# Aleutian Arc Geothermal Fluids: Chemical Analyses of Waters and Gases Sampled in Association with the Alaska Volcano Observatory

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## Data

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## Introduction

As part of ongoing efforts by the Alaska Volcano Observatory (AVO) to study and monitor volcanoes of the Aleutian Arc, samples of water and gas are occasionally collected from thermal springs, fumaroles, gas vents, and other features. These samples are analyzed in one or more laboratories at the U.S. Geological Survey (USGS). Some of the analytical results are eventually included in publications that summarize the field work or present major conclusions, but some data remains unpublished, especially results from single "grab" samples that are collected during the performance of other work. Such data could be useful for purposes such as constraining the strength of magmatic degassing, evaluating geothermal resources, or simply establishing baseline hydrologic conditions at remote volcanoes that are seldom visited. This report contains the chemical and isotopic data from thermal waters and gases collected from the Aleutian Arc (Figure 1) over the past 20 years, where such data remain unpublished or only published in part. We discuss some interesting features in the data, and offer brief overviews on what the data indicate about subsurface conditions. We emphasize however, that the datasets are small and the inferences drawn from them are preliminary and should not be considered as peer reviewed. One main goal in providing these overviews is to stimulate future research.

For completeness, this report also summarizes the focused investigations of thermal fluids and gases carried out in the past 20 years at Aleutian Arc volcanoes where the data have already been published (e.g., Chiginagak, Akutan, Ukinrek Maars). Results from ongoing investigations focused on the Katmai area (Lopez and others, in prep.) are not included. Brief statements about the volcanoes and their recent eruptive histories are mostly taken from the Alaska Volcano Observatory website (AVO, 2015) as of 1 April 2015, but derive in many cases from Miller and others (1998) or Wood and Kienle (1990).

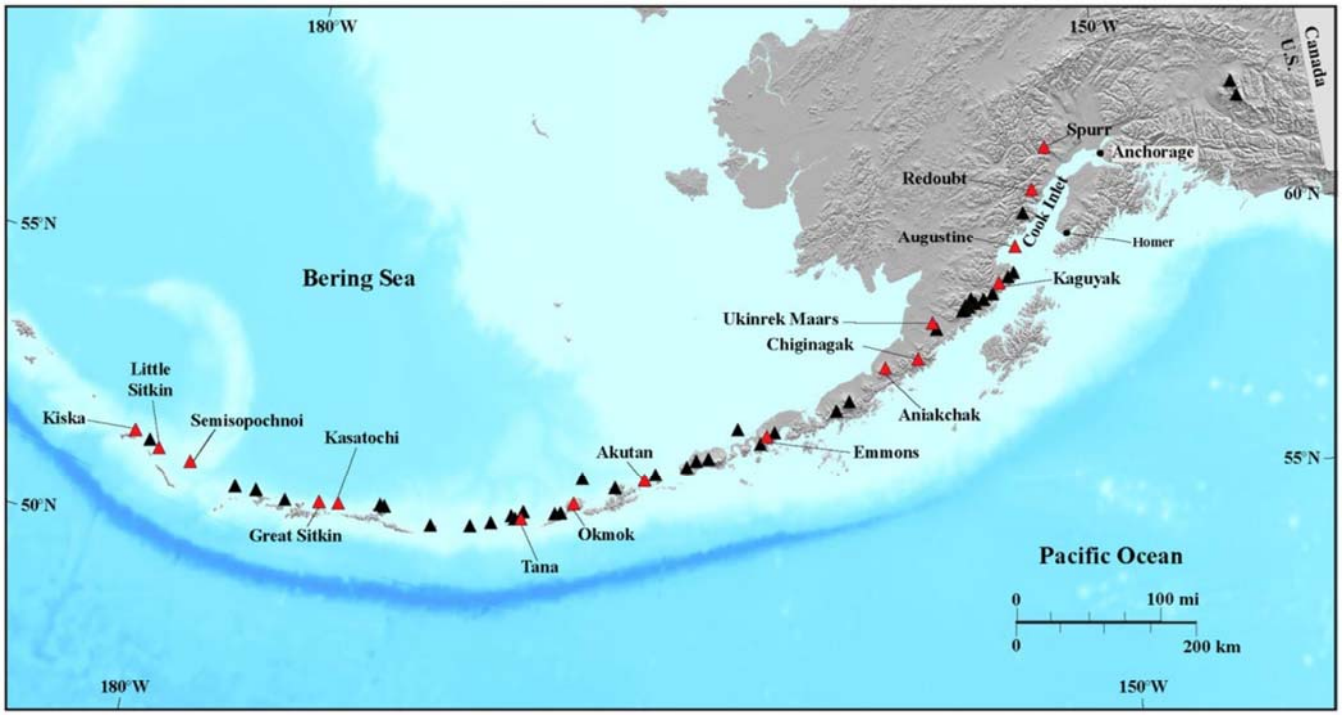


Figure 1. Map showing Aleutian Arc volcanoes (triangles). Red triangles with labels are volcanoes discussed in this report.

## Methods

A general summary of collection and analytical protocols was given by Bergfeld and others (2013). Gas samples discussed herein were collected in evacuated glass sample bottles without added caustic. Bubbling gases were collected from springs using an inverted funnel and water displacement. Fumarole gases were collected through a metal tube into a T-handle glass bottle with a downstream pinch clamp. Samples for dissolved inorganic carbon (DIC) and its isotopes were collected by injecting water into a septum-equipped evacuated glass bottle using a syringe. Helium isotope samples were collected in copper tubes sealed with refrigeration clamps.

Some water samples were collected according to established field protocols, including: on-site measurement of pH; filtration of water for chemical analysis through 0.45 µm membrane filters; acidification of cation samples; collection of isotope and alkalinity samples in tightly sealed glass bottles (Bergfeld and others, 2013). However, for some of the water samples, field measurements were minimal and consist of temperature and location, and only raw (unfiltered) water samples were collected. Unless otherwise specified, the pH, specific conductance, and alkalinity values presented in the tables are laboratory measurements, and filtration as needed prior to chemical analysis was performed in the laboratory. Lack of field processing probably has minimal negative impact on conservative species like Na, Cl and most major ions, but trace and redox-sensitive species like Fe or nutrients like $NO_3$ and $PO_4$ may have large uncertainties. A few samples were collected raw and acidified, which allows suspended particles to dissolve after collection and can greatly increase the concentrations of many of the metal species.

Chemical analyses of gas and water samples were carried out at USGS laboratories in Menlo Park, California, using methods described in Bergfeld and others (2013). Gases were analyzed by using gas chromatographs equipped with a thermal-conductivity detector. Water samples were analyzed for anions by ion chromatography except for $HCO_3$, which was analyzed by titration and should be considered as "total alkalinity as $HCO_3$" in all tables attached to this report. Cations were analyzed by argon plasma optical-emission spectrometry, and the results given in mg/L and µg/L. For some samples, major cation and trace element concentrations were determined at the USGS Minerals Program laboratories in Denver, Colorado, by inductively coupled plasma mass spectrometry (ICP-MS) using procedures described by Lamothe and others (1999). These results are usually given in ppm and ppb. Analytical results presented herein preserve the units of the reporting laboratory. For low salinity waters (dissolved solids <5000 mg/L), mg/L nearly equals ppm, and µg/L nearly equals ppb. Stable isotope analyses of waters, steam, DIC, $CO_2$, and $CH_4$ were performed by mass spectrometry at the USGS Stable Isotope Laboratory in Reston, Virginia, and are reported in per mil (Revesz and others, 2008a,b). Noble-gas ratios were determined by mass spectrometry at the USGS Noble Gas Laboratory in Denver, Colorado, using methods described in Hunt and others (2013). Reported $^3He/^4He$ ratios are corrected for air contamination and are given as $R_C/R_A$ values, where $R_A$ is the $^3He/^4He$ ratio in air.

## Akutan Volcano

Akutan Volcano in the east-central Aleutian Islands has erupted frequently during historic times, most recently in 1992 (AVO, 2015; McGimsey and others, 1995; Waythomas and others, 1998). Gas samples were collected from the summit crater in 2012 by Bergfeld and others (2013) during their study of geothermal features in a valley on the eastern side of the volcano. The geothermal features consist of fumaroles and acid-sulfate pools at higher elevations ("flank" geothermal area) and Cl-rich hot springs on the valley floor. The water and gas chemistry from all areas were interpreted and published by those authors.

The summit crater gas samples, though low in $O_2$, were heavily influenced by atmospheric circulation through the porous surface, and the hot spring study proved more interesting. The main finding of Bergfeld and others (2013) was that the output of heat, water, and geothermal solutes had increased substantially since the early 1980s when the system was studied by Motyka and others (1988). The reservoir at depth is of considerable interest as a potential source of geothermal power for the community of Akutan and a large seafood processing plant on the eastern shore of the island (Kolker and Mann, 2009; Kolker and others, 2012). Analyses of gas samples collected in 1996 from various thermal features are given in Symonds and others (2003a, b).

The δ13C-DIC values for the high-Cl hot springs sampled in 2012 were published in Bergfeld and others (2013). Table 1 [Download Data Tables] shows carbon isotope results for CO2 and CH4 gases that have since become available. The δ13C-CO2 values for high-Cl hot springs are slightly lighter (1–2‰) than the respective δ13C-DIC values, reflecting isotopic fractionation between the CO2 gas and dissolved carbonate species, but the overall similarity in δ13C values of the hot-spring DIC and the CO2 from all features is consistent with a common deep carbon source that has a $\delta^{13}C$ value in the –10 to –12.5‰ range.

Three $\delta^{13}C$-$CH_4$ values were obtained from the flank geothermal area and show a narrow spread near –32‰, in the range expected for thermal breakdown of buried organic matter. The difference between the $\delta^{13}C$-$CH_4$ and $\delta^{13}C$-$CO_2$ values (~21‰) corresponds to a calculated isotope equilibration temperature of ~370°C (Horita, 2001), much higher than the 200-235°C range obtained from three other gas geothermometers used by Bergfeld and others (2013). This discrepancy probably reflects the

sluggish rate of carbon isotope exchange between $CO_2$ and $CH_4$ in the absence of catalysts (Horita, 2001), and we suggest that the 370°C estimate is not reliable.

## Aniakchak Volcano

Aniakchak caldera formed about 3500 years ago and has been the site of numerous intra-caldera eruptions, the most recent being an explosive eruption in 1931 (Neal and others, 2001). A bubbling warm spring (Figure 2) discharges within the caldera and is informally called Bolshoi Spring because it emerges at the base of Bolshoi Dome, near the NW edge of Surprise Lake (Figure 3). Water temperature was 22.4 to 24.7°C when measured during the summers of 1992–1997 (Neal and others, 2001). The gas bubbles were sampled in 1997 by Symonds and others (2003b), who noted the magmatic $\delta^{13}C$ (–6.1‰) and $^3He/^4He$ (8.06 $R_A$) isotope values. The spring was resampled for helium isotopes in 2002 by Tina Neal. Water temperature ranged from 19.1 to 23.8°C at different spots around the pool. The $^3He/^4He$ ratio was 7.14 $R_A$ in spring water and 7.17 $R_A$ in gas bubbles. The close agreement in these two values suggested that the $^3He/^4He$ ratio had declined slightly between 1997 and 2002.

Figure 2. Bolshoi spring in Aniakchak caldera in 1992 (photo – C. Neal).

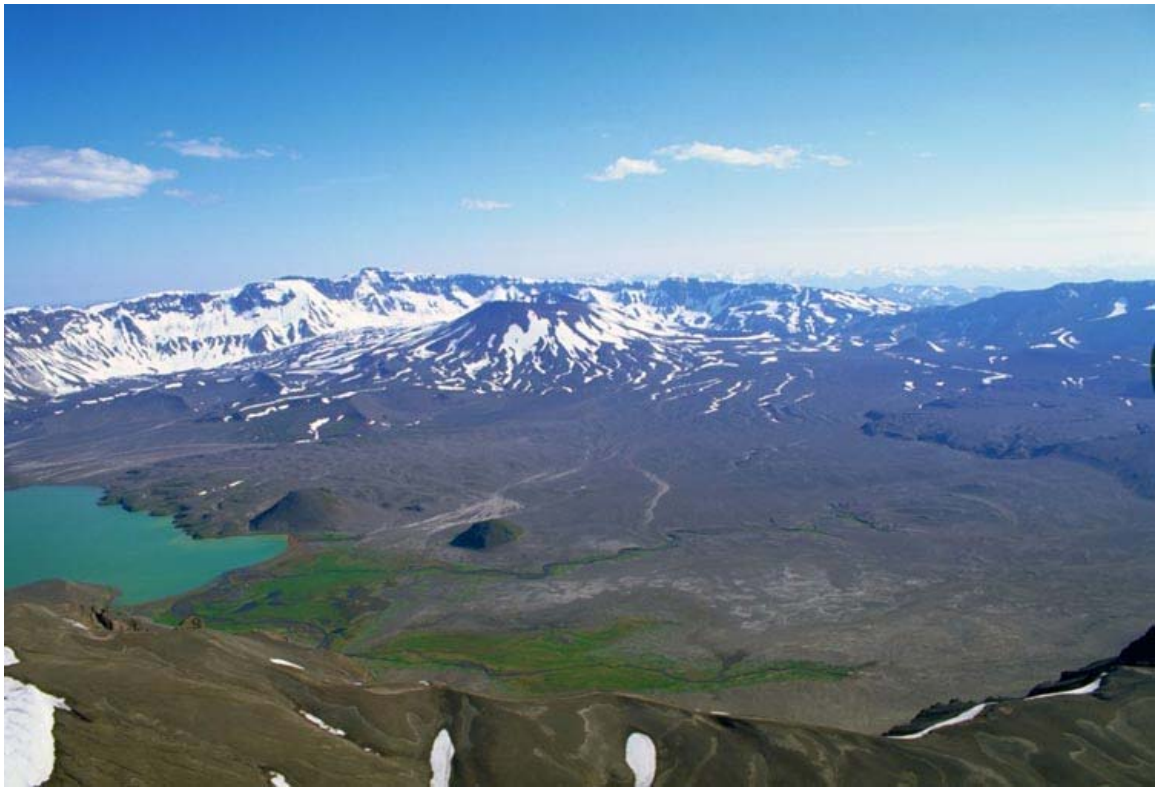

Figure 3. View from N rim of Aniakchak caldera. Faint red staining at right edge of Surprise Lake is location of Bolshoi spring. Similar warm springs discharge along two streams in foreground (photo – C. Neal).

A private citizen, Gary Freeburg, volunteered to visit the spring in 2014 and collected two water samples with similar chemistry at temperatures of 21.8 and 22.6°C (Table 2 [Download Data Tables]). Spring temperature and chemical composition are very similar to values reported by Motyka and others (1993) for a sample collected in the mid-1970s. Ivan Barnes collected a sample of "groundwater" from an "area of copious gas seeps" at this location in 1973 (Ivan Barnes' field notes). The cooler temperature and lower concentrations of most dissolved species in the 1973 sample suggest that the feature was diluted by lake water (Table 2 [Download Data Tables]).

Motyka and others (1993) applied several chemical geothermometers to the data from the warm spring water and obtained temperatures that range from 33°C for the Mg-corrected Na-K-Ca geothermometer up to 216°C for the Na-K geothermometer. Lower temperature estimates are probably more accurate given the high Mg concentration, but none of the geothermometers are necessarily reliable for this spring, a highly "immature" water under the classification scheme of Giggenbach (1988). The spring chemistry probably reflects absorption of magmatic $CO_2$ into groundwater, followed by rapid dissolution of, but not equilibration with, the rocks within the aquifer.

Bolshoi spring is just the largest of many carbonated and iron-rich warm springs that emerge over a large part of the NE caldera floor, with temperatures in the 18-22°C range (Cameron and Larson, 1992). The aggregate flow of these springs may constitute a substantial output of heat, even though their discharge temperatures are not impressive. The springs discharge into two streams that feed into Surprise Lake, and the mineralized water has a clear influence on lake characteristics (Cameron and Larson, 1992).

## Augustine Volcano

Augustine is a frequently active volcano near the mouth of Cook Inlet built upon a pre-existing island of Jurassic Naknek Formation, which is exposed on the southern flank (Waitt and Begét, 2009). Volcanic eruptions occurred in 1976, 1986, and 2006 (Power and others, 2010; AVO, 2015). Following the 1976 eruption, fumaroles in the summit area have been sampled repeatedly by several investigators (Viglino and others, 1985; Kodosky and others, 1991; Symonds and others, 1990; 2003a; 2003b). The changes in fumarole chemistry that have been observed over this time are complex and difficult to completely summarize, but in the years following both the 1976 and 1986 eruptions, fumaroles became progressively richer in steam and $H_2$ relative to $CO_2$ and $SO_2$. The ratio of $H_2/CO_2$ climbed from <1 in 1979 to 2–3 in 1984 in both raw and "reconstructed" gas analyses (Kodosky and others, 1991), and after dropping below 1 during 1986–1987, the ratio increased to 19 in 1992 (Symonds and others, 1990; 2003b). These trends were generally ascribed to increasing influx of water into the hot central conduit over the years following eruptions. The δD and $\delta^{18}O$ values of condensed fumarolic steam support the view that seawater and local meteoric water mix with primary magmatic water within the hot core of the volcano (Viglino and others, 1985; Symonds and others, 1990). In further support of seawater influx, Symonds and others (1990) noted a trend in Cl/Br ratios in the condensed steam toward a seawater ratio as fumarole temperatures decreased.

We present gas chromatographic analyses of fumarole samples (Table 3 [Download Data Tables]) collected in 2008 by Cynthia Werner (Figure 4) and in 2010 by Deborah Bergfeld and Taryn Lopez. Details of the 2008 gas sampling are as follows. Aug #1 was collected in the West moat region of the summit area from a wide orifice (T = 63°C), and air contamination was expected. Samples Aug #2 and Aug #3 (T = 95°C) were collected from steaming cracks on the tephra field at the summit of the volcano. Good flow was observed while sampling, yet samples were still air contaminated. Aug #4 and Aug #5 (T = 98°C) were collected from a mound on the west ridge from an audible fumarole with strong flow (Figure 5). The 2010 samples were collected using a titanium tube inserted into a steaming crack (T = 94.1 °C; AUG10-02) and from a pit (T = 92.4 °C; AUG10-03) near the base of the dome. At both sites the gas upflow was weak and it was necessary to use a hand pump to purge the collection apparatus. Sample AUG10-02 is from a site near the 2008 sample Aug #2.

Figure 4. Cindy Werner sampling fumaroles on Augustine in 2008.

Figure 5. Location of fumaroles sampled on W edge of summit in 2008.

All samples were collected in evacuated flasks. Acidic gases like HCl and HBr would dissolve into the condensed water and were not determined, while $SO_2$ would partition between the condensed water and the gas headspace. The $SO_2$ values in Table 3 [Download Data Tables] have been corrected for this effect using Henry law solubility data, and the other gas concentrations have been adjusted for this correction through normalization of the analyses to 100% dry gas.

Several of the samples contain large amounts of air, but 2 of the samples from 2008 are nearly air free. For the other 3 samples with 10.5-11% $CO_2$, it's unlikely that air contamination occurred during sample collection. These samples are likely from sites where air is drawn into the roots of the fumarole through a porous lava surface. Regardless, the samples from both years are strikingly low in $H_2$ even though their low gas/steam ratios show them to be water-rich. Overall, they reflect oxidized conditions, as $H_2S$ is not detected and CO is barely detectable in only one sample. These compositions appear to be unique in the record of Augustine fumarole samples. In part this may reflect the moderately high fO2 estimated for the 2006 magma (Webster and others, 2010), but shallow level processes likely also play a role given the low gas/steam ratios.

The complete absence of $H_2S$ could be due to its well-known instability in sample tubes containing $SO_2$ and liquid water. However, a low concentration of $H_2S$ would fit with emission results from nearly simultaneous air-borne measurements in the plume by McGee and others (2010). Those authors report 120 t/d of $SO_2$ on 7/17/2008 while $H_2S$ was not detected. During 2006–2008, their measured $H_2S/SO_2$ molar ratios in the plume were all $\leq 0.01$. McGee and others (2010) were able to detect, but not quantify, plume $CO_2$ on 7/17/2008. These authors do report a $CO_2/SO_2$ molar ratio of 4.3 on 5/18/2007, the last date during their measurement period on which $CO_2$ emissions could be quantified. That value matches the $CO_2/SO_2$ molar ratio in the 2008 fumarole samples, and as expected for times of relative quiescence, is higher than the C/S ratio of 0.5–2 observed during times of peak emissions at Augustine (McGee and others, 2010) and at other Cook Inlet volcanoes during actual or failed eruptions (Werner and others, 2011). Pfeffer and others (2013) estimate a molar $SO_2$/HCl ratio of 7 for the plume on 7/19/2008, based on two filter pack samples collected in the east and west moat regions for 1 hour, 20 minutes and 20 minutes, respectively. If this ratio is applied to the 2008 Aug#4 and Aug#5 samples (Table 3 [Download Data Tables]), fumarolic gases at that time would contain about 2% HCl.

The He isotope data (Table 3 [Download Data Tables]) show strong magmatic values similar to the 7.6 $R_A$ reported in 1982 (Kodosky and others, 1991). Symonds and others (2003b) attributed their much lower value of 4.28 $R_A$ in 1992 to progressive degassing of magma emplaced in prior eruptions. If so, the magma involved in the 2006 eruption appears to have recharged the fumarolic system with a more-mantle-like value. However, progressive degassing of magma should lead to lighter carbon isotope ratios, and the $\delta^{13}C$-$CO_2$ value that Symonds and others (2003b) report for 1992 (-5.4‰) is essentially identical to values found in 2008 (Table 3 [Download Data Tables]) or reported in 1982 (Kodoski and others, 1991). We argue that a local reservoir of $^4He$-rich gas exists, perhaps in the basement rocks, and can modulate the $^3He/^4He$ ratio in response to seismic fracturing. The shift to slightly lighter $\delta^{13}C$-$CO_2$ values in 2010 may reflect progressive degassing of the 2006 magma, but these samples were not analyzed for He isotopes.

Several fresh waters were collected on the island during 2010 by Deb Bergfeld and Taryn Lopez, and two sites were revisited in 2013 by J. Zebulon Maharrey (Table 4 [Download Data Tables]). Most of these features were spring-fed creeks sampled near sea level, as dense shrubbery typically rendered the source springs inaccessible (Figure 6). The waters are significantly enriched in dissolved solids relative to local rain and snowmelt, but they show little evidence for a thermal component: their temperatures are low, and thermophilic species such as Li and Rb are not detected.

The waters draining Augustine clearly contain more Cl than local precipitation (Table 4 [Download Data Tables]). Perhaps the most interesting feature of these waters is their high Cl/Br ratios, which range from 500 to 600 (Figure 7). These ratios are much higher than in either seawater (280) or in waters near the Ukinrek maars (~350) that are thought to contain a component of connate brine from the Jurassic Naknek Formation (Evans and others, 2009). Although boron was only detectable in a few of the samples (Table 4 [Download Data Tables]), a Cl/B ratio of 1000–2000 is indicated, which also differs from the ratios in seawater (4230) and the Naknek connate brine (~100).

Figure 6. Creek 1 at Augustine sampled in 2010 (photo – T. Lopez).

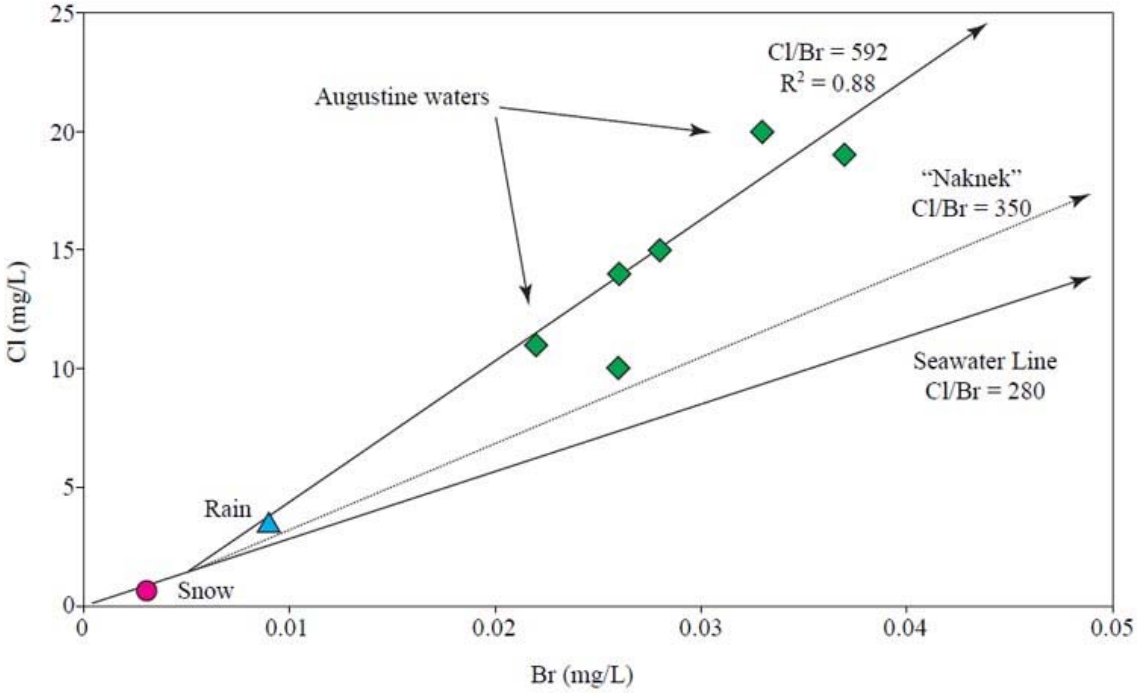


Figure 7. Cl-Br relations for waters draining Augustine compared to seawater and to groundwaters from the Naknek Formation (dotted line) in the Ukinrek Maars area (from Evans and others, 2009).

Comparably high Cl/Br ratios (525–667) were found in high-temperature (870°C) fumaroles collected from the summit dome in 1987 and were considered representative of magmatic values by Symonds and others (1990). Perhaps cold groundwaters are able to scavenge magmatic HCl and HBr without much seawater influence, and the resulting acidity catalyzes dissolution of cations from the young volcanic rocks. Alternatively, halide-rich salts have been observed in fumarole encrustations on lava flows (Kodosky and Keskinen, 1990), and such deposits might be plentiful enough to influence the halide chemistry of dilute groundwaters. These two possibilities are not distinguishable with the data currently available (Table 4 [Download Data Tables]). Groundwater scavenging of magmatic HCl and HBr should also scavenge some $CO_2$ and impart a magmatic $\delta^{13}C$ value to the DIC. The $\delta^{13}C$-DIC values are consistent with magmatic $CO_2$ in two waters and with organic $CO_2$ (soil respiration) in two others. Another complexity is that the water samples from two of the same creeks collected in 2013 gave slightly lower Cl/Br ratios of 400-467. Measurement of helium isotopes and collecting samples from the source spring vents might resolve the issue. Regardless, the Cl and $SO_4$ transport in the streams is trivial compared to the typical plume emissions of HCl and $SO_2$ at Augustine (Symonds and others, 1990; Kodosky and others, 1991; McGee and others, 2010). The two gaged streams (Table 4 [Download Data Tables]) transport 0.22 t/d of Cl and 0.19 t/d of $SO_4$, and scaling up the discharge to the average daily precipitation on the entire volcano implies that the groundwater system transports <10 t/d of each species.

## Chiginagak Volcano

Chiginagak is a stratovolcano on the Alaska Peninsula. The most recent reported, but unconfirmed, activity was a small ash eruption in 1971 (AVO, 2015). The volcano is topped by a small crater, and increased summit heating and gas upflow in 2004–2005 led to the rapid filling of this crater with acidic melt-water to a depth of about 100 m. Water eventually burst out through an ice tunnel and flowed down the Indecision Creek drainage into Mother Goose Lake, reducing the pH of this large body of water to below 3, and severely affecting the salmon run on the King Salmon River. An acidic aerosol cloud accompanied the flood and killed or damaged vegetation over a large part of the drainage. A discussion of this event and chemical analyses of stream and lake water were presented by Schaefer and others (2008). Follow-up sampling in subsequent years as the drainage of acidic crater water declined was detailed by Schaefer and others (2013). In the course of these investigations, samples were also collected from the Mother Goose hot springs at the northern base of Chiginagak, which had previously been studied by Motyka and others (1981). The hot springs showed no obvious effects from the acid lake drainage.

## Emmons Volcano

Mt. Emmons forms part of the Emmons Lake Volcanic Center (ELVC) on the lower Alaska Peninsula and rises within a complex of nested calderas (Waythomas and others, 2006). The ELVC includes several frequently active volcanoes, including Pavlov, which last erupted in 2014 (AVO, 2015). Emmons Lake lies at the southern base of Mt. Emmons, and thermal springs discharge into the lake on the NW shoreline. Water and gas bubbles were collected from one of these springs in 2005 by M. Mangan and T. Miller (Figure 8), who published the helium and carbon isotope results (Mangan and others, 2009). We provide here (Tables 5 and 6 [Download Data Tables]) the water and gas chemistry data for this spring and for a concurrently collected sample of lake water near the point of thermal water inflow. Chemical analyses from samples collected in 1980 (Motyka and others, 1981; 1993) and 1973 (Mariner and others, 2006) are given for comparison.

Figure 8. Hot spring near the base of Mt. Emmons in 2005 (photo – M. Mangan).

It is unclear whether the hot spring sampled in 2005 is the same spring that was sampled in earlier years. The similarity in the concentrations of many species (e.g., F, Cl, $SO_4$, Na, K) suggests that it might be, but several springs occur in the area. Regardless, the site seems to exhibit long-term stability in terms of both water and gas chemistry. Sodium is the dominant cation, but the water is clearly enriched in several thermophilic elements (Li, Rb, Cs). Bicarbonate is the dominant anion, but the water also contains considerable chloride. The Cl/Br ratio (378) and low Cl/B ratio (24) rule out modern seawater as the main source for these elements (seawater Cl/Br = 280; Cl/B = 4230). Magmatic degassing or circulation through old marine sediments buried beneath the volcanic rocks is a more likely source.

The hot spring is thought to be fed from a large hydrothermal system within the caldera that contains Mt. Emmons and the lake (Mangan and others, 2009). Motyka and others (1981; 1993) estimate a reservoir temperature of ~185°C for this system, based mainly on oxygen isotope equilibration between $H_2O$ and $SO_4$, and on the Na/K ratio. Other chemical geothermometers indicate lower temperatures (e.g., chalcedony gives 132°C), which also would be in line with the lack of any oxygen isotope shift in the hot spring water off of the Global Meteoric Water Line (GMWL).

Motyka and others (1981) suggest that the hot spring discharges a mixture of water from two reservoirs, and attribute disagreements between geothermometers to this possibility. The gas composition (Table 6 [Download Data Tables]) is consistent with this suggestion. Instead of being heavily dominated by $CO_2$, as is common in many volcano-hosted hydrothermal systems, the gas has an equal proportion of $N_2$. The $N_2$/Ar and $^{40}Ar/^{36}Ar$ ratios near those of air suggest a largely atmospheric $N_2$ source, but the low $O_2$ concentration rules out direct air contamination at the spring vent (sample #2 is slightly air contaminated). Rising $CO_2$-rich water from a deep, hot reservoir may mix with warm, air-

saturated but $O_2$-free, water at shallower depth, and then emerge as a mixture in the spring vent. Mixing of waters with different gas contents could explain the striking failure of the D'Amore-Panichi gas geothermometer (D'Amore and Panichi, 1980) to yield reasonable reservoir temperatures. The temperatures with this normally reliable tool are about 50°C below the actual spring temperature.

Mangan and others (2009) pointed out that the $^3He/^4He$ ratio (6.6 RA) and $\delta^{13}C$ value of the $CO_2$ gas (–9.8‰) show a strong magmatic source for these gases. A separate sample of dissolved inorganic carbon (DIC) was collected in 2005 and gave a $\delta^{13}C$ value of –8.3‰ for the $CO_2$ and carbonate species dissolved in the water. The $\delta^{13}C$ value of the bulk fluid would be between the two values (–9.8 and –8.3‰).

## Kaguyak Volcano

Kaguyak caldera is located in the Katmai National Park. The caldera formed about 6 ka and is presently filled with a lake about 2 km in diameter and 150 m deep (Fierstein and Hildreth, 2008). Those authors report gas bubbles at three locations in the lake and strong $H_2S$ odor during a survey by boat in 1999. Elevated concentrations of Cl, B, $SiO_2$, and a Cl/Br ratio of 515 in a sample of lake surface water were interpreted as evidence for hydrothermal input to the lake. Assumption of steady state conditions allowed Fierstein and Hildreth (2008) to estimate an annual input of hydrothermal Cl of ~200 tonnes.

## Kasatochi Volcano

Kasatochi is a small island volcano in the western Aleutian Arc that, prior to a sizeable eruption in August 2008, was an important bird nesting area. The 400-m-high crater rim encircled a picturesque lake with a surface elevation ~15 m above sea level. During observational visits to the island in 2005 and 2006 by U.S. Fish and Wildlife staff, areas of vigorous bubbling were clearly visible on the lake surface when viewed from the rim, but the steepness of the crater walls precluded access for any sampling of water or gas (McGimsey and others, 2008; Neal and others, 2008)

In 2008, thick eruption deposits buried rookeries and vegetation alike, leaving a sterile landscape that has provided a unique opportunity to study biological recovery on a relatively isolated island (Scott and others, 2010). The eruption led to the release of a large cloud of $H_2S$ (Clarisse and others, 2011), and sulfurous odors were reported 80-km downwind from Kasatochi for more than a year after the eruption. A field team visiting the island in summer 2009 was thus surprised by the absence of fumaroles and proposed that gases were being released diffusely through the deposits (Scott and others, 2010). Their discovery of dead insects and two dead birds in and near crevices in the deposits suggested that escaping gas, likely $CO_2$, was involved in the deaths.

Follow-up gas studies were conducted in June 2010 by Angie Diefenbach and included measurements of $CO_2$ concentration in the upper meter of the deposits along several transects. At each measurement point, a steel tube was inserted into the ground and subsurface gas was pumped out through a hand-held $CO_2$ meter (Figure 9). No sulfurous odors were detected, but a few areas had $CO_2$ concentrations greater than ambient values. Gas samples were collected at two such sites (Figure 10, Table 7 [Download Data Tables]) with variable results.

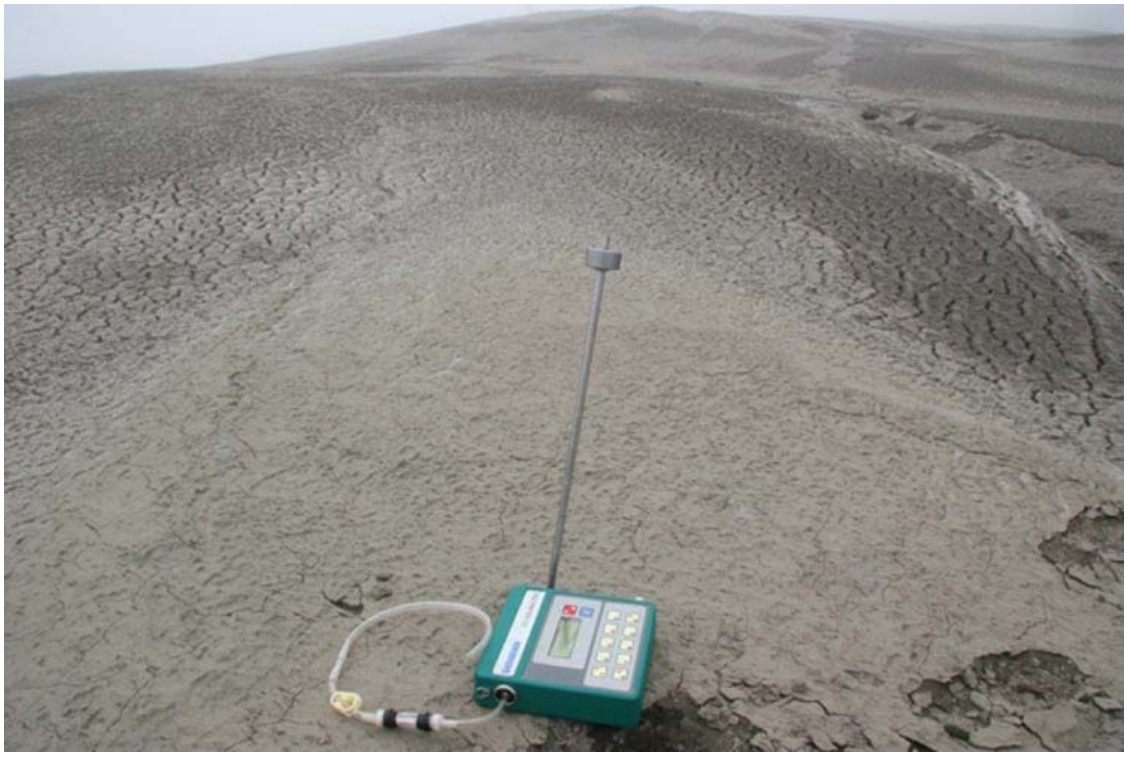

Figure 9. Soil probe and CO2 meter near the crater rim at Kasatochi (photo – A. Diefenbach).


Figure 10. Soil-gas sampling sites in 2010 and location of dead birds in 2009 (photo – A. Diefenbach).

At site K098, the $CO_2$ concentration in the sample tube was in good agreement with the field measurement of 4%. Site K108, the 2009 location of the dead birds, was an open hole emitting warm air. A field measurement of 60% $CO_2$ was obtained down in the hole, but strong wind gusts would reduce the readings and apparently caused substantial air contamination during sample collection. Two other similar vents of warm gas with ~50% $CO_2$ were found nearby.

No sulfur gases were detected in either gas sample (Table 7 [Download Data Tables]), and apart from $CO_2$ and a trace of $CH_4$ in one sample, the gases consisted of air components. $N_2$/Ar ratios near to that of air (83.6) rule out a significant non-atmospheric $N_2$ component, but the high $N_2/O_2$ ratio in sample K098 relative to the air ratio (3.73) attests to substantial removal of $O_2$ in the subsurface. A typical cause for $O_2$ removal in the shallow subsurface is microbial respiration, where consumption of organic matter produces $CO_2$, and the vegetation buried by the eruption deposits would be a likely source. To check this possibility, the $CO_2$ in K098 was analyzed for $^{14}C$ contents. The low result shows that <2% of the $CO_2$ could be produced from the recently buried vegetation. Extremely old organic matter (>30 ka) could produce such a low $^{14}C$ value, but such a source is unlikely. The $\delta^{13}C$-$CO_2$ value is much heavier than typical organic sources, is in the range of magmatic carbon, and is similar to the value obtained from site K108, where $O_2$ depletion is not observed. We conclude that the $CO_2$ at both sites is magmatic and that gas emission sites could be broadly if sparsely scattered around the island, as suggested by Figure 11.

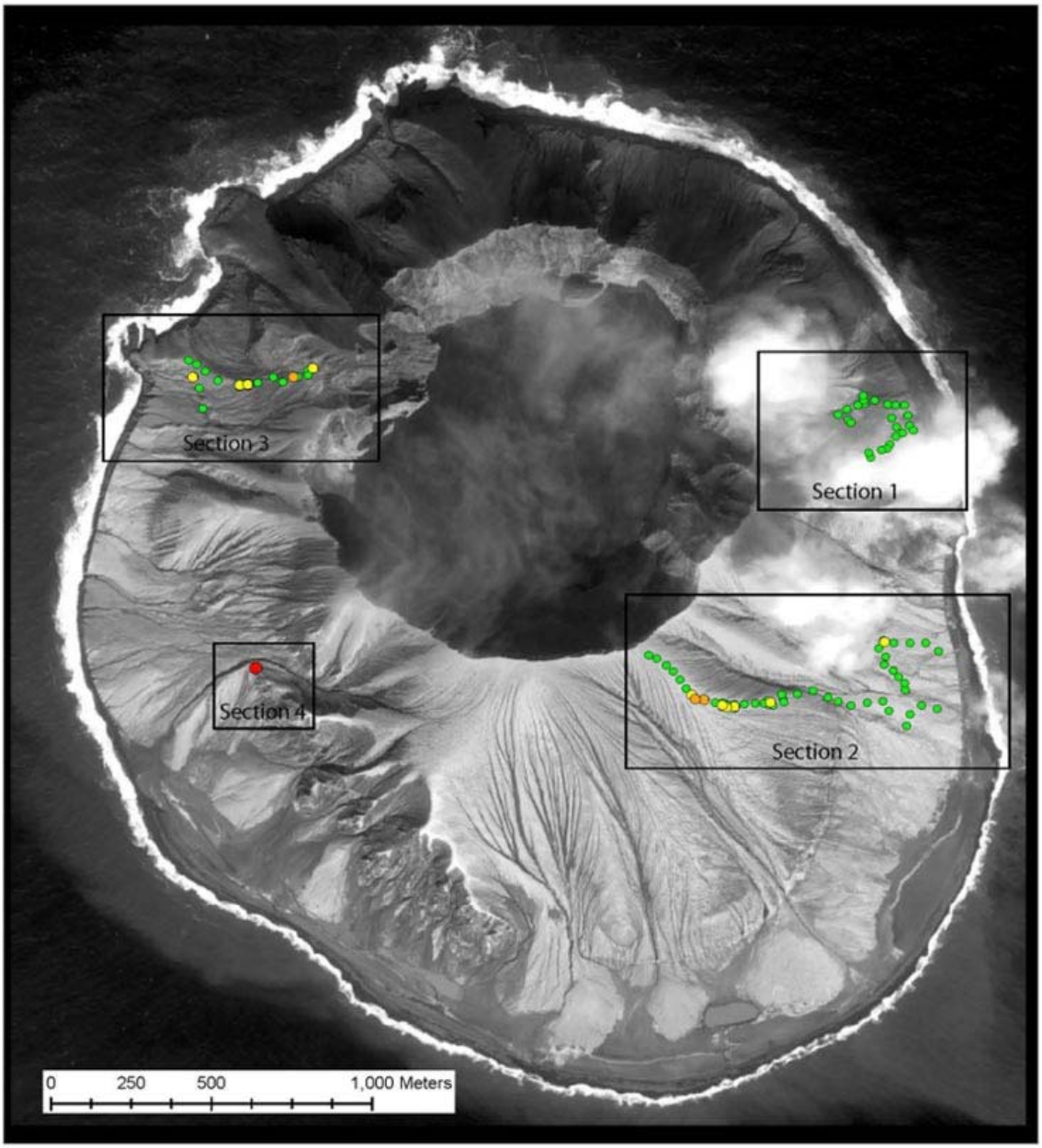


Figure 11. Worldview image of Kasatochi volcano (September 2009) with 2010 $CO_2$-survey sections outlined in boxes. $CO_2$ site locations represented by circles with gas concentrations color coded (0.3% green, 0.4-.9% yellow, 1-4% orange, and 47-60% red).

## Kiska Volcano

Kiska, located in the Rat Islands group, is the western-most active volcano in the Aleutian Arc. The most recent eruption occurred in 1990 (AVO, 2015). Gas investigations were carried out at Kiska in 2009 and 2010 in an attempt to determine the cause of peculiar groupings of dead birds in a steep-

walled canyon at the northern base of the volcano (Bond and others, 2012). Gas was collected from pits formed in the blocky lava where bird deaths were most common. Although most samples were similar to normal air, one sample had >1% $CO_2$, and the $\delta^{13}C$ value (–9.55‰) and low $^{14}C$ content (fraction modern = 0.0399) imply a magmatic source (Bond and others, 2012). $CO_2$ concentration is apparently variable at this site, and at times becomes toxic to bird life.

## Okmok Volcano

Okmok, on the northeast part of Umnak Island in the central Aleutians, is a large caldera that erupted explosively over a 5-week period in 2008 (Neal and others, 2010; Larsen and others, 2015). After the eruption, a water sample was collected from the expanded North Cone D lake by Tina Neal in 2008. The lake water was scooped up in a bucket from the unstable shoreline and carried inland where temperature, pH, and specific conductance were measured. In 2010, Janet Schaefer resampled the lake and collected additional water samples from the newly formed West Cone D lake, warm springs (Figure 12) at the base of Cone D along the south shore of North Cone D lake, and just below the falls (Figure 13) of Crater Creek in The Gates region (see Larsen and others (2015) for location of Okmok geographic features). The analytical results are given in Table 8 [Download Data Tables].

Figure 12. Warm springs at base of Cone D in Okmok caldera in 2010 (photo – J. Schaefer).

Figure 13. Falls of Crater Creek at Okmok caldera in 2010 (photo – J. Schaefer).

The 2008 eruption produced a thick blanket of tephra within the caldera, and the chemistry of the North Cone D lake no doubt reflects dissolution of material from this readily leachable layer. In the 2 years between the initial sample in 2008 and the resampling in 2010, most dissolved species dropped by a factor of 2-4, probably reflecting dilution by rainfall and snowmelt. Concentrations of a few species however, such as $HCO_3$, As, Mg, and $SiO_2$, increased. These are species that are much more abundant in the warm spring water, which drains into North Cone D lake, than in the lake when initially sampled in 2008. Thus the warm spring water has a clear impact on lake chemistry. West Cone D lake is chemically intermediate between the 2 samples of North Cone D lake in most of its dissolved constituents. The relative impact of tephra leaching vs. any possible thermal input is impossible to resolve on the basis of a single sample.

The warm spring water itself, in addition to being enriched in the 4 species listed above, would be rich in dissolved $CO_2$, ~470 mg/L at the measured $HCO_3$ and low pH. The warm spring is also high in Fe and Mn, which reflect anoxic conditions at depth. Neither species is stable for long periods in oxygenated lake waters.

One interesting characteristic of the warm spring water is its seawater-like Cl/Br ratio of 290 (Table 8 [Download Data Tables]). Whether or not the hydrothermal system taps a small component of seawater, this Cl/Br ratio readily distinguishes the warm spring water from the lake waters. The Cl/Br ratio of North Cone D lake dropped from 638 to 403 between 2008 and 2010, consistent with a shift from initial leaching of halogens from the tephra to a greater control by warm spring input over time. West Cone D lake had a Cl/Br ratio of 518 in 2010, consistent with but certainly not demonstrating a small input of warm water to that lake. The chemistry of Crater Creek at the caldera breach more or less resembles a mix of the 2 lake waters, suggesting that all of the shallow groundwater draining the caldera

is similar to the lake waters in composition. The Cl/Br ratio of 524 in Crater Creek shows that thermal water resembling the warm spring could contribute to, but not dominate, the Cl output in stream drainage from the caldera.

Byers and Brannock (1949) conducted a major study of warm springs at the base of Cone D in 1946, at which time numerous springs ranging up to 30°C discharged ~3250 L/s of aggregate flow. The warm spring discharge accounted for about 1/7th of the total water outflow from the caldera in Crater Creek as gaged at the breach. Based on an assumed background temperature of 3.9°C, the warm spring discharge corresponded to a convective heat output of ~90 MW, about 3 times larger than the combined heat output of the impressive Geyser Bight and Hot Springs Cove systems elsewhere on Umnak Island (Byers and Brannock, 1949).

Byers and Brannock (1949) report chemical analyses for 4 of the warm springs, but the warmest spring sampled had a temperature of 22°C. Minimum and maximum values for each parameter are included in Table 8 [Download Data Tables]. The springs sampled in 1946 were more dilute than the warm spring sampled in 2010, but the analyses show a general compositional similarity. Byers and Brannock (1949) noted a correlation between temperature and dissolved species, and thus their 30°C spring may have shown an even closer resemblance to the 29.6°C spring sampled in 2010. Regardless, the compositional similarity and locational correspondence clearly imply that the warm spring sampled in 2010 represents re-emergence of the spring discharge studied in 1946, as suggested by Larsen and others (2015). Interestingly, the spring vents became submerged in 1958, when a lava flow impoundment raised the level of North Cone D lake, and they remained visible but inaccessible for sampling when visited by Tina Neal in 2001. The temporary burial of this area by tephra in 2008 apparently allowed a minor on-shore discharge of spring water. The fact that warm spring input was apparently able to significantly influence the chemistry of North Cone D lake over the 2 years following 2008, as discussed above, shows that total spring discharge into the lake remained large, even if mainly below lake surface.

If the warm spring system still has a discharge near to that measured in 1946, it represents a large output of magmatic carbon. The pH and $HCO_3$ values in Table 8 [Download Data Tables] yield a calculated DIC value of 220 mg/L. A discharge of 3000 L/s of such fluid would equate to an output of 200 tonnes/day of magmatic carbon (expressed as $CO_2$). Although no isotopic analyses were conducted on the warm spring, fumarole gases sampled from Cone F within Okmok caldera in 1981 (Motyka and others, 1993) showed clear magmatic characteristics ($^3He/^4He = 6.5\ R_A$; $\delta^{13}C\text{-}CO_2 = -12.0‰$).

## Redoubt Volcano

Redoubt is one of the large Cook Inlet volcanoes where AVO monitoring often includes airborne measurements of plume emissions (Werner and others, 2011; 2013). It last erupted in March 2009. Pre-eruptive heating beginning in late 2008 led to substantial ice loss in the summit area (Bleick and others, 2013), with the melt-water emerging from beneath glacial ice at the head of the Drift River drainage on the north side of the volcano. The melt-water stream was sampled by Game McGimsey and Chris Waythomas on several occasions, from 7 November 2008 to 20 March 2009. Flow rates were highly variable even on short timescales, but the water chemistry showed a steady trend toward an acid sulfate composition with a cation abundance pattern near to that expected for dissolution of the summit dacite (Werner and others, 2012). Those authors argued that $SO_2$ gas was dissolving into ice-melt in the summit area, converting to sulfuric acid, and dissolving the dacitic dome rocks. They were able to

combine sulfate concentrations with estimated streamflows to constrain the amount of $SO_2$ scrubbed by the melting ice. The relatively low value led them to propose that high C/S ratios measured in the plume reflected intrusion of primitive $CO_2$-rich magma into the mid-crust during the lead-up to eruption.

An apparent enrichment in Ca in the melt-water relative to dacite composition was noted by Werner and others (2012), who speculated that a small fraction of the sulfate load could derive from dissolution of $CaSO_4$ somewhere in the flow system. An additional stream sample collected on 1 October 2012 shows this effect clearly, as by that time, the upflow of magmatic $SO_2$ and HCl was no longer sufficient to maintain stream acidity. The pH had risen above 7, and concentrations of dissolved species had dropped to much lower levels than in 2009 (Table 9 [Download Data Tables]).

The dilute nature of the 2012 sample supports the assumption of Werner and others (2012) that the high concentrations of $SO_4$ and Cl observed in 2008-2009 were mainly due to scrubbing of acid gases released from increasingly active magmatism. The complete loss of Fe in the 2012 sample reflects its low solubility in neutral pH waters, but the large proportional increase in Ca relative to other cations and to the dacite composition (Figure 14) shows that dissolution of a Ca-bearing mineral might contribute 30-50% of the Ca. For gypsum or anhydrite dissolution, the corresponding $SO_4$ contribution to the stream would be about 100 mg/L. Although the sulfate contribution from $CaSO_4$ was likely an insignificant part of the $SO_4$ load during the Redoubt unrest, this source should be considered in all volcano-related studies of stream chemistry. For example, extreme Ca enrichment in a drainage stream showed that $CaSO_4$ dissolution was a significant factor in the Chiginagak crater lake chemistry (Schaefer and others, 2008).

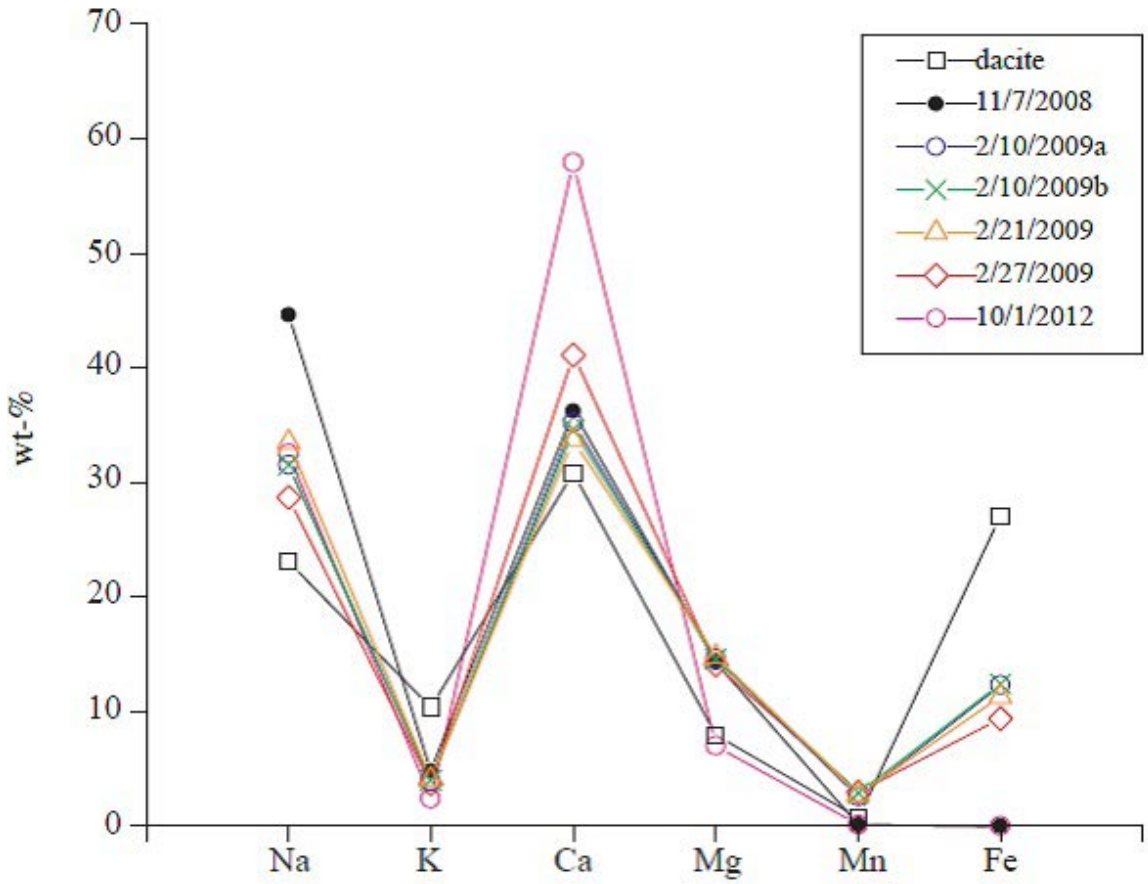


Figure 14. Cation abundance pattern for streamflow at Redoubt in 2012 compared to 2008-2009 data from Werner and others (2012) and to the dome dacite composition.

Figure 15 is a photograph of the stream taken at the sampling point in 2012. Previous samples were collected ~300 m downstream in the area of the waterfall where the stream first emerged from the winter snow pack.

Figure 15. Photograph of stream draining Redoubt taken from sampling point in October 2012 and showing location of previous samples near waterfall photo (photo – G. McGimsey).

## Semisopochnoi Volcano

Semisopochnoi is an island in the western Aleutians consisting of a caldera and several composite cones (Figure 16). The most recent activity appears to have been a minor ash eruption from one of the cones in 1987, but periods of elevated seismicity in 2014 and 2015 raised concerns about magmatic intrusions (AVO, 2015). Warm springs discharge along Fenner Creek within the caldera (Coombs and others, in prep.), and water was collected from the most vigorous spring by Tina Neal in 2005 (Figure 17). The chemical analysis is shown in Table 10 [Download Data Tables].

Figure 16. View to NE of Semisopochnoi. Warm spring is on Fenner Creek just downstream from lake at top center of photo (photo – R. Clifford).

Figure 17. Tina Neal sampling warm spring on Fenner Creek in 2005 (photo – M. Coombs).

The δD and $\delta^{18}O$ values of the spring water indicate a meteoric origin, suggesting that infiltrating groundwater acquires some heat and $CO_2$ in the subsurface. The $\delta^{13}C$-DIC value is consistent with a magmatic $CO_2$ source. The warm, carbonated groundwater dissolves the young volcanic rocks, and the release of cations is accompanied by conversion of dissolved $CO_2$ into $HCO_3$. The reaction does not go to completion and the water emerges at a slightly acid pH with approximately equal molar concentrations of $CO_2$ and $HCO_3$. The underground residence time is apparently too short to remove more of the $CO_2$, and the temperature too low to favor incorporation of Mg into alteration minerals; hence the high Mg concentration in the water. Conventional cation geothermometers are not reliable under these conditions. The high Mg concentration suggests the temperature at depth is unlikely to greatly exceed the discharge temperature. The chalcedony geothermometer yields a temperature of 108°C, which is almost certainly the maximum (amorphous silica yields 15°C).

The high Cl/Br ratio (465) rules out a significant seawater influence, as does the low Cl/B ratio of 58, which is close to that reported by Coats (1959) for samples of the local volcanic rocks. There is no evidence that the groundwater encounters high temperatures or acid gases (like HCl) at depth.

The 2005 expedition also included visits to Little and Great Sitkin volcanoes (discussed next). A small suite of unfiltered water samples was collected by Tina Neal and Michelle Coombs from all three volcanoes and analyzed for cations (and $SO_4$). Results are shown in Table 11 [Download Data Tables], and include a second analysis of the warm spring on Semisopochnoi (in Table 10 [Download Data Tables]) as well as Fenner Creek upstream of the thermal area. The two analyses of the warm spring show good agreement in most constituents. The Fenner Creek sample (Table 11 [Download Data Tables]) is somewhat elevated in a few constituents (Na, Li, Rb, $SO_4$) relative to normal cold groundwater values, suggesting that some in-seepage of thermal water may occur further upstream.

## Little Sitkin Volcano

Little Sitkin, one of the Rat Islands, hosts a young volcanic cone inside of a nested, double caldera. Eruptions have been reported over the past three centuries but are not confirmed or characterized by field studies (AVO, 2015). The volcano is morphologically quite young, and in 2012 a strong seismic swarm likely related to a magmatic intrusion was tracked by AVO (Herrick and others, 2014).

Fumarolic activity and sulfur deposition on the island were described by Snyder (1959). At least two significant thermal areas are known, and scattered other areas have been mapped (Herrick and others, 2014). Samples were collected from the largest and west thermal area (Figure 18) by Tina Neal in 2005. This thermal area consists of mud and clear-water pools, mud volcanoes, and pressurized steam vents. A field-filtered sample and a raw sample were collected from a mostly clear pool, and another raw sample was collected from a pool with some suspended mud. Two gas samples were collected from different but proximal pools that were hotter but more dilute than the spring sampled for water chemistry. An analysis of the field-filtered sample is shown in Table 12; analyses of the gas samples are shown in Table 13. Raw water analyses are shown in Table 11 [Download Data Tables].

Figure 18. Hot springs and muddy pools at Little Sitkin (photo – C. Neal).

The field-filtered sample 05LSCN08B (Table 12 [Download Data Tables]) and raw sample 05LSCN08D (Table 11 [Download Data Tables]) from the same pool differ in many aspects, and this may reflect a non-uniform composition in the pool itself. However the main difference is that the raw sample is much higher in Al (factor of 60) and $SiO_2$ than the field-filtered sample. This difference probably reflects the presence of Al-Si particles in the raw water that are removed by field filtering. The high sulfate concentration and extremely high Al and Fe concentrations in the raw water (05LSCN08A) from the other pool (Table 11 [Download Data Tables]) distinguish it as an acid sulfate water. A vapor-dominated geothermal system clearly underlies this area, as also shown by the low Cl in 05LSCN08B (Table 12 [Download Data Tables]). This water would normally be considered an acid sulfate water except that the pH is >4 and the major cation is ammonium. On a molar basis, $(NH_4)_2SO_4$ contributes nearly 90% of the ions in solution.

Ammonium sulfate waters occur in some vapor-dominated geothermal systems. Many examples can be found in samples from Lassen Volcano National Park, California (Janik and Bergfeld, 2010) and at several areas in Yellowstone National Park, Wyoming (Fournier, 1989). As temperature increases, $NH_3$ becomes more volatile and readily separates from the deep liquid into the overlying steam cap, along with other gases like $CO_2$ and $H_2S$. Near surface oxidation of $H_2S$ to sulfuric acid lowers the pH and converts the $NH_3$ to ammonium ion. Typically, sulfuric acid exceeds the stoichiometric balance with $NH_3$, and the resulting pH is in the 1–3 range. In a few cases, $NH_3$ exceeds the stoichiometric balance with sulfuric acid, and the resulting pH can exceed 7; for example, at Washburn Hot Springs in Yellowstone (Fournier, 1989). The water from Little Sitkin is a rarity in this regard, but is not unique.

The chemistry of these waters reflects near surface dissolution of the local rocks. In such a case, neither the cation composition nor the $SiO_2$ content reflect conditions at depth, and chemical geothermometers are not appropriate. On the other hand, the D'Amore-Panichi gas geothermometer (Table 13 [Download Data Tables]) should be reliable and indicates a temperature of 235°C for the relatively air-free sample (05LSCN08F). Thus this geothermal system might be one of the hottest in Alaska. The δD and $\delta^{18}O$ values (Table 12 ) are much heavier than meteoric waters of the Aleutian arc and are likely caused by extreme evaporative fractionation at low water discharge. However, a component of magmatic or connate water may also be present. Additional samples would be needed to evaluate these possibilities.

The $N_2$/Ar ratio in gas sample 05LSCN08F is substantially greater than the ratio in air (83.6) and signals a non-atmospheric component of $N_2$. This excess $N_2$ in the gas and the abundant ammonium in the water are no doubt cooked out of organic matter exposed to magmatic heating. The presence of higher hydrocarbons (to butane) along with the methane clearly point toward thermal degradation of organic matter within the hydrothermal system, just as they do in gases from the northeastern part of Yellowstone where hydrothermal circulation and petroleum migration are linked (Fournier, 1989). It is an interesting coincidence that Little Sitkin is far enough west in the Aleutian arc to be adjacent to the Bowers Basin, which hosts a thick sequence of sediments (Ehm, 1983). Despite the influence of sediments on gas composition, the $CO_2$ has a clear magmatic isotope signature.

## Great Sitkin Volcano

Great Sitkin Volcano occupies the northern half of Great Sitkin Island, located in the central Aleutian Islands well east of Little Sitkin, and has erupted numerous times in the past century (AVO, 2015). Hot springs, mud pots, and fumaroles occur over a large area at the head of Big Fox Creek (Figure 19). As discussed by Simons and Mathewson (1955), the rocks in this thermal area are mostly decomposed, and the ground surface overlying boiling pools of water is unstable. One raw water sample

collected by Tina Neal in 2005, and the results from this sample are compared in Table 11 [Download Data Tables] with a sample reported in Motyka and others (1993).

Figure 19. Hot spring area on Great Sitkin (photo – C. Neal).

Although the 2 samples are likely from different features, they show a general similarity in most species. The high concentrations of Al, Fe, and $SiO_2$ in the sample from 2005 are likely due to its collection as a raw acidified sample. These species are known to form colloids that would be removed during the filtering step used by Motyka and others (1993). The high $SO_4$/Cl ratio shows that the thermal area overlies a vapor-dominated system. The waters would normally be classified as acid-sulfate, but pH values in this area range from 2 to 7 (Simons and Mathewson, 1955). $NH_3$ concentrations were not determined, but near-equivalence between cations and anions in the 1981 sample rules out a large ammonium concentration, and suggests that rock dissolution is the main neutralizing agent for any sulfuric acid formed from $H_2S$ oxidation. Neither sample is particularly high in $SO_4$, so only a small amount of rock dissolution would be needed to achieve neutralization.

A partial gas analysis from Simons and Mathewson (1955) showed that $CO_2$ constitutes at least 80% of the gas, and an air-contaminated sample from Motyka and others (1993) shows an absence of $CH_4$. Geothermometry is questionable given the lack of a complete and uncontaminated gas sample, but a range of 129–167°C was estimated by Motyka and others (1993).

## Spurr Volcano

Mount Spurr, directly across Cook Inlet from Anchorage, is considered to mark the eastern end of active volcanism in the Aleutian Arc; all historic eruptions have occurred at Crater Peak, a satellite cone of Spurr (AVO, 2015). However, an episode of anomalous heating and ice-melt during 2004-2006 led to the formation of an ice-cauldron lake and fumaroles at the summit of Spurr. The event is well documented in Coombs and others (2006).

In the course of field investigations in 2006, an outflow of slightly thermal water from the west arm of the Kidazgeni Glacier was sampled for anion analysis by Tina Neal, and the results are given in Neal and others (2008). The water had an alkaline pH of 8.0 and an anion composition resembling water samples from long-known warm springs in the adjacent Crater Creek drainage (Neal and others, 2008). The Crater Creek warm springs have a large cumulative discharge and are thought to be associated with a geothermal reservoir of considerable size (Wescott and others, 1985), which has recently been targeted in drilling operations by geothermal interests. Given the high pH, the water sampled in 2006 from below the Kidazgeni Glacier appeared to have a source other than the summit crater lake, which was presumed to be highly acidic, and similar to the lake atop Crater Peak (Keith and others, 1995). This was a surprising find, because several outbursts of water and debris from the summit area had clearly impacted the Kidazgeni Glacier (Coombs and others, 2006). An outburst flood from the toe of the Kidazgeni Glacier was documented in 1993 by Nye and others (1995), but the ultimate source of the floodwater was not conclusively identified.

Although the source of the slightly warm water sampled in 2006 remains uncertain, experience gained from similar incidents of crater lake drainage at Redoubt and Chiginagak highlights the need for more complete analyses of distal streams to allow better understanding of relations between stream water chemistry and summit processes. For example, cation analyses at Redoubt and Chiginagak have shown that $CaSO_4$ can be an important source of sulfate, and the 2012 sample from Redoubt, with a pH of 8.66, indicates that acidic waters in the summit area can be neutralized by rock dissolution during outflow. Such rapid reaction rates may be characteristic of ice-clad volcanoes where flow paths might encounter an abundance of finely ground rock.

## Tana Volcano

The Tana volcanic complex occupies the eastern half of Chuginadak Island in the Islands of Four Mountains group. Tana is suspected of being active in the Holocene, but was thought to lack surficial thermal manifestations and was identified as a "poor" candidate for geothermal potential (Motyka and others, 1993). However, during the Islands of Four Mountains multidisciplinary project in 2014 (funded by the National Science Foundation, the USGS/AVO, and the Keck Geology Consortium) investigators located fumaroles, boiling hot springs, and geysers, the first time such features had been described. Water samples were collected by Kirsten Nicolaysen and Pavel Izbekov from the summit lake (Figure 20), and from two fumarolic areas that are about 6 km apart. The upper area is high on the NE flank (Figure 21), and samples were collected from two small boiling springs among the fumaroles. The lower area is near the eastern coastline (Figure 22) and hosts small geysers among the fumaroles. A stream emerging from a fumarole and the water from a geyser were sampled in this area.

Figure 20. Kirsten Nicolaysen collects water and hydrothermally altered rock at the summit lake on Tana (photo – D. Leary).

Figure 21. Pavel Izbekov approaches the fumarole field high on the NE flank of Tana (photo – K. Nicolaysen).

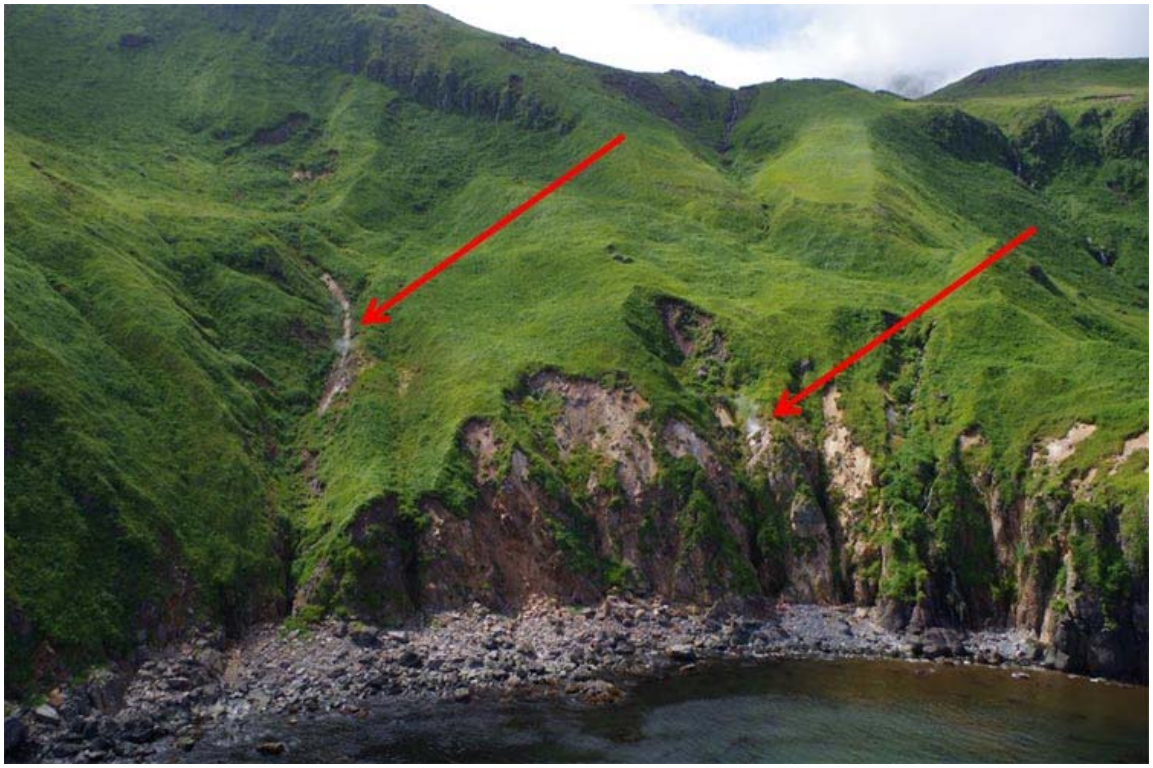

Figure 22. Hydrothermal area near eastern coastline of Tana; arrows point to fumaroles (photo – P. Izbekov).

The analyses (Table 14 [Download Data Tables]) show some characteristics that are readily explained. None of the waters are high in Cl, and this is clear evidence that the heat is carried by steam; that is, the underlying thermal regime is vapor-dominated. Sulfate is the main anion in the 4 acid water samples and derives from oxidation of $H_2S$ carried upward by the steam. Ammonium is particularly enriched in 2 of the waters, and is likewise transported upward with steam as $NH_3$ gas.

Tana's summit lake, though having a low temperature (9.1°C) and no visible steaming or fumaroles, nonetheless had rocks at shoreline that showed distinct bleaching, particularly along fractures (Figure 20). This plus thin rinds of iron hydroxides perhaps testifies to past hydrothermal activity at the summit, and the lake water was sampled to investigate continuing thermal input to the lake. The acidic pH, moderate sulfate concentration, and trace of ammonium in the lake water (Table 14 [Download Data Tables]) call for a continued input of geothermal vapor. The low Cl and Br concentrations and Cl/Br ratio of ~180 suggest that precipitation is the main source of these elements. The δD and $\delta^{18}O$ values of the lake water plot on the GMWL, indicating that ice-melt and precipitation inputs greatly exceed evaporation losses. Thus, seepage out of the lake basin must play a significant role in the water balance.

The two hot springs from the upper thermal area (14TAKN-008 and 14TAKN-009) are compositionally similar in many respects, but differ from each other enough that one cannot be a simple dilution of the other. On a molar basis, ammonium (derived from $NH_3$ gas) is the major cation in both waters. Other cations mainly represent rapid dissolution of the local rock in contact with the acidic waters, resulting in a mixed Na-K-Ca-Mg composition. Spring 14TAKN-008 is acidic enough to maintain high concentrations of Al and Fe in solution; 14TAKN-009 at a higher pH has substantially lower Al and Fe concentrations.

The two waters collected near the eastern coast show some enigmatic characteristics. The water draining the fumarole vent has a neutral pH while the water flowing out from the geyser is acid sulfate.

The reverse situation would normally be expected in a hydrothermal field, such as those at Yellowstone (Fournier, 1989). Further, the geyser outflow water plots off the GMWL and is the only one of the 5 Tana samples to do so. The two samples from the eastern coast appear to have a small seawater component to account for their slight elevation in Cl and for the predominance of Na among the cations. Nevertheless, they are clearly steam heated as shown by their dilute nature, and some of their unusual characteristics likely reflect the interplay between steam, dilute groundwater, and seawater at the island's edge. Two small mudpots in this area show that dissolution of cations from country rock is likely a factor in to the chemical budget as well.

The high concentrations of ammonium at Tana, while not as high as at Little Sitkin, are intriguing because they reveal an input of volatiles from buried sediments. At this location, west of the continental segment of the Aleutian Arc, incorporation of marine detritus into the volcanic pile perhaps offer the most likely source. Additional sampling of gases and analysis of nitrogen isotopes might help resolve the ammonium source.

## Ukinrek Maars Volcano

The Ukinrek Maars formed in 1977 at the northern base of Mount Peulik volcano on the upper Alaska Peninsula. They also lie 3 km south of The Gas Rocks, where a prominent vent of $CO_2$ gas lies just offshore in Becharof Lake. This gas vent was observed at least 60 years prior to maar formation. Several studies of gas and hot spring discharges have been carried out in this area after the eruptions (Barnes and McCoy, 1979; Motyka and others, 1993; Symonds and others, 1997), which mostly pointed to decreasing temperature and vigor over time. However, Symonds and others (1997) noted expanding areas of vegetation kill on the low ridge that hosts the maars and recommended that a study of diffuse gas emissions be conducted. That work was performed in 2004 by Evans and others (2009).

The diffuse efflux of $CO_2$ in 2004 was found to be moderately large, totaling 21–44 t/d from several spatially distinct areas of ground where plants were visibly unhealthy or dead. As at the well-known areas of tree-kill at Mammoth Mountain California, the diffuse gas emissions were not associated with a detectable thermal anomaly, but were similar in chemistry and C and He isotopes to the gas venting at The Gas Rocks. This similarity led Evans and others (2009) to propose that this gas vent (at The Gas Rocks) was a long-term precursor to the eruption of basalt at Ukinrek Maars. The study also helped to constrain the chemical characteristics of connate water in the Naknek formation, a Jurassic sedimentary body of broad extent in this part of the arc.

## Summary

This report presents the first published chemistry data on waters or gases from three Aleutian Arc volcanoes: Semisopochnoi, Little Sitkin, and Tana. Water chemistry at Little Sitkin and Tana shows that the hydrothermal systems are vapor-dominated, and high concentrations of ammonium reveal a significant interaction with buried organic matter. Gas geothermometry implies a reservoir temperature of 235°C at Little Sitkin, which would make this system one of the hottest in Alaska. This report also updates the record of fluid chemistry at several volcanoes; notably, several new gas analyses from

Augustine and a new stream sample at Redoubt, or fills in results for constituents not analyzed in previous studies, such as carbon isotopes.

The carbon isotope data presented in the tables here, or in the recent reports cited, can be combined with results from the two major compilations of carbon isotope values of fluids from Aleutian Arc volcanoes in the literature (Motyka and others, 1993; Symonds and others, 2003b) to fill in the pattern for the entire active part of the arc, from Spurr at the eastern end to Kiska at the western end. The combined carbon isotope dataset is given in Table 15 and plotted in Figure 23. For plotting purposes, values from multiple sites were averaged (for example several sites at Makushin; 3 sites at Atka) so that a single value for each volcano is plotted for each set of researchers. Where 2 or 3 groups of researchers give results, the agreement between the groups is generally fair, worst case being Makushin where the one data point from Symonds and others (2003b) is significantly heavier than all 9 values given by Motyka and others (1993). A few widely divergent values were not given in Table 15 or plotted in Figure 23. These include an extremely negative value from Akutan (-18.1‰) and a positive value from Augustine (+2.3‰) in Motyka and others (1993) and values obtained on cold dilute waters at Augustine and Ukinrek Maars.

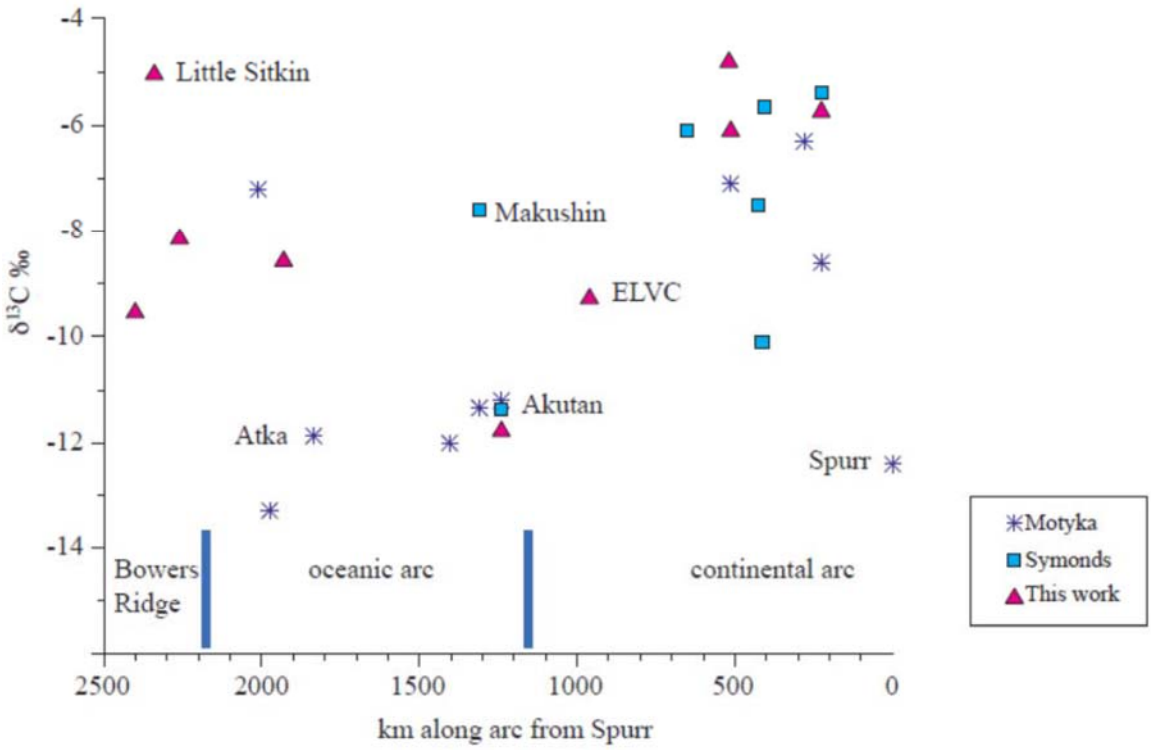


Figure 23. Variation in the isotopic composition of inorganic carbon (CO2 and DIC) along arc from Mt. Spurr to Kiska Island (see text and Table 15).

Most geoscientists accept the view that much of the carbon emitted by island arc volcanoes derives from subducted sediments and carbonate minerals, and that the mix between them is a controlling factor in the isotopic composition of the emitted $CO_2$ (Sano and Marty, 1995). The relative importance of shallow crustal carbon sources and losses is still debated, but was particularly emphasized by Symonds and others (2003a). Figure 23 suggests that the carbon isotope composition does vary in a systematic way along the arc, shifting from heavier values toward the east (Spurr excepted) to lighter values toward the center. The shift occurs close to the transition zone from a continental to an oceanic arc. However, a shift back to heavier values at the western end is very apparent, especially considering

the new data, and this shift does not correspond to an obvious change in geologic setting. The shift begins hundreds of km east of the intersection of the arc with the Bowers Ridge. Thus the cause of the carbon isotope variations along arc remains uncertain. Nevertheless, the pattern is intriguing and worthy of further investigation. Carbon isotope data are still lacking for known geothermal systems on many of the Aleutian Arc volcanoes. Searches for magmatic $CO_2$ in soil gases, as recently found at Kasatochi and Kiska, have rarely been done in the Aleutian Arc.

Work presented or described herein highlights the fact that thermal springs are not necessarily the most useful features in volcano monitoring. Thermal springs such as those at Aniakchak and ELVC often exhibit long-term stability in composition through the years (Tables 2 & 5). Gas samples from acid-sulfate areas and summit fumaroles, such as those at Augustine (Table 3), are more likely to respond quickly to magmatic unrest. Under certain conditions, streams draining the summit areas can provide useful information on magmatic gas flux, as at Chiginagak and Redoubt. Opportunities to monitor similar streams should not be overlooked, especially in cases when direct sampling in the summit area is precluded by inaccessibility or hazard issues.

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