

# **Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012**



Scientific Investigations Report 2013–5231

U.S. Department of the Interior U.S. Geological Survey

**Cover.** View to the southeast of the main stem of Hot Springs Creek, showing the outflow from the group A hot springs (lower far right edge of image) and steam from group B hot spring (near center). U.S. Geological Survey photograph by Deborah Bergfeld, July 28, 2012.

# Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012

By Deborah Bergfeld, Jennifer L. Lewicki, William C. Evans, Andrew G. Hunt, Kinga Revesz, and Mark Huebner

Scientific Investigations Report 2013–5231

U.S. Department of the Interior U.S. Geological Survey

## **U.S. Department of the Interior**

SALLY JEWELL, Secretary

### **U.S. Geological Survey**

Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit http://www.usgs.gov or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit http://www.usgs.gov/pubprod

To order this and other USGS information products, visit http://store.usgs.gov

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Bergfeld, D., Lewicki, J.L., Evans, W.C., Hunt, A.G., Revesz, K., and Huebner, M., 2014, Geochemical investigation of the hydrothermal system on Akutan Island, Alaska, July 2012: U.S. Geological Survey Scientific Investigations Report 2013–5231, 20 p., http://dx.doi.org/10.3133/sir20135231.

ISSN 2328-0328 (online)

## Contents

Abstract	1
Introduction	1
Methods	3
Site Descriptions	3
Hot Springs	3
Other Waters	8
Gas Vents	8
Results	9
Water and Gas Chemistry	9
Discharge	9
Discussion	9
Hot-Spring Water Geochemistry	9
Hot-Spring Geothermometry	12
Gases at Akutan	12
Thermal Chloride Flux	15
Change in the Akutan Hydrothermal System	16
Summary	16
Acknowledgments	18
References Cited	

# Figures

1.	Topographic map of northeastern part of Akutan Island, showing locations of caldera and modern cinder cone of Akutan Volcano, flank fumarole field, and Akutan village	2
2.	Photos showing features in Hot Springs valley. Aerial photograph of Hot Springs valley, with steam plume visible from group C hot spring. Vent-type hot spring in group A. Pool-type hot spring with gas bubbles in group B	8
3.	Scatterplots showing positive correlation between Cl concentration and other components in Akutan hot-spring waters and negative correlation between Cl and Mg concentrations	13
4.	Plots of isotopic composition and chloride concentrations for Akutan hot springs and local cold creek water in 2012. $\delta D$ versus $\delta^{18}O$ values of hot springs and cold creek water relative to World Meteoric Water Line. Cl concentration versus $\delta^{18}O$ values in hot-spring water, showing positive correlation	14
5.	Ternary N <sub>2</sub> -He-Ar diagram for gas samples collected at Akutan Volcano in 1981, 1996, and 2012	15
6.	Scatterplots showing differences in water chemistry for Akutan hot springs in 1980–81 and 2012	17
7.	Schematic cross section of hydrothermal system on Akutan Island	18

## **Tables**

1.	Sample-collection parameters, chemical analyses and isotope values for	
	waters from Akutan Volcano, Alaska sampled during 1996 and 2012	4
2.	Sample locations, gas chemistry and noble-gas data for degassing features around Akutan Volcano, Alaska, sampled during 2012	10
3.	Chloride concentrations and stream discharges used to determine geothermal flux and heat output from hot springs along sections of Hot Springs Creek near Akutan Volcano, Alaska, in 1981 and 2012	12

## **Conversion Factors**

Multiply	Ву	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square meter (m <sup>2</sup> )	0.0002471	acre
square meter (m <sup>2</sup> )	10.76	square foot (ft <sup>2</sup> )
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
	Volume	
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
	Flow rate	
liter per second (L/s)	15.85	gallon per minute (gal/min)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
metric tonnes per day (t/d)	1.102	tons per day (ton/d)
	Energy	
joule (J)	0.0000002	kilowatthour (kWh)

### SI to Inch/Pound

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  $^{\circ}F=(1.8\times^{\circ}C)+32$ 

Vertical coordinate information is referenced to the World Geodetic System of 1984 (WGS 84). Horizontal coordinate information is referenced to the World Geodetic System of 1984 (WGS 84). Altitude, as used in this report, refers to distance above the vertical datum.

## **Abbreviations**

ASMW	Air-saturated meteoric water
DIC	Dissolved inorganic carbon
EFHSC	East fork of Hot Springs Creek
FF	Flank fumarole field
Q	Discharge
$R_{c}/R_{A}$	<sup>3</sup> He/ <sup>4</sup> He corrected for atmospheric air
TI	Thermal influx
VPBD	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
WMWL	World Meteoric Water Line

#### **Chemical unit abbreviations**

J/g	Joules per gram
mS/cm	millisiemens per centimeter
µS/cm	microsiemens per centimeter
MW	megawatts

#### Chemical symbols and chemical species abbreviations

Ar	Argon
В	Boron
Br	Bromine; bromide (Br-)
Са	Calcium
CH4	Methane
CI	Chlorine; chloride (Cl-)
CO <sub>2</sub>	Carbon dioxide
δ <sup>13</sup> C	$^{\rm 13}{\rm C}/^{\rm 12}{\rm C}$ in sample compared to that of a standard reference rock
δ <sup>18</sup> 0	$^{\rm 18}{\rm O}/^{\rm 16}{\rm O}$ in sample compared to that of standard mean ocean water
δD	<sup>2</sup> H/ <sup>1</sup> H in sample compared to that of standard mean ocean water
H <sub>2</sub>	Molecular hydrogen
$H_20$	Water
$H_2S$	Hydrogen sulfide
HCO <sup>3</sup>	Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )
Не	Helium
<sup>3</sup> He	Helium-3 atom
К	Potassium
Li	Lithium
Mg	Magnesium
N <sub>2</sub>	Molecular nitrogen
Na	Sodium
Si	Silicon
SiO <sub>2</sub>	Silica
SO <sub>4</sub>	Sulfate

# Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012

By Deborah Bergfeld, Jennifer L. Lewicki, William C. Evans, Andrew G. Hunt, Kinga Revesz, and Mark Huebner

## Abstract

We have studied the geochemistry of the hot springs on Akutan Island in detail for the first time since the early 1980s. Springs in four discrete groups (A-D) along Hot Springs Creek showed generally higher temperatures and substantially higher Na, Ca, and Cl concentrations than previously reported, and total hot-spring discharge has also increased markedly. The springs now account for a heat output of ~29 MW, about an order of magnitude more than in 1981. Gas samples from the hot springs and from a fumarolic area on the flank of Akutan Volcano show high  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios (>6.4 R<sub>4</sub>) after correction for air contamination and reveal a common magmatic heat source. Hot-spring gases are unusually rich in N<sub>2</sub>, Ar, and CH<sub>4</sub>, suggesting that the water has boiled and lost CO<sub>2</sub> during upflow beneath the flank fumarole field. Gas geothermometry calculations applied to the flank fumarole field implies temperatures of 200-240 °C for the reservoir, and Na-K-Ca geothermometry implies temperatures near 180 °C for the outflow waters that feed the hot springs. The results of our study confirm the existence of a substantial geothermal resource on the island.

## Introduction

Akutan Volcano is an active stratovolcano in the eastcentral Aleutian Islands that has erupted at least 27 times since the late 1700s (Finch, 1935; Byers and Barth, 1953; Waythomas, 1999). The most recent eruption, in 1992, was followed by a seismic crisis in March 1996 (McGimsey and others, 1995; Waythomas and others, 1998). The summit caldera, at an elevation of 1,100 m, contains an active cone and icecovered lakes (Waythomas and others, 1998). During our site visit in July 2012, we observed degassing from fumaroles and steaming ground on the cone. Surface expressions of the hydrothermal system on Akutan Island include a ~5,000-m<sup>2</sup> fumarole field (Motyka and others, 1988) on the northeast flank of the volcano, at an elevation of ~400 m, and a series of hot springs that discharge at elevations close to sea level along lower parts of the northeast-trending Hot Springs valley (fig. 1). Additional warm water discharges from diffuse seeps at the mouth of Hot Springs Bay.

Reconnaissance surveys of the hot springs on Akutan Island began as early as 1953 (Byers and Barth, 1953). The first detailed geochemical and geophysical investigations to assess geothermal potential occurred during the early 1980s (Motyka and Nye, 1988). Motyka and others (1988) categorized the hot springs as belonging to one of five groups (A-E, fig. 1) from southwest to northeast. Between 1980 and 1983, Motyka and coworkers collected water and gas samples from the springs and made discharge and load measurements of the creek above and below the hot-spring inputs; they also collected gas from the flank fumarole field. Additional investigations at Akutan took place in 1996, several months after the seismic crisis (Symonds and others, 2003a, b). Studies at Akutan beginning in 2009 were related to renewed interest in geothermal development of the Akutan hydrothermal system for use by the City of Akutan and other population centers on the island. (Kolker and Mann, 2009; Kolker and others, 2012). That work included geochemical sampling, geophysical studies, and the drilling of two small-diameter temperaturegradient wells in Hot Springs valley (Kolker and others, 2012) but no new investigation of the hot-spring chemistry.

We report here the results of a 5-day survey of the hydrothermal system on Akutan Island during July 2012. Samples of gas and water were collected from the hot springs, and gas was collected from fumaroles on the flank of the volcano and from an area of acid-altered steaming ground on the cone. Fumaroles were also present on the cone but not readily accessible. We made discharge measurements on the main stem of Hot Springs Creek and two of its tributaries (fig. 1).



Figure 1. Topographic map of northeastern part of Akutan Island (after Richter and others, 1998), showing locations of caldera and modern cinder cone of Akutan Volcano, flank fumarole field, and Akutan village. A, B, C, D, and E, hot spring groups defined by Motyka and others (1988) and retained in this study. FF, flank fumarole field; S, snow sample location; R, rain sample location; SG, area of summit gas discharge.

3 MILES

## **Methods**

General information on sample collection and analytical techniques was presented by Bergfeld and others (2011). We used digital meters to measure water temperature, specific conductance and pH at each water-sampling site. Samplingsite locations were determined by using a handheld Global Positioning System device. Whenever possible, hot-spring waters were collected from the spring orifice, but at springs with deep pools we collected from the side of the pool. We collected two samples of filtered  $(0.45 \text{ }\mu\text{m})$  water in plastic bottles for bulk chemistry (including major ions and trace metals), and two samples of raw water in glass bottles for stable isotope ( $\delta D$ ,  $\delta^{18}O$ ) analysis and for determination of alkalinity at all of the springs and most of the creeks. At five springs we collected an additional sample of filtered water, using a 0.1-µm filter specifically for determination of Al concentrations. Samples for cation analysis were acidified in the field to pH <2, using ultrapure nitric acid. Alkalinity titrations were performed by using sulfuric acid and a digital titrator. The titrations were typically performed on the day of sample collection, but when this procedure was impossible, the sample was stored in a refrigerator.

At five of the hot springs we collected a 60-mL water sample for determination of dissolved inorganic carbon (DIC) concentration. The water was collected in a syringe and injected into a preweighed evacuated glass tube through a rubber septum and acidified in the field by injecting 0.5 mL of 6N HCl.

No spring produced a vigorous gas upflow, but four springs had sufficient gas discharge to allow for sample collection into an evacuated tube. The gas was collected by connecting the sample bottle to the neck of a funnel and placing the mouth of the funnel over the bubble train. Narrow-gauge tubing was threaded through the funnel into the neck of the sample bottle, attached to a syringe, and used to pump away trapped atmospheric gas. After the atmospheric components were purged, the small tubing was removed, and the bottle was opened and allowed to fill. At two of the group A hot springs we collected a second aliquot of gas for analysis of noble-gas ratios including <sup>3</sup>He/<sup>4</sup>He. These samples were collected in a copper tube sealed at both ends with refrigeration clamps.

Three types of gas samples were collected from fumaroles and steaming ground on the flanks and cone of Akutan Volcano. At some sampling sites, the gas was collected into empty evacuated bottles, using a funnel or metal tube to focus the gas flow. Before opening the sample bottle, we flowed gas through the collection apparatus to purge any trapped atmospheric gas. Gas collected in evacuated bottles was used for determination of bulk chemistry (for example, CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>) and for determination of the  $\delta^{13}$ C composition of CO<sub>2</sub> and CH<sub>4</sub>. When a sufficient quantity of steam condensed in the bottles, the water was sent for  $\delta$ D and  $\delta^{18}$ O analysis. We also collected gas in evacuated bottles containing 4N NaOH solution. This method was used for determinations of bulk chemistry, concentrations of trace-gas species, and H<sub>2</sub>S, which might not be preserved in the evacuated bottles. A third set of gas samples was collected in copper tubes for analysis of noble-gas ratios.

Discharge was measured at four sites, using a standard USGS wading rod and pygmy meter. The sites include Hot Springs Creek above the group A hot-spring inputs and below the group D inputs, a tributary containing the outflow from group A hot springs, and a tributary flowing from the east side of the valley that discharges into Hot Springs Creek (fig. 1). Water samples collected at three of the discharge-measurement sites were used to calculate the flux of dissolved constituents.

Chemical analyses of gas and water samples were determined at USGS laboratories in Menlo Park, Calif. Gases were analyzed by using gas chromatographs equipped with thermalconductivity and flame-ionization detectors. Water samples were analyzed for anions by ion chromatography, and for cations by argon plasma optical-emission spectrometry. Stable isotope analyses of waters, steam, DIC, CO<sub>2</sub>, and CH<sub>4</sub> were performed by mass spectrometry at the USGS Stable Isotope Laboratory in Reston, Va. Noble-gas ratios were determined by mass spectrometry at the USGS Noble Gas Laboratory in Denver, Colo. Reported <sup>3</sup>He/<sup>4</sup>He ratios are corrected for minor amounts of air and are given as  $R_C/R_A$  values.

## **Site Descriptions**

### **Hot Springs**

On the basis of the map by Motyka and others (1988), the layout of the hot springs in 2012 was apparently much like that in the 1980s. In this report, we retain their nomenclature for the hot-spring groups (fig. 1). Group E waters are thermal seeps in the intertidal zone that discharge diffusely and mix with seawater. We report the water chemistry for one group E site in table 1 but omit additional discussion of those data.

Hot-spring groups A through D occur along a ~850-m section of lower Hot Springs valley at elevations close to sea level (fig. 1; table 1). Most of the hot springs discharge from the northwest side of Hot Springs Creek (fig. 2*A*). Some hot springs discharge from shallow discrete vents along the margin of volcaniclastic deposits (fig. 2*B*), and others originate on the valley floor and collect in pools that drain into the creek (fig. 2*C*). Water temperatures ranged from 60 °C to ~100 °C, with the higher temperatures at vent-type springs.

The uppermost hot springs (group A, fig. 1) consist of two vents and a pool that are closely clustered and discharge into a small tributary stream on the west side of Hot Springs Creek. We collected water from all three hot springs (AKU12-01, AKU12-02, AKU12-03, table 1), and gas from the pool and the lowermost vent (AKU12-01 and AKU12-03, respectively). Water in the pool was cool enough to support aquatic plants, but the flow was sufficient that the surface of the pool was clear. 
 Table 1.
 Sample-collection parameters, chemical analyses and isotope values for waters from Akutan Volcano, Alaska, sampled during 1996 and 2012.

[All analyses in milligrams per liter except as noted. Stable isotope values in per mil (‰) relative to Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation (VSMOW-SLAP) for  $\delta D$  and  $\delta_{18}O$  or relative to Vienna Pee Dee Belemnite-Space Vacuum Epitaxy Center (VPDB-SVEC) for  $\delta^{13}C$ ; ---, no data. Water geothermometers: chalcedony ( $T_{CH}$ ) and quartz conductive ( $T_{QC}$ ) from Fournier (1981); Na-K-Ca ( $T_{NKC}$ ) from Fournier and Truesdell (1973). Datum for Universal Transverse Mercator (UTM) coordinates is referenced to WGS84 zone 3U. Analytical uncertainties ±5 percent at 1 $\sigma$  level for major species; 0.2 and 2 per mil at  $2\sigma$  level for  $\delta^{18}O$  and  $\delta D$ , respectively]

Sample number	Description	Date	Easting (meters)	Northing (meters)	Elevation (meters)	Temp. (°C)	Cond. (µS/cm)	рН	δ <sup>18</sup> 0 (‰)	δD (‰)
Hot springs										
AKU12-01	Group A pool	07/25/2012	444006	6000806	18	60.5	1,920	6.44	-9.2	-69
AKU12-02	Group A upper vent	07/25/2012	443989	6000805	16	84.3	3,200	6.33	-8.6	-69
AKU12-03	Group A lower vent	07/25/2012	444032	6000819	18	94.0	3,050	7.00	-8.7	-69
AKU12-04	Group B upper pool	07/25/2012	444132	6000890	19	76.8	2,300	6.67	-8.9	-69
AKU12-11	Group B lower pool	07/27/2012	444255	6001052	14	75.2	1,472	6.49	-9.3	-69
AKU12-05	Group C geysering vent	07/25/2012	444349	6001222	18	100.8	3,240	6.69	-8.4	-67
AKU12-13	Group C east bank vent	07/27/2012	444461	6001338	18	73.0	1,836	6.88	-9.2	-69
AKU12-14	Group C west bank vent	07/27/2012	444339	6001217	18	99.5	2,670	6.65	-8.9	-69
AKU12-12	Group D vent spring	07/27/2012	444498	6001442	16	83.8	2,360	7.47	-8.9	-69
Cold waters										
AKU12-15	Upper Hot Springs Creek	07/28/2012	441925	5999860	73	5.3	55	7.49	-10.7	-74
AKU12-16	Hot Springs Creek, lower gage	07/29/2012	444721	6001526	54	10.5	266	6.86		
AKU12-18	Upper Hot Springs Creek at gage	07/29/2012	443357	6000037	31	5.8	60.2	7.02		
AKU12-19	Snow	07/30/2012	439151	5996100	505		33.4			
AKU12-20	East Fork Hot Springs Creek	07/30/2012	444634	6001377	16	5.7	115	6.71		
AKU12-21	Rain; Akutan Harbor	07/29/2012	449488	5998752	10					
Other										
AKU12-17	Seep on beach	07/29/2012	444833	6001800	8	49.4	14,400	5.79	-6.3	-46
1996 Akutan v	vaters									
AK-01	Vig. bubbling spring	7/27/1996				97.4	2,490	6.89	-9.2	-69
AK-08	Green pool	7/30/1996				60.6	1,250	6.94	-9.6	-67
AK-11	Small green pool	7/30/1996				64.2	2,470	6.49	-9.5	-65
AK-02	Acidic water in fumarole field	7/28/1996				90.7	2,290	2.50	-8.4	-57

# Table 1. Sample-collection parameters, chemical analyses and isotope values for waters from Akutan Volcano, Alaska, sampled during 1996 and 2012.—Continued

[All analyses in milligrams per liter except as noted. Stable isotope values in per mil (‰) relative to Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation (VSMOW-SLAP) for  $\delta D$  and  $\delta_{18}O$  or relative to Vienna Pee Dee Belemnite-Space Vacuum Epitaxy Center (VPDB-SVEC) for  $\delta^{13}C$ ; ---, no data. Water geothermometers: chalcedony ( $T_{CH}$ ) and quartz conductive ( $T_{QC}$ ) from Fournier (1981); Na-K-Ca ( $T_{NKC}$ ) from Fournier and Truesdell (1973). Datum for Universal Transverse Mercator (UTM) coordinates is referenced to WGS84 zone 3U. Analytical uncertainties ±5 percent at 1 $\sigma$  level for major species; 0.2 and 2 per mil at  $2\sigma$  level for  $\delta^{18}O$  and  $\delta D$ , respectively]

Sample number	δ <sup>13</sup> C-DIC (‰)	AI	As	В	Ba	Br	Ca	Cd	CI	Co	<b>CO</b> <sub>3</sub>	Cr	Cu
Hot springs													
AKU12-01		< 0.03	0.76	14.0	0.04	1.6	37.4	0.01	530	< 0.006	0	< 0.006	< 0.006
AKU12-02		< 0.055	1.51	25.1	0.05	3	61.8	0.02	980	< 0.011	0	< 0.011	< 0.011
AKU12-03	-10.7	< 0.055	1.50	23.4	0.04	2.8	41.0	0.02	920	< 0.011	0	< 0.011	< 0.011
AKU12-04	-11.6	< 0.055	1.16	18.1	0.02	2.1	45.1	0.01	700	< 0.011	0	< 0.011	< 0.011
AKU12-11	-11.7	< 0.03	0.55	10.1	0.05	1.2	39.1	< 0.006	410	< 0.006	0	< 0.006	< 0.006
AKU12-05	-9.9	< 0.055	1.69	25.2	0.04	3.3	73.2	0.02	1100	< 0.011	0.1	< 0.011	< 0.011
AKU12-13		< 0.03	0.57	12.1	0.26	1.5	96.5	< 0.006	510	< 0.006	0.1	< 0.006	< 0.006
AKU12-14		< 0.055	1.22	17.9	0.04	2.7	52.1	0.01	880	< 0.011	0	< 0.011	< 0.011
AKU12-12	-11.4	< 0.055	0.63	16.2	< 0.011	2.5	64.5	< 0.011	800	< 0.011	0	< 0.011	< 0.011
Cold waters													
AKU12-15		0.01	< 0.001	0.01	0.01	0.0039	5.3	< 0.001	3.6	< 0.001	0	< 0.001	< 0.001
AKU12-16		0.01	0.05	1.20	0.01	0.16	11.7	< 0.001	58	< 0.001	0	< 0.001	< 0.001
AKU12-18		0.01	< 0.001	0.01	0.01	0.006	6.0	< 0.001	4.3	< 0.001	0	< 0.001	< 0.001
AKU12-19		0.05	< 0.001	0.01	0.002	0.0014	0.57	< 0.001	6.8	< 0.001		< 0.001	0.005
AKU12-20		< 0.005	0.00	0.13	0.01	0.026	10.0	< 0.001	13	< 0.001		< 0.001	< 0.001
AKU12-21						0.057			12				
Other													
AKU12-17		< 0.25	0.36	6.30	< 0.05	23	209.5	< 0.05	7,300	< 0.05	0	< 0.05	< 0.05
1996 Akutan	waters												
AK-01		0.10	1.30	14.1		2.24	32.0		623		0		
AK-08		0.07	0.325	5.31		0.89	27.8		252		0		
AK-11		0.13	0.87	10.2		1.42	52.7		426		0		
AK-02		25.1	0.0051	0.059		< 0.02	26.0		3.66		0		

#### 6 Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012

 Table 1.
 Sample-collection parameters, chemical analyses and isotope values for waters from Akutan Volcano, Alaska, sampled during 1996 and 2012.—Continued

[All analyses in milligrams per liter except as noted. Stable isotope values in per mil (‰) relative to Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation (VSMOW-SLAP) for  $\delta D$  and  $\delta_{18}O$  or relative to Vienna Pee Dee Belemnite-Space Vacuum Epitaxy Center (VPDB-SVEC) for  $\delta^{13}C$ ; ---, no data. Water geothermometers: chalcedony ( $T_{CH}$ ) and quartz conductive ( $T_{QC}$ ) from Fournier (1981); Na-K-Ca ( $T_{NKC}$ ) from Fournier and Truesdell (1973). Datum for Universal Transverse Mercator (UTM) coordinates is referenced to WGS84 zone 3U. Analytical uncertainties ±5 percent at 1 $\sigma$  level for major species; 0.2 and 2 per mil at  $2\sigma$  level for  $\delta^{18}O$  and  $\delta D$ , respectively]

Sample number	F	Fe	HCO <sub>3</sub>	К	Li	Mg	Mn	Мо	Na	$\mathbf{NH}_{4}$	Ni	NO <sub>3</sub> -N <sup>1</sup>	PO <sub>4</sub> -P <sup>1</sup>
Hot springs													
AKU12-01	0.4	0.86	111	29.2	0.94	5.84	0.24	< 0.006	325		< 0.006	0.1	< 0.1
AKU12-02	0.5	0.03	111	49.2	1.72	4.55	0.25	< 0.011	578		< 0.011	0.1	< 0.1
AKU12-03	0.7	0.03	97	48.0	1.62	2.93	0.18	< 0.011	557		< 0.011	0.4	< 0.1
AKU12-04	0.6	1.10	111	38.6	1.25	4.03	0.25	< 0.011	434		< 0.011	0.1	< 0.1
AKU12-11	0.4	1.70	128	26.1	0.63	8.04	0.51	< 0.006	246		< 0.006	0.2	< 0.1
AKU12-05	0.8	0.04	44	51.4	1.56	2.04	0.16	< 0.011	636		< 0.011	0.3	< 0.1
AKU12-13	0.3	0.75	134	32.9	0.64	17.1	0.75	< 0.006	228		< 0.006	< 0.1	< 0.1
AKU12-14	0.6	0.35	42	40.5	1.27	3.89	0.26	< 0.011	494		< 0.011	0.1	< 0.1
AKU12-12	0.5	< 0.022	81	37.8	1.14	4.47	0.05	< 0.011	452		< 0.011	< 0.1	< 0.1
Cold waters													
AKU12-15	0.03	0.04	16	0.34	< 0.001	0.86	0.02	< 0.001	3		< 0.001	0.02	< 0.01
AKU12-16	0.06	0.35	35	3.17	0.08	2.02	0.10	< 0.001	33		< 0.001	0.01	< 0.01
AKU12-18	0.04	0.03	18	0.38	< 0.001	1.00	0.02	< 0.001	4		< 0.001	0.02	< 0.01
AKU12-19	0.01	0.03		0.82	< 0.001	0.50	0.03	< 0.001	4		< 0.001	0.03	< 0.01
AKU12-20	0.04	0.33		0.68	0.00	2.12	0.08	< 0.001	9		< 0.001	< 0.01	< 0.01
AKU12-21	0.074											0.89	< 0.065
Other													
AKU12-17	bdl	< 0.1	69	137	1.51	610	0.28	< 0.05	3,578		< 0.05	<1	<1
1996 Akutan w	aters												
AK-01	0.81	0.08	176	39.2	1.40	2.74	0.15		433	0.99		< 0.05	
AK-08	0.41	< 0.01	117	15.0	0.48	2.90	< 0.01		184	0.55		0.35	
AK-11	0.60	1.66	159	27.6	0.83	5.79	0.35		266	1.33		< 0.02	
AK-02	0.22	41.0	0	2.59	< 0.01	8.92	0.71		14.1	12.8		< 0.02	

# **Table 1.** Sample-collection parameters, chemical analyses and isotope values for waters from Akutan Volcano, Alaska,sampled during 1996 and 2012.—Continued

[All analyses in milligrams per liter except as noted. Stable isotope values in per mil (%) relative to Vienna Standard Mean Ocean Water-Standard
Light Antarctic Precipitation (VSMOW-SLAP) for $\delta D$ and $\delta_{18}O$ or relative to Vienna Pee Dee Belemnite-Space Vacuum Epitaxy Center (VPDB-SVEC) for $\delta^{13}C$ ;
, no data. Water geothermometers: chalcedony ( $T_{CH}$ ) and quartz conductive ( $T_{OC}$ ) from Fournier (1981); Na-K-Ca ( $T_{NKC}$ ) from Fournier and Truesdell (1973).
Datum for Universal Transverse Mercator (UTM) coordinates is referenced to WGS84 zone 3U. Analytical uncertainties ±5 percent at 1σ level for major species;
0.2 and 2 per mil at $2\sigma$ level for $\delta^{18}$ O and $\delta$ D, respectively]

Sample number	Rb	Se	SiO <sub>2</sub>	<b>SO</b> <sub>4</sub>	Sr	Zn	TDS	Cation	Anion	Balance	Т <sub>сн</sub> (°С)	Τ <sub>αc</sub> (° <b>C</b> )	Т <sub>лкс</sub> (°С)
Hot springs				·					·				
AKU12-01	0.15	< 0.006	122	22	0.39	< 0.012	1,202	17.4	17.3	0.9%	123	148	181
AKU12-02	0.26	< 0.011	155	31	0.69	< 0.022	2,004	30.1	30.2	-0.3%	140	163	184
AKU12-03	0.26	< 0.011	158	37	0.56	0.025	1,891	27.9	28.4	-1.5%	141	164	188
AKU12-04	0.19	< 0.011	147	29	0.58	< 0.022	1,534	22.7	22.2	2.0%	146	160	184
AKU12-11	0.14	< 0.006	161	17	0.47	< 0.012	1,050	14.2	14.1	0.8%	136	166	184
AKU12-05	0.30	< 0.011	169	54	1.14	< 0.022	2,165	33.0	33.0	0.1%	129	169	181
AKU12-13	0.13	< 0.006	134	28	0.95	< 0.012	1,198	17.1	17.2	-0.4%	142	154	192
AKU12-14	0.22	< 0.011	140	43	0.83	< 0.022	1,721	25.6	26.5	-3.2%	133	157	180
AKU12-12	0.20	< 0.011	141	41	0.85	< 0.022	1,643	24.4	24.8	-1.7%	133	157	178
Cold waters													
AKU12-15	< 0.01	< 0.001	7	5.5	0.03	< 0.002	42	0.5	0.5	3.6%			
AKU12-16	0.01	< 0.001	21	6.7	0.10	0.005	172	2.3	2.4	-2.8%			
AKU12-18	< 0.01	< 0.001	8	5.3	0.04	0.002	47	0.6	0.5	8.1%			
AKU12-19	< 0.01	< 0.005	0.28	1.1	0.01	0.064	14	0.3					
AKU12-20	< 0.01	< 0.001	15	3.2	0.05	0.008	53	1.1					
AKU12-21				5.7									
Other													
AKU12-17	< 0.5	< 0.05	116	970	4	< 0.1	13,024	217.3	224.5	-3.3%			
1996 Akutan w	vaters												
AK-01			175	49.0	0.42		1,552	21.9	22.2	-1.4%	149	171	188
AK-08			88.6	33.0	0.31		729	10.1	10.0	1.2%	103	131	168
AK-11			126	36.0	0.52		1,118	15.7	15.9	-1.4%	126	151	182
AK-02			121	662	0.11		918	11.6	13.9	-18.0%	122	148	34

<sup>1</sup>Nitrate is reported as milligrams per liter nitrogen; phosphate reported as milligrams per liter phosphorus.

#### 8 Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012

The hot springs in groups B, C, and D (fig. 1) discharge into the main stem of Hot Springs Creek. We sampled gas and water at two pools in group B ~200 m apart (AKU12-04, AKU12-11, table 1). Some pools of thermal water along the B-C traverse were either shallow and muddy or stagnant and choked with mats of vegetation. Given time constraints, these waters were not sampled.

No significant gas was discharging at any of the hot springs below group B (fig. 1). All of the samples collected downstream of the group B hot springs were from vents. We sampled three group C hot springs along the edge of the creek (AKU12-05, AKU12-13, AKU12-14) and a single group D hot spring (AKU12-12) that discharged close to the creek. Two of the group C hot springs on the west side of Hot Springs Creek were boiling. At one site, the boiling water created a small geyser that fountained to ~40 cm, with a highly visible steam cloud. The water filled its basin and roiled violently for more than a minute before draining away. The fill-drain cycle repeated within 5 to 10 minutes.

### **Other Waters**

Creek waters were collected concurrently with gaging at Hot Springs Creek below the hot springs (AKU12-16, table 1) at a tributary that flows in from the east (AKU12-20; denoted as the east fork of Hot Spring Creek [EFHSC] by Motyka and others, 1988) and at Hot Springs Creek above Hot Springs valley (AKU12-18, fig. 1). We also collected creek water above the upper gage site (AKU12-15), two samples of precipitation that included "old" snow on the northwest flank of an unnamed peak ~4 km southeast of the summit caldera, and a rain sample along the coast in the village of Akutan (AKU12-19 and AKU12-21, respectively, fig. 1).

#### **Gas Vents**

We observed gas discharging at several sites on the modern cinder cone within the summit caldera, the most accessible of which was a steeply sloping area of acid-altered ground (SG, fig. 1). A few spots had a focused discharge, but the overall discharge was weak across a broad area encrusted with sulfur-bearing minerals. The ground surface was dry, but the steam upflow created muddy conditions under the first few centimeters of crust.

The area of degassing vents on the flank of the volcano (FF, fig. 1) was described in earlier studies as containing "geothermal fumaroles," distinct from the "volcanic fumaroles" on the summit cone (Motyka and others, 1993). This area is larger and more active than the degassing sites on the cone. Large plumes of steam discharge from fumaroles and roiling mud pots, rivulets of acidic water flow through the area, and the ground surface is acid-altered with little vegetation. In 2012, we observed evidence of a recent mudflow from the lower part of the active area down into a ravine. The 2012 sampling sites included a vent fumarole with a strong focused discharge and a drowned fumarole, herein called a frying pan. A



В





**Figure 2.** Photos showing features in Hot Springs valley. *A*, Aerial photograph of Hot Springs valley, with steam plume visible from group C hot spring. View northwestward. *B*, Vent-type hot spring (AKU12-02) in group A. *C*, Pool-type hot spring with gas bubbles (AKU12-04) in group B.

## **Results**

### Water and Gas Chemistry

The locations and chemical data for waters sampled in 2012 are listed in table 1, which includes four previously unpublished analyses of Akutan waters collected by R.B. Symonds in 1996. The 1996 data lack precise coordinates, and so we cannot relate the results to a specific hot-spring group. The hot springs are composed of neutral-chloride geothermal waters (Goff and Janik, 2000) and have Cl concentrations ranging from 410 to 1,100 mg/L, with Na as the main cation. In comparison, the local meteoric waters show a mixed cation composition and have Cl and  $SO_4$  concentrations as high as 12.0 and 5.7 mg/L, respectively, greater than for typical continental precipitation (Root and others, 2005) but much lower than in the hot springs. The water in EFHSC contained 13 mg/L Cl, just slightly greater than in the rain sample. The Cl concentration in Hot Springs Creek at the lower gage (downstream of all the hot springs and the confluence with EFHSC) was 58 mg/L, demonstrating a considerable flux of geothermal chloride contributed from the springs.

The  $\delta D$  and  $\delta^{18}O$  values of the spring waters range from -69 to -67 per mil and from -9.3 to -8.4 per mil, respectively, relative to Vienna Standard Mean Ocean Water (VSMOW), in comparison with the values of -74 and -10.7 per mil, respectively, of creek water (table 1). DIC concentrations of waters in the five sampled hot springs are relatively low (0.5–3.7  $\mu$ mol CO<sub>2</sub>/mg H<sub>2</sub>O), with  $\delta^{13}$ C-DIC values ranging from -11.7 to -9.9 per mil relative to Vienna Pee Dee Belemnite (VPDB).

The chemical compositions of the collected gases are diverse (table 2). Gas from the crater and the hot-spring pools has high N<sub>2</sub> and Ar concentrations. In general, these samples are not air contaminated; only one sample (AK12-01, table 2) contained significant oxygen. Gas from the pools is distinguishable from crater gas by having high CH<sub>4</sub> and low H<sub>2</sub>S concentrations. Gas from the group A vent hot spring (AKU12-03) is similar to that from the flank fumarole field in its high CO<sub>2</sub> and much lower N<sub>2</sub> concentrations. He concentrations are generally low in all gas samples. He isotopes in the gas from group A hot springs and the flank fumarole have  $R_C/R_A$  ratios >6.4 that show strong inputs of <sup>3</sup>He from a magmatic source.

### Discharge

Discharge measurements on Hot Springs Creek above and below the hot springs, on a small tributary to Hot Springs Creek that receives the discharge of the group A hot springs, and on EFHSC near the confluence with Hot Springs Creek (fig. 1) are listed in table 3. The upstream discharge in Hot Springs Creek was 890 L/s, and the downstream discharge was 1,348 L/s. The discharge of EFHSC was 245 L/s, suggesting that the hot springs could add as much as ~200 L/s to the flow of Hot Springs Creek.

## Discussion

### Hot-Spring Water Geochemistry

Chloride is a useful tracer of source fluids because it behaves conservatively and Cl concentrations are low in meteoric water and relatively high in the hot springs. Our results indicate that large variations in Cl concentrations occur within each hot-spring group and that pool waters typically have lower Cl concentrations than the waters in vent hot springs (table 1). We observed no correlation between Cl concentrations and the locations of springs along the flowpath of Hot Spring Creek. In contrast, strong positive correlations  $(R^2 = 0.86 - 0.99)$  exist between Cl and Br, Na, B, Li, and specific conductance (fig. 3). The strong correlations between Cl and the conservative species Br and B suggest that all of the hot-spring waters are varyingly diluted from a common source that is not seawater. Concentrations of less conservative species, such as SO<sub>4</sub>, Si, and Ca, correlate somewhat with Cl but are more scattered.

Waters in high-temperature geothermal systems typically have low Mg contents (Nicholson, 1993). The water from a group C vent hot spring that discharges from the east side of the creek is unusual in that it had relatively high Mg concentrations (AKU12-13, table 1). Excluding that site, a clear negative correlation exists between Mg and Cl in the spring waters ( $R^2 = 0.80$ , fig. 3). Extrapolation of the Mg trendline to zero suggests that the source fluid has a Cl concentration of ~1,300 mg/L.

Figure 3*A* shows that the  $\delta^{18}$ O values of hot-spring waters are shifted to the right of the World Meteoric Water Line (WMWL) by ~1.0 to 1.5 per mil. Although such a shift could indicate a component of magmatic water, similar shifts have been observed in numerous geothermal systems with neutral-chloride waters and result from oxygen-isotope exchange between the reservoir rocks and hydrothermal fluids (Craig, 1963; Sheppard, 1986). Typically, no correlative change occurs in  $\delta$ D values because rocks contain little deuterium, and the hydrogen-isotope systematics are buffered by the water (Craig, 1963; Sheppard, 1986).

Examination of the hot-spring waters on Akutan Island shows slight differences in the isotopic composition of pools and vents. Water in the geysering spring has the highest  $\delta D$  and  $\delta^{18}O$  values and is an outlier relative to the other hot springs. These high values could result from vigorous boiling and loss of isotopically light steam. Water in the pools has slightly lower  $\delta^{18}O$  values than that in most vent hot springs. The shift cannot be a function of evaporation, which would raise  $\delta D$  and  $\delta^{18}O$  values, and likely indicates that the pools are mixed with slightly more meteoric water than the vent hot springs.

We note that, except for the geysering spring, the waters have a limited range of  $\delta D$  values, from -69.4 to -68.6 per mil. We can extrapolate back to the WMWL and derive an estimate of -9.95 to -9.80 per mil for the  $\delta^{18}O$  content of the cold groundwater that dilutes the hot springs and pools (fig. 4*A*).

Sample locations, gas chemistry and noble-gas data for degassing features around Akutan Volcano, Alaska, sampled during 2012. Table 2. [All gas compositions in volume percent; dashes, no data. Types: E, empty bottle; N, bottle containing NaOH solution. R/R, <sup>3</sup>He/<sup>4</sup>He ratio relative to air;  $R_{c}/R_{c}$ , <sup>3</sup>He/<sup>4</sup>He ratio corrected for atmospheric components. Gas geothermometers:  $T_{2n}$ , from D'Amore and Panichi (1980);  $T_{co2;cH4}$  from Giggenbach (1996);  $T_{c1,c2}$  from Darling (1998). Datum for Universal Transverse Mercator (UTM) coordinates is referenced to WGS84 zone 3U. See Bergfeld and others (2011) for details on analytical uncertainties]

Sample number	Location	Date	Easting (meters)	Northing (meters)	Elevation (meters)	Type	Temp (°C)	CO <sub>2</sub>	H <sub>z</sub> S	He	Ξ <sup>2</sup>	CH₄	Z	Ar
Hot springs														
AKU12-01	Group A pool	07/25/12	444006	6000806	18	Щ	60.5	7.2	<0.0005	0.0012	0.0002	2.4	86.4	1.19
AKU12-03	Group A lower vent	07/25/12	444032	6000819	18	Щ	94.0	95.7	<0.0005	0.0002	0.0016	0.61	3.45	0.11
AKU12-04	Group B upper pool	07/25/12	444132	6000890	19	Щ	76.8	25.9	0.0056	0.0006	0.0054	9.4	63.6	1.04
AKU12-11	Group B lower pool	07/27/12	444255	6001052	14	Ш	75.2	24.3	0.0012	0.0011	0.0010	6.7	67.8	1.11
Akutan flank														
AKU12-09	Flank fumarole	07/26/12	440550	6000347	379	Щ	98.6	94.4	2.1	0.0009	0.67	0.22	2.57	0.005
AKU12-09A	Flank fumarole	07/26/12	440550	6000347	379	Z	98.6	94.6	1.7	0.0007	0.62	0.22	2.71	0.004
AKU12-09B	Flank fumarole	07/26/12	440550	6000347	379	Z	98.6	94.5	2.0	0.0008	0.65	0.23	2.60	0.004
AKU12-10	Flank frying pan	07/26/12	440547	6000367	381	Щ	83.4	91.4	2.2	0.0008	0.59	0.21	4.87	0.034
AKU12-10	Flank frying pan	07/26/12	440547	6000367	381	Z	83.4	90.7	1.8	0.0008	0.59	0.22	6.56	0.059
Akutan crater														
AKU12-07	Crater site 2	07/26/12	436319	6000281	1070	Щ	95.0	14.8	2.1	0.0004	0.54	0.17	81.3	0.89
AKU12-08	Crater site 3	07/26/12	436326	6000265	1082	Z	95.0	13.3	0.60	<0.002	0.97	0.13	83.8	1.06

Table 2. Sample locations, gas chemistry and noble-gas data for degassing features around Akutan Volcano, Alaska, sampled during 2012.—Continued

Sample number	02	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>.</sub> H <sub>s</sub>	C4H10	HCI	뽀	NH <sub>3</sub>	R/R	R <sub>c</sub> /R <sub>A</sub>	40 <b>Ar/<sup>36</sup>Ar</b>	T D-P (°C)	T CO₂-CH₄ (°C)	T C <sub>1</sub> -C <sub>2</sub> (°C)
Hot springs														
AKU12-01	2.8	<0.001	0.0083	<0.0005	<0.0005	ł	ł	ł	4.79	6.88	297	1	1	ł
AKU12-03	0.17	7.8E-07	0.0086	<0.0005	<0.0005	-	1	-	5.85	6.49	296	44	163	204
AKU12-04	0.07	3.2E-07	0.0271	0.0009	0.0011		-	-	1	1	-	1	1	-
AKU12-11	0.05	<0.001	0.0269	0.0021	0.0011	ł		ł	1	ł		1	1	-
Akutan flank														
AKU12-09	0.062	3.6E-04	0.0015	<0.0005	<0.0005	-	1	-	7.63	7.64	297	236	199	223
AKU12-09A	0.002	3.7E-04	0.0017	<0.0001	<0.002	0.0009	0.0253	0.026	1	1	-	231	199	219
AKU12-09B	<0.03	3.9E-04	0.0016	0.0002	<0.002	0.0032	0.0497	0.001	1	1		234	198	222
AKU12-10	0.69	6.1E-04	0.0015	<0.0005	<0.0005	-	1	-	0.967*	0.835*	295	235	200	220
AKU12-10	<0.03	6.6E-04	0.0017	<0.0001	<0.002	0.0049	0.0158	<0.025	1	1		232	199	218
Akutan crater														
AKU12-07	0.14	<0.001	<0.0002	<0.0005	<0.0005	ł	ł	ł	1.41	2.09	288	1	1	1
AKU12-08	<0.03		0.0011	-	-	0.0303	0.1582	0.00	1.80	3.80	291	-	1	1

#### 12 Geochemical Investigation of the Hydrothermal System on Akutan Island, Alaska, July 2012

**Table 3.**Chloride concentrations and stream discharges used to determine geothermal flux and heat output from hot springs alongsections of Hot Springs Creek near Akutan Volcano, Alaska, in 1981 and 2012.

[Q, stream discharge; ---, no data]

		2012	2			19	81	
Description	Sample number	CI (mg/L)	0 (L/s)	CI (t/d)	Sample number	Cl (mg/L)	0 (L/s)	CI (t/d)
Upper Hot Springs Creek	AKU12-18	4.3	890	0.33				
Group A tributary		<sup>1</sup> 196	84	1.41	11	41	71	0.25
East fork Hot Springs Creek	AKU12-20	13	245	0.3				
Lower Hot Springs Creek	AKU12-16	58	<sup>2</sup> 1,348	6.8	14	10	878	0.76
Geothermal Cl flux (corrected for background)				6.15				
Average Cl 2012 hot springs (mg/L)		759						
Discharge of spring water (L/s)		93.8						
Enthalpy change (J/g)		305						
Heat output (MW)		28.7						

<sup>1</sup> Calculated from specific conductance.

<sup>2</sup> Includes flow from the east fork of Hot Springs Creek, without which Q = 1,103 L/s. Enthalpy estimate is calculated by using the steam tables of Keenan and others, (1969).

The strong correlation between Cl concentration and  $\delta^{18}$ O value ( $R^2 = 0.958$ , fig. 4B) can also be used to derive information about the isotopic composition of thermal and nonthermal endmembers. As noted earlier, Mg and Cl concentrations in the springs suggest that the thermal end member has a Cl concentration of ~1,300 mg/L. Extrapolation of the Cl- $\delta^{18}$ O trendline to a Cl concentration of 1,300 mg/L yields a  $\delta^{18}$ O value for this fluid of about -8.25 per mil, whereas extrapolating the data to zero Cl gives a  $\delta^{18}$ O value of about -9.80 per mil for the cold groundwater, in agreement with the value derived from  $\delta D$ - $\delta^{18}$ O relations (fig. 4A). These mixing lines (fig. 4A, B) reflect the isotopic composition of the cold groundwater more accurately than does the single cold creek sample that was analyzed.

### **Hot-Spring Geothermometry**

The average temperatures estimated from silica and alkali geothermometers for the least diluted hot-spring waters, those with Cl concentrations of  $\geq$ 800 mg/L, range from 129 °C to 188 °C (table 1). Using the quartz conductive geothermometer on the least diluted hot-spring water gives a maximum estimated temperature of 169 °C. Temperatures estimated from the Na-K-Ca thermometer (178–188 °C) of Fournier and Truesdell (1973) are less likely to be affected by dilution and closely agree with the measured downhole temperature of 182 °C at ~178 m in the thermal-gradient well TG-2, located near the group B hot springs (Kolker and others, 2012). The 1996 waters from sampling sites along Hot Springs Creek have lower Cl concentrations and Na-K-Ca temperatures of 168–188 °C.

### Gases at Akutan

The composition of the gas on Akutan Island varies widely (table 2), and much of the variation likely results from shallow processes that greatly affect the final gas chemistry. He isotope ratios in five samples indicate that the degassing features at all sampling sites (summit crater, flank, lower Hot Springs valley) have some input of magmatic gas that is varyingly diluted with crustal gas before discharging. A sixth sample was badly air contaminated.

The gas collected from the flank fumarole field on Akutan Volcano has high  $CO_2$  and  $H_2S$  concentrations and relatively low concentrations of air-derived gas (table 2) and has more geothermal characteristics than the gas from other sites on Akutan Island. On a ternary He-Ar-N<sub>2</sub> diagram (fig. 5), gas from the flank fumarole falls along a trend defined by gas from other Cascade Range and Aleutian Arc (CRAA) volcanoes (fig. 2; Symonds and others, 2003b). Gas from the flank frying pan falls off the CRAA trend because of its higher N<sub>2</sub> and Ar concentrations and shows some influence of air-derived components. Calculations using three gas geothermometers suggest equilibration temperatures for gas in the flank fumarole field of ~200–240 °C (table 2).

Gas from two sampling sites in the summit crater had elevated  $H_2$  and  $H_2S$  concentrations similar to typical volcanic gas (table 2), whereas high  $N_2$  and Ar concentrations indicate that the deep-sourced component has been substantially diluted by the addition of atmospheric air (fig. 5). The absence of  $O_2$  indicates that the samples were not air contaminated during collection. Similar trends are evident for the composition of summit and flank gases collected from fumaroles in





**Figure 4.** Plots of isotopic composition and chloride concentrations for Akutan hot springs and local cold creek water in 2012. *A*,  $\delta D$  versus  $\delta^{18}O$  values of hot springs and cold creek water relative to World Meteoric Water Line. Horizontal lines show range of  $\delta D$  values in all hot-spring waters except that from geysering spring; vertical lines show range of  $\delta^{18}O$  values predicted for cold groundwater that dilutes hot springs. *B*, Cl concentration versus  $\delta^{18}O$  values in hot-spring water, showing positive correlation. Line of linear regression is extrapolated to 0 and 1,300 mg/L Cl to estimate  $\delta^{18}O$  values for groundwater diluting hot springs and for undiluted thermal fluid, respectively. SMOW, Standard Mean Ocean Water.

1996, although the amount of atmospheric dilution for the gas from the summit crater was lower than in 2012. A sample of gas from an acidic spring on the flank in 1981 is similar to the 2012 sample from the frying pan and plots along the atmospheric-dilution trend (Motyka and others, 1988). Altogether, it is reasonable to assume that the gases emitting from features on the flank and summit share a common deep magmatic source. The gas composition is consistent with a weak flow of gas to the summit crater within a permeable volcanic cone that acts as a chimney and allows atmospheric air to enter the system. As the mixed gas rises to the surface, it is heated, and atmospheric O<sub>2</sub> is consumed in the process.

Gas discharge from the hot springs in 2012 was weak and produced only small bubble trains that rose through the water. The <sup>3</sup>He/<sup>4</sup>He ratios in gas from two of these hot springs demonstrate magmatic helium inputs, but the bulk gas composition of most samples had high N, and low CO, concentrations (table 2) that are unlike most geothermal gas emissions (for example, Goff and Janik, 2000). High N<sub>2</sub> concentrations have been a pervasive feature of the gas at the hot springs over the years. Gas from a group A hot spring in 1981 consisted of

10.3 volume percent CO, and 76.7 volume percent N, (Motyka and others, 1988). A vigorously degassing hot spring in 1996 contained 89.1 volume percent CO, and 8.8 volume percent N<sub>2</sub> (Symonds and others, 2003a). This sample is similar to the gas from the 2012 group A vent hot spring that had the highest CO<sub>2</sub> concentration of any sample from the hot-spring area, but even this sample is low in gases (H<sub>2</sub>S, H<sub>2</sub>) that are typical of high-temperature geothermal systems.

#### Thermal Chloride Flux

Using mass balance with the discharge measurements and the Cl concentrations in waters from the creeks and springs, we can calculate the thermal influx (TI) to Hot Springs Creek. The flux of dissolved Cl  $(F_{Cl})$  is calculated from streamdischarge measurements (Q) and the collocated Cl concentrations of the water [Cl], such that for each discharge point *i*:

$$(F_{\rm Cl})_i = Q_i^*[\rm Cl]_i$$

Figure 5. Ternary N<sub>2</sub>-He-Ar diagram for gas samples

N<sub>2</sub>/100 collected at Akutan Volcano in 1981, 1996, and 2012. **EXPLANATION** Pre-2012 data are from Motyka and others (1988) and 2012 Flank Symonds and others (2003a). Numbers in parentheses,  $R_{c}/R_{A}$  ratios. Tielines on 2012 flank fumarole samples  $\diamond$ 2012 Summit indicate that multiple samples were collected for  $\diamond$ 2012 Hot Springs valley chemistry and only one He sample was collected for 1996 Flank 0 isotopic analysis. Arrow indicates that flank and summit 0 1996 Summit samples fall along a mixing line between deep-sourced  $\bigcirc$ 1996 Hot Springs valley gas and air. Trendlines are derived from data of Symonds (2003b) for Cascade Range and Aleutian Arc (CRAA), 1981 Flank FUM (7.3) Bergfeld and others (2011) for Yellowstone National Park, (7.6) Δ **1981 Hot Springs valley** and Lowenstern and others (1999) for The Geysers, Calif. ASMW, air-saturated meteoric water; (7.2)FUM, flank fumarole, FP, frying pan.  $\bigcirc$ - Case and Balle and Aleutian Archine (6.9)(6.0 - 6.3)ASMW (6.5)Yellowstone trend (5.8)Ar

10 x He

We correct for the chloride in meteoric water above the group A hot springs (U) and for the input from EFHSC. Assuming that the remaining chloride in the downstream site (D) is provided from the hot spring system,

 $TI = (F_{CI})_{D} - ((F_{CI})_{U} + (F_{CI})_{EFHSC}).$ 

These calculations indicate that a thermal influx of  $\sim$ 6.15 metric tonnes of chloride is released by the hot-spring system each day (t/d).

We can refine our understanding of individual hot-spring inputs by using the discharge measurement for the tributary below the group A hot springs. Although we did not collect a water sample, the overall excellent correlation between specific conductance and Cl concentration of the hot springs (fig. 3) allows us to calculate a chloride flux for the group A hot-spring waters. Using a linear regression of Cl concentration and specific conductance for all of the hot springs, we estimate that the tributary water with a specific conductance of 745 mS/cm had a Cl concentration of ~196 mg/L (table 3). The discharge of 84 L/s yields a chloride flux of ~1.4 t/d. The remaining 4.7 t/d of thermal influx is contributed below the group A hot springs.

### Change in the Akutan Hydrothermal System

Comparison of the hot-spring water chemistry from the early 1980s through July 2012 shows large changes in the hydrothermal system on Akutan Island (fig. 6). In general, the concentrations of most dissolved components in each spring group were higher in 2012 than in the 1980s, and we specifically note the high Ca, Cl, and Na concentrations in 2012. Excluding the intertidal springs, the maximum Cl concentration was 424 mg/L in the early 1980s, 623 mg/L in 1996, and 1,100 mg/L in 2012 (table 1; Motyka and others, 1988, table 6-1). Only HCO<sub>3</sub> and SO<sub>4</sub> lack evidence of a consistent increase from the 1980s to 2012 (fig. 6). A maximum temperature of 84 °C was recorded for the hot springs in 1980, in comparison with 97.4 °C at a vigorously bubbling hot spring in 1996 and two hot springs with temperatures of >99 °C in 2012 (table 1).

The discharge data for Hot Springs Creek from 1981 and 2012 are comparable, even though gaging locations are not identical. A direct comparison of discharge from the tributary below the group A hot springs is possible because the stream is short and places to make measurements are limited. Discharge from the tributary in 1981 was 71 L/s, in comparison with 84 L/s in 2012 (table 3). The July 1981 discharge of 878 L/s in lower Hot Springs Creek was obtained above the confluence with EFHSC, whereas the 2012 measurement (1,348 L/s) was obtained below. Subtracting the 2012 discharge of EFHSC (245 L/s) results in a discharge of 1,103 L/s in Hot Springs Creek above the confluence. Thus, the flow in both the group A tributary and Hot Springs Creek appears to be 20–25 percent higher in 2012 than in 1981.

This increase in flow could simply be attributed to seasonal or interannual changes, but the large increase in

stream Cl concentrations (table 3) is clear evidence of a large increase in the hydrothermal component in Hot Springs Creek. The Cl concentration in the group A tributary increased by a factor of ~5 between 1981 and 2012, and a similar increase occurred in Hot Springs Creek below the group D hot springs, from 10 mg/L in 1981 to 58 mg/L in 2012. Because of the additional dilution from EFHSC, the measured fivefold increase for lower Hot Springs Creek considerably underestimates the actual change. As described earlier, the Cl concentration in EFHSC was similar to precipitation, with little evidence of thermal inputs to this stream. Thus, the Cl concentration in the creek increased by a greater factor than in the hot springs, a result that can be explained only by an increase in hot-spring discharge rate.

We can estimate the heat output associated with the chloride flux by using the average hot-spring temperature of 83 °C and average Cl concentration of 759 mg/L for the hot springs in 2012 (table 3). A thermal chloride flux of 6.15 t/d yields a hot-water discharge of 93.8 L/s. The enthalpy anomaly of this hot water relative to the annual land-surface temperature of 10 °C (Selkregg, 1976) is 305.5 J/g, yielding a heat output of 29 MW. This value is approximately an order of magnitude higher than the heat-discharge estimate of 2.2 to 4.1 MW from 1981 (Motyka and others, 1988).

### Summary

The existing conceptual model of the geothermal system on Akutan Island (Kolker and others, 2012) places the reservoir in the vicinity of the flank fumarole field, which caps an upflow zone. The rising hot water loses gas and steam before flowing laterally as an outflow plume northeastward, where it discharges at the springs in Hot Springs valley after varying dilution with groundwater (fig. 7). This model fits well with our new results, particularly the gas data. The most robust gas samples that were collected from the flank fumarole had a <sup>3</sup>He/<sup>4</sup>He ratio ( $R_c/R_A = 7.6$ ) and N<sub>2</sub>-He-Ar concentrations typical of other CRAA volcanoes (Symonds and others, 2003a, b). In contrast, the chemical compositions of the hot-spring gases are strongly influenced by shallow processes. Low CO<sub>2</sub> concentrations in most samples reflects the previous loss of this gas in the flank fumarole field, allowing N<sub>2</sub> and Ar from the diluting groundwater and CH<sub>4</sub> from organic sources to dominate the gas composition. Although the gas compositions are reset by low-temperature processes and are not representative of deep reservoir conditions, the similarity in the isotope compositions of He in the gas and C in DIC to those in the gas from the flank fumarole field, -11.2 to -10.8 per mil (Motyka and others, 1988), support a connection between the two areas through the envisioned outflow plume.

Samples collected since 1981 indicate that flank fumaroles provide the most reliable information on the deep reservoir temperature. Kolker and others (2012) used a gas geothermometer based on the ratios of CO, and H, to Ar (Powell and



**Figure 6.** Scatterplots showing differences in water chemistry for Akutan hot springs in 1980–81 and 2012. A through D, hot-spring groups of Motyka and others (1988). Results for 1980s analyses with poor charge balance are omitted, and no comparisons of B and Br concentrations are made because recent changes in analytical procedures have greatly improved precision and detection limits. Diamonds, waters measured in this study; circles, compositions from Motyka and others (1988).

Cumming, 2010) to propose reservoir temperatures well above 200 °C. We obtain a temperature range of 200–240°C by using three non-Ar-based gas geothermometers. Lower temperature estimates are obtained by applying solute geothermometers to the hot-spring waters, and these temperatures reflect the cooling and mixing that occur on the outflow path. Temperatures of 178–188 °C calculated from the Na-K-Ca geothermometer are consistent with a measured temperature of 182 °C from a thermal-gradient well in Hot Springs valley (Kolker and others, 2012).

Results from our study document increasing concentrations of hydrothermal components in the spring waters and an increase in the volume of water discharging from the hot spring system. Taken together, these findings provide unequivocal evidence that large changes in the hydrothermal system on Akutan Island have occurred over the past ~30 years. We estimate the heat output of the current hydrothermal system at 29 MW, approximately an order of magnitude higher than in the early 1980s (Motyka and others, 1988). We are unaware of any other neutral-chloride hydrothermal



**Figure 7.** Schematic cross section of hydrothermal system on Akutan Island. Cold groundwater infiltrates in summit region, feeding reservoir situated somewhere near flank fumarole field. Heat and gases are supplied to reservoir by underlying magmatic intrusion. Hot water rising from the reservoir boils, providing steam and gas to flank fumarole field. Degassed hot water forms an outflow plume that discharges in Hot Springs valley after varying dilution by cold groundwater.

systems that have shown this kind of change. Many causes could be invoked, but a permeability enhancement somewhere in the system, such as in the outflow zone, would logically explain the increase in hot-spring discharge. It is tempting to link such a process to fault movement during the seismic crisis of March 1996, given that a hot spring sampled by Symonds later in that year had a higher Cl concentration than that reported by Motyka and others (1988). The infrequency of sampling may obscure the exact timing, but if the tenfold increase in heat output dates back to 1996, it can hardly be considered a short-term transient, and so the increased heat resource available for power generation over a 30-year timespan may be much larger than indicated by the resource data of Motyka and others (1988).

## Acknowledgments

We thank Colin Williams (USGS, Menlo Park, Calif.) and John Power (USGS, Alaska Volcano Observatory, Anchorage) for supporting this project, and Michelle Coombs, Kristi Wallace, and Chris Waythomas (USGS, Alaska Volcano Observatory, Anchorage) for logistical assistance in planning and executing the fieldwork. Additional thanks go to Timothy Brabets (USGS, Anchorage) for the loan of some gaging equipment. Helpful reviews of the manuscript were provided by Fraser Goff (New Mexico Institute of Mining and Technology, Socorro) and Cynthia Werner (USGS, Alaska Volcano Observatory, Anchorage).

## **References Cited**

- Bergfeld, D., Lowenstern, J.B., Hunt, A.G., Shanks, W.C.P., III, and Evans, W.C., 2011, Gas and isotope chemistry of thermal features in Yellowstone National Park, Wyoming: U.S. Geological Survey Scientific Investigations Report 2011–5012, 26 p.
- Byers, F.M., and Barth, T.F.W., 1953, Volcanic activity on Akun and Akutan Islands: 7<sup>th</sup> Pacific Science Congress, Auckland, New Zealand, 1951, Proceedings, v. 2, p. 382–397.
- Craig, H., 1963, The isotopic geochemistry of water and carbon in geothermal areas, *in* Tongiogi, E., ed., Nuclear geology on geothermal areas: Pisa, Consiglio Nazionale delle Ricerche, p. 17–53.
- D'Amore, F., and Panichi, C., 1980, Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer: Geochimica et Cosmochimica Acta, v. 44, p. 549–556.
- Darling, W.G., 1998, Hydrothermal hydrocarbon gases—1, Genesis and geothermometry: Applied Geochemistry, v. 13, p. 815–824.
- Finch, R.H., 1935, Akutan volcano: Zeitschrift für Vulkanologie, v. 16, no. 3, p. 155–160.
- Fournier, R.O., 1981, Application of water geochemistry to geothermal exploration and reservoir engineering, *in* Rybach, L., and Muffler, L.J.P., eds., Geothermal systems; Principles and case histories: New York, J. Wiley & Sons, p. 109–143.

Fournier, R.O., and Truesdell, A.H., 1973, An empirical Na-K-Ca geothermometer for natural waters: Geochimica et Cosmochimica Acta, v. 37, p. 1255–1275.

Giggenbach, W.F., 1996, Chemical composition of volcanic gases, *in* Scarpa, M., and Tilling, R.I., eds., Monitoring and mitigation of volcano hazards: New York, Springer, p. 222–256.

Goff, F., and Janik, C.J., 2000, Geothermal systems, *in* Sigurdsson, H., Houghton, B.F., McNutt, S.R., Rymer, H., and Stix, J., eds., Encyclopedia of volcanoes—San Diego, Calif., Academic Press, p. 817834.

Keenan, J.H, Keyes, F.G., Hill, P.G., and Moore, J.G., 1969, Steam tables—thermodynamic properties of water including vapor, liquid, and solid phases: New York, Wiley, 162 p.

Kolker, A., and Mann, R., 2009, Heating up the economy with geothermal energy—a multi-component sustainable development project at Akutan, Alaska: Geothermal Resources Council Transactions, v. 33, p. 7–11.

Kolker, A., Stelling, P., Cumming, W., and Rohrs, D., 2012, Exploration of the Akutan geothermal resource area, *in* 37<sup>th</sup> Stanford University Workshop on Geothermal Reservoir Engineering, Stanford, Calif., 2012, Proceedings, SGP-TR-194.

Lowenstern, J.B., Janik, C.J., Fahlquist, L., and Johnson, L.S., 1999, Gas and isotope geochemistry of 81 steam samples from wells in the Geysers geothermal field, Sonoma and Lake Counties, California: U.S. Geological Survey Open-File Report 99–304, 28 p.

McGimsey, R.G., Neal, C.A., and Doukas, M.P., 1995, Volcanic activity in Alaska—summary of events and response of the Alaska Volcano Observatory 1992: U.S. Geological Survey Open-File Report 9583, 26 p.

Motyka, R.J., and Nye, C.J., 1988, A geological, geochemical, and geophysical survey of the geothermal resources at Hot Springs Bay valley, Akutan Island, Alaska: Alaska Division of Geological & Geophysical Surveys Report of Investigations 88–3, 115 p.

Motyka, R.J., Moorman, M.A., and Poreda, R.J., 1988, Geochemistry of thermal springs and fumaroles, Hot Springs Bay Valley Akutan Island, Alaska, *in* Motyka, R.J., and Nye, C.J., eds., A geological, geochemical, and geophysical survey of the geothermal resources at Hot Springs Bay valley, Akutan Island, Alaska: Alaska Division of Geological & Geophysical Surveys Report of Investigations 883, p. 71–104. Motyka, R.J., Liss, S.A., Nye, C.J., and Moorman, M.A., 1993, Geothermal resources of the Aleutian Arc: Alaska Division of Geological and Geophysical Surveys Professional Report 0114, 17 p., 4 sheets, scale 1:1,000,000.

Nicholson, K., 1993, Geothermal fluids—chemistry and exploration techniques: New York, Springer Verlag, 263 p.

Powell, T., and Cumming, W., 2010, Spreadsheets for geothermal water and gas geochemistry: Stanford University 35<sup>th</sup> Workshop on Geothermal Reservoir Engineering, Stanford, Calif., Proceedings, SGPTR188.

Richter, D.H., Waythomas, C.F., McGimsey, R.G., and Stelling, P.L., 1998, Geologic map of Akutan Island, Alaska: U.S. Geological Survey Open-File Report 98–0135, 22 p., scale 1:48,000.

Root, E., Gibbons, J., Jones, W., Schwarz, B., Hynek, S., and Haileab, B., 2005, National trends in rainwater chemistry: Geological Society of America, North-Central Section, 39<sup>th</sup> annual meeting, Abstracts with Programs, Paper No. 24–16.

Selkregg, L.L., 1976, Southwest Region, v. 3 *of* Alaska regional profiles: Anchorage, University of Alaska, Arctic Environmental Information and Data Center, 313 p.

Sheppard, S.M.F, 1986, Characterization and isotopic variations in natural waters, chap. 6 of Valley, J.W., Taylor, H.P., Jr., and O'Neil, J.R., eds., Stable isotopes in high temperature geological processes: Reviews in Mineralogy, v. 16, p. 165–183.

Symonds, R.B., Janik, C.J., Evans, W.C., Ritchie, B.E., Counce, D., Poreda, R.J., and Iven, M., 2003a, Scrubbing masks magmatic degassing during repose at Cascade-Range and Aleutian-Arc volcanoes: U.S. Geological Survey Open-File Report 03–435, 22 p.

Symonds, R.B., Poreda, R.J., Evans, W.C., Janik, C.J., and Ritchie, B.E, 2003b, Mantle and crustal sources of carbon, nitrogen, and noble gases in Cascade-Range and Aleutian-Arc volcanic gases: U.S. Geological Survey Open-File Report 03–436, 26 p.

Waythomas, C.F., 1999, Stratigraphic framework of Holocene volcaniclastic deposits, Akutan Volcano, east-central Aleutian Islands, Alaska: Bulletin of Volcanology, v. 61, no. 3, p. 141-161.

Waythomas, C.F., Power, J.A., Richter, D.H., and McGimsey, R.G., 1998, Preliminary volcano-hazard assessment for Akutan Volcano, east-central Aleutian Islands, Alaska: U.S. Geological Survey OpenFile Report 98–0360, 36 p. Manuscript approved September 16, 2013

Menlo Park Publishing Service Center, California Manuscript approved for publication December 5, 2013 Edited by George Havach and Claire Landowski Design and layout by Ron Spencer

ISSN 2328–0328 (online) http://dx.doi.org/10.3133/sir20135231