a hydrothermal system. Gas geothermometry (e.g., D'Amore and Panichi, 1980) might be able to detect such heating. For instance, increases in gas geothermometer temperatures accompanied seismic unrest at Campi Flegrei in 1994 (Tedesco and Scarsi, 1999). Precursory increases in gas geothermometer temperatures seem most promising for fumaroles that show consistent geothermometer results such as at selected fumaroles at Mount Mageik, Trident, Mount Baker, and Mount Shasta (Figure 3). In addition, fumaroles that vent deeper hydrothermal systems (e.g., Trident, Mount Mageik; Figure 3) might show earlier increases in geothermometer temperatures than fumaroles that vent shallow systems (e.g., Mount Baker, Mount Shasta; Figure 3).

Isotopic changes in the discharge gases may also precede eruptions at some CRAA volcanoes. In particular, future unrest at CRAA volcanoes may produce changes in $\delta^{13}\text{C}$ of CO₂ if the activity modifies the proportions of mantle and organic sedimentary C implied in Table 1; such change might occur along with magma movement. In addition, magma intrusion or seismic unrest is often accompanied by increases in ³He/⁴He (Tedesco and Scarsi, 1999; Sorey and others, 1993). However, significant increases in ³He/⁴He appear unlikely at many CRAA volcanoes because they already discharge near-magmatic He (Table 1). But the lower values of 5.90 and 4.28 R_C/R_A at summit fumaroles on Mount Shasta and Augustine Volcano, respectively, suggest that these magmatic systems are relatively degassed and that intrusion of new magma prior to the next eruptions at these volcanoes might produce precursory increases in ³He/⁴He. Indeed, between the 1976 and 1986 eruptions of Augustine Volcano, values of R_C/R_A were 7.66 (1978) and 7.60 (1982) (Poreda and Craig, 1989). Increases in ³He/⁴He are also potential

precursors at flank vents at Mount Rainier (Longmire Springs) and Makushin, which currently have R_C/R_A values of 2.76 and 4.81. In addition, intrusion of new magma at Mount Rainier might produce significant increases in He concentrations in the Longmire gases since the leak-resistant noble-gas subsamples from Longmire only contain 30 to 50 ppb He.

Hazards implications

By producing acidic fluids, scrubbing contributes to ongoing and potentially hazardous hydrothermal alteration at CRAA volcanoes. Acidic fluids dissolve and alter competent volcanic rock, processes that may influence edifice stability by forming zones of weakness along fractures, dikes, and bedding surfaces (López and Williams, 1993; Scott and others, 1995; Crowley and Zimbelman, 1997). Clay-size minerals in hydrothermal alteration can also contribute to the formation of debris flows that can travel farther as a cohesive unit than more granular flows (Scott and others, 1995).

To determine the impact of ongoing scrubbing on rock-alteration hazards at CRAA volcanoes, we need estimates of the scrubbing rates. Mount Baker is an example where we can estimate scrubbing rates using CO_2 emission rates and bulk-gas compositions. In July 1998 Mount Baker was emitting $2.0 - 2.5 \times 10^5$ kg/day of CO_2 (M. P. Doukas and T. M. Gerlach, personal communication, 1999). Similar CO_2 emission rates of $1.87 \pm 0.26 \times 10^5$ kg/day were measured in September 2000 (McGee and others, 2001). Using the 1998 CO_2 emission rate and the $\text{H}_2\text{S}/\text{CO}_2$ and HCl/CO_2 ratios from August 1997 gas samples (Symonds, Counce, and Janik, unpublished data), we estimate discharge rates of only $7.1 - 15 \times 10^3$ kg/day for H_2S and $10 - 65$ kg/day for HCl . The molar C/S (13 - 22) and C/Cl (3200 - 17000) ratios in the discharged gases are substantially higher than in typical andesitic-dacitic convergent-plate HTMG (Symonds and others, 1994), implying that the Mount Baker hydrothermal system scrubs $1.0 - 8.4 \times 10^4$ kg/day of S and $1.1 - 6.7 \times 10^4$ kg/day of Cl. In addition, several Aleutian-Arc volcanoes probably have high scrubbing rates based on visual degassing rates, although CO_2 emission rates have not yet been measured at these sites. Mount Mageik is by far the most vigorously degassing volcano in our study and it clearly has high rates of scrubbing. But Mount Griggs, Trident, Akutan, and Makushin also display significant amounts of degassing and therefore probably have notable rates of scrubbing. However, we think it likely that Mounts Shasta and Hood have low scrubbing rates because these volcanoes have very low CO_2 emission rates compared to Mount Baker (M. P. Doukas and T. M. Gerlach, personal communication, 1999). Nonetheless, we cannot preclude the possibility that Mount Shasta, Mount Hood, and other CRAA volcanoes have high scrubbing rates even without significant CO_2 degassing or surficial evidence of degassing; it is possible that scrubbing is so severe that it even prevents significant CO_2 emissions.

We expect that most of the ongoing alteration in CRAA volcanoes is associated with primary scrubbing in hydrothermal systems. Using the predicted depths to the tops of the hydrothermal systems for 8 CRAA volcanoes (Figure 3), we infer that alteration is occurring high within the edifices of Mounts Shasta, Griggs, and Baker, but near or below the base of the edifices of Mount Mageik, Makushin, Trident, and Mount Hood; at Akutan, alteration occurs both at the summit and the base. Secondary scrubbing can also produce shallow alteration when acidic gases boiled from these hydrothermal systems are scrubbed by groundwater. Such secondary alteration may be most effective for the deep but hot hydrothermal systems at Mount Hood, Trident, Makushin, and Mount Mageik since high-pressure boiling hydrothermal systems

release gases that are richer in H₂S and HCl than gases from low-pressure boiling systems (Symonds and others, 2001). Secondary scrubbing is also more effective at boiling-point fumaroles than at superheated fumaroles where more of the acidic gases vent into the atmosphere. For instance, the boiling-point fumarole fields at Makushin and Trident display extensive advanced argillic alteration. Generation of alteration from secondary scrubbing also seems promising for Mount Mageik where some of the hydrothermal gases are scrubbed by an acidic summit-crater lake that may drain into and alter the edifice.

Ultimately, the potential hazards associated with hydrothermal alteration at each CRAA volcano depends on the spatial distribution of hydrothermal alteration and the proximity of the volcano to civilization. Mount Rainier is an example of a CRAA volcano that is both close to Washington's crowded Puget Sound region and also displays extensive hydrothermal alteration that may contribute to edifice instability and the generation of cohesive debris flows (Scott and others, 1995; Crowley and Zimbelman, 1997). Recently, high-resolution airborne magnetic and electromagnetic surveys have been used to map the volume and extent of hydrothermal alteration at Mount Rainier (Finn and others, 2001). These maps help constrain modeling of the role of hydrothermal alteration in potential edifice failures at Mount Rainier (Reid and others, 2001). Based on our work, we recommend additional geophysical surveys and edifice-stability modeling at Mount Baker where there is evidence of substantial ongoing shallow alteration within the upper edifice. Mount Baker displays extensive upper-edifice alteration, and has produced several Holocene debris flows that contain significant amounts of the alteration minerals, kaolinite and alunite (Frank, 1983). Mount Baker is also close enough to civilization that debris flows or edifice failure could be hazardous (Gardner and others, 1995). Another potential target is the upper edifice of Mount Mageik, which shows evidence of substantial ongoing alteration, although Mageik is too remote to have significant debris-flow or edifice-failure hazards. Though close to civilization, the south side of Mount Hood and the summit region of Mount Shasta appear less promising because surficial alteration is not particularly extensive at these sites and, as discussed above, scrubbing rates appear relatively low.

Finally, hydrothermal systems themselves can be hazardous. Precipitation of silica and minerals can cause self sealing of hydrothermal systems, producing rapid increases in pressure that sometime lead to hydrothermal eruptions (e.g., the 1843 eruption of Mount Baker). Intrusions or heating of deeper hydrothermal systems also generates rapid excursions in pressure that might help trigger deep-seated edifice collapse.

CONCLUSIONS

While most potentially restless CRAA volcanoes have not erupted for decades to centuries, many degas small to moderate amounts of HTMG from 3-10 km deep magma reservoirs. The magma reservoirs are apparently at least partially resupplied during repose—otherwise, how can one account for near-mantle ³He/⁴He values at CRAA volcanoes without recent magmatic eruptions (e.g., Mounts Baker and Griggs)? Prior to discharge from ≤ 173°C fumaroles and springs, the HTMG are heavily modified from variable amounts of scrubbing by deep hydrothermal and shallow meteoric water. The concept of scrubbing enables one to view these hydrothermal gases as part of the continuum of reaction products between HTMG and water.

By masking magmatic degassing, scrubbing presents a challenge for gas-monitoring of CRAA volcanoes. We concur with other recent studies (Doukas and Gerlach, 1995; McGee and

others, 2000; Symonds and others, 2001) that the best strategies for detecting gas precursors to future CRAA eruptions are to measure periodically the emission rates of CO₂ and SO₂, and to monitor continuously CO₂ concentrations in soils around volcanic vents. CO₂ is the second-most abundant species in magmatic gases and has a relatively low solubility in water and magma; hence, it is an ideal candidate for monitoring magma movement. In contrast, SO₂—third in abundance behind CO₂—has a relatively high solubility in water making it an ideal candidate to detect drying out of degassing pathways. Timely sampling of fumaroles can augment the geochemical surveillance program by providing complete chemical and isotopic compositions of the gas discharges. In particular, the extent of scrubbing can be determined by measuring the relative proportions of CO₂ to total S to HCl (Figure 4), the vent temperatures, and the concentrations of SO₂ and HCl. The chemical compositions of gases can also constrain gas geothermometers to help detect changes the temperature of the hydrothermal systems; this might be particular effective for selected vents at Mount Mageik, Trident, Mount Baker, and Mount Shasta, which exhibit relatively constant geothermometry temperatures. In addition, changes in δ¹³C of CO₂ might indicate magma movement, since the δ¹³C values of the CRAA gases indicate mixing between magmatic and organic sedimentary sources. Finally, intrusion of new magma might be accompanied by increases in ³He/⁴He R_C/R_A values at Mount Rainier (Longmire Springs), Augustine Volcano, Makushin, and Mount Shasta, since these sites currently have relatively low R_C/R_A values. Precursory increases in R_C/R_A values at other CRAA volcanoes seem unlikely because they already are close to the mantle value.

Through hydrolysis of SO₂, H₂S, and HCl, scrubbing creates acidic fluids that hydrothermally alter rocks in 0.2- to 3-km-deep hydrothermal systems and in fields of boiling-point fumaroles near the surface at many CRAA volcanoes. Hydrothermal alteration is potentially hazardous because it may influence edifice stability and contribute to the formation of more-hazardous cohesive debris flows. There is evidence of significant rates of scrubbing and hence alteration at Mount Baker, Mount Griggs, Trident, Akutan, and Makushin. Mount Baker raises concern because the ongoing scrubbing occurs high in the edifice, it has significant amount of upper edifice alteration, it has produced several alteration-rich Holocene debris flows, and it is close enough to civilization that debris flows or edifice failure could be hazardous. Therefore, we recommend aerogeophysical and hazard-modeling studies of the volume, extent, and hazards of hydrothermal alteration at Mount Baker, similar to recent investigations of Mount Rainier (Finn and others, 2001; Reid and others, 2001). Other potential hazards associated with the CRAA volcano hydrothermal systems include hydrothermal eruptions and, for deeper systems intruded by magma, deep-seated edifice collapse.

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Table 1. Representative chemical compositions (in mol% in total gas for fumaroles and mol% in dry gas for springs), $^3\text{He}/^4\text{He}$ ratios (in R_C/R_A values), and $\delta^{13}\text{C}$ of CO_2 (in ‰ relative to PDB) for gases from Cascade-Range and Aleutian-Arc volcanoes

Volcano	Sub-sample ^a	Vent type ^b	T (°C)	H ₂ O	CO ₂	H ₂ S	N ₂	CH ₄	H ₂	HCl	HF	NH ₃	Ar	O ₂	He	$^3\text{He}/^4\text{He}$ R_C/R_A	$\delta^{13}\text{C}$ (‰)
Boiling-point and Superheated Fumaroles																	
Akutan	960729-1	SF	96.6	99.212	0.710	0.0495	0.0250	0.0025	5.2x10 ⁻⁴	5.7x10 ⁻⁹	<3x10 ⁻⁶	<3.1x10 ⁻⁶	1.5x10 ⁻⁴	1.9x10 ⁻⁴	4.5x10 ⁻⁶	7.24	-12.0
"	960728-1	FF	97.8	94.404	5.33	0.114	0.113	0.0129	0.0273	<5.3x10 ⁻⁷	<4x10 ⁻⁶	2.6x10 ⁻⁴	3.1x10 ⁻⁴	2.5x10 ⁻⁴	1.9x10 ⁻⁵	7.26	-9.70
Augustine	920713-2	SF	97.0	99.84	0.0073	0.0046	0.0025	9.5x10 ⁻⁷	0.1399	1x10 ⁻⁴	1x10 ⁻⁴	ND	ND	5.7x10 ⁻⁴	BD	4.28 ^c	-5.43 ^c
Baker	970807-5	SF	134.4	98.267	1.623	0.0916	0.00720	0.00709	0.00381	5.1x10 ⁻⁴	<0.0016	2x10 ⁻⁵	1x10 ⁻⁵	9x10 ⁻⁶	1x10 ⁻⁵	7.70	-6.88
"	970807-8	SF	107.7	98.201	1.655	0.126	0.00751	0.00746	0.00271	<1x10 ⁻⁴	<0.0018	1x10 ⁻⁵	9x10 ⁻⁶	5x10 ⁻⁶	1x10 ⁻⁵	ND	-6.12
Griggs	950722-1	SF	93.8	98.878	1.06	0.0290	0.0288	<1.7x10 ⁻⁵	7.9x10 ⁻⁴	<0.0032	ND	1.5x10 ⁻⁴	4.5x10 ⁻⁴	1.1x10 ⁻⁴	ND	8.11	-6.29
"	970718-1	FF	99.2	96.741	2.951	0.252	0.0204	2.46x10 ⁻⁴	9.8x10 ⁻⁵	0.0341	<0.0017	<9x10 ⁻⁶	1.3x10 ⁻⁴	1x10 ⁻⁵	6.4x10 ⁻⁵	7.94	-5.59
Hood	970508-1	SF	90.3	98.495	1.172	0.260	0.0331	<7x10 ⁻⁶	0.0396	<1x10 ⁻⁴	<0.0015	<9x10 ⁻⁶	2.3x10 ⁻⁴	6x10 ⁻⁵	4x10 ⁻⁵	ND	ND
"	970909-2	SF	91	97.650	2.156	0.115	0.0286	<8x10 ⁻⁶	0.0504	7.8x10 ⁻⁵	<0.0030	<1x10 ⁻⁵	2.4x10 ⁻⁴	4x10 ⁻⁵	2x10 ⁻⁵	7.60	-9.08
Mageik	970719-5	SF	172.9	96.003	3.485	0.366	0.0319	0.00103	0.0636	0.0484	<0.0044	0.00120	1.1x10 ⁻⁴	4x10 ⁻⁵	<1x10 ⁻⁵	7.57	-6.75
Makushin	960724-1	FF	100	99.870	0.109	0.0110	0.00876	1.2x10 ⁻⁵	0.0014	7.7x10 ⁻⁹	<2x10 ⁻⁶	2.6x10 ⁻⁶	1.5x10 ⁻⁴	4x10 ⁻⁵	BD	4.81	-7.57
Trident	970717-1	FF	94.2	89.15	8.188	0.346	0.192	0.231	1.87	0.0011	0.011	0.0155	0.002	0.001	<2x10 ⁻⁴	7.82	-10.51
Thermal and Cold Springs																	
Akutan	960727-2	FSS	97.4	NA	89.1	<0.004	8.83	1.65	0.014	3.7x10 ⁻⁴	<0.0002	3.1x10 ⁻⁴	0.37	0.074	5.3x10 ⁻⁴	5.78	-12.34
Aniakchak	970712-2	SSS	25	NA	63.02	<0.009	36.0	0.26	0.073	0.014	<0.50	<0.001	0.519	0.055	0.02	8.06	-6.11
Rainier	970808-5	FSS	20	NA	99.78	<0.001	0.144	0.0020	5.3x10 ⁻⁴	<0.003	<0.039	<1x10 ⁻⁴	0.00295	0.0699	4x10 ⁻⁵	2.76	-12.95
Shasta	970626-1	SAP	80.2	NA	94.44	0.279	2.95	1.00	0.952	0.0078	0.21	<3x10 ⁻⁴	0.016	0.135	<5x10 ⁻⁴	5.90	-11.4

NA, not applicable; ND, not determined; BD, below detection.

CO is below detection in all but the Augustine sample (8x10⁻⁴).

^aRepresents year, month, day, and subsample sequence.

^bSF, summit fumarole; FF, flank fumarole; SSS, summit soda spring; FSS, flank soda spring; SAP, summit acid pool.

^cSubsample collected on 7/28/94.

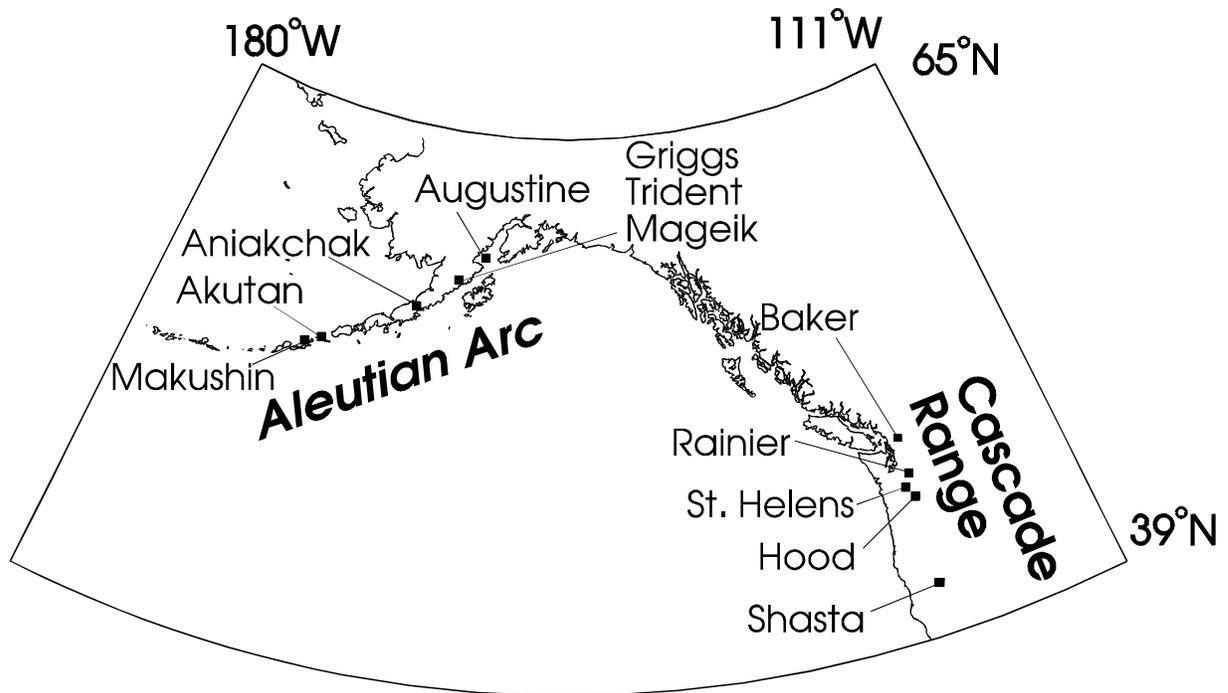


Figure 1. Map of northwestern North America showing location of volcanoes sampled in the Cascade Range and Aleutian Arc.

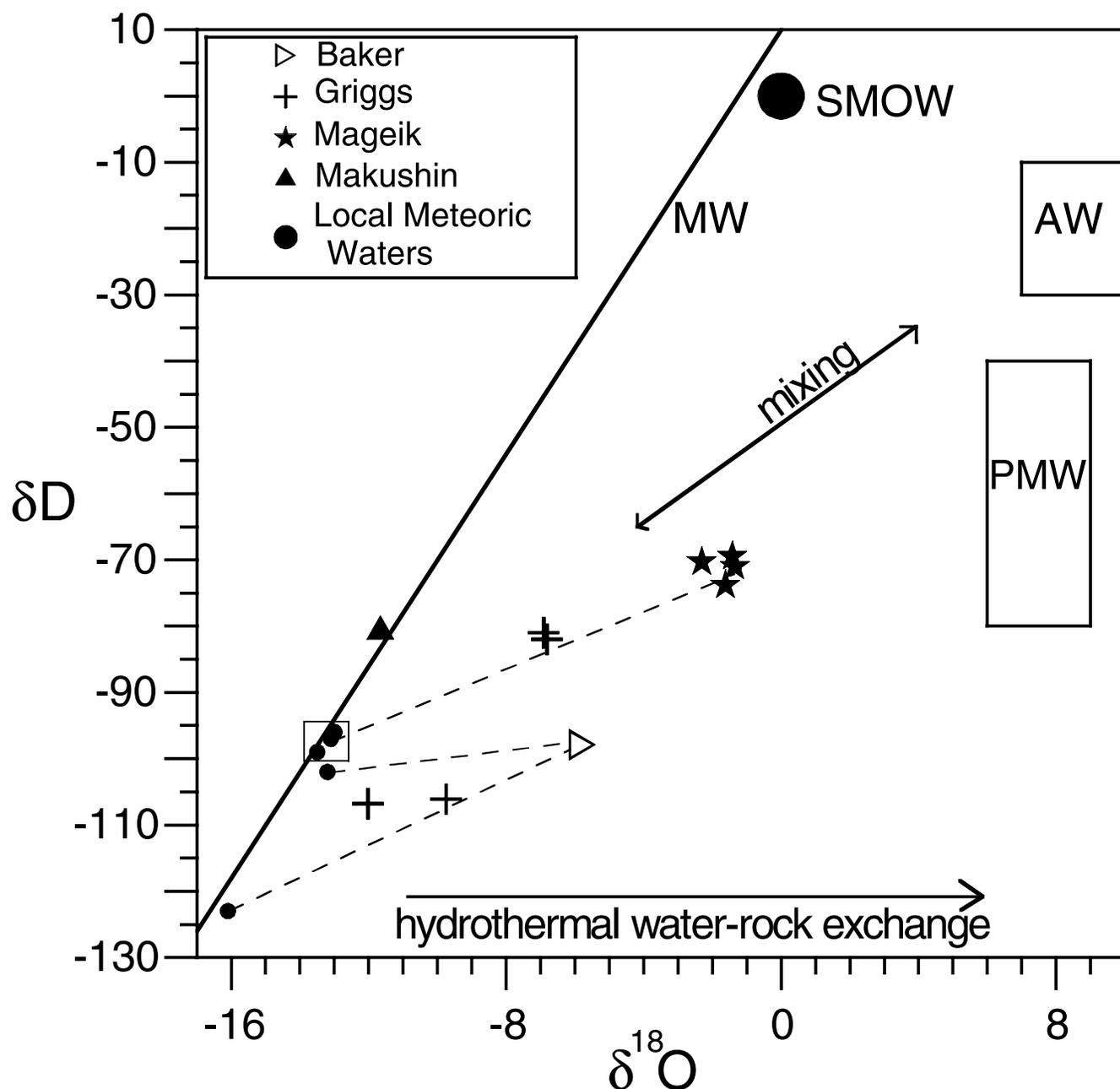


Figure 2. Plot of $\delta^{18}\text{O}$ and δD values for condensed water from superheated fumaroles at Mounts Baker, Griggs (two highest δD points), and Mageik, and from boiling-point fumaroles at Mount Griggs (two lowest δD points) and Makushin. Dashed lines connect values for condensates at Mounts Baker and Mageik with their respective local meteoric waters. Plotted meteoric waters for Mount Mageik are from nearby sites (Keith and others, 1992); the two plotted meteoric waters for Mount Baker are estimates for the elevation of the sampling site and the summit derived from data from nearby Mount Rainier (Frank, 1995). Also shown for reference are the meteoric water (MW) line (Craig, 1961), standard mean ocean water (SMOW), the andesitic water (AW) box (Giggenbach, 1992), and the primary magmatic water (PMW) box (Sheppard and others, 1969). All data reported as per mil values relative to SMOW.

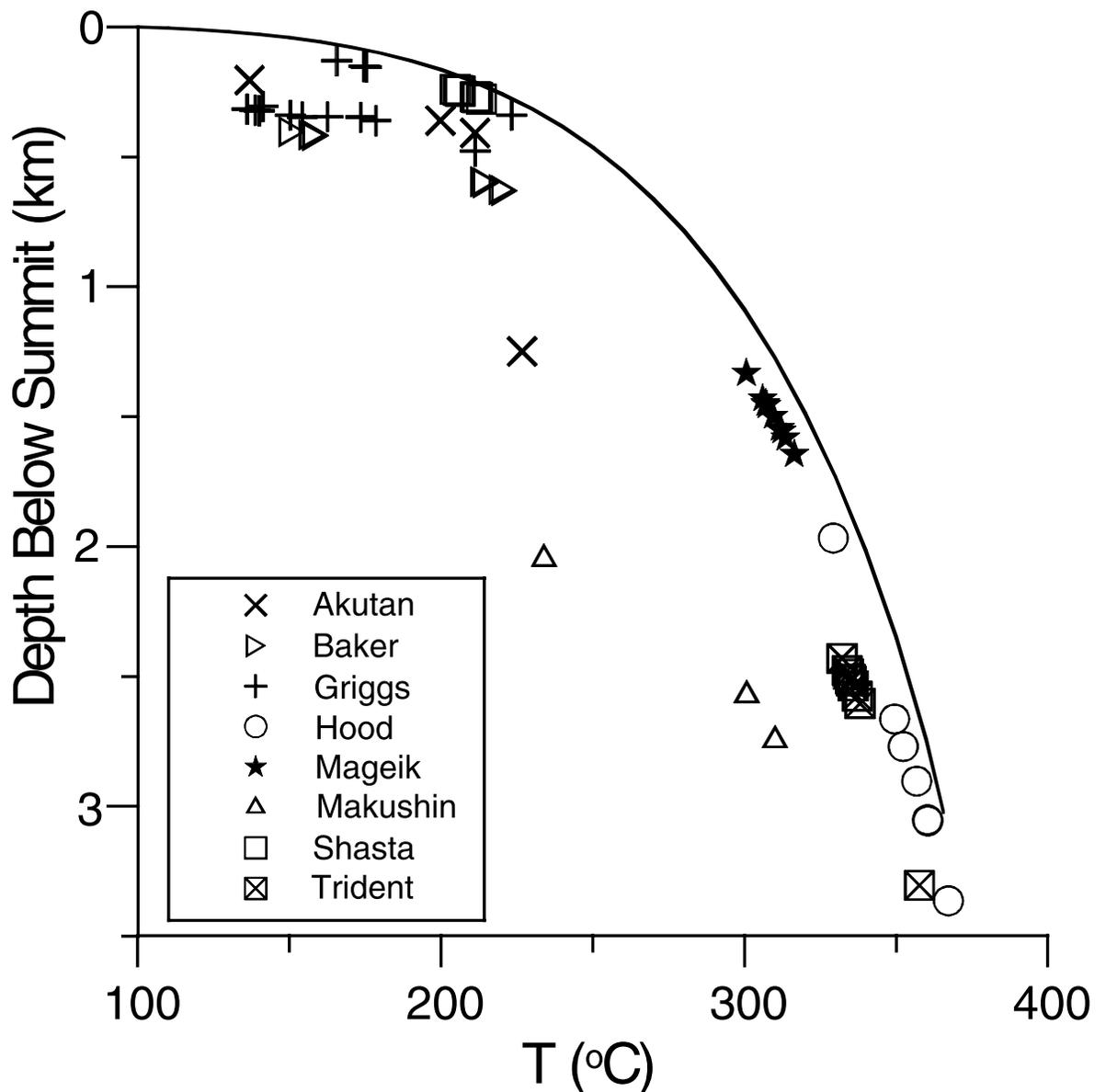


Figure 3. Diagram showing relation between reservoir temperature and inferred depth below summit for eight CRAA volcanoes. The boiling curve of water is shown for reference. Subsurface temperatures estimated by applying an empirical $\text{H}_2\text{S}-\text{H}_2-\text{CH}_4-\text{CO}_2$ geothermometer (D'Amore and Panichi, 1980) to the bulk-gas analyses. Depth below summit estimated by adding the boiling-curve depth for the geothermometer temperature to the elevation difference between the site and the summit. Note that summit-to-site elevation differences explain why the points plot beneath the boiling curve; the site-to-reservoir depth can be determined by extrapolating from the plotted points to the boiling curve with a vertical line.

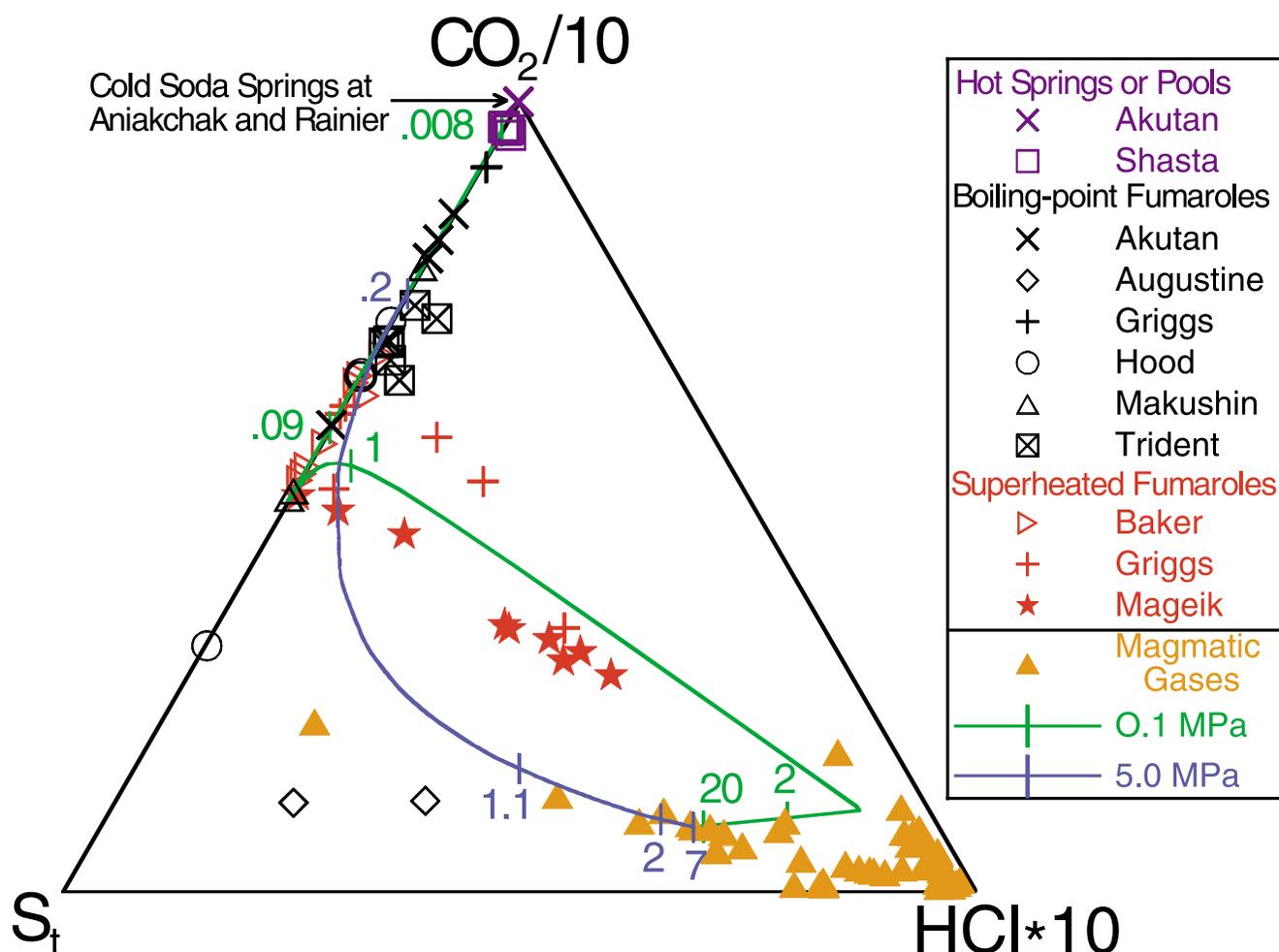


Figure 4. Ternary diagram of CO₂, total S, and HCl for gas discharges from CRAA volcanoes. Plot distinguishes between gases from cold soda springs (arrow near CO₂/10 apex), hot springs or pools (blue), boiling-point fumaroles (black), and superheated fumaroles (red). For comparison, we plot HTMG (orange) from convergent-plate volcanoes (Symonds and others, 1994). Green line shows evolution of "scrubbed" gas composition produced by injecting increasing amounts of hot magmatic gas into 1 kg of 25°C air-saturated water at 0.1 MPa using a thermochemical modeling approach (Symonds and others, 2001). The injected gas, representative of convergent-plate HTMG, is a 915°C gas from Merapi volcano, Indonesia (Le Guern and others, 1982). The numbers next to green line denote kg of gas added; as the calculations proceed, the mixture changes from liquid-plus-gas (0.008 to 1.7 kg of gas added; T = 81° - 106°C) to gas-only (1.7 to 100 kg of gas added; T = 106° - 895°C). Navy line shows "scrubbed" gas composition for the same reaction at 5.0 MPa (Symonds and others, 2001).

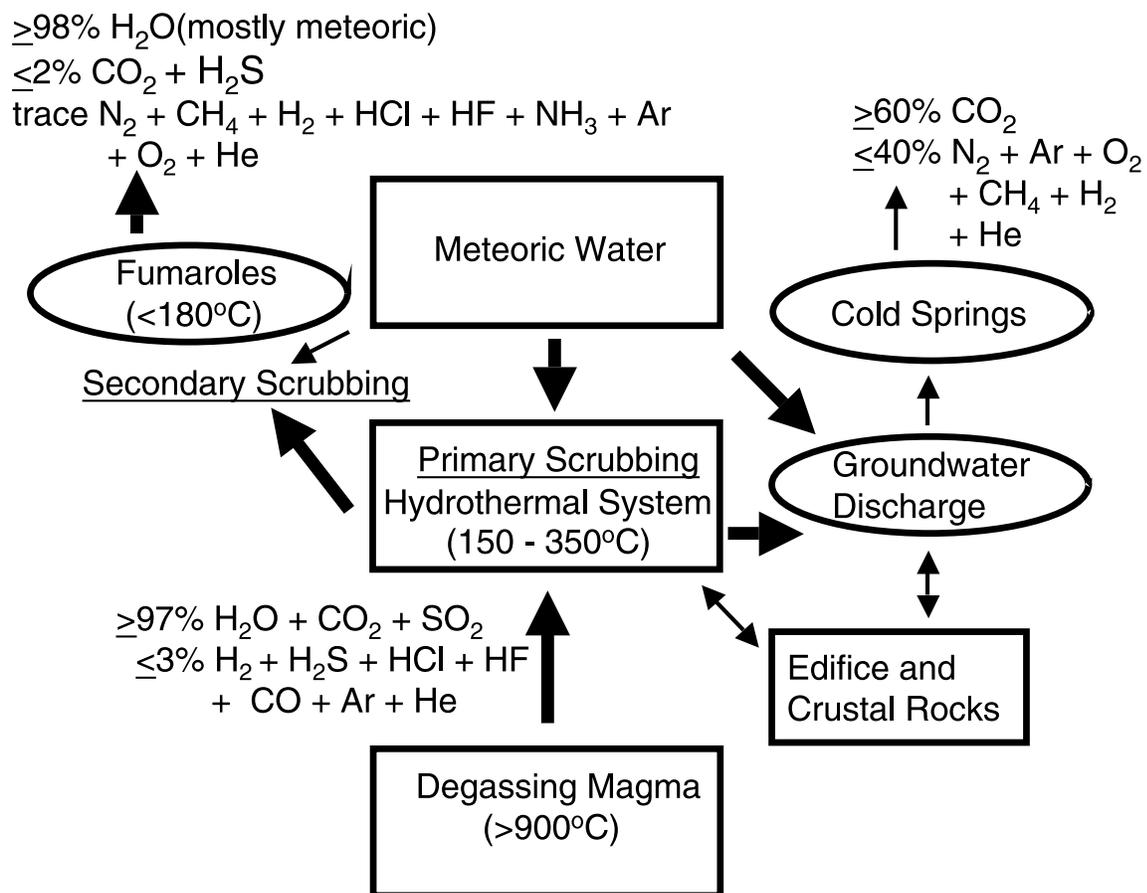


Figure 5. Simplified box model of inputs (rectangles) and outputs (ellipses) of gases in a typical CRAA volcanic system during repose between eruptions (see text). Note zones of primary and secondary scrubbing as discussed in text. Thick and thin arrows indicate dominant and less important flow paths, respectively. Double arrows mark two-way flow paths.