Gas Emissions From the Western Aleutians Volcanic Arc

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The Aleutian Arc is remote and highly active volcanically. Its 4,000 km extent from mainland Alaska to Russia’s Kamchatka peninsula hosts over 140 volcanic centers of which about 50 have erupted in historic times. We present data of volcanic gas samples and gas emission measurements obtained during an expedition to the western-most segment of the arc in September 2015 in order to extend the sparse knowledge on volatile emissions from this remote but volcanically active region. Some of the volcanoes investigated here have not been sampled for gases before this writing. Our data show that all volcanoes host high-temperature magmatic-hydrothermal systems and have gas discharges typical of volcanoes in oceanic arcs. Based on helium isotopes, the western Aleutian Arc segment has minimal volatile contributions from the overriding crust. Volcanic CO₂ fluxes from this arc segment are small, compared to the emissions from volcanoes on the Alaska Peninsula and mainland Alaska. The comparatively low CO₂ emissions may be related to the lower sediment flux delivered to the trench in this part of the arc.

Keywords: Aleutians, volcano, gas, volatiles, geochemistry

INTRODUCTION

The Aleutian Arc is one of the most volcanically active and remote arcs in the world. The arc extends ~4,000 km from mainland Alaska to Russia’s Kamchatka Peninsula and separates the Bering Sea to the North from the Pacific Ocean to the South (Figure 1). The eastern 2,500 km of the arc represents the region of active volcanism and is undergoing subduction of the Pacific plate beneath the North American plate. The arc has ~142 volcanic centers, of which 54 volcanoes have been historically active (Cameron et al., 2020). At the time of writing (2021), Semisopochnoi, Great Sitkin and Pavlof volcanoes are currently erupting, and Gareloi and Cleveland volcanoes have shown signs of unrest (GVP, 2015; GVP, 2019; GVP, 2021a; GVP, 2021b; GVP, 2021c; GVP, 2021d). The type of volcanic activity is highly variable throughout the arc, with eruptions ranging from nearly continuous Strombolian-style basaltic eruptions (e.g. Pavlof 2014) to infrequent, discrete Plinian events such as the 1912 Katmai/Novarupta eruption (Fierstein and Hildreth, 1992). The frequent eruptions occurring in the Aleutian Arc often produce high-altitude ash clouds that are hazardous to the numerous aircraft that fly over the North Pacific Ocean. Previous studies have investigated volcanic gas emissions from many Eastern and Central Aleutian volcanoes; however at the time of this study little was known about volcanic gas emissions from the Western Aleutian volcanoes.
We characterize volcanic gas emissions from the sparsely studied and highly remote Western Aleutians volcanic islands (from west to east) of Kiska, Little Sitkin, Semisopochnoi, Gareloi, Tanaga and Kanaga (Figure 1B). These volcanoes are all considered to be historically active by the Alaska Volcano Observatory, defined as having a known or suspected eruption, persistent fumaroles, a volcanic deformation signal, and/or seismic swarm of volcanic origin since 1700 (Cameron et al., 2020). Because the Western Aleutians volcanoes are some of the most remote in Alaska, many eruptions in this region have been poorly documented throughout historic time and little is known in general about these volcanic systems.

In this publication we present the first constraints on the chemical composition of volcanic gases from Western Aleutians
volcanoes of Gareloi, Kiska and Kanaga. We also present new measurements from hydrothermal gas discharges from Semisopochnoi, Tanaga and Little Sitkin volcanoes to complement previous studies. We targeted these volcanoes during an expedition that was jointly supported by NSF, the USGS and the Deep Carbon Observatory in 2015 and involved transportation by a combination of boat, helicopter and foot to reach most of the volcanic centers. Prior to this study, several field efforts since the 1980s have been aimed at measuring volatile emissions within the Aleutian Arc, including collection and analysis of Eastern and Central Aleutian volcanic gas and water samples for chemical and isotopic composition (Motyka et al., 1993; Symonds et al., 2003a; Symonds et al., 2003b; Evans et al., 2015); annual to bi-weekly surveys of plume composition and flux for volcanoes within the Cook Inlet and Katmai Volcanic Cluster regions were performed by Alaska Volcano Observatory scientists (Casadevall et al., 1994; Gerlach et al., 1994; Doukas, 1995; Doukas and McGee, 2007; McGee et al., 2010; Werner et al., 2011; Werner et al., 2013) and targeted gas composition and flux measurements at the individual volcanoes of Akutan (Bergfeld et al., 2013), Ukinrek-Maars (Evans et al., 2009) and Mount Martin, Mount Mageik, and Trident (Lopez et al., 2017). While these studies provide significant information on volcanic gas discharges from the Aleutians and the processes controlling the compositions of these emissions, the main degassing features from the Western Aleutian arc segment were virtually uncharacterized before this work. We also present the first SO₂ flux measurements obtained from Gareloi and Kiska volcanoes. Together, these new constraints on volcanic gas composition and flux allow us to make inferences about the subsurface volcanic systems and current state of volcanic activity at these remote volcanoes. The Western Aleutians, like other remote island arcs that are built on oceanic crust (i.e. Kuril, Izu-Bonin Marianas), have gas compositions that appear to be minimally affected by contributions from the overriding arc crust, providing a relatively undistorted view into slab- and mantle-derived volatiles.

MATERIALS AND METHODS

Volcano Settings

Figure 1B shows the location of Western Aleutian volcanoes sampled in this study and Figure 2 shows some of their fumaroles and thermal features. Kiska Volcano is the westernmost historically active volcano within the Aleutian Arc (Figure 1B). Kiska is a stratovolcano with volcanic rocks of basaltic to andesitic composition (Miller et al., 1998). Confirmed historic eruptions consisted of ash and gas emissions in 1990 and lava effusion in 1962, 1964, 1969 and 1990 (https://volcano.si.edu/volcano.cfm?vn=31102). Other reported volcanic activity has comprised primarily volcanic gas emissions. This study sampled volcanic fluids from Kiska Volcano (52.1056 N, 177.5994 E, 1,049 m) that were emanating from a roaring ∼10 m diameter fumarole vent on the upper west flank of the volcanic edifice. The vent consisted of a depression containing ∼10–20 vigorously-degassing and audibly-jetting fumaroles whose emissions coalesced into a coherent plume (Figure 2A). The ground surrounding the vent was yellow in color and contained native sulfur deposits. The apparent high gas flux and confined emission location prevented safe access to sample the fumaroles by inserting a titaneum tube directly into the vents when we visited this site.
Due to this situation, we were able to approach the site only to collect a gas sample from the plume above the vents that was affected by atmospheric contamination.

Little Sitkin volcano is a stratovolcano within a system of nested calderas (Miller et al., 1998). No confirmed eruptions from Little Sitkin have occurred in historic time, though observations are limited for this remote location. Volcanic rocks are primarily andesitic in composition, and range from basalt to dacite (Snyder, 1959; Larsen et al., 2020). Gas emissions from Little Sitkin emanate primarily from a geothermal region located on the western flank of the volcanic edifice (51.96117 N, 178.49226 E, 166 m), and this was the target of our study. Gas emissions in this region were released via three degassing manifestations: fumarolic emissions, bubbling springs and mud pools. Fumarolic regions near the summit and the northwest shore of the island have been previously reported (Snyder, 1959), but were not sampled during this study.

Semisopochnoi island is composed of scattered volcanic vents, the prominent caldera of Semisopochnoi volcano, and older, ancestral volcanic rocks. Volcanic rocks on Semisopochnoi range from basalt to dacite in composition (Miller et al., 1998; Coombs et al., 2007). Reports of volcanic eruptions prior to our 2015 field study occurred in 1772, 1790, 1792, 1830, 1873, and 1887 (https://volcano.si.edu/volcano.cfm?vn=311060). The 1987 eruption occurred from the extracaldera Sugarloaf Peak. Since 2018 Semisopochnoi has been undergoing intermittent eruptive activity from Mount Cerberus (GVP, 2021d). At the time of our study the volcano was in a period of quiescence, with no persistent fumaroles present to our knowledge. Water samples were collected from a warm spring next to Fenner Creek in the caldera with no visible bubbles (51.93636 N, 179.65459 E, 1,332 m).

Gareloi volcano is a stratovolcano comprising two overlapping volcanic edifices, referred to as the South and North Peaks, respectively. It is one of the most active volcanoes of the Western Aleutians with at least nine confirmed eruptions since 1791 (https://volcano.si.edu/volcano.cfm?vn=311070). Gareloi has also had persistent fumarolic activity since a seismic network was installed in 2005 (Coombs et al., 2008). Gareloi’s erupted products are potassium rich in composition and range primarily from shoshonite to latite in composition, with sparse andesite (Coombs et al., 2012). Gareloi’s largest historical eruption occurred in 1929 (Coombs et al., 2008) and likely formed the South Peak’s asymmetrical crater that opens to the southeast. The South Peak Crater (51.7646 N, 178.80697 W, 1,326 m) is the home of the primary degassing region on Gareloi, an active fumarole field on the crater wall, whose gas emissions coalesce into a coherent plume (Figure 2B). These gases were targeted during this study. The North Peak contains a steeply walled crater that was observed to contain a crater lake and potentially an active fumarole field at the lake’s edge at the time of our study, but was not targeted here.

Tanaga Island is home to three volcanic centers: Tanaga, Sajaka and Takawangha. Of these Tanaga is thought to be the youngest and only historically active vent of the three. The only confirmed historic eruption from Tanaga occurred in 1914, with suspected eruptions occurring in 1773–1770, 1791 and 1829 (www.alaska.edu). Little information is available on these eruptions, and they may have originated from the other volcanic centers (Miller et al., 1998). The erupted products from the three volcanic centers range from basalt to dacite in composition. While no known fumarole fields exist on Tanaga Island, natural hot springs (Figure 2C) are located on the edge of Hot Springs Bay (51.77175 N, 177.79955 W, 1 m), southeast of Takawangha. These hot springs were targeted during our study.

Kanaga volcano is the easternmost volcano discussed here. It is a stratovolcano within an older caldera on the north end of Kanaga island (Miller et al., 1998). Kanaga has had several confirmed historic eruptions including 1786, 1904, 1906, 1942, 1994–95 and most recently in 2012 (GVP, 2013). Erupted products range from basalt to andesite. Volcanic fluids from Kanaga Volcano (51.9230167 N, 177.161,083 W, 1,237 m) were released from two main sources in 2015: 1) numerous individual fumaroles dispersed along the ~10 m wide southwest to southeast trending fracture that has dissected the summit since its 2012 eruption (Figure 2D); and 2) hot springs located ~7.3 km southeast of the summit. Yellow sulfur deposits surround the active fumaroles and travertine deposits are prominent in the hot springs region.

**Sampling and Analytical Techniques**

We utilized a number of techniques for the collection of gas samples depending on the specific situation at the volcano. When possible, we collected direct gas samples from vents or bubbling springs in the crater or on the volcano’s flanks using pre-evacuated Giggenbach bottles containing NaOH (Giggenbach and Goguel, 1989b). Where vents were not accessible, we measured plume gas composition by Multi-GAS (Aiuppa et al., 2005) and collected gas samples in Tedlar Bags for immediate subsequent carbon isotope analysis by Infrared Isotope Ratio Analyzer (Delta Ray) located on our boat (Rizzo et al., 2014; Fischer and Lopez, 2016). If there was a substantial plume, we made SO2 flux measurements using a miniDOAS system (Galle et al., 2002) from the ground or helicopter. We collected water and gas samples from hot springs where no fumaroles were present or accessible.

Direct fumarole sampling involves inserting a titanium tube into a volcanic vent and drawing gases directly into previously evacuated glass bottles (i.e. Giggenbach bottles). The bottles contain a 5N NaOH solution that absorbs the acid gases (CO2, SO2, H2S, HCl, HF) and heat vapor allowing the non-reactive gases (noble gases, H2, N2, O2, CH4, CO) to accumulate in the head space. This technique has been described in Giggenbach and Gougel (1989a) and more recently in Oppenheimer et al. (2014).

Gas and water samples were also collected in copper tubes clamped or crimped at both ends for noble gas analyses (Sano and Fischer, 2013). The gas composition of Giggenbach bottles was analyzed in the Volatiles Laboratory at UNM using a combination of gas chromatography and quadrupole mass spectrometry following established procedures (de Moor et al., 2013a; Lee et al., 2017; Ilanko et al., 2019).

Helium isotopes were analyzed in splits from the Giggenbach bottles or from separately collected copper tubes. The samples were analyzed in the noble gases isotope laboratory at INGV,
Sezione di Palermo (Italy), following the analytical procedures outlined in e.g. Rizzo et al. (2016). The \(^{3}\)He/\(^{4}\)He ratio is expressed as \(R/Ra\) (where \(Ra\) is the ratio in air and equal to \(1.39 \times 10^{-6}\)) and was corrected for air contamination \((Rc/Ra)\) using the He/Ne ratio following the equation proposed by Sano et al. (1987). Nitrogen isotopes were analyzed for select gas samples at the University of New Mexico using a stable isotope ratio mass spectrometer with gas bench following the techniques described in Ilanko et al. (2019). Air standards were analyzed every 3–4 analyses to correct raw \(\delta^{15}\)N values. A blank was also run for each sample or air standard and the peak areas were subtracted from those subsequently measured in the sample. The blank-corrected air values were then subtracted from the blank-corrected sample values. Reported errors are given in 1 s.d. over 4–6 peaks. Although the number of peaks for calculations varies between samples, the same peak numbers were used for the blank corrections and the air standard associated with each sample. Unfortunately, as shown in the results section, \(\delta^{15}\)N values for these samples are burdened with high standard deviations due to interferences with unidentified peaks or low signals, making the data of limited value.

Water samples for water anion and cation analyses were collected at warm and hot spring sites using standard collection procedure that involved transfer of water into a 60 ml plastic syringe, and filtering through 0.2 micron millipore filters into Nalgene bottles. Samples were analyzed at the analytical chemistry laboratory in the Department of Earth and Planetary Sciences at the University of New Mexico using established IC and ICP OES methods (i.e. ASTM 300.1 and US EPA 200.7).

**Multi-GAS**

The Multi-GAS used in the work was provided by Alessandro Aiuppa (University of Palermo) and was equipped with an infrared CO\(_2\) sensor and electrochemical sensors for SO\(_2\) and H\(_2\)S (Aiuppa et al., 2014). The sensor unit was placed close to the fumarolic vents in campaign style while other samples were collected, usually for 1–2 h. The derived concentration data (acquired at 0.5 Hz) were post-processed to derive ratios between volatile species, using a routine procedure (Aiuppa et al., 2014). In brief, co-acquired gas concentration data for pairs of gas species were compared in scatter plots (see Figure 3), and the gas/gas ratios were derived from the slopes of the best fit linear regression lines for each volcano’s dataset.

**miniDOAS**

The miniDOAS used in this work follows the design and approach of Galle et al. (2002) and has previously been used at Anatahan volcano, Mariana Islands (Hilton et al., 2007) at Erta Ale volcano, Ethiopia and Masaya, Nicaragua (de Moor et al., 2013b). The data processing is performed using DOASIS software (Kraus, 2006) that enables real-time calculation of the plume SO\(_2\) burden. The SO\(_2\) burden combined with constraints on windspeed allow emission rates to be calculated (Stoiber et al., 1983). At Kiska Volcano we performed several walking traverses along the crater rim on September 10 and measured wind-speed using a hand-held anemometer at the same time we measured plume SO\(_2\) burden. At Gareloi we mounted the miniDOAS in the helicopter with the telescope positioned vertically out the small window and performed flight traverses under the plume on September 14 at an average altitude of 470 m above sea level. We had measured wind speed using the wind circle method (Doukas, 2002) during a previous trip to the summit (September 13) and asked the pilot to estimate wind speed during the flight. At Kanaga we performed a helicopter traverse as well as a walking traverse and constrained wind speed via the wind circle method at the same time as the plume SO\(_2\) burden measurements (September 21). During the walking traverse, we were only able to partially capture the plume, due to inaccessible terrain.

**RESULTS**

Generally speaking, our results presented in this section show that the SO\(_2\) fluxes were quite low and typical for volcanoes at a low state of activity (Fischer et al., 2019; Werner et al., 2019). Gas discharges are dominated by H\(_2\)O, followed by CO\(_2\) and the sulfur species. Except for Gareloi, which has a fumarole temperature up
to 270°C and displays a magmatic gas composition, all other volcanoes discharge gases that have a mixed magmatic-hydrothermal character. Helium isotopes of gas samples are within the MOR range (Graham, 2002) implying no or only minor contributions of radiogenic helium from the overriding crust. CO₂-N₂-³He relative abundances allow for the assessment of the contributions of these volatiles from of from the mantle wedge and subducted materials (Sano and Marty, 1995; Sano et al., 2001). Our data of gas chemistry are consistent with minor slab-derived volatile contributions to a predominantly mantle-derived source for CO₂ and N₂. A detailed evaluation of the carbon contributions from the subducted slab and how it varies along the entire Aleutian volcanic arc is presented in Lopez et al. (in prep.). The results from direct gas samples are shown in

### TABLE 1 | Gas chemical composition in mmol/mol total gas. All samples were collected in September 2015.

| Volcano/sample ID | Temp. °C | H₂O | CO₂ | SO₂ | H₂S | HCl | HF | He | Ar | O₂ | N₂ | CH₄ | CO |
|-------------------|----------|-----|-----|-----|-----|-----|----|----|----|----|----|-----|----|
| Kanaga Fum 1a S21 | 95       | 921.03 | 34.55 | 3.60 | 2.13 | 1.47 | 0.09 | <0.001 | 0.0015 | 0.561 | 0.624 | 0.001 | 39.54 | 0.00082 | 0.00081 |
| Kanaga Fum 1b S27 | 95       | 971.58 | 9.059 | n.a | n.a | n.a | n.a | 0.0007 | 0.267 | 0.289 | 0.008 | 18.79 | 0.00039 | 0.00039 |
| Kanaga Fum 2a S10 | n.d      | 908.06 | 24.71 | 0.44 | 0.41 | 0.03 | 2.08 | <0.001 | 0.00086 | 0.124 | 0.693 | 11.90 | 51.99 | <0.0002 | <0.0002 |
| Kanaga Fum 2 S11 | n.d      | 927.51 | 14.97 | n.d | n.d | n.d | 1.89 | <0.001 | 0.0007 | 0.044 | 0.452 | 8.008 | 47.11 | <0.0002 | <0.0002 |
| Gareloy Fum 1a S1 | 102      | 985.51 | 1.982 | 7.17 | 5.81 | 1.26 | 2.80 | 0.001 | 1.157 | 0.013 | 0.000 | 0.935 | 0.00400 | 0.1195 |
| Gareloy Fum 1b S14 | 102     | 983.51 | 7.99 | 5.99 | 1.48 | 2.11 | 0.001 | 0.0001 | 1.512 | 0.016 | 0.000 | 0.935 | 0.00400 | 0.1195 |
| Gareloy Fum 2a S8 | 270      | 983.46 | 4.185 | 10.1 | 9.05 | 1.07 | 0.60 | 0.27 | 0.0001 | 1.572 | 0.013 | 0.000 | 0.935 | 0.00400 | 0.1195 |
| Gareloy Fum 2b S29 | 270     | 953.64 | 11.30 | 28.1 | 24.1 | 4.02 | 0.40 | 0.45 | 0.0004 | 3.003 | 0.037 | 0.000 | 3.024 | 0.02407 | 0.00170 |
| Little Sitkin 1a S5 | 66     | 795.80 | 164.9 | 10.7 | 0.96 | 9.74 | 0.65 | <0.001 | 0.0231 | 0.808 | 0.050 | 0.093 | 20.10 | 6.84929 | <0.0002 |
| Little Sitkin BS2 S26 | 55 | 446.49 | 492.4 | 16.2 | 0.84 | 15.4 | 0.32 | <0.001 | 0.0209 | 1.194 | 0.184 | 0.054 | 32.10 | 11.0480 | <0.0002 |
| Little Sitkin Fum 1a S3 | 97 | 893.18 | 98.00 | 1.91 | 0.24 | 1.66 | 0.07 | <0.001 | 0.0030 | 0.148 | 0.013 | 0.000 | 5.148 | 1.52506 | <0.0002 |
| Little Sitkin Fum 1b S9 | 97 | 878.77 | 115.0 | n.a | n.a | n.a | 1.89 | <0.001 | 0.0054 | 0.172 | 0.016 | 0.000 | 4.324 | 1.72416 | <0.0002 |
| Kiska Fumarole KIF S16 | n.d | 536.94 | 44.59 | 8.77 | n.a | n.a | 0.39 | 0.12 | 0.30 | 0.09 | — | — |
| Tanaga Hot Spring Gas 1 S22 | 62 | 970.00 | 1.048 | 0.16 | n.a | n.a | 1.41 | <0.001 | 0.0001 | 0.043 | 1.536 | 4.727 | <0.0002 | <0.0002 |

n.a, not analyzed; n.d. not determined.

### TABLE 2 | Noble gas and nitrogen stable isotopes.

| Noble gases | R/Ra | He/Ne | Rc/Ra | +/- | Ar⁴⁰/Ar³⁶corr | +/- | δ¹⁵N |
|-------------|------|-------|-------|-----|--------------|-----|-------|
| Kanaga Fum 1a S21 | 5.95 | 1.1 | 7.96 | 0.0662 | 295.32 | 0.16 | —0.42 |
| Kanaga Fum 1b S27 | 5.99 | 1.13 | 7.93 | 0.0657 | 294.61 | 0.16 | —0.45 |
| Kanaga Fum 1c | 5.76 | 0.95 | 8.14 | 0.0589 | 295.55 | 0.15 | —— |
| Kanaga Fum 2a S10 | n.a | n.a | — | — | — | — | 0.39 |
| Kanaga Fum 2 S11 | n.a | n.a | — | — | — | — | 0.30 |
| Gareloy Fum 1a S1 | 7.76 | 5.88 | 8.15 | 0.0658 | 295.31 | 0.07 | —1.59 |
| Gareloy Fum 1a S10 | 7.71 | 3.82 | 8.31 | 0.0674 | 293.85 | 0.26 | —— |
| Gareloy Fum 2a S8 | 6.80 | 4.74 | 7.22 | 0.0581 | 279.03 | 0.08 | —— |
| Gareloy Fum 2b S29 | 6.91 | 6.63 | 7.20 | 0.0515 | 294.19 | 0.21 | —— |
| Little Sitkin 1a S5 | 7.08 | 93.12 | 7.10 | 0.0557 | 299.30 | 0.09 | —— |
| Little Sitkin 1b S9 | 7.02 | 325.44 | 7.02 | 0.0566 | 301.19 | 0.09 | —— |
| Kiska Fumarole KIF S16 | n.a | n.a | — | — | — | — | — |
| Tanaga Hot Spring Gas 1 S22 | 0.97 | 0.39 | n.d | — | 296.16 | 0.15 | —— |

Noble gas isotopes and He/Ne from Cu tube. Heavily air contaminated samples - unreliable values due to analytical issues.

### TABLE 3 | Multi GAS data collected in September 2015.

| Molar ratios | H₂/SO₂ | H₂S/SO₂ | CO₂/SO₂ | CO₂/H₂S | CO₂/H₂S | H₂O/SO₂ | H₂O/CO₂ | H₂O/H₂S | H₂O |
|--------------|--------|---------|---------|---------|---------|---------|---------|---------|------|
| Kiska | Nd | 1.8 | 6.9 | 3.8 | 2.5 | nd | Nd | nd | — |
| Little Sitkin | Nd | nd | nd | 98 | 98 | nd | 11 | 1.078 | 91.6 |
| Gareloy | 0.11 | 0.1 | 0.26 | 2.6 | 0.2 | 83 | 320 | 832 | 98.4 |
| Kanaga | Nd | 9.5 | 186 | 19.6 | 18 | 6,696 | 36 | 705 | 97.1 |

| mole % | CO₂ | SO₂ | H₂S |
|-------|-----|-----|-----|
| 71 | 10.3 | 18.6 |
| 8.3 | — | 0.08 |
| 91.6 | — | — |
| 4.3 | 1.2 | 0.12 |
Tables 1 and 2, water chemistry of spring samples is in Supplementary Table S1 and the results of the Multi-GAS and SO2 flux measurements are shown in Table 3 and Table 4, respectively.

Direct Samples of Gas and Water Phase

The complete gas chemistry is shown in Table 1 and compositions are typical of magmatic and hydrothermal gas discharges from volcanoes in arc settings (Fischer and Chiodini, 2015). We obtained gas samples from the plume formed above the fumarolic vents at Kiska (unknown temperature), Little Sitkin (97°C), Gareloi (102°C and 270°C), and Kanaga (95°C). We also obtained gas samples from bubbling hot springs at Little Sitkin (55°C and 66°C) and Tanaga (62°C). The sample from Kiska is heavily air contaminated and is not discussed further because we have reliable Multi-GAS data for this plume/vent. All fumarole gases are dominated by H2O (879–986 mmol/mol), followed by CO2 (4–115 mmol/mol) and total sulfur (S, = SO2 + H2S, 0.4–28 mmol/mol). Kanaga and Gareloi had comparatively high HCl contents of up to 2 mmol/mol. Trace gases include He, H2, CH4, CO. CH4 reached up to 1.7 mmol/mol at Little Sitkin. The gases from bubbling springs and extracted from the water phase are dominated by CO2 with minor H2S and CH4.

Noble gas and nitrogen isotope data are reported in Table 2. The 3He/4He ratios corrected for air contamination range from 7.0 to 8.3 Ra. These values are within the MORB range (8 ± 1 Ra; Graham, 2002), and at the high end of values typical for arc volcanoes (Hilton et al., 2002; Sano and Fischer, 2013). Although the Gareloi samples are somewhat air contaminated, with He/Ne of 3.8–6.6, the corrected value of 8.3 Ra approaches some of the highest measured values at arcs to date: 8.6 Ra at Goryachii Klyuch in the Kurile Islands (Taran, 2009; Tolstikhin, 1986), 8.8 Ra at Galeras Volcano, Colombia, although the latter sample is highly air contaminated, resulting in a large correction (Sano et al., 1997), and 9.0 Ra at Pacaya volcano, Guatemala, in olivine-hosted fluid inclusions (Battaglia et al., 2018). The helium isotope ratios of our samples indicate that the Western Aleutian volcanoes are among the least influenced by crustal helium of any arc volcano. Two samples from bubbling springs at Tanaga and Little Sitkin are heavily air contaminated and not further discussed. The 40Ar/36Ar ratios of gas samples are similar to the air value of 295 with the highest ratio reaching 301, typical of arc gases (Sano and Fischer, 2013). As can be seen from Table 2, duplicate samples (e.g. Gareloi Fum 1a and 1b; and 2a and 2b) from the same fumarole with one collected in a Cu-tube and the other in a Giggenbach bottle, followed by splitting in the lab, have indistinguishable He- and Ar- isotope values. This underscores the notion that both types of samples are valid for noble gas isotope sampling; however, if highly acid gases are sampled, Cu-tubes are better to be trapped in the field, rather than cold-welded (Sano and Fischer, 2013).

Nitrogen isotope data were only obtained from two localities. The Kanaga fumaroles have values of δ15N from −0.4 to +0.4‰, consistent with significant air contamination (δ15Nair = 0.0‰) while the Gareloi fumarole gas has a value of -1.6 ± 0.9‰, also within error of air but potentially more negative. As mentioned above, these analyses were burdened with significant analytical issues, due to low signal and unidentified peaks resulting in high standard deviations, making them of limited value.

Water cation and anion data are shown in Supplementary Table S1. We collected water samples from springs on Kanaga, Little Sitkin, Semisopochnoi and Tanaga. Prior to our expedition, the only reported water sample data were from Semisopochnoi and Little Sitkin (Evans et al., 2015). Water temperatures range from 23°C for Semisopochnoi to 86°C at Kanaga, pH varies from acid at Little Sitkin to neutral at Semisopochnoi. Kanaga and Tanaga springs are located on the volcanoes’ flanks and characterized by high Na, K, and Ca values while Semisopochnoi and Little Sitkin springs are located within the volcanoes’ craters or calderas and characterized by lower, Na, K, and Ca values. SO4 contents are highest at Little Sitkin and Cl is highest at Tanaga and Kanaga.

Multi-GAS Major Gas Ratios

We obtained Multi-GAS data from Kiska, Little Sitkin, Gareloi and Kanaga volcanoes. The results are shown in Table 3. Consistent with direct gas samples, the dominant gas species is H2O, followed by CO2 or SO2. CO2/SO2 ratios show a wide range from 0.2 at the high-temperature vents of Gareloi to 98 at the low-temperature hydrothermal system of Little Sitkin. Kiska (2.5) and Kanaga (18) have intermediate CO2/SO2 ratios. Notably, at Gareloi,

### TABLE 4 | SO2 fluxes measured by miniDOAS and calculated CO2 fluxes using indicated gas ratios from direct samples or Multi-GAS.

| SO2 flux (t/day) | MG CO2/St | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 | MG CO2/SO2 |
|------------------|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
the amount of SO₂ detected by Multi-GAS in the gas plume was higher than the mean fumarole composition, resulting in lower average H₂O/SO₂ of 83 than that of the direct gas samples (average H₂O/SO₂ = 120). We were not able to reliably measure H₂O at Kanaga. Figure 3 shows the Multi-GAS correlation plots with $R^2$ values as a measure of data quality.
SO₂ Fluxes

We successfully obtained SO₂ fluxes from Gareloi and Kanaga by helicopter traverse and from Kiska by walking traverse. The SO₂ flux data are summarized in Table 4 and Figure 4 shows an example of the two walking traverses performed at Kiska volcano.

At Kanaga wind speed of 12 m/s was measured and the SO₂ flux calculated by averaging 7 helicopter traverses was 70 ± 30 tons SO₂/day. At Kiska the average flux of two walking traverses was only 3.6 ± 0.1 tons SO₂/day, using a measured wind speed of 4.6 m/s. For Gareloi, we use the wind speed of 13.6 m/s to obtain a SO₂ emission rate of 320 ± 80 tons SO₂/day, averaged over 5 helicopter traverses. This was the highest average flux observed during our field campaign. The flight path of the helicopter and obtained SO₂ burdens are shown in Figure 5.

DISCUSSION

Major Gases

The compositions of the major gases are shown in Figure 6, along with a compilation of high-temperature arc gases from the literature (Henley and Fischer, 2021; Taran and Zelenski, 2015). Notably, the ratios obtained by the Multi-GAS are within the range of gas compositions obtained by direct fumarole sampling, supporting the notion that the two measurement and sampling approaches are complementary and can be used interchangeably depending on which approach is more feasible in a given situation. At Gareloi (270°C) the CO₂/Si ratio between the four collected samples ranges from 0.3–0.6 while the H₂O/Si ratio of three direct gas samples ranges from 97 to 137, with the fourth sample being an outlier with much lower H₂O/Si ratio of 35. Given that the Multi-GAS recorded a H₂O/St ratio of 75, we attribute the low H₂O/Si ratio of sample 2bS29 to water loss during sampling, consistent with significantly lower water contents of that sample compared to the three others (953 mmol/mol vs 983 mmol/mol). The low CO₂/SO₂ ratio signature is consistent with that previously proposed for the Aleutian-Kamchatka Pacific arc segment indicating relatively low slab-derived carbon contribution to gas discharges compared to other arcs (Aiuppa et al., 2017; Aiuppa et al., 2019). Low CO₂/Si ratios may also indicate an extensively degassed magma that has lost most of its CO₂ compared to S (Giggenbach, 1996). The low temperature (~boiling point) samples from Kiska, Kanaga, and Little Sitkin display significantly higher CO₂ contents and CO₂/Si ratios in excess of 4 with most samples’ CO₂/Si > 8. Little Sitkin gases are typical low temperature hydrothermal gases dominated by H₂O and CO₂. In terms of their H₂O/Si ratios, Little Sitkin, Kiska and Gareloi fall within 40–150, a typical range for arc gases. Notably, the Multi-GAS data set collected for Little Sitkin has a higher H₂O/St (~1,000) compared to the gas samples (~50). This is likely due to the high and variable humidity at Little Sitkin fumarole and spring area that may have compromised the Multi-GAS H₂O measurements, as suggested by the low R² value (Figure 3). Kanaga gases have the highest H₂O/Si ratios of all the gases sampled or measured, likely due to the addition of significant meteoric water in the subsurface. The sample collected at the bubbling spring of Tanaga is dominated by H₂O. Gareloi and Kiska gas compositions lie in the typical range of high temperature arc gases, even though they have significantly lower outlet temperatures (although we were not able to measure Kiska temperature), suggesting that these volcanic
gases have had minimal interaction with hydrothermal systems
(Giggenbach, 1996). This notion is also supported by data
presented in Figure 7 that show the highest SO2/H2S ratios
for Gareloi, indicating a stronger magmatic gas signature, and
significantly lower SO2/H2S for Little Sitkin and Kanaga,
indicating mixed magmatic-hydrothermal signatures. Multi-
GAS data from Kiska shows significantly lower SO2/H2S than
Gareloi but overall higher sulfur contents than the two volcanoes
dominated by hydrothermal gas discharges (Little Sitkin and
Kanaga). In summary, there is good agreement between data
collected by Multi-GAS and by direct gas sampling of fumaroles
irrespective of gas outlet temperature or magmatic/hydrothermal
character of the gases. Gareloi and Kiska have the most magmatic
major gas compositions of the Western Aleutians volcanoes
investigated and their compositions overlap with global high
temperature arc gases from the literature.

FIGURE 7 | CO2, SO2 and H2S relative abundances of gases collected during this study. Magmatic gases are characterized by relatively high SO2 contents while hydrothermal gases are dominated by CO2 and H2S (Giggenbach, 1996).

FIGURE 8 | N2, He, Ar relative abundances of gas samples collected in this study. Also shown are data from volcanoes in Alaska and the Aleutians (Symonds et al., 2003b; Evans et al., 2015). Subduction zone gases are characterized by high N2/He, while upper mantle gases have low N2/He at high He/Ar (Giggenbach, 1996).
Minor Gases and Redox Pairs

Trace gas $N_2$, $He$, and $Ar$ of Western Aleutian samples are shown in Figure 8 along with data from gas samples collected at other Alaska-Aleutian volcanoes (Evans et al., 2015; Symonds et al., 2003a) and from the geographically similar Kuril Island Arc (Taran et al., 2018). Our data display a range in compositions typical of arc gases world-wide (Giggenbach, 1996) with $N_2/He$ ratios generally $>1,000$ and $He/Ar$ ratios affected by variable amounts of mixing with air or air-saturated water. Gases from Little Sitkin show the lowest $N_2/He$ ratios with samples from both the fumarole and bubbling spring plotting at values close to or below the typical arc-type range. We note that the definition of the arc-type field with $N_2/He$ values from 1,000–10,000 by Giggenbach (1996) was based on significantly fewer data available at the time. More recent additions of data from samples collected from gas discharges of volcanoes in oceanic arc settings (Kurile Islands (Taran et al., 2018), Izu Bonin Marianas (Mitchell et al., 2010), Sangihe (Clor et al., 2005)) display $N_2/He$ values at the lower end of this range, in the mantle field or in some cases between these endmembers. The upper mantle-like $^3He/^4He$ values (7.0–8.3 Ra) that preclude significant crustal contamination of the gases and the higher than mantle $N_2/He$ ratios are indicative of $N_2$ addition from the subducted slab. Recent thermochemical modeling work by Epstein et al. (2021) in the Hikurangi margin suggests that $N$ generally is better retained than $C$ during subduction an observation that may explain some of the lower $N_2/He$ ratios in some arcs and supports the idea of subduction of some of the $N$ past the zone of arc magma generation (Busigny et al., 2003; Mitchell et al., 2010). The Western Aleutians data also overlap with the Kuril Islands data; however, some of the Kuril volcanoes indicate a more dominant mantle source for $N_2$, i.e. low $N_2/He$ at high $He/Ar$ values, displacing them close to the mantle gas field (Figure 8). Like the Western Aleutians gases, the Kuril $^3He/^4He$ values of the least air contaminated samples have air-corrected values ranging between 7.0 and 8.3 Ra (Taran et al., 2018). This consistency in $^3He/^4He$ ratios between these two oceanic arcs implies that oceanic arc gases are generally less affected than those from continental arcs by contributions of volatiles from crustal sources (Sano and Fischer, 2013), providing the opportunity to investigate slab-derived volatile sources.

**FIGURE 9 |** $CO_2$, $^3He$, $^4He$ relative abundances of gases sampled in this study. Upper mantle gases are characterized by $CO_2/^3He$ of $\sim 2 \times 10^9$ and $N_2/^3He$ of $\sim 1 \times 10^6$. Subducted organic sediments have significantly higher $CO_2/^3He$ and $N_2/^3He$ and are dominated by $N_2$ over $CO_2$ (Marty and Jambon, 1987; Sano et al., 2001), resulting in molar $N_2/CO_2 < 1$. Subducted carbonates have $CO_2/^3He$ of $1 \times 10^{13}$ (Sano and Marty, 1995) and the $N$ content of AOC is on the order of 2–20 ppm (Li et al., 2007) while $CO_2$ in the AOC is around 2000 ppm (Alt and Teagle, 1999). Assuming a 10 ppmw $N$ content and a 2,000 ppmw $CO_2$ content of the AOC would result in a $N_2/CO_2$ molar ratio of $\sim 0.02$ or less (Taran et al., 2018).
mixture of predominantly mantle and AOC sources. Gases from Gareloi have the most organic sedimentary ± AOC contributions, based on their relatively high N₂/³He and high N₂/CO₂, while gases from Kanaga and Tanaga can be explained by a predominantly mantle source mixing with air. It is also apparent that gases from Little Sitkin and Gareloi have CO₂/³He ratios that overlap with or are only slightly higher than the mantle endmember, indicating that slab-derived carbon addition in this part of the arc is likely minor. However, we note that samples from Gareloi display N₂-He-Ar relative abundances (Figure 8) that indicate significant air contamination and therefore, N₂ and CO₂ sources need to be treated with caution. Samples from Kanaga and Tanaga are also displaced towards the air component in Figure 8, compromising any evaluation of deep source contributions of N₂ to these gas discharges. Our samples from the Western Aleutians generally display lower CO₂/³He ratios than the samples from the Kuril arc (Taran et al., 2018), suggesting that gases in the Western Aleutians have a lower slab CO₂ contribution than gases from the Kuril Islands. Lopez et al (in prep) utilize C-isotopes to investigate in detail the contribution of slab-derived carbon and how it varies along the Aleutian Arc, and find predominantly mantle and/or AOC carbon sources in the Western Aleutians.

Figure 10 shows that for commonly used redox pairs for H₂/H₂O and CO/CO₂ (Chiodini and Marini, 1998) and using the buffer system of D’Amore and Panichi (1980), the samples for which CO was detected (Kanaga and Gareloi) would have equilibrium temperatures of around 350°C. We note, however, that both Kanaga and Gareloi gas compositions are widely dispersed on this diagram making this assessment qualitative only. If correct, the high equilibrium temperatures in the liquid plus vapor field for Kanaga are consistent with the comparatively high CO₂/S₈ and low SO₂/H₂S ratios (Figures 6, 7) that suggest S deposition at depth and production of H₂S according to the following from (Giggenbach, 1996):

\[
\begin{align*}
3\text{SO}_2 + 2\text{H}_2\text{O} &= \text{2H}_2\text{SO}_4 + \text{S}(0) & (1) \\
\text{SO}_2 + 2\text{H}_2\text{S} &= 3\text{S}(0) + 2\text{H}_2\text{O} & (2) \\
4\text{S}(0) + 4\text{H}_2\text{O} &= 3\text{H}_2\text{S} + \text{H}_2\text{SO}_4 & (3)
\end{align*}
\]

Therefore, Kanaga likely remains a highly active volcano with a high temperature magmatic-hydrothermal system just below the surface, although SO₂ degassing levels are low (70 ± 30 t SO₂/day) and fumaroles are diffuse. For Gareloi, one sample (1a S1) has unusually high CO contents, compared to the duplicate sample (1b S14) and the other samples from Gareloi that were collected at higher temperature sites (2a and 2b), resulting in unrealistically high log(CO/CO₂) values of ~2.2. We assume that this is likely due to an analytical issue. All other Gareloi samples lie within the vapor field at high temperatures (>350°C) consistent with the magmatic character of these fumarole gases. Unfortunately, the inaccessibility of the Kiska fumarole precluded adequate collection of gas samples, making an evaluation of the equilibrium temperatures impossible. However, the extensive deposition of native sulfur around the vent area (Figure 2A) strongly suggests reactions of SO₂ according to 1) and 2) implying that Kiska also hosts pressurized magmatic-hydrothermal system, which is emitting roaring gases at the one fumarole. We also plotted the data for the Little Sitkin fumarole gas using the detection limit for CO (0.0002 mmol/mol), and the resulting minimum equilibrium temperatures are 250°C in a mixed liquid + vapor phase. We note that CO contents of Little Sitkin gases could be lower resulting in temperatures below 250°C. Therefore, quantitative assessment of Little Sitkin deep temperatures in not possible with these data.

**Thermal Waters**

Thermal water from the Western Aleutians are shown in the classic plot of Giggenbach (1988) in Figure 11 with the theoretical lines representing equilibrium compositions with a typical hydrothermal mineral composition including K- and Na feldspars, micas and chloride. The intersection of each isotherm with the full equilibrium line indicates that the waters are in full equilibrium with this mineral assemblage at the indicated temperature. Displacement towards the Mg-rich corner of the diagram indicates that the sampled waters are either mixtures of hydrothermal fluids with shallow groundwaters or that the reactions involving Mg have quickly equilibrated during ascent of the thermal waters to the surface (i.e. Chiodini et al. (2015)). In both instances, as long as the waters lie between the fully and partially equilibrated curves, the Na-Mg and Na-K
geothermometers still provide a valid estimate of the hydrothermal temperatures. The Mg-rich waters of Semisopochnoi and Little Sitkin lie close to the Mg-apex and overlap with the typical rock composition, indicating that these waters are immature waters and have not equilibrated with the alteration mineral assemblage. The Kanaga water sample approaches the partial equilibrium line but its composition also suggests immature water composition, out of equilibrium with relevant alteration mineral assemblages. Only Tanaga has a composition that lies in the field of partially equilibrated waters. Its Na-Mg temperature is around 220°C, consistent with a high temperature hydrothermal system at depth. Tanaga water temperature was measured at 62°C but no fumaroles were available for gas sampling to evaluate deep temperatures using gas geothermometry.

**SO₂ and CO₂ Fluxes**

SO₂ fluxes from Western Aleutian volcanoes are 3.6 ± 0.1 t/day (Kiska), 70 ± 30 t/day (Kanaga) and 320 ± 80 t/day (Gareloi) and are typical of the low to moderate fluxes similar to many passively degassing arc volcanoes (Shinohara, 2013; Carn et al., 2017; Fischer et al., 2019; Werner et al., 2019). CO₂ fluxes can be estimated by combining the CO₂/SO₂ ratios of direct gas emissions with measured SO₂ fluxes (Fischer et al., 1998; Aiuppa et al., 2019; Fischer et al., 2019). While this common approach provides reasonable estimates, it has been pointed out that crater plume or fumarole C/S ratios may not always be representative of the overall C/S ratios in the plume, especially if not measured at the same time as SO₂ flux, and may lead to erroneous CO₂ fluxes (Burton et al., 2013). These authors argue that direct airborne measurements of CO₂ in the plume and contemporaneous C/S ratio measurements improve the accuracy of the CO₂ estimates. Recently Fischer and Aiuppa (2020) showed that high-temperature fumarole compositions and multi-GAS measurements obtained from crater plumes combined with ground-based or satellite-based SO₂ emission provide robust CO₂ fluxes for volcanoes where degassing is dominated by crater emissions. However, estimating the CO₂ fluxes of volcanoes that have SO₂ emissions that are not detectable by satellite, and therefore are likely dominated by hydrothermal and diffuse emissions rich in H₂S and CO₂, provides a significant challenge in estimating a global CO₂ flux that also includes low emitters (Fischer et al., 2019; Werner et al., 2019; Fischer and Aiuppa, 2020). Due to constraints on time and access, we were unable to measure diffuse CO₂ emissions by accumulation chamber (Chioldini et al., 1998) and we did not have the necessary instrumentation to measure CO₂ concentrations in the plume by airborne techniques (Werner et al., 2009). However, our data from direct fumarole samples and from crater plume multi-GAS measurements enable the estimation of CO₂ flux from these volcanoes while addressing some of the issues mentioned above. For Gareloi, the high temperature (270°C) fumarole and multi-GAS CO₂/SO₂ and CO₂/Si ratios agree well (Table 4). The direct fumarole samples have a CO₂/Si of 0.41 ± 0.11 while the Multi-GAS shows 0.20 for that same ratio. The Multi-GAS CO₂/SO₂ ratio (0.26) is essentially identical to that CO₂/Si ratio (0.20) and the direct samples’ CO₂/SO₂ and CO₂/Si ratios (0.34–0.69 and 0.28 to 0.55, respectively) due to the predominance of SO₂ as the S species degassing from high T fumaroles. Using these ratios, we obtain a CO₂ flux from Gareloi of 1.17 × 10⁸ mol C/yr or 5.14 × 10⁷ g/yr (5.14 ± 1.3 × 10⁻⁷ Tg/yr). Similarly for Kiska, where we observed degassing from one massive fumarole, the CO₂/Si and CO₂/SO₂ ratios obtained by Multi-GAS are within a factor of two (2.5 and 5.09, respectively). Using this ratio, the CO₂ flux from Kiska is 3,090 ± 1,445 mol/yr or 1.3 ± 0.6 × 10⁻⁷ Tg/yr.
For Kanaga, the Multi-GAS CO$_2$/S$_2$ ratios and CO$_2$/SO$_2$ ratios differ significantly (18 and 186, respectively). Likewise, CO$_2$/S$_2$ and CO$_2$/SO$_2$ ratios from direct samples differ significantly and differ between gases collected from different fumaroles. At Kanaga, H$_2$S is a significant sulfur species and ten times more abundant than SO$_2$ as measured by Multi-GAS. Notably, the direct samples have variable H$_2$S contents, likely due to the low overall S concentrations in the gas, making SO$_2$ versus H$_2$S distinction challenging using our wet-chemistry based analytical methods. We therefore consider the Multi-GAS CO$_2$/SO$_2$ and CO$_2$/H$_2$S ratios more reliable. While it has been shown that H$_2$S will readily oxidize to SO$_2$ during high temperature (1,000 °C) mixing of magmatic gases with the atmosphere (Martin et al., 2006), low temperature oxidation is likely to be much slower. Because Kanaga equilibrium temperature is ~300 °C and outlet temperatures are only boiling, extensive high temperature oxidation of H$_2$S to SO$_2$ is unlikely and we therefore use the Multi-GAS CO$_2$/SO$_2$ ratio for our flux estimate. This approach results in a Kanaga CO$_2$ flux of 2.38 × 10$^6$ mol/yr or 1.05 ± 0.45 × 10$^{-4}$ Tg/yr. Our data show that while Gareloi is the largest SO$_2$ emitter of the Western Aleutians, Kanaga is the largest CO$_2$ emitter. Our data do not include any diffuse degassing or any flank degassing, only crater degassing.

The volcanoes of the Western Aleutians emit about 1 ± 0.4 × 10$^{-4}$ Tg CO$_2$/yr, a small fraction of the 1.66 Tg CO$_2$ (taking into account extrapolations of non-measured volcanoes) emitted by the entire Alaska-Aleutian volcanic arc (Fischer et al., 2019). Using these workers’ data, it is interesting to note that the volcanic CO$_2$ emissions increase significantly from the Western Aleutians (0.0001 TgCO$_2$/yr) to the Central (0.1 ± 0.09 TgCO$_2$/yr) and Eastern Aleutians (0.12 ± 0.08 TgCO$_2$/yr) and to the Alaska Peninsula (1.03 ± 0.48 TgCO$_2$/yr). When we normalize these fluxes by approximate arc segment lengths (Western Arc 500 km, Central Arc 750 km, Eastern Arc 1,100 km, Figure 1), we notice orders of magnitude changes in CO$_2$ fluxes per km with the Western Arc emitting only 2.2 × 10$^{-7}$ TgCO$_2$/yr/km, the Central Arc emitting 1.3 × 10$^{-4}$ TgCO$_2$/yr/km and the Eastern Arc emitting 1.05 × 10$^{-3}$ TgCO$_2$/yr/km. The above values take into account only the volcanoes that have been measured and reported in Fischer et al. (2019). Applying these authors’ extrapolation method, to include not measured volcanoes does not significantly change these fluxes for the eastern and central segments (1.13 × 10$^{-3}$ TgCO$_2$/yr/km for eastern, 1.46 × 10$^{-4}$ TgCO$_2$/yr/km for central) but increases the flux of the western segment to 1.04 × 10$^{-4}$ TgCO$_2$/yr/km. The remote western segment has four volcanoes that are hydrothermally active (Great Sitkin, Moffet, Tanaga and Little Sitkin) but have not been measured for CO$_2$ emissions. As these volcanoes have been ascribed a flux of 0.013 TgCO$_2$/yr each in (Fischer et al., 2019), this extrapolated flux of 0.052 TgCO$_2$/yr is larger than what we measured for all western Aleutian volcanoes combined (0.001 TgCO$_2$/yr/km), leading to a significantly higher estimated flux. Future studies should focus on measuring CO$_2$ fluxes from these volcanoes.

Plate convergence is near orthogonal in the eastern and central portion of the arc and gradually becomes more oblique in the western region of the Aleutian Arc, with plate motion eventually transitioning to strike-slip near ~170°E (Figure 1) (DeMets et al., 1996; Buurman et al., 2014). The varying convergence angles, combined with the thickness of subducted sediment, result in highly variable subducted sediment fluxes along the length of the arc, with a maximum in the central Aleutians and a minimum in the western Aleutians (Kelemen et al., 2003). The Eastern Aleutians are characterized by thicker continental crust (Fliedner and Klemperer, 2000). These along-strike variations in subduction parameters and crustal thickness may potentially affect the observed volcanic CO$_2$ output along the strike of the arc as is discussed in more detail in (Lopez et al., in preparation).

CONCLUSION

Our new data of gas and spring discharges from the Western Aleutian volcanoes provide key information about the nature of the volcano-hydrothermal systems in this region. The results indicate that all the volcanoes investigated host high-temperature mixed liquid-vapor systems that are fed by volatiles primarily sourced from the mantle wedge and the subducted slab, with negligible crustal contamination. In particular, Kiska, Kanaga and Gareloi have gas compositions that indicate a significant magmatic degassing component. Our measured SO$_2$ and CO$_2$ fluxes provide background values during a low-level of activity that provide a baseline against which future fluxes can be compared and evaluated in light of changes in volcanic activity. The Aleutian Arc is well known for its along-strike variations in subduction parameters such as convergence angle, amount of sediment delivery to the trench and crustal thickness. While more work on volcanic gas fluxes is needed, especially in the remote regions of the arc, our data suggest that volcanic CO$_2$ fluxes are lowest where convergence angle is most oblique and sediment delivery to the trench is at its minimum.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

TF helped obtain the funding, collected most of the samples and data, coordinated the analyses, made most of the figures and wrote the article. TL helped obtain the funding collected some of the samples and data, performed most of the analyses and contributed to the article. AA provided instrumentation to make some of the measurements, plotted some of the data and contributed to the article AR analyzed some of the samples and contributed to the article TI analyzed some of the samples and data, performed most of the analyses and contributed to the article KK obtained funding, was co-Scientist in Charge of the cruise and contributed to the article EC obtained funding, was co-Scientist in Charge of the cruise, provided a figure and contributed to the article.
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SUPPLEMENTARY MATERIAL
The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.786021/full?supplementary-material
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