



Mantle and crustal sources of carbon, nitrogen, and noble gases in Cascade-Range and Aleutian-Arc volcanic gases

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ABSTRACT

Here we report anhydrous chemical (CO_2 , H_2S , N_2 , H_2 , CH_4 , O_2 , Ar, He, Ne) and isotopic ($^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $\delta^{13}\text{C}$ of CO_2 , $\delta^{13}\text{C}$ of CH_4 , $\delta^{15}\text{N}$) compositions of virtually air-free gas samples collected between 1994 and 1998 from 12 quiescent but potentially restless volcanoes in the Cascade Range and Aleutian Arc (CRAA). Sample sites include $\leq 173^\circ\text{C}$ fumaroles and springs at Mount Shasta, Mount Hood, Mount St. Helens, Mount Rainier, Mount Baker, Augustine Volcano, Mount Griggs, Trident, Mount Mageik, Aniakchak Crater, Akutan, and Makushin. The chemical and isotopic data generally point to magmatic (CO_2 , Ar, He), shallow crustal sedimentary (hereafter, SCS) (CO_2 , N_2 , CH_4), crustal (He), and meteoric (N_2 , Ar) sources of volatiles. CH_4 clearly comes from SCS rocks in the subvolcanic systems because CH_4 cannot survive the higher temperatures of deeper potential sources. Further evidence for a SCS source for CH_4 as well as for non-mantle CO_2 and non-meteoritic N_2 comes from isotopic data that show wide variations between volcanoes that are spatially very close and similar isotopic signatures from volcanoes from very disparate areas. Our results are in direct opposition to many recent studies on other volcanic arcs (Kita and others, 1993; Sano and Marty, 1995; Fischer and others, 1998), in that they point to a dearth of subducted components of CO_2 and N_2 in the CRAA discharges. Either the CRAA volcanoes are fundamentally different from volcanoes in other arcs or we need to reevaluate the significance of subducted C and N recycling in convergent-plate volcanoes.

INTRODUCTION

The concentrations and isotopic compositions of CO_2 , N_2 , CH_4 , Ar, and He in convergent-plate volcanic gases help provide insight on several aspects of volcanic degassing. First, such data help constrain the sources of these species, thereby illuminating subvolcanic processes (Craig and others, 1978; Matsuo and others, 1978; Allard, 1983; Poreda and Craig, 1989; Magro and Pennisi, 1991; Kita and others, 1993; Sorey and others, 1993; Giggenbach, 1995; Sano and Marty, 1995; Hulston and Lupton, 1996; Fischer and others, 1998; Sorey and others, 1998; Pedroni and others, 1999; Tedesco and Scarsi, 1999). Secondly, the origins of species in volcanic emissions also has important implications for geochemical monitoring of volcanic activity and contributes additional insights to seismic and geodetic monitoring. For example, increased emissions of CO_2 , the second most abundant species in convergent-plate magmatic gases (Symonds and others, 1994; Giggenbach, 1996), may portend magma intrusion even when other gas species show either no change or are below analytical detection (McGee and others, 2000; Symonds and others, 2003). Increases in $^3\text{He}/^4\text{He}$ may also signify magma intrusion (Sorey and others, 1993). Obviously, it is critical to know the sources of gas species in volcanic discharges to use them to monitor volcanic activity. Finally, the concentrations and isotopic compositions of carbon and nitrogen species contributes to the understanding of the geochemical cycles of C and N. Many recent geochemical studies of convergent-plate volcanic gases conclude that these discharges contain a significant component of subducted C and N, which has important implications for the cycling of volatiles in subduction zones (Kita and others, 1993; Sano and Marty, 1995; Fischer and others, 1998).

In this study, we use a large body of chemical and isotopic data on virtually air-free samples to investigate the origin of carbon, nitrogen, and noble gases in discharges from 12

Cascade Range and Aleutian Arc (CRAA) volcanoes (Figure 1). This work builds on a large body of previous work on CRAA discharges. Numerous papers have discussed carbon and, occasionally, nitrogen isotopic compositions of discharges from individual CRAA volcanoes (Evans and others, 1981; Welhan and others, 1988; Motyka and others, 1988a; Motyka and others, 1988b; Motyka and others, 1993; Zimbelman and others, 2000). Taking a broader perspective, Poreda and Craig (1989) show that discharges from 12 CRAA volcanoes have $^3\text{He}/^4\text{He}$ ratios between 6.0 and 7.9 R_C/R_A indicating a mantle source for most of the He in the CRAA discharges. Recent work (Symonds and others, 2001; Symonds and others, 2003) shows that these hydrothermal gases contain a magmatic component that is heavily modified by meteoric-water scrubbing. However, this is the first paper to discuss the origin of CO_2 , N_2 , CH_4 , and Ar in the CRAA discharges from an arc-wide perspective. We also publish the first (1) $^3\text{He}/^4\text{He}$ data for Aniakchak Crater, Mount Mageik, Mount Rainier, and Trident, (2) $^{40}\text{Ar}/^{36}\text{Ar}$ data for Akutan, Aniakchak Crater, Augustine Volcano, Mount Griggs, Mount Hood, Mount Mageik, Makushin, Mount Rainier, Mount Shasta, and Trident, (3) $\delta^{13}\text{C}$ of CO_2 data for Aniakchak Crater, Mount Baker, Mount Hood, Mount Mageik, Mount Shasta, and Trident, (4) $\delta^{13}\text{C}$ of CH_4 for Mount Baker, Mount Shasta, and Trident, and (5) $\delta^{15}\text{N}$ data for Mount Baker, Mount Griggs, Mount Mageik, Mount Shasta, and Trident.

Our data show that carbon, nitrogen, and noble gases in the CRAA discharges come from a mixture of mantle, shallow crustal sedimentary (SCS), crustal, and meteoric sources. Moreover, our data fail to support a significant subducted component of carbon and nitrogen. The absence of significant subducted carbon and nitrogen in the CRAA discharges contradicts recent work on other arc discharges (Kita and others, 1993; Sano and Marty, 1995; Fischer and others, 1998) and has implications for the cycling of carbon and nitrogen in subduction zones.

GEOLOGIC SETTING

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. While the CR exists in continental crust, the AA extends from continental crust in the east to oceanic crust west of 163°W (Fournelle and others, 1994). The present subduction rates and eruptive activity in the AA (Fournelle and others, 1994) exceed those in the CR.

The last eruptive activity at each of the 12 studied CRAA volcanoes (Figure 1) ranges from <10 to several thousand years ago. With at least 27 eruptive episodes since 1790, Akutan is one of the most active CRAA volcanoes and it erupted most recently with steam and ash emissions in 1992; a seismic swarm associated with intrusive activity also occurred in March 1996. Augustine Volcano last erupted in 1986, but other recent eruptions occurred in 1976, 1963-1964, 1935, 1883, and 1812. Mount St. Helens produced a number of explosive and dome-building eruptions between 1980 and 1986; it also erupted several times between 1800 and 1857. Significant recent eruptions have also occurred at a satellite cone on the SW flank of Trident in 1953-1974, at Aniakchak in 1931, at Mount Rainier in the 1840's, at Mount Hood about 200 years ago, at Makushin in 1826, and at Mount Shasta in 1786. At Mount Baker, a hydrothermal eruption formed Sherman Crater in 1843 and an aseismic

increase in heat flow occurred at Mount Baker in 1975. Mount Griggs and Mount Mageik have erupted in the Holocene, but not in historic times.

SAMPLING AND ANALYTICAL METHODS

During 1994-8, R. Symonds and B. Ritchie made two to four site visits to each of the studied CRAA volcanoes (Figure 1), except for Akutan and Makushin (only sampled in 1995), to sample the hottest or most vigorous summit or flank fumaroles (Table 1). In some cases, only springs effervescing CO₂ (soda springs) or bubbling acidic pools are available to sample (Table 1). At each site, they collected several subsamples for later analysis to characterize the chemical (H₂O, CO₂, H₂S, N₂, CH₄, H₂, HCl, HF, NH₃, Ar, O₂, He) and isotopic ($\delta^{13}\text{C}$ of CO₂, $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$ of CH₄, $\delta^{15}\text{N}$, and δD and $\delta^{18}\text{O}$ of water) compositions of the gas discharges (Symonds and others, 2003). In this study, we only discuss the results from the noble-gas subsamples, which constrain several noble-gas isotopic ratios and the dry-gas compositions, and the C-isotope subsamples, which provide data on $\delta^{13}\text{C}$ of CO₂, $\delta^{13}\text{C}$ of CH₄, and $\delta^{15}\text{N}$. The dry-gas compositions of the noble-gas subsamples are particularly useful because they are virtually free of sampling-induced air contamination (see below).

To sample fumaroles, a Ti tube was inserted into the vent and attached to a dewatered 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). Prior to sample collection, we purged air from the sampling train by flushing the tubing and bottle ports with vent gas.

Over the sampling period, 31 noble-gas subsamples were collected in leak-resistant bottles made of Corning-1720 glass and fitted with double-port vacuum stopcocks. These subsamples were analyzed by R. Poreda for dry-gas composition (CO₂ + H₂S, N₂, H₂, CH₄, O₂, Ar, He, Ne, Kr) and noble-gas isotope ratios using mass spectrometry and other methods as described elsewhere (Poreda and others, 1992; Poreda and Farley, 1992). Then we estimated the CO₂ and H₂S concentrations by using the measured amounts of CO₂ + H₂S and the CO₂/H₂S ratios from analyses of concomitant bulk-gas samples (Symonds and others, 2003). 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 $^{40}\text{Ar}/^{36}\text{Ar}$.

Thirty seven C-isotope subsamples were also collected in evacuated bottles for later analysis by W. Evans. First, these samples were analyzed by gas chromatography for dry-gas composition (CO₂, H₂S, N₂, H₂, CH₄, O₂, Ar, He, C₂H₆, CO, SO₂). Then they were purified using liquid nitrogen traps on a high-vacuum line and analyzed for $\delta^{13}\text{C}$ of CO₂, $\delta^{13}\text{C}$ of CH₄, and $\delta^{15}\text{N}$ of N₂ using a Finnigan MAT 251. Most of the C isotope samples have less than 0.5% air contamination. Analytical precision is ± 0.1 per mil for $\delta^{13}\text{C}$ of CO₂, ± 0.5 per mil for $\delta^{13}\text{C}$ of CH₄, and ± 0.2 per mil for $\delta^{15}\text{N}$ of N₂.

RESULTS

The chemical and isotopic analyses of the noble-gas subsamples for 11 CRAA volcanoes are reported in Table 2. The chemical analyses constrain only the dry-gas compositions; representative analyses of the complete gas compositions, including H₂O, HCl,

HF, and NH₃, are reported elsewhere (Symonds and others, 2003). The ³He/⁴He ratios are reported as R/R_A and R_C/R_A values where R_C and R are the ratio in the subsample with and without correction for atmospheric contamination (Poreda and Craig, 1989), respectively, and R_A is the atmospheric ratio, using air helium as the absolute standard. Results for a 1998 sample from Mount St. Helens are not reported because this sample contains over 95% air and only 3.7% CO₂ (R/R_A = 1.18, R_C/R_A = 1.54), reflecting the poor quality of this sampling site.

In general, the dry-gas analyses of the noble-gas subsamples are in excellent agreement with dry-gas analyses of concomitant bulk-gas subsamples, except that most of the noble-gas subsamples are virtually free of sampling-induced air contamination that exists in some bulk-gas samples (Symonds and others, 2003). As described elsewhere (Giggenbach, 1995; Fischer and others, 1998), the relative proportions of N₂, He, and Ar can help determine the sources of these species in samples of volcanic gases. Figure 2 shows that most of our CRAA samples plot in the range typical for arc-type gases (high N₂ concentrations, N₂/Ar > 200, N₂/He > 1000) and mantle-derived gases (low N₂ concentrations, N₂/He < 200) with minimal contributions from air (low He concentrations, N₂/Ar = 83.6) and air-saturated water (ASW; low He concentrations, N₂/Ar = 38.4). Only samples from bubbling springs at Mount Rainier, Akutan, and Aniakchak Crater, and from boiling-point fumaroles at Augustine Volcano and Trident (1994 sample) contain significant amounts of ASW N₂ and Ar, and the 1994 Trident sample is atypical of our other Trident samples. The Makushin sample also contains a significant component of meteoric N₂ and Ar, which probably comes from anoxic ASW as the sample's N₂/O₂ and He/Ne ratios are 47 and 43 times that for air, respectively. The low amount of air in the CRAA noble-gas subsamples is confirmed by the He/Ne ratios, which are hundreds to thousands times that of air, except for samples from Mount Rainier, Augustine Volcano, Akutan (AK1 site), and Aniakchak Crater (Table 2).

The carbon and nitrogen isotope analyses of the C-isotope subsamples from all 12 CRAA volcanoes are reported in Table 3. The δ¹³C of CO₂ and δ¹³C of CH₄ data are reported as per mil values (‰) relative to PDB. The δ¹⁵N data are reported as ‰ values relative to air, after correcting the δ¹⁵N analyses for small amounts of air contamination in these samples.

SOURCES OF VOLATILES

Helium

Our measured ³He/⁴He ratios of the CRAA gases range from 2.76 to 8.12 R_C/R_A, but exceed 7 R_C/R_A at eight volcanoes (Table 2, Figure 3). Poreda and Craig (1989) also report >7 R_C/R_A values for gas discharges from Augustine (in 1978 and 1982), Lassen Peak (1970), Makushin (summit fumarole in 1983), Mount Douglas (1982), and Okmok (1981). Hence, in the past 3 decades, at least 12 CRAA volcanoes have discharged gases with >7 R_C/R_A values. Elevated R_C/R_A values between 6 and 8 are common for gas discharges from convergent-plate volcanoes around the World and are thought to represent mixtures of mostly mantle He (assumed to be similar to that for mid-oceanic-ridge basalts or MORB at 8 ± 1 R/R_A) and minor crustal He (0.02 R/R_A) (Craig and others, 1978; Poreda and Craig, 1989). Therefore, we support previous conclusions that the mantle is the dominant source of He in the CRAA gases (Poreda and Craig, 1989).

Our R_C/R_A values are slightly higher than past results (Poreda and Craig, 1989) at Makushin (4.30 in 1982 and 4.58 in 1981 both at a vent near the GV-2 site), Mount Griggs (7.66 at Flank 3 site in 1978), and Mount Hood (7.20 in 1978); at Akutan, our values are higher than past results at the AK2 site (7.10 in 1981), but lower at the AK1 site (6.10 in 1981). Our higher R_C/R_A values at these sites probably reflects less air contamination in our samples rather than any change in volcanic activity. In fact, our R_C/R_A values for the Summit 1 site at Mount Griggs (8.12 in 1998) and Mount Baker (7.70 in 1997) are the highest values ever reported for AA and CR volcanoes, respectively. In contrast, our reported R_C/R_A values are considerably lower than previous results at Augustine Volcano (7.66 in 1978 and 7.60 in 1982; Poreda and Craig, 1989), slightly lower than earlier data for Mount Shasta (6.23 in 1980; Welhan and others, 1988), and, generally, slightly lower than past results at Mount Baker (7.62 in 1978; Poreda and Craig, 1989). Such decreases in R_C/R_A values may indicate dilution of magmatic He with crustal He as the magma reservoirs of these systems become more degassed and therefore depleted in He and other volatiles.

Using a simple mixing model between our assumed values for mantle and crustal He, we estimate for each analysis He_M , the percentage of He derived from the mantle (Poreda and Craig, 1989). All of our CRAA sites, discharge gases with $He_M \geq 91\%$, except for summit sites at Mount Shasta ($He_M = 73-74\%$) and Augustine Volcano ($He_M = 53\%$), or flank vents several km from the central conduit (site AK1 at Akutan, $He_M = 72\%$; Makushin, $He_M = 60\%$; Mount Rainier, $He_M = 34-38\%$). Because He_M exceeds 91% in the gases from Mount Griggs, Aniakchak Crater, Trident, Mount Baker, Mount Hood, Mount Mageik, and Akutan (sites AK2 and AK3), we infer the degassing of relatively fresh <5-km-deep magma at these sites. Our inference is supported by gas geothermometry that indicates <3-km-deep hydrothermal systems at all of the above sites except Aniakchak Crater (Symonds and others, 2003). Also, we think it likely that if the gases came from deep (e.g., >10 km depth) or relatively degassed magma reservoirs, they would have lower R_C/R_A values due to dilution by crustal He.

We speculate that sustained high He_M values, such as observed over 16-to-20-year periods at Akutan, Mount Baker, Mount Griggs, and Mount Hood require periodic additions of magma. Frequent magma recharge is obvious at Akutan which has erupted at least 27 times between 1760 and present. Periodic resupply of magma also seems reasonable at Mount Hood due to annual seismic swarms even though the last magmatic eruption was about 200 years ago. However, for volcanoes like Mounts Baker and Griggs, which last erupted juvenile magmatic products in the mid-Holocene, periodic magma recharge may seem less credible. Nonetheless, we find it implausible that such high He_M values can be sustained in the decades to centuries between eruptions without periodic magma recharge, especially since some CRAA volcanoes (e.g., Augustine Volcano, Mount Shasta) discharge gases with low He_M values.

Lower R_C/R_A values for more distal vents at Makushin and Akutan (AK1 site) reflect the flank or basal locations of these sites rather than deeper or more degassed magmas at these volcanoes. Previous work at Makushin between 1980 and 1983 (Motyka and others, 1988b; Poreda and Craig, 1989) shows that R_C/R_A values decrease dramatically with distance from the summit with an overall range of 7.83 at the summit and 3.91 at the most distal vent. This trend probably indicates increasing additions of crustal He with distance from the central conduit (Motyka and others, 1988b). At Akutan, we measured higher (near mantle) R_C/R_A values at the flank AK2 site and the near-summit AK3 site than at the most

distal AK1 site (Table 2; Figure 3). An increase in magmatic C in the July 1996 gas discharges at Akutan is consistent with the change of volcanic activity from relative quiescence in the early 1980's to the 1992 eruption and the intrusion in March 1996. However, at Makushin, there was no significant change in volcanic activity over the same time period.

However, the low R_C/R_A values of Soda Spring on the flank of Mount Rainier (Table 2, Figure 3) may reflect deeper or more degassed magma in addition to its distance from the summit. Gases from this site not only have the lowest R_C/R_A values of the studied CRAA volcanoes (Figure 3), excluding the air-contaminated vent at Mount St. Helens, but they also exhibit the lowest ^4He concentrations (Table 2). Summit fumaroles from Mount Rainier are weak and discharging mostly air (Zimbelman and others, 2000). These observations suggest that the present magmatic system at Mount Rainier may be relatively weak.

In addition, we speculate that the low R_C/R_A values at Augustine Volcano and Mount Shasta may also indicate the absence of fresh near-surface magma. Between the 1976 and 1986 eruptions, Augustine Volcano discharged high-temperature magmatic gases up to 754°C in 1979, 472°C in 1982, and 357°C in 1984 (Kodosky and others, 1991) with $\text{He}_M = 94\text{-}5\%$ (see above), indicating the presence of a vigorous shallow magmatic system at that time. Emission of high-temperature magmatic gases (up to 870°C in 1987) continued after the 1986 eruption (Symonds and others, 1990) and temperatures up to 640°C were measured as late as 1989 (Symonds, unpublished results). However, by 1992 the temperature of the hottest vents had cooled to the boiling-point of water and R_C/R_A was only 4.28 in 1994. Therefore, we speculate that Augustine Volcano no longer has a vigorously degassing near-surface magmatic system. Likewise, at Mount Shasta where the volcanic gases emanate from a shallow (probably less than 0.3 km) magmatic hydrothermal system (Symonds and others, 2003), we speculate that the low R_C/R_A values indicate a relatively degassed source magma. Interestingly, the R_C/R_A values at Mount Shasta have declined from 6.23 in 1980 (Welhan and others, 1988) to between 5.85 and 5.94 in 1995-7 (Table 2). This suggests that the crustal component in the Mount Shasta gases is increasing with time, possibly due to progressive outgassing of the magmatic system.

Argon

Our measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for the CRAA gases range from 288 at Augustine Volcano to 530 at Mount Shasta (Table 2). In contrast to $^3\text{He}/^4\text{He}$, fewer data exist on $^{40}\text{Ar}/^{36}\text{Ar}$ in volcanic discharges and these are the first published $^{40}\text{Ar}/^{36}\text{Ar}$ data for CRAA volcanoes. Previous work on volcanic discharges from the Lesser Antilles Islands Arc (Pedroni and others, 1999), the Taupo Volcanic Zone (Hulston and Lupton, 1996), and the Aeolian Arc (Magro and Pinnisi, 1991; Tedesco and Scarsi, 1999) show that $^{40}\text{Ar}/^{36}\text{Ar}$ ratios generally indicate mixing between a dominant meteoric component near 295.5, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for air and ASW, and a more radiogenic component, dominated by ^{40}Ar , from the mantle or crust.

Thirteen of our 29 measurements are within 10% of 295.5, indicating a strong meteoric component of Ar in gas discharges from Augustine Volcano, Mount Rainier, Aniakchak Crater, Akutan, Mount Mageik, and Makushin (Figure 4). The Ar in these 13 samples probably comes from ASW rather than air because (1) He/Ne (R/R_A) ratios between 3.2 and 595 indicate that these samples are not heavily air contaminated (Figure 4), and (2)

the relative proportions of N₂, He, and Ar in these samples (Figure 2) point to an ASW source of Ar (see above).

However, samples from Trident, Mount Baker, Mount Shasta, Mount Hood, and Mount Griggs, in that order, exhibit increasingly higher ⁴⁰Ar/³⁶Ar ratios indicating increasing contributions from a ⁴⁰Ar-rich component (Figure 4). Potential sources of this ⁴⁰Ar-rich component are the mantle and the radioactive decay of ⁴⁰K in the crust. However, in samples from these 5 CRAA volcanoes, the ⁴⁰Ar/³⁶Ar ratio correlates positively with He/Ne (R/R_A), suggesting mixing of ASW and a deeper component rich in ⁴⁰Ar and ⁴He (Figure 4). Therefore, we think that the mantle is the most likely source for the ⁴⁰Ar-rich component given the mantle origin of He (see above). Several recent studies estimate that ⁴⁰Ar/³⁶Ar ratios in the mantle (MORB) are up to two orders of magnitude greater than in air (e.g., Staudacher and others, 1989), suggesting that the mantle is a negligible source of ³⁶Ar. Assuming two-source mixing between ASW Ar and mantle ⁴⁰Ar, we estimate for these 5 volcanoes Ar_M, the percentage of mantle-derived Ar:

$$Ar_M = 100((^{40}Ar - ^{36}Ar * 295.5) / ^{40}Ar),$$

where ⁴⁰Ar and ³⁶Ar are molar concentrations in the sample. Our estimates for Ar_M are 4 - 22% at Trident, 10 - 27% at Mount Baker, 0 - 44% at Mount Shasta, 15 - 37% at Mount Hood, and 11 - 36% at Mount Griggs.

Methane and nitrogen

The dry-gas analyses of the CRAA gases contain between 0.001% (Mount Rainier) and 7.57% (Trident) CH₄ and between 0.014% (Mount Griggs) and 4.22% (Trident) non-meteoritic N₂, excluding samples from Mount Rainier, Akutan (AK1 site), Aniakchak Crater, Augustine Volcano, Trident, and Makushin that contain significant amounts of ASW N₂ as in the “Results” section (Table 2). We think CH₄ in the CRAA hydrothermal discharges comes mostly from reactions between subvolcanic hydrothermal fluids and sedimentary rocks, although discharges from some sites contain minor amounts of inorganic hydrothermal CH₄. Although CH₄ is a significant minor species in <300°C hydrothermal gases (Giggenbach, 1980), only trace amounts of CH₄ exist in high-temperature magmatic gases from convergent-plate volcanoes (HTMG) (Giggenbach, 1996) and even these trivial amounts of CH₄ exceed predicted equilibrium concentrations of CH₄ in HTMG by several orders of magnitude (Symonds and others, 1994; Symonds and others, 1996). Therefore, it is generally accepted that CH₄ in HTMG probably comes from the subvolcanic hydrothermal system either from reactions between hydrothermal fluids and sedimentary rocks (Symonds and others, 1996) or from an inorganic reaction between CO₂ and H₂ deep within the hydrothermal systems (Giggenbach, 1980; Giggenbach and Matsuo, 1991):



The lower temperatures and higher pressures of hydrothermal systems drive reaction (1) to the right, whereas magmatic temperatures force the reaction to the left; the latter explains why only trivial amounts of CH₄ are in equilibrium with HTMG (Symonds and others, 1996).

The above reasoning and the fact that the gas discharges from many CRAA volcanoes

(Trident, Mount Shasta, Aniakchak, Akutan, Mount Baker, Mount Mageik, Makushin) contain 10-to-10000-times more CH_4 than HTMG (Giggenbach, 1996) point clearly to a non-magmatic source of CH_4 in these hydrothermal discharges. A sedimentary source of CH_4 is supported by the $\delta^{13}\text{C}$ of CH_4 data for Mount Shasta, Trident, and Akutan (Table 3), which are much lighter than the -15‰ to -20‰ range for mantle CH_4 (Welhan, 1981). Somewhat heavier $\delta^{13}\text{C}$ of CH_4 values for Mount Baker (Table 3) may indicate mixing of sedimentary and inorganic CH_4 , the latter forming in the hydrothermal system by reaction (1) involving magmatic CO_2 . The most likely source of the sedimentary CH_4 is shallow crustal sedimentary (SCS) rocks in the subvolcanic system. Deeper sources of sedimentary CH_4 such as subducted sediments or magmatically heated deep crustal rocks seem unlikely because, as discussed above, CH_4 cannot survive the magmatic temperatures of these deeper processes.

As discussed in the “Results” section, analyses from 7 of our sampled CRAA volcanoes contain N_2 that comes almost exclusively from non-meteoritic sources; these samples span the range from mantle-type gases with $\text{N}_2/\text{Ar} = 166$ (Mount Griggs) to N_2 -rich arc gases with $\text{N}_2/\text{Ar} = 1350$ (Mount Shasta) (Figure 2). Such high N_2/Ar ratios and the corresponding (non-meteoritic) N_2 concentrations (Table 2) are within the range reported for HTMG and geothermal gases from convergent-plate settings (Matsuo and others, 1978; Magro and Pennisi, 1991; Kita and others, 1993; Giggenbach, 1996; Fischer and others, 1998); these studies all propose that such high N_2/Ar ratios and non-meteoritic N_2 concentrations indicate a sedimentary source of N. The $\delta^{15}\text{N}$ of our non-meteoritic N_2 samples from Mount Shasta, Mount Mageik, Trident, Mount Baker, and Mount Griggs range from +1.1‰ to +4.8‰ (Table 3), which are significantly heavier than reported $\delta^{15}\text{N}$ values of -3.5‰ for MORB (Javoy and Pineau, 1991) but similar to calculated $\delta^{15}\text{N}$ values of -1.5‰ to +5.5‰ for fluids derived from metamorphism of sedimentary rocks (Bebout and Fogel, 1992). Several studies (Shinohara and Matsuo, 1986; Fischer and others, 1998) report similarly heavy $\delta^{15}\text{N}$ values and interpret these high values to indicate sedimentary N (Shinohara and Matsuo, 1986; Fischer and others, 1998). We concur with the above studies and think the high N_2/Ar ratios, high non-meteoritic N_2 concentrations, and heavy $\delta^{15}\text{N}$ values in our non-meteoritic N_2 samples indicate a sedimentary source of N.

Potential sources of sedimentary N in the CRAA gases include subducted sediments, deep crustal rocks, or SCS rocks. Previous studies have proposed that non-meteoritic N in HTMG or geothermal gases from convergent plate settings comes from subducted sediments (Matsuo and others, 1978; Magro and Pennisi, 1991; Kita and others, 1993; Giggenbach, 1996; Fischer and others, 1998). If the non-meteoritic N in the CRAA gases comes predominantly from subducted sediments, we might expect to see variations in N_2/Ar ratios associated with regional tectonic differences, such as reported for northern and southern Japan (Kita and others, 1993). Instead, we find that the three Katmai volcanoes, Mount Griggs, Mount Mageik, and Trident, all within 20 km of each other, cover almost the entire range of observed N_2/Ar ratios for the CRAA samples (Figure 2). The Katmai volcanoes are clearly associated with subduction of the same part of the Pacific Plate. Moreover, Akutan (AK2 and AK3 sites) and Mount Mageik discharge gases with similar N_2/Ar ratios (Figure 2), even though they exist in oceanic and continental sectors, respectively, of the AA (Fournelle and others, 1994). Finally, N_2/Ar ratios in the CR discharges (Mounts Baker, Hood, and Shasta) display almost as much variation as discharges from the above AA volcanoes, which conceals any obvious difference in subducted N between the two arcs

(Figure 2). We conclude that variations in N_2/Ar ratios in our non-meteoritic-N samples are explained better by diversity in (shallow or deep) crustal inputs of N into the magma-plumbing system at each volcano rather than by regional differences in subducted sediments.

A crustal source of N is also supported by a strong correlation (lognormal $R = 0.58$) between $CH_4/^3He$ and $N_2/^3He$ in the non-meteoritic-N samples (Figure 5). As discussed above, 3He in the CRAA gases comes predominantly from the mantle. Therefore, wide variations in the ratio of a species, such as CH_4 or N_2 , to 3He support a non-mantle origin assuming that mantle-derived gases are much more homogeneous. In fact, $CH_4/^3He$ and $N_2/^3He$ in the non-meteoritic-N samples vary by over 5 and 3 orders of magnitude, respectively, strongly supporting non-mantle sources for both CH_4 and N_2 . Using the same arguments as with the N_2/Ar ratios, we rule out a subducted source for N_2 and CH_4 . In addition, we propose that N_2 come from a SCS source rather than a deep-crustal source because (1) the excellent correlation between $CH_4/^3He$ and $N_2/^3He$ in the non-meteoritic-N samples suggests a similar source for both N_2 and CH_4 , and (2) CH_4 cannot survive magmatic temperatures of the deeper crust.

Carbon dioxide

Our $\delta^{13}C$ of CO_2 values for the CRAA gases range from -5.0‰ to -13.5‰ (Table 3; Figure 6). The range of $\delta^{13}C$ of CO_2 values for the CRAA gases extend from typical mantle values of -5‰ to -8‰ (Allard, 1983) towards lighter values in the direction of organic C in recent sediments of -10‰ to -30‰ (Faure, 1986) and terrestrial plants of -24‰ to -34‰ (Smith and Epstein, 1971) (Figure 6). This suggests that the CRAA discharges contain mixtures of magmatic and organic sedimentary CO_2 .

The $CO_2/^3He$ ratios in the CRAA gases also support mixing between magmatic and organic sedimentary CO_2 . The $CO_2/^3He$ ratios in CRAA gases extend from the mantle range of $1-3 \times 10^9$ (Marty and Jambon, 1987) to 10^{11} , except for samples from Aniakchak Crater and Mount Rainier (Figure 7). Values of $CO_2/^3He$ that exceed the mantle range by factors up to 100 are common for convergent-plate volcanic gases and probably indicate mixing of magmatic and sedimentary CO_2 (Fischer and others, 1998; Sano and Marty, 1995). However, the anomalous $CO_2/^3He$ ratios for discharges from Aniakchak Crater and Mount Rainier may reflect interactions with near-surface waters. CO_2 has a much higher water-solubility than He. Thus, the less-than-mantle $CO_2/^3He$ value at the Aniakchak-Crater cold spring may reflect preferential scrubbing and removal of CO_2 in near-surface waters. In contrast, the $\sim 10^4$ -times-mantle $CO_2/^3He$ values at Longmire Springs on the flank of Mount Rainier (Figure 7) may reflect preferential degassing of He, such as suggested for gas discharges from Long Valley caldera (Sorey and others, 1998), as water-dissolved gases are transported laterally to flank vents.

Potential sources of the organic-sedimentary CO_2 component in the CRAA gases include subducted sediments, deep crustal rocks, or SCS rocks. Many recent studies (Fischer and others, 1998; Sano and Marty, 1995) have proposed that elevated $CO_2/^3He$ ratios and variable $\delta^{13}C$ of CO_2 values in convergent-plate volcanic gases indicate three-way mixing between CO_2 from the mantle (MORB C), CO_2 from organic sediment, and CO_2 from subducted carbonate as depicted in Figure 8. However, we rule out a subducted source of CO_2 by using the trends in $CO_2/^3He$ ratios (Figure 7) and the same reasoning as discussed above for N_2/Ar , $CH_4/^3He$, and $N_2/^3He$ ratios. Instead, we again favor a SCS source for CO_2 .

because of (1) the strong correlation between $\text{CH}_4/{}^3\text{He}$ and $\text{CO}_2/{}^3\text{He}$, suggesting a similar source for both CO_2 and CH_4 , and (2) the arguments above, which suggest that CH_4 cannot survive deep crustal temperatures.

There are some interesting comparisons between our $\delta^{13}\text{C}$ of CO_2 values and those obtained previously. Our $\delta^{13}\text{C}$ data for Augustine Volcano are within the limits of the 1979-1984 results (mostly between -5.2‰ and -9.2‰; Kodosky and others, 1991). However, our $\delta^{13}\text{C}$ data are higher than past results at Akutan (-18.1‰ at AK1 and -10.8‰ to -11.2‰ at AK2 in the early 1980's; Motyka and others, 1988a) and Makushin (-10.2‰ to -13.0‰ at GV-2 in the early 1980's; Motyka and others, 1988b), which may indicate an increase in magmatic C in these gas discharges. An increase in magmatic C in the July 1996 gas discharges at Akutan is consistent with the change of volcanic activity from relative quiescence in the early 1980's to the 1992 eruption and the intrusion in March 1996. However, at Makushin, there was no significant change in volcanic activity over the same time period. In contrast, our $\delta^{13}\text{C}$ data for Mount St. Helens are slightly lower than the 1980 results of -10.4‰ to -10.8‰ in 1980 (Evans and others, 1981), suggesting a decrease in magmatic C in the gases since the 1980-6 eruptions. However, the fact that our $\delta^{13}\text{C}$ data for Longmire on the flank of Mount Rainier are slightly lower than 1997 results at the summit of -11.1‰ to -12.5‰ (Zimbelman and others, 2000) probably reflects more SCS carbon in the flank gases rather than a temporal change in magmatic degassing. Temporal changes in $\delta^{13}\text{C}$ of CO_2 values are consistent with a magmatic-SCS source for CO_2 in the CRAA discharges, and suggest that $\delta^{13}\text{C}$ of CO_2 values may change with volcanic activity.

VARIABLE CRUSTAL INPUTS OF CO_2 , N_2 , AND CH_4

Based on the data presented above, we examine the amounts of SCS CO_2 , N_2 , and CH_4 in the CRAA discharges. In summary, gases from Mount Shasta and Trident have the largest SCS inputs of CO_2 , N_2 , and CH_4 ; Mount Rainier discharges also contain large SCS inputs of CO_2 and CH_4 . Gas discharges from Akutan contain moderate SCS inputs of CO_2 and N_2 , and moderate (AK2 and AK3 sites) to large (AK1 site) crustal inputs of CH_4 . Gases from Mounts Baker and Mageik contain moderate amounts of SCS CO_2 , N_2 , and CH_4 ; Makushin discharges have moderate SCS inputs of CO_2 and CH_4 . Discharges from Mount Griggs and Mount Hood contain the smallest SCS inputs of CO_2 , N_2 , and CH_4 ; gases from Aniakchak Crater and Augustine Volcano also contain small SCS inputs of CO_2 and CH_4 .

The close proximity of Trident, Mount Mageik, and Mount Griggs in the Katmai region provides a unique opportunity to use geological evidence to explain why their discharges have such variable amounts of SCS CO_2 , N_2 , and CH_4 . The Jurassic Naknek Formation forms the basement in the Katmai region and is the logical source of SCS CO_2 , N_2 , and CH_4 . Hildreth (1983) shows that (1) eruptive products from Mount Mageik and Trident are chemically similar, but their trace-element compositions imply independent storage systems beneath each volcano; and (2) erupted products from Mount Griggs are chemically and isotopically distinct from the other two, and its plumbing extends to mantle depths. Thus, we speculate that differences in magma storage reservoirs and their interactions with the Naknek Formation at these three Katmai volcanoes cause the wide variations in the amounts of SCS CO_2 , N_2 , and CH_4 in their respective gas discharges.

If similar processes apply at the other studied CRAA volcanoes, we use the estimated amounts of SCS CO_2 , N_2 , and CH_4 in their respective discharges to infer the following about

these magmatic hydrothermal systems: (1) The systems at Mount Shasta and Mount Rainier have large interactions with SCS rocks. (2) The systems at Akutan, Mount Baker, and Makushin have moderate interactions with SCS rocks. (3) The systems at Aniakchak Crater, Augustine Volcano, and Mount Hood interact little with SCS rocks.

CONCLUSIONS

This study enables us to reach the following conclusions:

1. The anhydrous compositions of the studied CRAA volcanic discharges are dominated by CO₂ and H₂S with minor to trace amounts of N₂, H₂, CH₄, O₂, Ar, He, and Ne, excluding minor amounts of HCl, HF, and NH₃ as reported elsewhere (Symonds and others, 2003). The chemical and isotopic (³He/⁴He, ⁴⁰Ar/³⁶Ar, δ¹³C of CO₂, δ¹³C of CH₄, δ¹⁵N) compositions generally point to magmatic and SCS sources for CO₂, SCS and meteoric source of N₂, a SCS source for CH₄, meteoric and magmatic sources for Ar, and magmatic and crustal sources of He.
2. Our reported ³He/⁴He ratios of >7R_C/R_A indicate degassing of relatively fresh near-surface magma at Mount Griggs, Aniakchak, Trident, Mount Baker, Mount Hood, Mount Mageik, and Akutan. Lower R_C/R_A values point to more degassed magma reservoirs at Mount Shasta, Augustine Volcano, and Mount Rainier. Our R_C/R_A values of 8.12 for Mount Griggs and 7.70 for Mount Baker are the highest values ever reported for AA and CR volcanoes, respectively.
3. This study suggests that future unrest might produce precursory changes in ³He/⁴He and δ¹³C of CO₂. In particular, intrusion of new magma might produce increases in R_C/R_A values in discharges from Mount Shasta, Augustine Volcano, and Mount Rainier since these gases currently have relatively low R_C/R_A values. In contrast, intrusion of new magma at any of the seven CRAA volcanoes that currently discharge gases with >7 R_C/R_A values would probably produce very little change in R_C/R_A values. Magma movement might also produce changes in δ¹³C of CO₂ since CO₂ in the CRAA discharges comes from magmatic and SCS sources; such changes seem more likely for Mount Rainier, Akutan, Mount St. Helens, Mount Shasta, Trident, Mount Hood, Makushin and Mount Mageik, which have significant SCS components of CO₂.
4. The CRAA discharges lack significant subducted components of C and N. Either the CRAA volcanoes are significantly different from volcanoes in other arcs or we need to rethink the significance of subducted C and N recycling in convergent-plate volcanoes. This has major implications for the C and N cycles.

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Table 1. Sites sampled in this study

| Volcano | Vent | Vent type ^a | Description | Latitude | Longitude |
|------------|----------------|------------------------|--|-------------|--------------|
| Akutan | AK1 | FSS | Spring on Hot Springs Creek | 54° 09' 11" | 165° 51' 16" |
| " | AK2 | FF | Vent in upper Hot Springs Creek valley | 54° 08' 55" | 165° 54' 30" |
| " | AK3 | SF | Vent on summit cinder cone | 54° 08' 55" | 165° 58' 25" |
| Aniakchak | Bolshoi | SSS | Spring at southwestern shore of Surprise Lake | 56° 55' 44" | 158° 07' 24" |
| Augustine | Spine | SF | At base of spine on 1986 dome | 59° 21' 43" | 153° 25' 40" |
| Baker | North Wall | SF | Vent in Sherman crater | 48° 46' 14" | 121° 48' 58" |
| " | Smiley | SF | Vent in Sherman crater | 48° 46' 11" | 121° 49' 07" |
| " | West Main | SF | Vent in Sherman crater | 48° 46' 09" | 121° 49' 06" |
| Griggs | Flank 3 | FF | Most vigorous vent at Griggs. Located on western flank | 58° 20' 56" | 155° 06' 41" |
| " | Summit 1 | SF | Vent on the summit | 58° 21' 11" | 155° 06' 19" |
| Hood | Crater Rock | SF | One of the most vigorous vents on east side of Crater Rock | 45° 22' 14" | 121° 41' 54" |
| " | Devils Kitchen | SF | Most vigorous vent in Devil's Kitchen | 45° 22' 12" | 121° 41' 50" |
| Mageik | N-crater | SF | Most vigorous vent on north wall of crater | 58° 11' 45" | 155° 14' 54" |
| " | S-crater | SF | Most vigorous vent at Mageik. Located on south side of summit crater | 58° 12' 00" | 155° 14' 41" |
| Makushin | GV-2 | FF | Vent in Glacier Valley | 53° 51' 30" | 166° 52' 29" |
| Rainier | Soda | FSS | Soda Spring at Longmire | 46° 45' 05" | 121° 48' 42" |
| " | Travertine | FSS | Travertine Mound at Longmire | 46° 45' 06" | 121° 48' 48" |
| Shasta | Summit | SAP | Bubbling pool near summit | 41° 24' 34" | 122° 11' 40" |
| St. Helens | Sept. Lobe | SF | Hottest vent on September 1984 lobe of lava dome | 46° 12' 03" | 122° 11' 24" |
| Trident | Trident-SE | FF | Fumarole field on southeastern flank of pre-1963 edifice | 58° 13' 52" | 155° 04' 56" |

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

Table 2. Chemical and noble-gas isotope analyses (in molar quantities) of noble-gas subsamples collected from selected CRAA volcanoes

| Volcano | Vent ^a | Date | T (°C) | CO ₂ (%) | H ₂ S (%) | N ₂ (%) | H ₂ (%) | CH ₄ (%) | O ₂ (ppm) | ⁴⁰ Ar (ppm) | ⁴ He (ppm) | Ne (ppb) | ³ He/ ⁴ He (R/R _A) | He/Ne (R/R _A) | ³ He/ ⁴ He (R _C /R _A) | ⁴⁰ Ar/ ³⁶ Ar |
|-----------|-------------------|------------|-----------|------------------------|-------------------------|-----------------------|-----------------------|------------------------|-------------------------|---------------------------|--------------------------|-------------|---|------------------------------|---|------------------------------------|
| Akutan | AK1 | 30-07-1996 | 97.4 | 58.4 | <0.008 | 34.4 | --- | 4.93 | 5070 | 11700 | 10.0 | 6100 | 4.94 | 6 | 5.78 | 295 |
| " | AK2 | 28-07-1996 | 97.8 | 95.6 | 2.0 | 2.10 | --- | 0.20 | 34 | 40 | 6.8 | 60 | 7.25 | 391 | 7.26 | 301 |
| " | AK3 | 29-07-1996 | 96.6 | 92.0 | 6.4 | 1.41 | --- | 0.14 | 60 | 25 | 4.6 | 43 | 7.23 | 370 | 7.24 | 300 |
| Aniakchak | Bolshoi | 12-07-1997 | 25 | 58.8 | <0.008 | 39.6 | 0.03 | 0.59 | 940 | 5740 | 232 | 9200 | 7.98 | 88 | 8.06 | 297 |
| Augustine | Spine | 28-07-1994 | 97 | 2.7 | 0.19 | 42.6 | 51.5 | <0.12 | 19500 | 7900 | 4.5 | 6500 | 3.61 | 4.9 | 4.28 | 288 |
| Baker | Smiley | 10-06-1994 | 135 | 93.8 | 5.1 ^b | 0.54 | 0.31 | 0.23 | <5 | 13 | 6.3 | 9.6 | 7.42 | 2300 | 7.42 | 403 |
| " | North Wall | 06-09-1994 | 150 | 93.6 | 5.1 ^b | 0.59 | 0.29 | 0.38 | <20 | 16 | 9.1 | 32 | 7.48 | 1000 | 7.49 | 385 |
| " | Smiley | 23-08-1996 | 137 | 93.9 | 5.1 | 0.47 | --- | 0.47 | 6 | 14 | 7.4 | 23 | 7.44 | 1120 | 7.45 | 328 |
| " | Smiley | 07-08-1997 | 134.4 | 93.0 | 5.2 | 1.06 | 0.25 | 0.44 | 100 | 12 | 10.7 | 39 | 7.69 | 964 | 7.70 | 329 |
| Griggs | Flank 3 | 22-07-1995 | 99.8 | 90.6 | 9.2 | 0.22 | --- | 0.006 | 5 | 13 | 9.6 | 23 | 8.03 | 1440 | 8.04 | 432 |
| " | Summit 1 | 22-07-1995 | 93.8 | 97.3 | 2.7 | 0.014 | --- | 0.0004 | 2 | 0.5 | 5.7 | 26 | 8.11 | 766 | 8.11 | 466 |
| " | Flank 3 | 18-07-1997 | 99.2 | 90.6 | 7.7 | 1.56 | 0.007 | 0.015 | 260 | 83 | 37.2 | 690 | 7.90 | 187 | 7.94 | 330 |
| " | Summit 1 | 16-07-1998 | 93.1 | 97.6 | 0.82 | 1.49 | 0.06 | 0.003 | 28 | 69 | 53.2 | 250 | 8.11 | 726 | 8.12 | 399 |
| Hood | Crater Rock | 18-10-1994 | 88.8 | 91 | 4.8 ^b | 1.05 | 2.90 | 0.015 | <10 | 37 | 12.9 | 24 | 7.51 | 1900 | 7.51 | 470 |
| " | Devils Kitchen | 23-06-1995 | 89.5 | 89.6 | 8.7 | 1.74 | --- | 0.006 | 12 | 59 | 15.2 | 23 | 7.48 | 2290 | 7.48 | 391 |
| " | Crater Rock | 09-09-1997 | 91.0 | 91.4 | 4.9 | 1.21 | 2.47 | 0.009 | 180 | 35 | 21.4 | 110 | 7.59 | 662 | 7.60 | 341 |
| Mageik | S-crater | 26-07-1995 | 167.4 | 90.2 | 8.6 | 1.23 | --- | 0.058 | 16 | 37 | 1.9 | 11 | 7.47 | 595 | 7.48 | 321 |
| " | S-crater | 19-07-1997 | 172.9 | 87.7 | 8.8 | 1.44 | 1.96 | 0.032 | 240 | 31 | 4.4 | 53 | 7.55 | 293 | 7.57 | 302 |
| " | N-crater | 22-07-1998 | 101.6 | 86.0 | 8.5 | 1.54 | 3.94 | 0.057 | 99 | 33 | 9.5 | 64 | 7.63 | 517 | 7.64 | 316 |
| " | S-crater | 22-07-1998 | 166.6 | 85.8 | 8.9 | 1.52 | 3.70 | 0.052 | 140 | 35 | 9.4 | 60 | 7.60 | 544 | 7.61 | 307 |
| Makushin | GV-2 | 24-07-1996 | 100 | 83.8 | 8.5 | 7.49 | --- | 0.023 | 430 | 640 | 5.8 | 470 | 4.72 | 43 | 4.81 | 321 |
| Rainier | Soda | 08-08-1997 | 18 | 99.6 | --- | 0.37 | 0.006 | 0.002 | 170 | 39 | 0.05 | 55 | 2.21 | 3.2 | 2.76 | 295 |
| " | Soda | 29-09-1998 | 14.2 | 99.8 | <0.0002 | 0.11 | 0.001 | 0.001 | 520 | 25 | 0.03 | 28 | 2.57 | 4.1 | 3.07 | --- |
| Shasta | Summit | 07-09-1995 | 82.1 | 98.1 | <0.36 | 1.38 | --- | 0.58 | 6 | 12 | 1.8 | 10 | 5.93 | 606 | 5.94 | 326 |
| " | Summit | 15-08-1996 | 80.4 | 95.0 | 0.32 | 3.30 | --- | 1.37 | 76 | 24 | 0.6 | 8.9 | 5.83 | 236 | 5.85 | 530 |
| " | Summit | 26-06-1997 | 80.2 | 95.0 | 0.28 | 2.87 | 0.92 | 0.88 | 12 | 35 | 3.3 | 69 | 5.87 | 165 | 5.90 | 299 |
| Trident | Trident-SE | 13-07-1994 | 93.9 | 74.8 | 3.1 ^b | 1.27 | 18.4 | 2.15 | <20 | 350 | 1.8 | 4.1 | 7.48 | 1560 | 7.48 | 380 |
| " | Trident-SE | 24-07-1995 | 94.2 | 82.8 | 5.4 | 4.22 | --- | 7.57 | 47 | 85 | 1.5 | 17 | 7.64 | 298 | 7.66 | 339 |
| " | Trident-SE | 17-07-1997 | 94.2 | 78.9 | 3.3 | 1.50 | 14.4 | 1.83 | 140 | 16 | 2.0 | 22 | 7.80 | 313 | 7.82 | 327 |
| " | Trident-SE | 18-07-1998 | 94.0 | 62.2 | 3.0 | 2.07 | 29.2 | 3.52 | 280 | 40 | 2.8 | 32 | 7.67 | 305 | 7.69 | 316 |

---, not determined; BD, below detection.

^aSampling sites described in Table 1.^bConcentration of H₂S estimated using CO₂/H₂S ratio from bulk gas samples collected in 1992, 1995, or 1996.

Table 3. Carbon and nitrogen isotope analyses of C-isotope subsamples collected at selected CRAA volcanoes

| Volcano | Vent | Date | $\delta^{13}\text{C}$ | $\delta^{13}\text{C}$ | $\delta^{15}\text{N}$ |
|-----------|--------------------------|------------|-----------------------|-----------------------|-----------------------|
| | | | CO_2 | CH_4 | |
| | | | (‰) | (‰) | (‰) |
| Akutan | AK1 | 30-07-1996 | -12.4 | -39.7 | --- |
| " | AK2 | 28-07-1996 | -9.7 | --- | --- |
| " | AK3 | 29-07-1996 | -12.0 ^a | --- | --- |
| Aniakchak | Bolshoi | 12-07-1997 | -6.1 | --- | --- |
| Augustine | Spine | 28-07-1994 | -5.4 ^b | --- | --- |
| Baker | Smiley | 10-06-1994 | -6.1 ^b | -22.9 | --- |
| " | North Wall | 06-09-1994 | -5.9 ^b | -24.3 ^b | --- |
| " | Smiley | 23-08-1996 | -6.7 | -21.7 | --- |
| " | West Main | 23-08-1996 | -6.1 | -22.4 | --- |
| " | Smiley | 07-08-1997 | -6.9 | -22.0 | 1.9 |
| " | West Main | 07-08-1997 | -6.1 | -22.0 | 4.8 |
| Griggs | Flank 3 | 22-07-1995 | -5.0 | --- | --- |
| " | Summit 1 | 22-07-1995 | -6.3 | --- | --- |
| " | Flank 3 | 18-07-1997 | -5.6 | --- | --- |
| " | Flank 3 | 16-07-1998 | -5.1 | --- | 4.3 |
| " | Summit 1 | 16-07-1998 | -6.3 | --- | --- |
| Hood | Devils Kitchen | 23-06-1995 | -8.3 | --- | --- |
| " | Crater Rock | 08-10-1996 | -9.6 | --- | --- |
| " | Crater Rock ^c | 08-10-1996 | -9.8 | --- | --- |
| " | Crater Rock | 09-09-1997 | -9.1 ^b | --- | --- |
| Mageik | S-crater | 26-07-1995 | -6.6 | --- | --- |
| " | S-crater | 19-07-1997 | -6.8 | --- | --- |
| " | N-crater | 22-07-1998 | -8.4 | --- | 2.1 |
| " | S-crater | 22-07-1998 | -8.2 | --- | 2.5 |
| Makushin | GV-2 | 24-07-1996 | -7.6 | --- | --- |
| Rainier | Soda | 08-08-1997 | -13.0 | --- | --- |
| " | Travetine | 29-09-1998 | -12.8 | --- | --- |
| " | Travetine | 29-09-1998 | -13.5 | --- | --- |
| Shasta | Summit | 07-09-1995 | -11.3 | --- | --- |
| " | Summit | 15-08-1996 | -11.2 | -27.9 | --- |
| " | Summit | 26-06-1997 | -11.4 | -28.6 | --- |
| " | Summit | 08-07-1997 | -11.1 | -28.9 | 1.1 |
| St Helens | Sept. Lobe | 29-06-1998 | -11.9 | --- | --- |
| Trident | Trident-SE | 13-07-1994 | -10.2 | -22.8 | --- |
| " | Trident-SE | 24-07-1995 | -10.1 | --- | --- |
| " | Trident-SE | 17-07-1997 | -10.5 | --- | --- |
| " | Trident-SE | 18-07-1998 | -9.6 | -29.9 | 3.2 |

---, not determined.

^aDetermined from bulk-gas sample collected into a flask filled partly with NaOH solution.

^bAverage of two samples.

^cAdjacent to main Crater Rock vent.

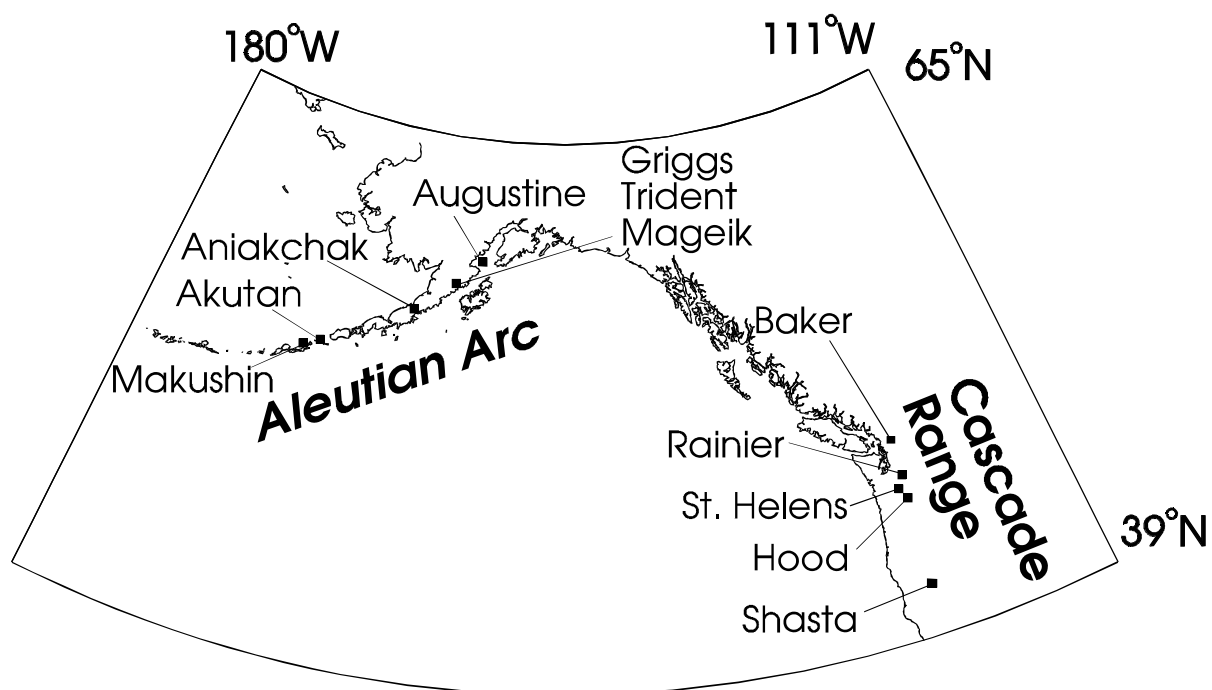


Figure 1. Map of northwestern North America showing location of volcanoes sampled in the Cascade Range and Aleutian Arc.

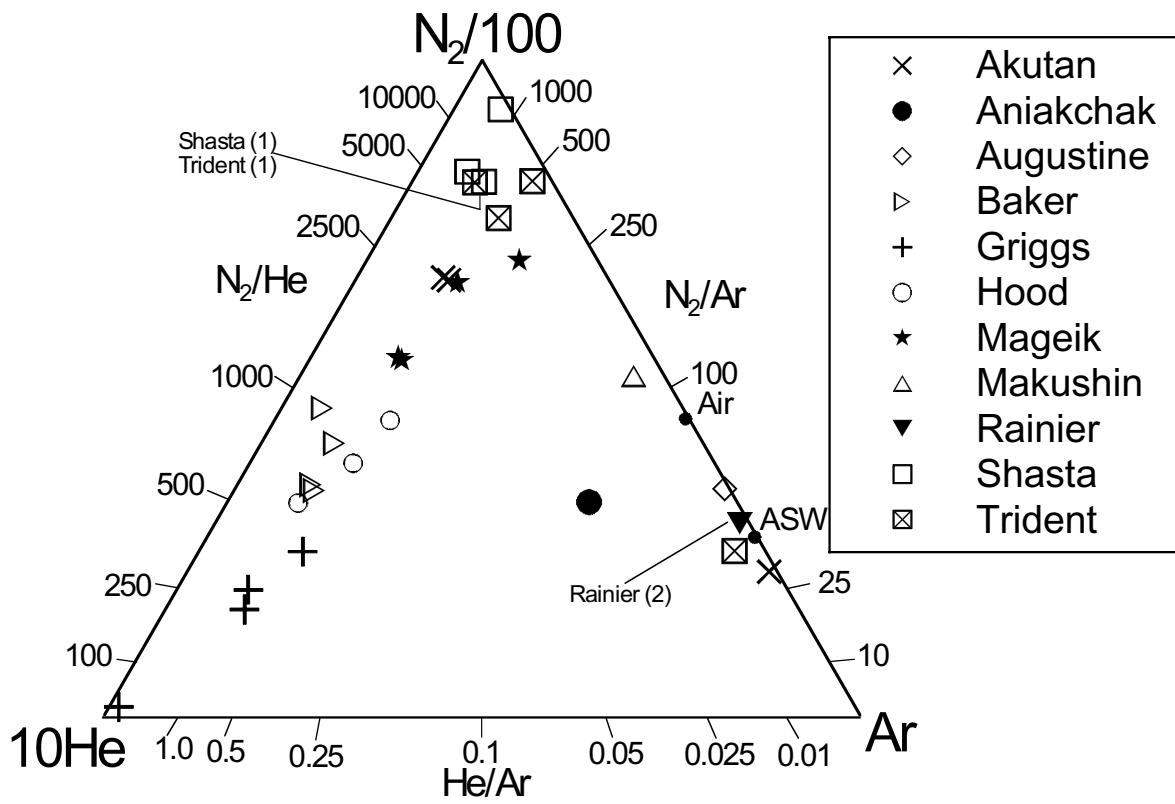


Figure 2. Molar proportions of N_2 , He, and Ar in CRAA gases. All data are from Table 2. Sampling sites described in Table 1.

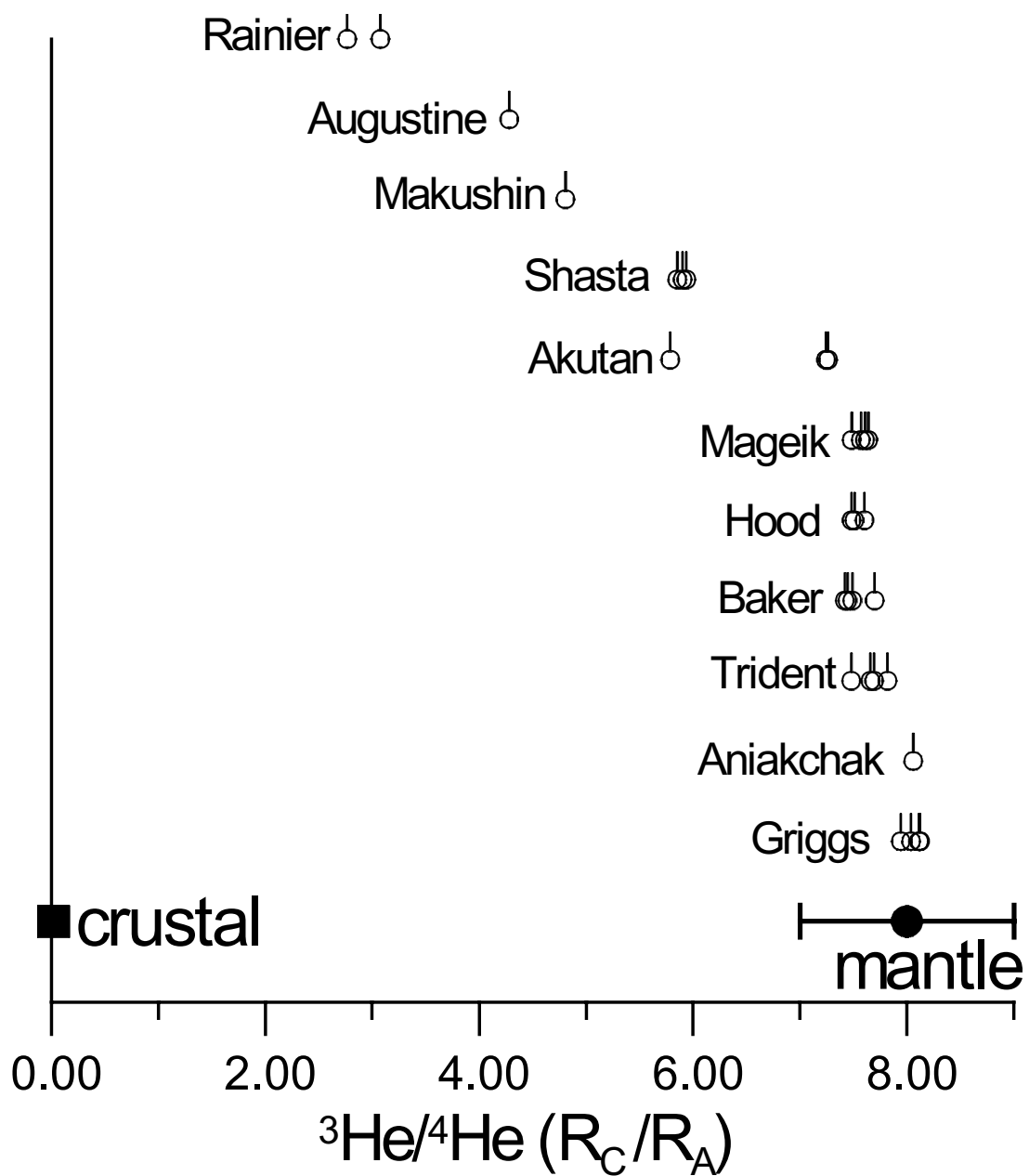


Figure 3. Plot of $^3\text{He}/^4\text{He} (R_C/R_A)$ values for CRAA gases. All data are from Table 2. Sampling sites described in Table 1. For reference, we plot values for mantle and crustal He (Poreda and Craig, 1989).

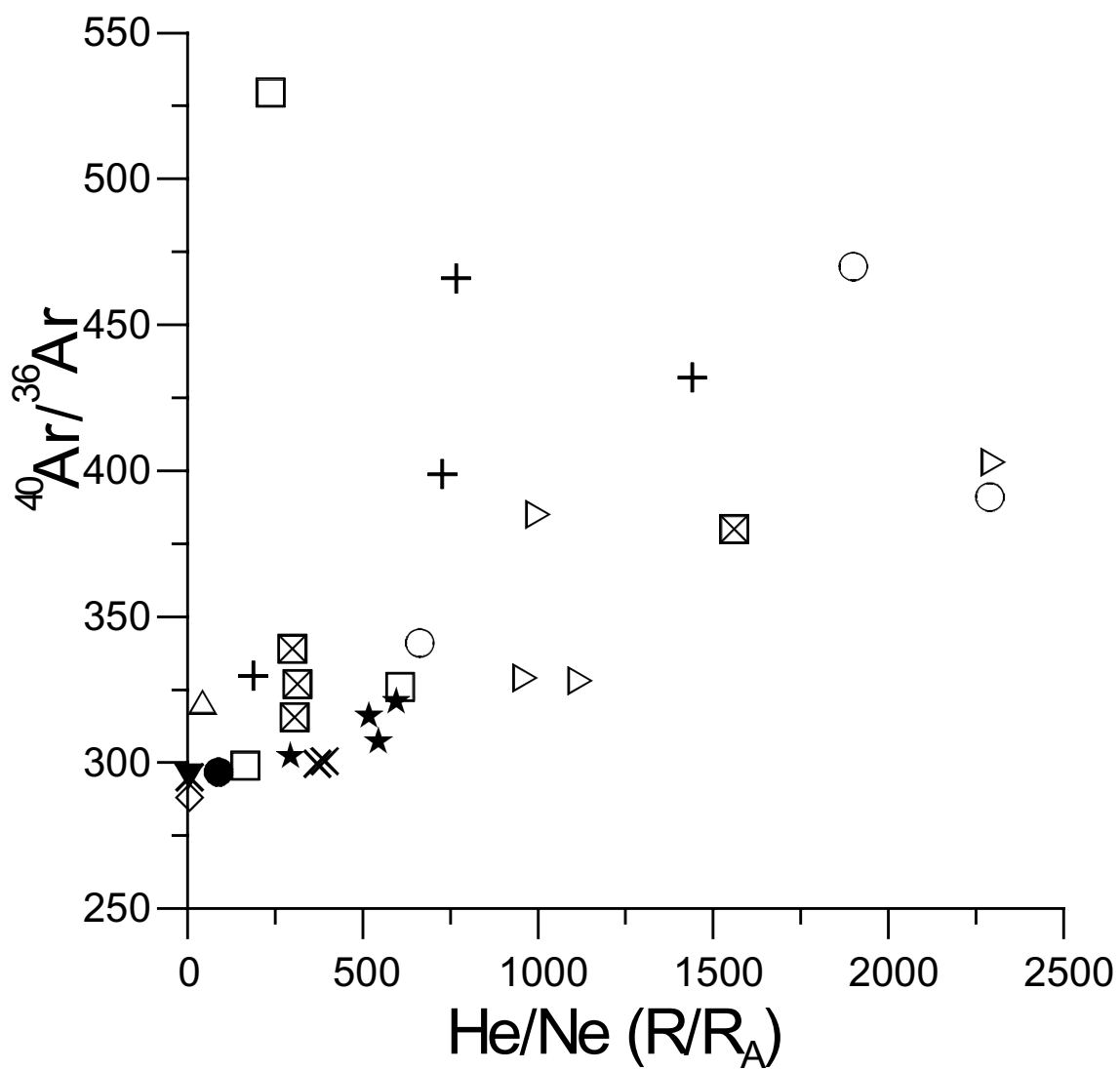


Figure 4. Plot of $^{40}\text{Ar}/^{36}\text{Ar}$ versus $\text{He}/\text{Ne} (R/R_A)$ for the CRAA gases. All data are from Table 2. Sampling sites described in Table 1. Symbols given in Figure 2.

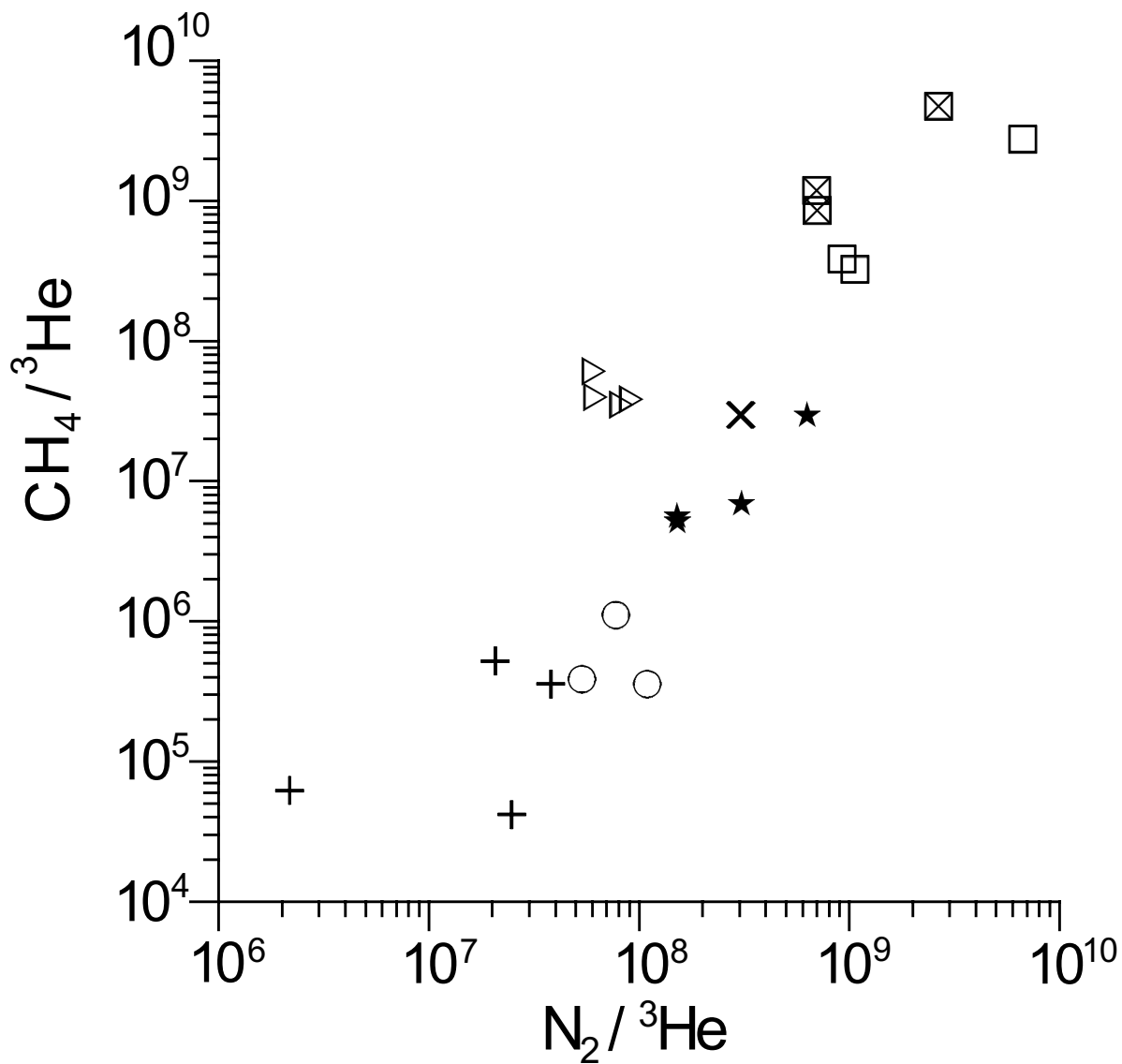


Figure 5. Plot of $\text{CH}_4/{}^3\text{He}$ versus $\text{N}_2/{}^3\text{He}$ for the CRAA analyses with non-meteoritic N_2 ($\text{N}_2/\text{Ar} \geq 166$). All data are from Table 2. Sampling sites described in Table 1. Symbols given in Figure 2.

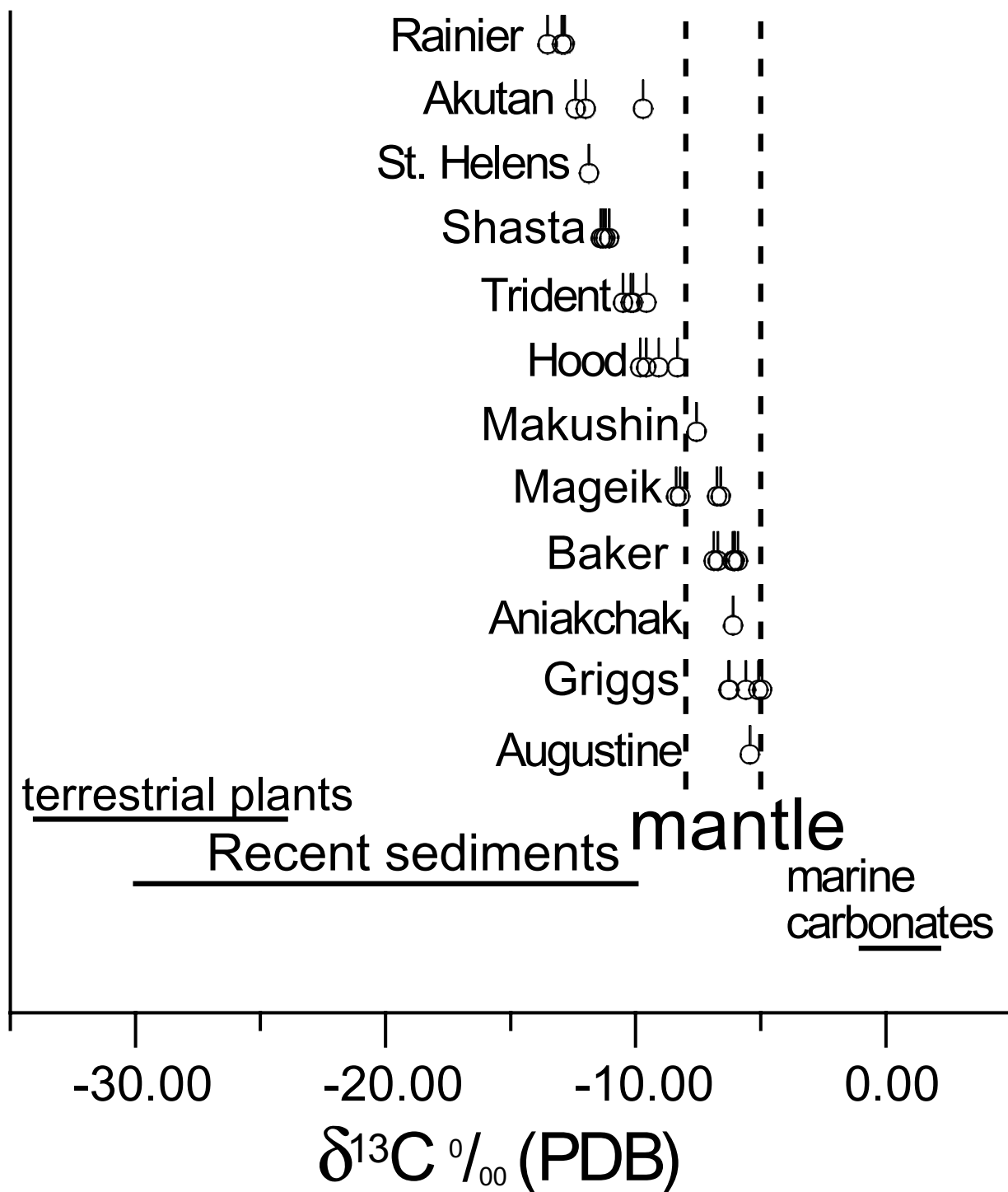


Figure 6. Plot of $\delta^{13}\text{C}$ of CO_2 values for CRAA gases. All data are from Table 3. Sampling sites described in Table 1. For reference, we plot $\delta^{13}\text{C}$ values for mantle C (Allard, 1983), Cambrian - Tertiary marine carbonates (Keith and Weber, 1964), organic matter in Recent sediments (Faure, 1986), and terrestrial plants (Smith and Epstein, 1971).

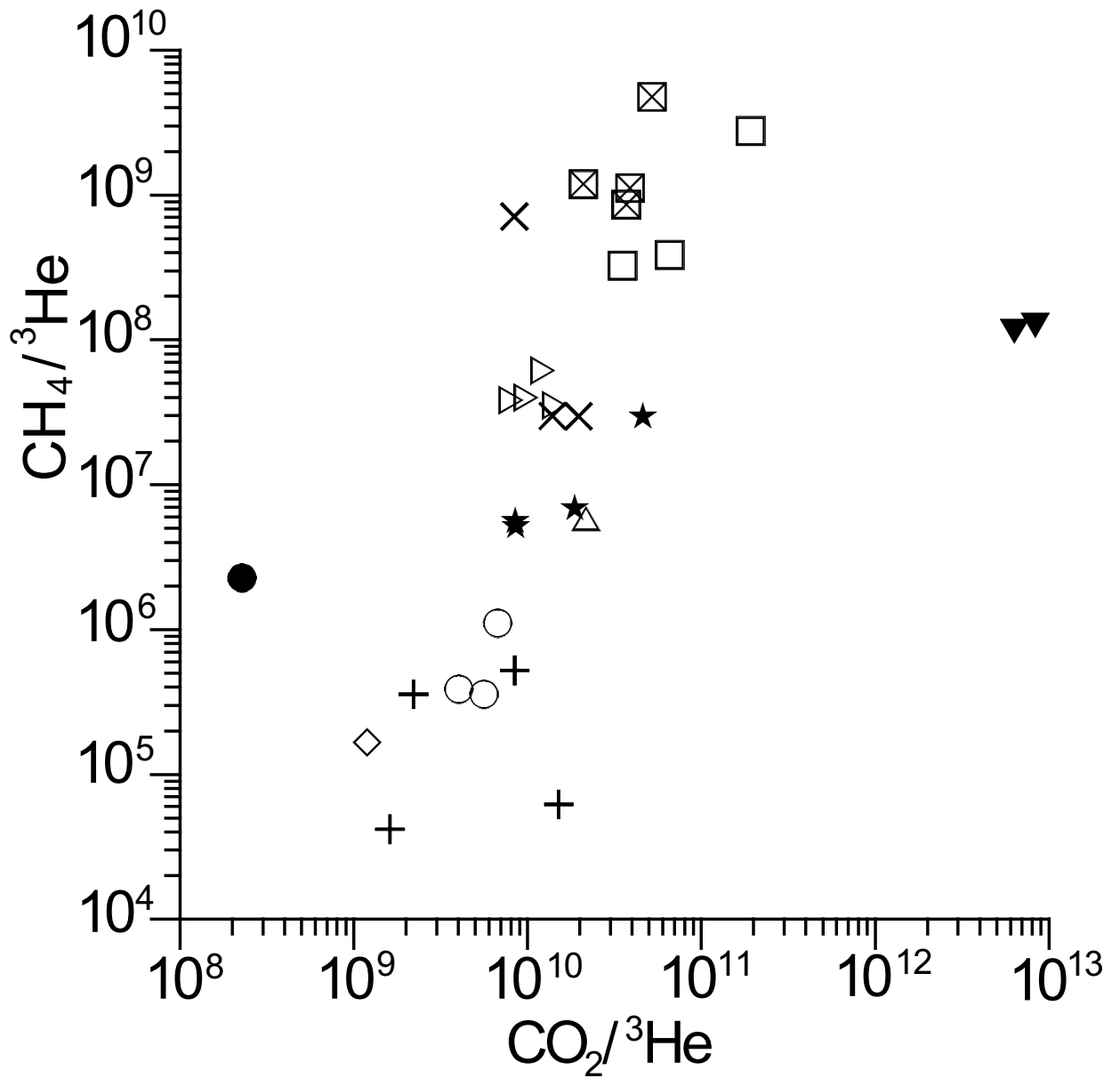


Figure 7. Plot of $\text{CH}_4/{}^3\text{He}$ versus $\text{CO}_2/{}^3\text{He}$ for the CRAA analyses. All data are from Table 2. CH_4 concentration for Augustine Volcano is estimated using the reported CO_2 concentration and the CH_4/CO_2 ratio from 1992 bulk-gas analyses (Symonds and others, 2003). Sampling sites described in Table 1. Symbols given in Figure 2.

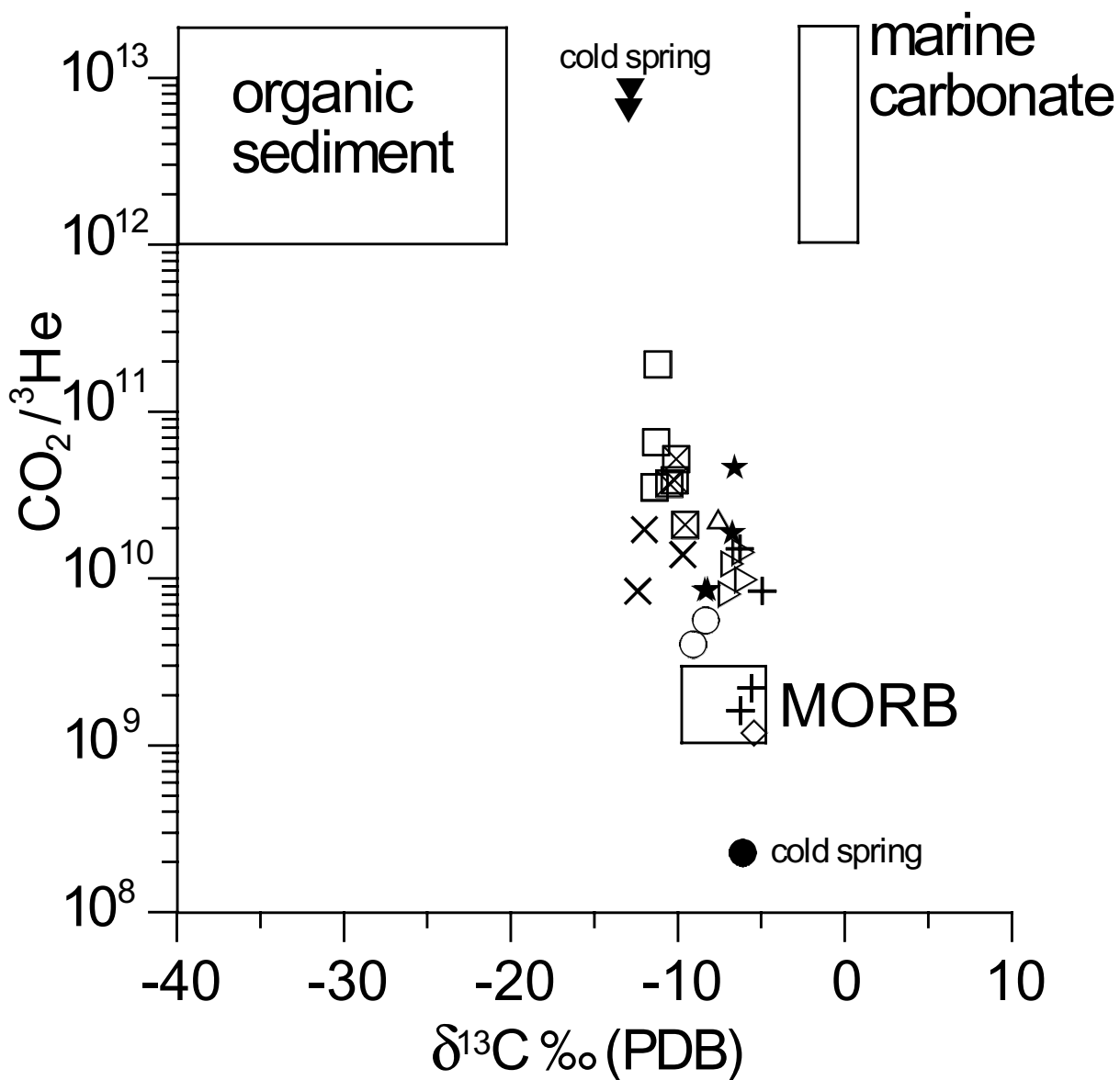


Figure 8. Plot of $\text{CO}_2/{}^3\text{He}$ versus $\delta^{13}\text{C}$ of CO_2 values for the CRAA analyses. Diagram depicts the mixing model (Sano and Marty, 1995) between MORB CO_2 , subducted organic sedimentary CO_2 , and subducted carbonate CO_2 . All data are from Tables 2 and 3. Sampling sites described in Table 1. Symbols given in Figure 2.