



## Deep magmatic degassing versus scrubbing: Elevated CO<sub>2</sub> emissions and C/S in the lead-up to the 2009 eruption of Redoubt Volcano, Alaska

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[1] We report CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S emission rates and C/S ratios during the five months leading up to the 2009 eruption of Redoubt Volcano, Alaska. CO<sub>2</sub> emission rates up to 9018 t/d and C/S ratios  $\geq 30$  measured in the months prior to the eruption were critical for fully informed forecasting efforts. Observations of ice-melt rates, meltwater discharge, and water chemistry suggest that surface waters represented drainage from surficial, perched reservoirs of condensed magmatic steam and glacial meltwater. These fluids scrubbed only a few hundred tonnes/day of SO<sub>2</sub>, not the >2100 t/d SO<sub>2</sub> expected from degassing of magma in the mid- to upper crust (3–6.5 km), where petrologic analysis shows the final magmatic equilibration occurred. All data are consistent with upflow of a CO<sub>2</sub>-rich magmatic gas for at least 5 months prior to eruption, and minimal scrubbing of SO<sub>2</sub> by near-surface groundwater. The high C/S ratios observed could reflect bulk degassing of mid-crustal magma followed by nearly complete loss of SO<sub>2</sub> in a deep magmatic-hydrothermal system. Alternatively, high C/S ratios could be attributed to decompressional degassing of low silica andesitic magma that intruded into the mid-crust in the 5 months prior to eruption, thereby mobilizing the pre-existing high silica andesite magma or mush in this region. The latter scenario is supported by several lines



of evidence, including deep long-period earthquakes (−28 to −32 km) prior to and during the eruption, and far-field deformation following the onset of eruptive activity.

**Components:** 10,700 words, 8 figures, 3 tables.

**Keywords:** CO<sub>2</sub>; Redoubt Volcano; SO<sub>2</sub>; degassing; hydrothermal; scrubbing.

**Index Terms:** 8419 Volcanology: Volcano monitoring (4302, 7280); 8424 Volcanology: Hydrothermal systems (0450, 1034, 3017, 3616, 4832, 8135); 8430 Volcanology: Volcanic gases.

**Received** 12 July 2011; **Revised** 25 January 2012; **Accepted** 1 February 2012; **Published** 20 March 2012.

Werner, C., W. C. Evans, P. J. Kelly, R. McGimsey, M. Pfeffer, M. Doukas, and C. Neal (2012), Deep magmatic degassing versus scrubbing: Elevated CO<sub>2</sub> emissions and C/S in the lead-up to the 2009 eruption of Redoubt Volcano, Alaska, *Geochem. Geophys. Geosyst.*, 13, Q03015, doi:10.1029/2011GC003794.

## 1. Introduction

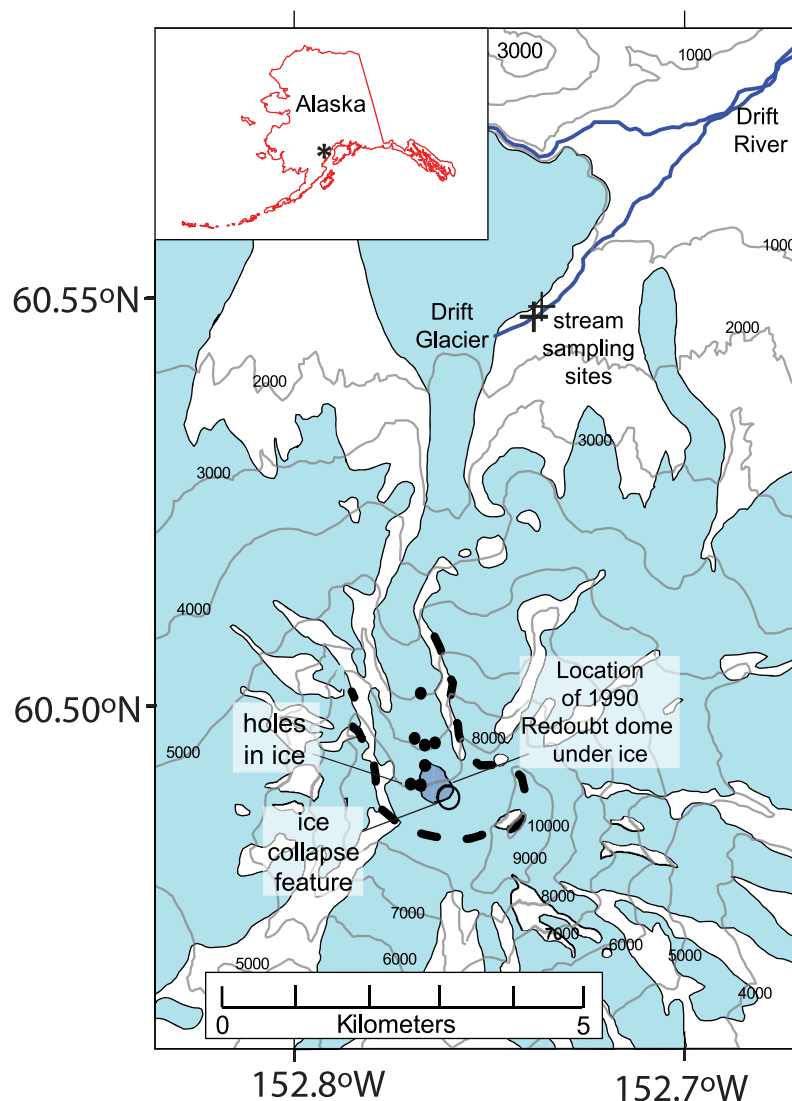
[2] Measurements of pre-eruptive carbon dioxide (CO<sub>2</sub>) emissions have long been recognized as a forecasting tool for volcanic eruptions due to the low solubility of CO<sub>2</sub> in magmas even at deep crustal conditions [Giggenbach, 1996; Newman and Lowenstern, 2002], its abundance in volcanic gases [Symonds et al., 1994], and because of its low solubility in groundwater relative to sulfur and halogen gases [Symonds et al., 2001]. However, there are still relatively few observations of pre-eruptive CO<sub>2</sub> emissions from volcanic systems [Aiuppa et al., 2009, 2010] or of CO<sub>2</sub> emissions from active arc volcanoes in general [Werner et al., 2006, 2008; Christenson et al., 2010]. At basaltic volcanoes, the C/S molar ratio in volcanic gas (typically derived from CO<sub>2</sub>/SO<sub>2</sub> measurements in plumes) has been observed to increase in the hours to weeks before eruptions, a pattern interpreted as the geochemical signature of mafic, CO<sub>2</sub>-rich magmas intruding from lower crustal reservoirs [Aiuppa et al., 2006, 2009]. At “wet” volcanoes, typical of many found in the Cascade and Alaskan volcanic arcs [Symonds et al., 2003], scrubbing of volcanic SO<sub>2</sub> can also cause the C/S ratio to exceed typical magmatic values, complicating the interpretation of this parameter [Doukas and Gerlach, 1995; Symonds et al., 2001, 2003; Gerlach et al., 2008; Werner et al., 2011].

[3] In this study we present a sequence of airborne measurements of CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S emission rates from Redoubt Volcano beginning 5 months prior to the March 2009 eruption and compare the magnitude of emissions for this pre-eruptive period to ‘failed’ eruptions (or magmatic intrusions) from the Cook Inlet region of Alaska [Werner et al., 2011]. We assess the role of sulfur scrubbing, both near

the surface and in a deeper hydrothermal system, as a mechanism for creating high C/S gas ratios prior to an eruption as opposed to solely the degassing of a CO<sub>2</sub>-rich primitive magma. This study is one of a few that document elevated CO<sub>2</sub> emission rates from an arc volcano prior to eruption, and highlights the importance of measuring the emission rates of CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S in the volcanic plumes as an element of eruption forecasting. The degassing during the eruption itself of Redoubt in 2009 is reported elsewhere (T. Lopez et al., Ozone Monitoring Instrument (OMI) measurements of sulfur dioxide during the 2009 eruption of Redoubt volcano, submitted to *Journal of Volcanology and Geothermal Research*, 2012; C. Werner et al., Degassing of CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S associated with the 2009 eruption of Redoubt Volcano, Alaska, submitted to *Journal of Volcanology and Geothermal Research*, 2012).

## 2. Redoubt Volcano and the 2009 Eruptive Activity

[4] Redoubt Volcano (3108 m) is an extensively glaciated stratovolcano (Figure 1) ~170 km SW of Anchorage in the rugged wilderness of Lake Clark National Park and Preserve. It is one of the most active volcanoes in the Cook Inlet region of south-central Alaska with historical eruptions in 1902, 1966–68, 1989–90 [Miller and Chouet, 1994], and 2009 [Schaefer et al., 2011]. Eruptions during and since 1966 have all occurred through glacial ice that fills a ~1.5 km wide summit crater. The crater itself is breached to the north by a deep glacial canyon known informally as Drift canyon. No springs are known around the volcano on the south, east, and west flanks, and thus we infer that all water exiting the summit crater drains to the north down Drift

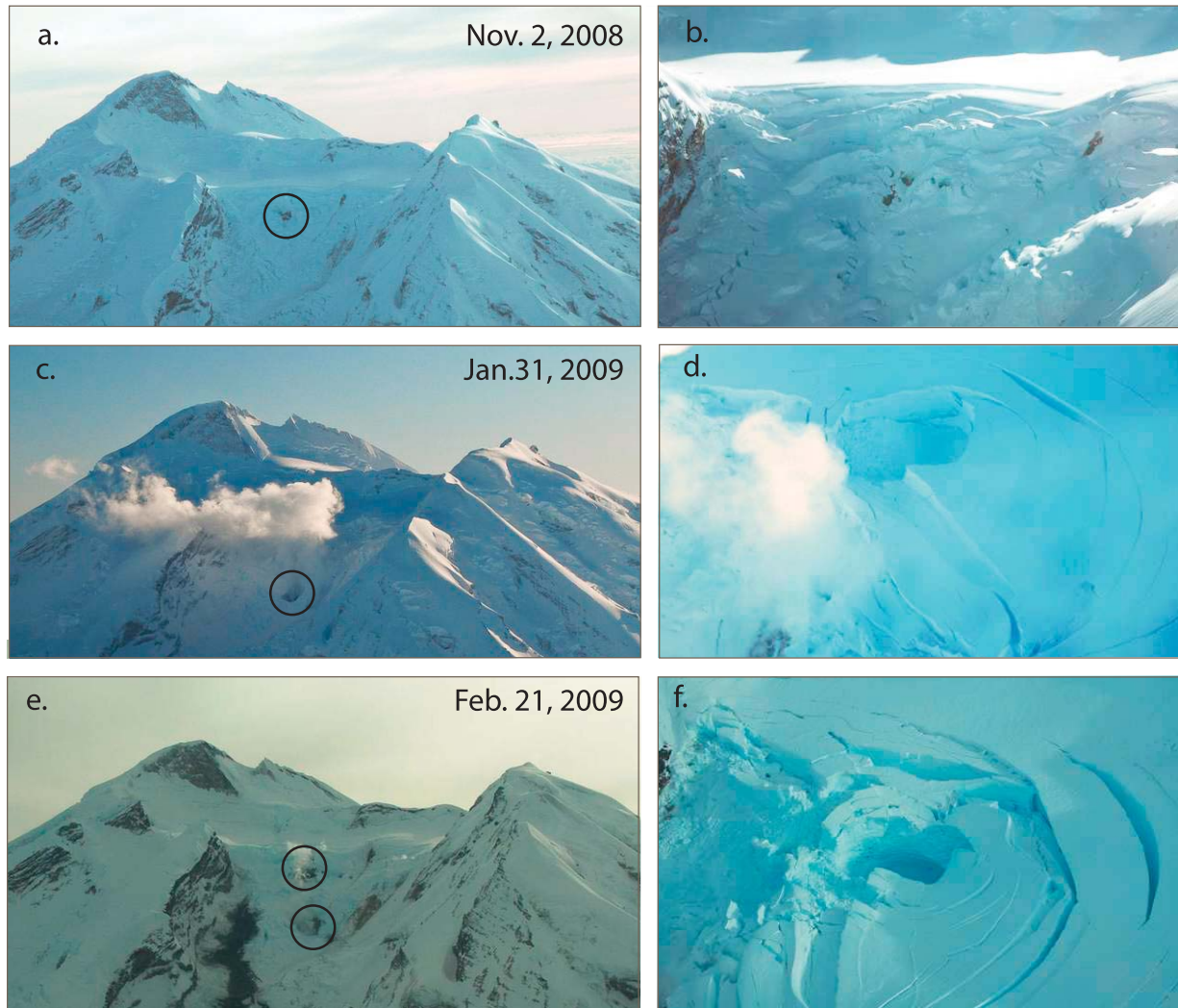


**Figure 1.** Map of Redoubt Volcano, Alaska, showing extensive glacial coverage (in blue). Stream sampling locations (crosses) are approximately 6.5 km from the dome and the closest place where meltwaters from the dome area exit from beneath the Drift Glacier. No other streams were observed around the volcano. The black dots show the locations of the ice holes where the plume first appeared, which is directly above the snow covered 1990 dome. The dotted line shows the approximate boundary of the summit crater which is breached to the north.

canyon (Figure 1). Between the 1989–1990 and 2009 eruptions, emissions were generally <60 t/d CO<sub>2</sub> and <10 t/d SO<sub>2</sub> [Doukas and McGee, 2007], and occasional minor vapor emission from the site of the penultimate 1990 lava dome suggested episodic low level activity from the volcano between eruptions. One background measurement of minor degassing in May 2005 yielded a C/S ratio of ~8 [Doukas and McGee, 2007].

[5] Little is known about the Redoubt hydrothermal system, or if the volcano indeed supports a hydrothermal system. No thermal manifestations are known to exist beyond the central crater [Motyka

*et al.*, 1993], which stands in contrast to neighboring volcanic vent Crater Peak (2309 m), where five areas of surface thermal manifestation exist, including a 1-km long zone of warm springs that discharge from the base of the volcano about 4 km downslope from the vent [Motyka *et al.*, 1993]. The extent of glacial coverage on Redoubt (Figure 1) could mask any hydrothermal expression within several kilometers of the main vent, but significant glacial coverage would also act to limit meteoric recharge to the volcano and a hydrothermal system [Hurwitz *et al.*, 2003]. Altered volcanic rock is found on the upper east side of Redoubt, though the central crater is relatively free of extensive



**Figure 2.** Series of photographs of Redoubt Volcano showing the change in the ice melting prior to the March 15, 2009 phreatic eruption. (a, c, and e) Note that very little visible plume existed in late February (in contrast to late January) even though large peaks of CO<sub>2</sub> were measured during this entire period (Figure 4). Circled locations are the main holes in the glacier where plume was observed to escape through the glacier; in Figure 2a this hole is over the 1990 dome. The field of view is approximately 4 km, and the distance between the peaks is approximately 2.5 km. (b, d, and f) The progression of the large ice collapse feature above the 1990 dome. The final dimension of the ice collapse feature was hundreds of meters across as shown in Figure 2f. Bleick et al. (submitted manuscript, 2012) discuss melting of the glacial ice in detail.

hydrothermal alteration [Till et al., 1994]. Evidence of extensive hydrothermal activity near the surface in the summit region in the past is recognized from deposits of the Rust Slough lahar, which contains ample hydrothermal material, and is thought to be the product of a massive slope failure of hydrothermally altered material from the north side of Redoubt approximately 200–400 yr B.P [Bégét and Nye, 1994; Till et al., 1994]. A similar lahar was formed on Mount Rainier, WA, and the lack of significant alteration in Rainier’s core as observed by geophysical techniques [Finn et al., 2001] is

thought to be a result of these deposits being previously removed.

[6] The 2009 eruption was preceded by six months of unrest. The first unambiguous seismic activity in the precursory period was the detection of deep long-period earthquakes (28–32 km) beneath the summit in mid-December, 2008 (J. Power et al., Seismic observations of Redoubt Volcano, Alaska 1989–2010 and forecasting of the 2009 eruption, submitted to *Journal of Volcanology and Geothermal Research*, 2012), although a couple of short



**Table 1.** Gas Emission Rates, Wind Speeds, and Ratios at Redoubt Volcano During 2008–2009<sup>a</sup>

Date	SO <sub>2</sub> (t/d)	n	SO <sub>2</sub> s.d. (t/d)	CO <sub>2</sub> (t/d)	H <sub>2</sub> S (t/d)	Wind Speed (m/s)	Wind stdev (m/s)	Molar C/S From CO <sub>2</sub> /SO <sub>2</sub>	Molar C/S From CO <sub>2</sub> /(SO <sub>2</sub> +H <sub>2</sub> S)
13-Oct-08	28 <sup>b</sup>	3	–	1368	11	6.8	0.3	71	41
02-Nov-08	31 <sup>b</sup>	3	–	1220	4	3.0	0.0	57	47
26-Jan-09	177	2	48	–	–	5.9	0.1	–	–
31-Jan-09	180	4	19	7326	–	3.9	0.2	59	–
02-Feb-09	157	4	36	3628	<1	7.2	1.1	34	33
07-Feb-09	88	3	8	9018	–	9.0	0.3	149	–
21-Feb-09	46	1	–	5980	–	7.0	0.1	189	–
27-Feb-09	34	4	4	–	–	3.7	0.2	–	–
15-Mar-09	3850	2	139	6588	–	7.4	1.1	2.5	–
20-Mar-09	938	4	141	3858	–	5.5	0.1	6.0	–
26-Mar-09	3585	3	629	10776	–	5.4	0.2	4.4	–
04-Apr-09	16646	5	1336	20716	586	11.0	0.8	1.8	1.7
05-Apr-09	11353	7	880	12820	198	6.2	0.6	1.6	1.6
16-Apr-09	1952	4	138	8827	202	2.6	0.5	6.6	5.5
20-Apr-09	12733	6	1316	12887	312	5.3	0.2	1.5	1.4
28-Apr-09	13276	5	2594	17220	536	10.7	1.1	1.9	1.8

<sup>a</sup>Significant digits on emission rates are retained to be consistent with Werner et al. (submitted manuscript, 2012) where cumulative emissions are calculated. Uncertainties for emission rates are estimated at ±20% (see text for details); nd means not detected, and dash indicates not measured.

<sup>b</sup>October and November 2008 SO<sub>2</sub> emission rates determined by InterScan contouring, COSPEC was below detection limits.

duration ‘tremor-like’ seismic traces were observed as early as September 2008. The degassing measurements reported in this study were initiated following several pilot reports of very strong H<sub>2</sub>S odors [Neal et al., 2011]. One report stated that the smell of H<sub>2</sub>S was strong enough to give several people headaches at 9000 ft and approximately 35–40 km downwind of Redoubt in late September 2008, as documented in the Alaska Volcano Observatory internal logs. Another pilot report from 6500 to 7000 ft and 110 km downwind away stated the smell was ‘very strong’ on September 30, 2008. Likewise, AVO field crews doing work on the volcano in July 2008 reported smelling H<sub>2</sub>S even when ~4 km from the volcanic vent (K. Bull, personal communication, 2012), and had noted fumarolic activity. During this period (July - September, 2008), however, no unambiguous volcanic seismicity had been detected [Schaefer et al., 2011], and the summit appeared relatively unperturbed (no significant increase in ice melting or crevassing observed). Glacial melting increased substantially following an increase in seismic activity in late January, 2009 (Figure 2).

[7] The eruption began on March 15, 2009 with a phreatic eruption, followed by the first magmatic eruption on March 23. The volcano experienced a total of 19 explosions interspersed with dome growth for two weeks, before settling into the final dome growth that lasted from April 4, 2009 until July, 2009 [Diefenbach et al., 2012]. The 2009 eruptive products show compositional and textural evidence for three magma bodies that all had their

final staging at 3.5–6 km depth prior to eruption [Coombs et al., 2012]. The first eruptive product was a low silica andesite (LSA) that is thought to have risen from depth in the months prior to eruption. These products were dominant in the first five days of explosion and were more mafic than any of the andesites in the 1989–90 eruption. The two other erupted magma types were high and intermediate silica andesites (HSA and ISA) which dominated the later part of the eruption. The ISA has a phenocryst population that suggests it was a hybrid between the LSA and the HSA [Coombs et al., 2012]. Given the similarity between the later eruptive products (HSA and ISA) and the andesites of the 1989–90 eruption, Coombs et al. [2012] suggest that the ascent of the LSA from depth through stagnant mushy magma in the mid-crust mobilized this magma, which drove the later half of the eruption.

### 3. Measurements

#### 3.1. Airborne Gas Measurements

[8] Emission rate measurements were made by flying a series of traverses perpendicular to the volcanic plume downwind of the summit with an instrumented fixed-wing aircraft. Closed-path LICOR spectrometers (LI-6252 or LI-7000, LI-COR Inc.) were used to measure CO<sub>2</sub> using the contouring method [Gerlach et al., 1997] and SO<sub>2</sub> emission rates were measured using a correlation spectrometer (COSPEC). On two occasions (October 13 and November 2, 2008) when emissions were still low

**Table 2.** Chemical and Isotope Data for Stream-Water Samples Draining the Summit Area of Redoubt Volcano (2008–2009)<sup>a</sup>

Parameter	Units	Collection Date					
		11/7/2008	2/10/2009: Low Flow	2/10/2009: High Flow	2/21/2009	2/27/2009	3/20/2009
T	°C	1.5	1.5	0.4	1.1	1.3	1.7
pH (lab)	–	7.2	5.4	5.45	5.06	4.15	4.39
Na	ppm	230	300	310	350	260	na
K	ppm	25	37	40	42	33	na
Ca	ppm	190	330	340	350	370	na
Mg	ppm	74	140	140	150	130	na
Li	ppm	0.50	1	1	1.2	0.75	na
Mn	ppm	0.27	25	29	29	27	na
Fe	ppm	<1	120	120	120	85	na
SiO <sub>2</sub>	ppm	63	120	120	140	130	na
B	ppm	6.3	8.3	7.9	10.7	7.1	na
Cr	ppb	<200	<200	<200	<200	<200	na
Co	ppb	<5	19	22	20	31	na
Ni	ppb	<20	<20	<20	<20	<20	na
Cu	ppb	<20	30	<20	20	500	na
Zn	ppb	<40	720	760	800	740	na
Al	ppb	10	1020	940	1400	6300	na
Cd	ppb	<20	<20	<20	<20	<20	na
Pb	ppb	<10	<10	<10	<10	<10	na
Mo	ppb	<20	<20	<20	<20	<20	na
V	ppb	7	<7	<7	<7	<7	na
Ti	ppb	<100	<100	<100	<100	<100	na
Ba	ppb	22	59	49	56	72	na
Sr	ppb	600	940	940	980	1050	na
As	ppb	<50	<50	<50	<50	<50	na
Rb	ppb	59	96	120	120	85	na
Cs	ppb	<2	5	6	15	3	na
U	ppb	<10	<10	<10	<10	<10	na
F	ppm	0.6	2.4	2.8	2.6	2.4	2.8
Cl	ppm	500	680	740	730	560	440
SO <sub>4</sub> <sup>2-</sup>	ppm	660	1400	1450	1400	1500	1450
Br	ppm	1.2	1.6	1.7	1.6	1.1	0.8
NO <sub>3</sub> -N	ppm	0.2	0.14	0.12	0.22	0.14	0.14
PO <sub>4</sub> -P	ppm	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
HCO <sub>3</sub>	ppm	42	<10	<10	<10	<10	<10
NH <sub>4</sub>	ppm	na	na	<0.2	na	na	na
δ <sup>18</sup> O	‰	–134		–133	–130	na	na
δD	‰	–17.0		–16.6	–16.0	na	na

<sup>a</sup>Typical analytical uncertainties are ±10% for cations, ±5% for anions, ±2% for δD, and ±0.1‰ for δ<sup>18</sup>O; na means not analyzed.

(not detectable with COSPEC), the SO<sub>2</sub> emission rate was measured using the contouring method and an electrochemical SO<sub>2</sub> analyzer (model 4240–1999b, Interscan, Inc.). Generally the emission rates calculated using COSPEC and contouring are comparable, but COSPEC measurements are considered more reliable due to the sampling biases easily introduced in contouring. A detailed comparison and discussion of all SO<sub>2</sub> emission rate measurements made using both methods during the entire Redoubt eruption is discussed by Werner et al. (submitted manuscript, 2012). H<sub>2</sub>S was measured using an electrochemical instrument (model 4170–1999b, Interscan, Inc.), but only

constituted a significant proportion of total S (S<sub>Total</sub> = SO<sub>2</sub> + H<sub>2</sub>S) during October and November, 2008. We report molar C/S ratios derived from the CO<sub>2</sub>/S<sub>Total</sub> emissions ratios (Table 1).

[9] The methods for measuring and calculating the gas emission rates in this study are described in previous publications [Gerlach et al., 1997; McGee et al., 2001; Doukas and McGee, 2007], and emission rate uncertainties are estimated as about ±20%. Consequently the derived C/S ratio has an estimated uncertainty of about ±30%. Wind circles [Doukas, 2002] were used for measuring wind speeds downwind of the plume at the height of the plume core, and associated uncertainty with this

method is approximately  $\pm 5\%$ . Measured standard deviations of the wind velocity measurements in this study were  $\sim \pm 7\%$ . Short-term temporal variability due to varying plume conditions probably represents one of the largest uncertainties in the data values, and varies based on type of activity at the volcano and meteorological conditions. For average COSPEC emission rates measured between January and March 15, 2009, the temporal variability averaged  $\pm 10\%$  for days with multiple passes under the plume.

### 3.2. Stream Sampling

[10] Water samples were collected from an outflow stream along the eastern margin of the piedmont lobe of the Drift glacier (Figure 1), the closest accessible fluid sampling point, located  $\sim 6.5$  km from the 1990 lava dome. Temperatures at the time of sampling were  $0$ – $2^\circ\text{C}$ ; all other drainages around the volcano remained frozen in the months preceding the eruption when average surface temperatures at the nearest reporting station were  $< 0^\circ\text{C}$  at sea level. The stream was sampled five times between November 2008 and March 2009, and the bulk samples of turbid water were filtered and analyzed using the methods of *Hurwitz et al.* [2010]. Three samples were sealed into glass bottles and sent to the USGS Reston Stable Isotope Lab, VA for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotopic analysis. All geochemical data for the stream waters are found in Table 2.

[11] Streamflow rates could not be measured as the sampling site was too hazardous to visit for more than a couple of minutes, or only long enough to collect a water sample. Scaled pictures and video were used to estimate streamflow rates, and these estimates were compared to ice-melt estimates calculated by H. A. Bleick et al. (Volcano-ice interactions during the precursory phase of unrest preceding the 2009 eruption of Redoubt Volcano, Alaska, submitted to *Journal of Volcanology and Geothermal Research*, 2012).

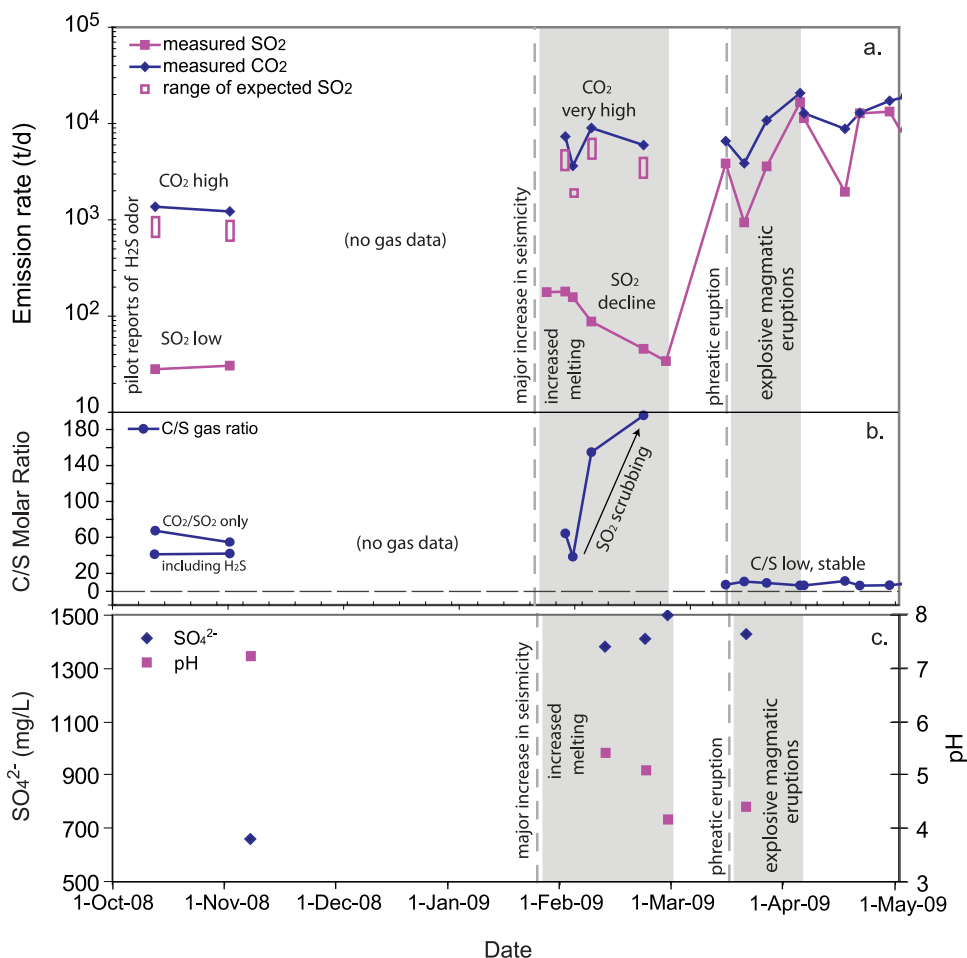
## 4. Observations

[12] Increased monitoring of Redoubt began in October, 2008. Visual observations documented increasing surface heat as reflected in the growing area of bare rock on the 1990 dome, subaerial flow of meltwater and mixed snow-ice-rock debris flows, and a small vapor plume emanating from a new hole in the glacier below the 1990 dome (Figures 2a and 2b) [*Neal et al.*, 2011]. Emission

rates of CO<sub>2</sub> were 1220–1368 t/d during the initial flights in October and November, 2008;  $\sim 20$  times above the  $\sim 60$  t/d measured during the preceding period of dormancy. SO<sub>2</sub> emission rates were on the order of 30 t/d, and 4–11 t/d H<sub>2</sub>S were detected (Figure 3a), resulting in a molar C/S emission ratio of  $\sim 40$ – $50$  (Table 1 and Figure 3b). Stream water showed a neutral pH and a relatively low SO<sub>4</sub><sup>2-</sup> (Figure 3c), with SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> concentrations of 660 and 500 mg/l, respectively.

[13] The next full gas measurement was made on January 31, 2009 following an increase in seismicity on January 21, 2009, and showed that CO<sub>2</sub> emissions had increased to 7326 t/d and SO<sub>2</sub> to 180 t/d (H<sub>2</sub>S measurements were not made on this day). This and another gas measurement on February 2nd resulted in C/S ratios of 59 and 33–34 (Table 1), respectively, both indistinguishable within uncertainties from ratios measured in late 2008. By this time, a larger area of bare rock had formed in the crater above the 1990 dome and a vigorous steam plume (Figure 2c) emanated from a new hole in the glacier. A large ice-collapse feature in the glacier in the upper plateau of the summit crater was beginning to form as well (Figure 2d). No stream samples were taken at this time, but observations of significant increases in the flow of dark muddy waters from the Drift glacier on Jan 26th and 27th suggested that the heat flux also increased at this time producing additional meltwater and entraining debris during runoff.

[14] CO<sub>2</sub> emission remained high (3628–9018 t/d) during late January and all of February. Examples of CO<sub>2</sub> concentrations recorded while flying through the volcanic plume in January and February 2009 are shown in Figure 4 and illustrate the extremely strong CO<sub>2</sub> signals (in excess of 14 ppm above local atmospheric concentration) observed, even on days when there was practically no visible plume near the volcano (Figure 2e) and while SO<sub>2</sub> was near the detection limit. The SO<sub>2</sub> emissions were initially stable from 157 to 180 t/d from January 26 to February 2 (H<sub>2</sub>S was  $< 1$  t/d), but then SO<sub>2</sub> started to decline. These changes resulted in an increasing C/S ratio in February (Figures 3a and 3b). At the same time, the circular collapse structure in the ice near the summit of the volcano grew substantially (Figure 2f); we infer that this indicated continued melting of ice over a broad area of the summit crater floor and subsidence of the overlying ice (Figure 2d). Based on observations of the ice crater growth, AVO scientists estimated that  $\sim 6.6$  million cubic meters of ice



**Figure 3.** Emission rate data plotted for the precursory and eruptive period from October, 2008 through April, 2009. (a) Measured CO<sub>2</sub> and SO<sub>2</sub> emission rates plotted in t/d, and the ‘expected’ SO<sub>2</sub> emission rate calculated from the CO<sub>2</sub> emission rate and a C/S molar plume ratio of 2–2.4, which represents bulk degassing of a mid- to upper-crustal magma with a low C/S ratio (see text and *Werner et al.* [2011]). (b) The C/S molar ratio calculated from emission rate measurements (Table 1). Note the increase in C/S in February 2009 coincident with declining SO<sub>2</sub> emissions during this period. Uncertainties as stated in text: ±20% for emission rates and ±30% for ratios. (c) SO<sub>4</sub><sup>2-</sup> and pH measurements from stream water samples taken at the base of the Drift Glacier approximately 6.5 km from the 1990 lava dome. pH was initially neutral and decreased following increases in melting, whereas the SO<sub>4</sub><sup>2-</sup> load increased. While not shown, Cl<sup>-</sup> increased between November and the first February sample, but declined starting February 21, reflecting that there was likely relatively less HCl to scrub compared to SO<sub>2</sub>. Dashed lines and colored periods indicate major phases of activity of the volcano until the end of April, 2009.

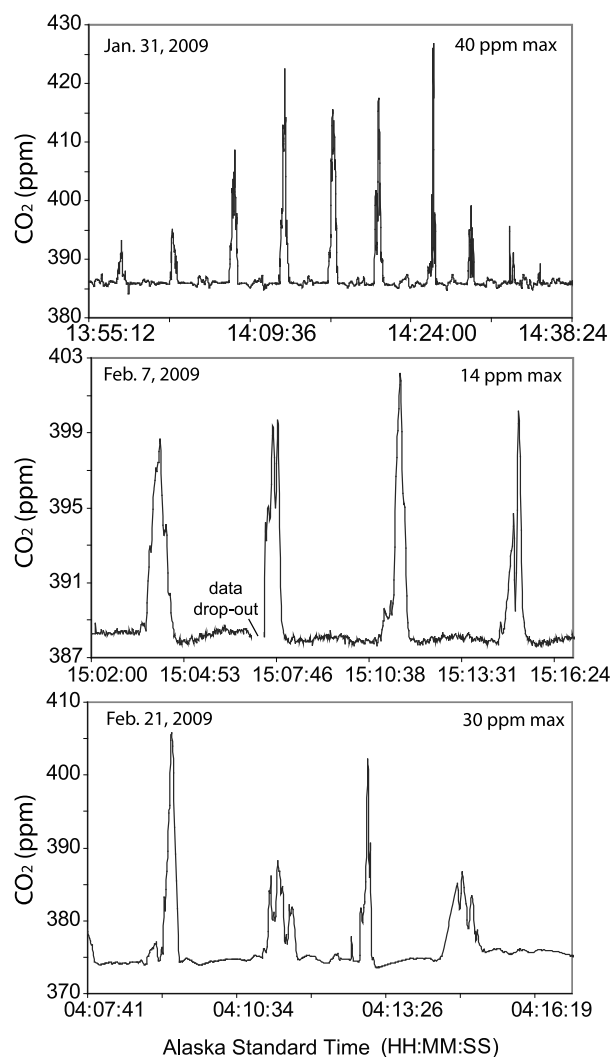
melted between January 31 and March 1, 2009 (Bleick et al., submitted manuscript, 2012).

[15] Following the apparent acceleration in heat output and subsequent ice melting at the summit in February (Figure 2f), the molar C/S ratio of the volcanic plume increased to a maximum of 190 (Figure 3b). Meanwhile the SO<sub>4</sub><sup>2-</sup> concentrations in stream water increased to more than twice that in the November sample, and the pH decreased to 4.15 by February 27 (Figure 3c). Cl<sup>-</sup> concentrations increased from 498 ppm in November to 738 ppm in early February, but then started to

decrease again while SO<sub>4</sub><sup>2-</sup> stayed fairly constant (Table 2). Concurrently, the fluoride content of the stream water increased from 0.6 to 2.4 ppm from November to February and then stayed roughly stable.

[16] On March 15, 2009, SO<sub>2</sub> emissions increased dramatically to 3850 t/d, coincident with a minor phreatic eruption, but CO<sub>2</sub> stayed roughly constant at 6588 t/d (Figure 3a). These were the last emission measurements before the first explosive magmatic event on March 23. Starting March 15, the molar C/S ratio decreased and remained between





**Figure 4.** Plume transects of CO<sub>2</sub> concentrations during January to February 2009 measured using a LICOR CO<sub>2</sub> analyzer in an aircraft flying through the core of the plume at distances of ~5 km downwind of the vent. Maximum concentrations measured on February 7th were very high (14 ppm) even though only a minor plume was visible on this day (Figure 2).

1.6 and 6 (average ~2.4) for the remainder of the eruption (Figure 3b) (Werner et al., submitted manuscript, 2012). One meltwater sample collected after the first magmatic explosion indicated similar SO<sub>4</sub><sup>2-</sup> as pre-eruptive samples and a pH still at 4.4.

[17] From November 2008 to February 2009, cation concentrations in stream water increased along with SO<sub>4</sub><sup>2-</sup>. Ca increased proportionately more than other cations and eventually exceeded Na as the dominant cation (Figure 5). The relative proportion of major cations in the stream water was similar to that from a major-element whole rock analysis of 1990 Redoubt dome lava (Figure 5) apart from Fe,

which was always depleted and essentially absent from the neutral-pH November sample. Note that the composition of the stream water differs from that of typical hydrothermal waters such as those from Akutan and Mount St. Helens (Figure 5). The  $\delta D$  and  $\delta^{18}O$  of stream waters (Figure 6) fall to the right of the global meteoric water line (GMWL) and toward the region expected for magmatic water [Giggenbach, 1992]. Furthermore, the sample compositions moved progressively more toward the magmatic water region with time.

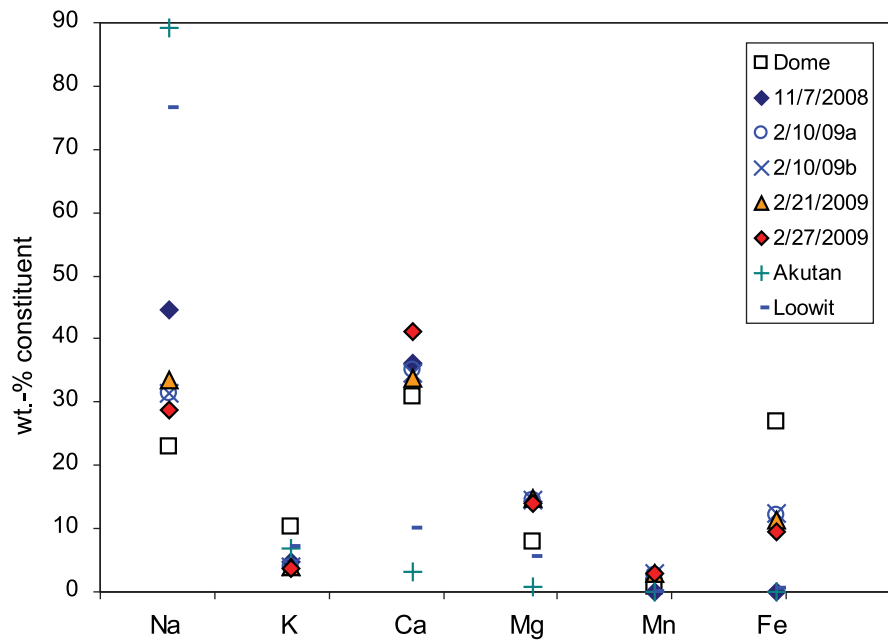
[18] Streamflow rates estimated from pictures and videos ranged from 1 to 10 m<sup>3</sup>/s, which encompass the average estimate of meltwater derived from ice (2.5 m<sup>3</sup>/s ice melt = 2.3 m<sup>3</sup>/s meltwater) in the precursory period through to February 2009. Meltwater production increased to 3.8 m<sup>3</sup>/s in March prior to the eruption (Bleick et al., submitted manuscript, 2012). One episode of increased flow rate was observed while stream sampling, which lasted on the order of minutes, but the morphology of the stream channel suggested that increased flow events happened intermittently. The increased flow event contained blocks of ice and sediment.

## 5. Discussion

### 5.1. Gas Emissions and C/S Ratios

[19] A recent analysis of gas emissions from Cook Inlet volcanoes highlights several important similarities of the degassing sequences from eruptions and non-eruptive unrest events (likely related to small magmatic intrusions) between 1989 and 2006 [Werner et al., 2011]. First, gas emissions in excess of 1500 t/d CO<sub>2</sub> or 1000 t/d SO<sub>2</sub> have only been observed at volcanoes that erupted, and typically these emission rates were measured during periods of explosive activity. Second, all degassing sequences with sufficient data early in the period of activity, whether the activity had culminated in an eruption or not, began with a C-rich compositions (high C/S), which decreased with time to molar C/S ratios between 0.5 and 2 for the volcanoes studied.

[20] To put the 2008–09 Redoubt gas data in context, CO<sub>2</sub> emissions in October and November, 2008 (1220–1368 t/d CO<sub>2</sub>), were noteworthy given there was little other indication of increasing unrest. Gas emission data were a significant influence on the decision to increase the aviation color code and volcano alert level for Redoubt from a GREEN/NORMAL to exhibiting signs of unrest (YELLOW/ADVISORY). However, low SO<sub>2</sub> at this time (<50 t/d) resulted in a high molar C/S ratio (40–50).



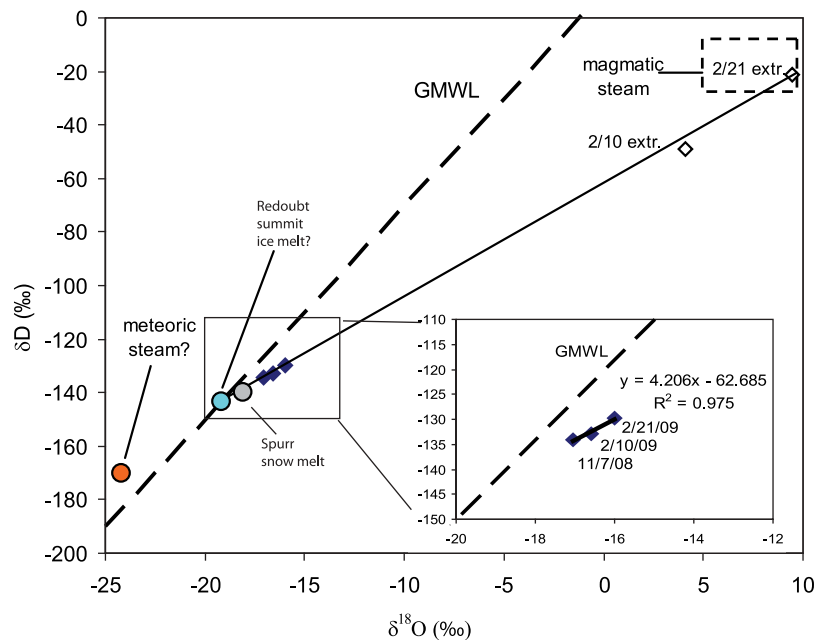
**Figure 5.** Relative wt.% proportions of major cations in stream water compared to the final 1990 dome lava composition [Nye *et al.*, 1994]. Cation composition was similar to the dome lava composition, becoming more so with time for Na, but less so for Fe and Ca. The composition of the stream water varies significantly from that of springs with known hydrothermal sources; e.g., Loowit springs at Mount St. Helens, WA [Bergfeld *et al.*, 2008], which has an estimated subsurface temperature of  $\sim 150^{\circ}\text{C}$ , and the hot spring on Akutan Volcano [Motyka *et al.*, 1993], where a geothermal well reached  $180^{\circ}\text{C}$ . These waters show the strong Na enrichment expected in hydrothermal waters.

[21] In the past, elevated C/S ratios at Cook Inlet volcanoes and elsewhere have often been attributed to scrubbing of SO<sub>2</sub> from the gas stream either at the surface or extending to several kilometers depth [Symonds *et al.*, 2001; Gerlach *et al.*, 2008; Werner *et al.*, 2008]. Recently, however, high molar C/S ratios coupled with high emission rates have been interpreted at open-system basaltic volcanoes as the consequence of injection of CO<sub>2</sub>-rich magma from the lower crust into the upper crust, which then acts as an eruption trigger [Aiuppa *et al.*, 2006, 2009]. As mafic magma injection is inferred as a mechanism to drive volcanism at Redoubt and other Cook Inlet volcanoes [Nye *et al.*, 1994; Larsen *et al.*, 2010], it is reasonable to question if the prolonged period of elevated C/S ratios could in part represent the degassing of a new CO<sub>2</sub>-rich magma intruded beneath the mid-crustal storage region as an alternative to a scrubbing hypothesis. The data set presented here provides an opportunity for this question to be investigated.

## 5.2. Scrubbing as a Mechanism for High C/S in Gas Emissions

[22] Large-scale scrubbing of SO<sub>2</sub> is often called on to maintain the high C/S ratios in volcanic

environments prior to or during eruptions [Doukas and Gerlach, 1995; Symonds *et al.*, 2001; Gerlach *et al.*, 2008; Werner *et al.*, 2008]. In this scenario, magmatic gases originally enriched in CO<sub>2</sub> and SO<sub>2</sub> preferentially lose sulfur either to magmatic-hydrothermal brines or mineralization within the volcanic edifice, or near the surface to groundwater or lakes [Symonds *et al.*, 2001, 2003]. In a report on several volcanic systems in the Cascades and Alaska, Symonds *et al.* [2003] discuss these possibilities as primary (within the volcanic edifice or deeper) and secondary (near the surface) scrubbing, respectively. These studies suggest that monitoring the C/S plume ratio would allow the ‘drying out’ of the volcano to be observed as emission rates increased and subvolcanic water available for scrubbing was eliminated. At Redoubt, even though the volcano was monitored regularly for 5 months prior to eruption, no clear ‘drying out’ period was observed, even when CO<sub>2</sub> emissions reached  $>9,000$  t/d. C/S ratios were high in the earliest measurements and, as will be discussed below, the ever-increasing supply of meltwater produced in the summit area in the precursory period resulted in higher C/S in gas emissions, the opposite of what was predicted by earlier studies [Symonds *et al.*, 2001, 2003].

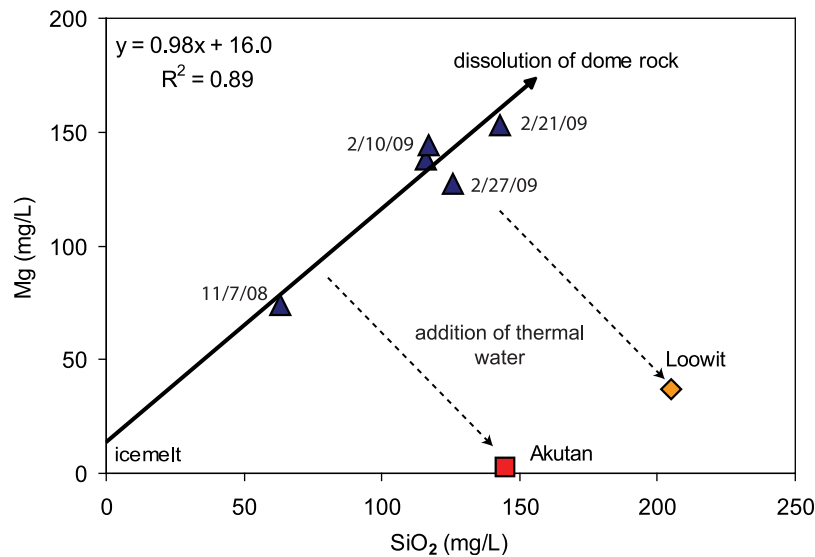


**Figure 6.** Deuterium and oxygen isotopic composition of stream water from November to February (versus VSMOW). Compositions move toward the magmatic steam region [Giggenbach, 1992] over time. The regression line shows that February samples could be ~8:1 mixtures of two hypothetical end-members: Redoubt ice-melt extrapolated from measured data to the GMWL using equation in inset (blue circle,  $\delta^{18}\text{O} = -19.2$  and  $\delta\text{D} = -143$ ), and estimated compositions of magmatic steam (hollow diamonds). The estimated value for Redoubt ice-melt is very similar to published values for snowmelt from the neighboring volcano, Mount Spurr (gray circle,  $\delta^{18}\text{O} = -18$  and  $\delta\text{D} = -141$ ) [Viglino *et al.*, 1985]. Orange circle shows isotopic composition of steam in equilibrium with the ice-melt end-member at 100°C. A mixture of such a “meteoric steam” and ice melt would plot left of the GMWL. Magmatic steam region from Giggenbach [1992] and liquid-steam fractionation factors from Friedman and O’Neil [1977].

### 5.2.1. Scrubbing at the Surface: Stream Samples and Water-Rock Interaction

[23] This eruption offers an unusual opportunity to estimate the amount of gas scrubbed at the surface because only one outflow stream is known at this otherwise “frozen” volcano, and both the composition and flow rate of outflow were tracked with time. The close correspondence between the cation composition of stream samples and Redoubt dome lava (Figure 5) suggests rapid dissolution of the rock by acidic meltwater that did not reach a high temperature or have time to equilibrate with secondary minerals. No hydrothermal fluid component (high SiO<sub>2</sub> and Na, and low Mg and Ca) is identifiable in any of the stream samples (Figure 5). Mg and SiO<sub>2</sub> show a strong positive correlation with increasing concentration with time until the end of February and differ compositionally from spring waters with a known hydrothermal source (Figure 7). Slight proportional enrichment in Ca relative to the dome lava (Figure 5) suggests possible addition of S from CaSO<sub>4</sub> dissolution, but depletion in Fe may reflect minor S removal to iron-sulfide minerals (Figure 5).

[24] Stream water chemistry thus suggests that the SO<sub>4</sub><sup>2-</sup> load in the stream could approximate the amount of SO<sub>2</sub> scrubbed out of the gas stream by meltwater, followed by oxidation of SO<sub>2</sub> to sulfuric acid. This approximation rests on the assumption that the SO<sub>4</sub><sup>2-</sup>-rich meltwater was not accumulating at shallow depths (<500 m) inside the volcano. While there is a large uncertainty here, stream outflow rates were estimated for each sampling and average values increased with time from ~1 to perhaps a maximum of 10 m<sup>3</sup>/s in late February (C. Waythomas, personal communication, 2010). These values bracket the meltwater production rate estimated from observations of ice melting at the summit (6.6 × 10<sup>6</sup> m<sup>3</sup> of ice over 30 days over February, 2009, or 2.3 m<sup>3</sup>/s of meltwater assuming a bulk ice density of 0.9). The general agreement between observed and expected streamflow rates argues against a large meltwater accumulation within the edifice along the outflow pathway, or progressive expulsion of a subvolcanic groundwater body, which might be expected with progressive heating following magma emplacement into the mid- to upper-crust. Further, the stable-isotope values of the stream samples are consistent



**Figure 7.** Mg versus SiO<sub>2</sub> in stream water showing positive correlation characteristic of waters lacking a hydrothermal component. Akutan and Loowit hot springs data are shown for comparison (Motyka *et al.* [1993] and Bergfeld *et al.* [2008], respectively).

with declining involvement of any near-surface groundwater over time due to an increase in the proportion of magmatic steam to meltwater with increasing emissions (Figure 6), as is discussed below.

[25] The isotopic composition of hydrogen and oxygen in stream samples from November to February gradually became heavier, moving away from average values of snowmelt in the region [Vigilino *et al.*, 1985] and the GMWL (Figure 6), and progressively toward the composition expected for a magmatic water component [Giggenbach, 1992]. Under the simplest-case assumption that the streamflow is derived entirely from adiabatic condensation of steam and melted ice, the ratio of meltwater to condensed steam would equal  $H_{\text{vap}}/\Delta H_{\text{fus}}$ , where  $\Delta H_{\text{fus}}$  is the heat required to melt the ice (333 J/g). The enthalpy of steam,  $H_{\text{vap}}$ , is 2676 J/g at 100°C, yielding a value of  $\sim 8$  for the ratio. Applying this ratio to the stream waters suggest that the condensed steam would constitute 11% of the streamflow, and meltwater 89%, and thus the waters should lie close to the value for snowmelt at similar altitudes in the region [Vigilino *et al.*, 1985] (Figure 6). If the steam is superheated,  $H_{\text{vap}}$  would be larger (e.g., 50% larger at 730°C), and some steam would escape to the plume. Thus, the condensed-steam component of streamflow could be  $<11\%$ . Nevertheless, for the isotopic compositions of streamflow measured in February, attributing 11% of flow to condensed steam yields an original steam composition that plots near the magmatic

water field of Giggenbach [1992]. This interpretation of only three isotopic data points is speculative, but the shift in these points is comparable to that observed in waters draining the crater of Mount St. Helens in the 1980s, which were attributed to a 10% mixture of magmatic steam in meteoric water [Shevenell and Goff, 1995]. If the steam component arose from boiling of a meteoric groundwater, the isotopic composition of streamflow would likely trend toward the left of the GMWL (Figure 6). Alternatively, if the isotopic shift was due to water-rock interaction, only a shift in oxygen would be observed, as shown by Symonds *et al.* [2003]. The isotopic data coupled with the evidence that streamflow and ice-melt rates were roughly consistent supports the interpretation that magmatic steam was able to exit the edifice and melt ice without the opportunity to condense in thermal or non-thermal groundwater, and thus we argue that SO<sub>2</sub> was largely unaffected by groundwater within the upper edifice as well. Rather, the small amount of scrubbing that did occur happened at the surface as the magmatic steam condensed and melted ice and snow from the glacier. This water built up in small surficial pools or perched reservoirs that drained continuously through the stream, but occasionally resulted in sediment-laden water/ice-block slurries that were observed as glacial outbursts and high streamflow events.

[26] Data collected in February 2009 points to an increase in scrubbing by meltwater at this time.



**Table 3.** Estimation of the Required Sulfur Scavenging by a Hypothetical Hydrothermal Brine at Redoubt Prior to the 15 March 2009 Eruption<sup>a</sup>

Date	Cum. Days	E SO <sub>2</sub> Rate <sup>b,c</sup> (t/d)	E CO <sub>2</sub> Rate <sup>b</sup> (t/d)	Exp. SO <sub>2</sub> , C/S = 2.4 (t/d)	Avg. Ice Loss <sup>d</sup> (m <sup>3</sup> /s)	Meltwater Estimate (10 <sup>6</sup> L/d)	Surficial SO <sub>2</sub> , Scrubbed, SO <sub>4</sub> <sup>2-</sup> = 1.5 g/L (t/d)	Loss SO <sub>2</sub> to Deep Brine (by Diff.) (t/d)	S Loss to Brine (t/d)	Cum. S Loss to Brine (t S)
13-Oct-08	0	28	1368	829	0.1	7.8	8	793	397	397
02-Nov-08	19	31	1220	739	0.1	7.8	8	701	351	7491
31-Jan-09	108	180	7326	4440	2.5	197	197	4063	2032	113476
02-Feb-09	109	157	3628	2199	2.5	197	197	1845	922	114953
07-Feb-09	114	88	9018	5465	2.5	197	197	5180	2590	123735
21-Feb-09	128	46	5980	3624	2.5	197	197	3381	1690	153701
27-Feb-09	134	34	5980 <sup>e</sup>	3624	2.5	197	197	3393	1697	163862

<sup>a</sup>Abbreviations are as follows: E SO<sub>2</sub>, emission of SO<sub>2</sub>; E CO<sub>2</sub>, emission of CO<sub>2</sub>; Cum., cumulative; Exp., expected; Avg., average; Diff., difference.

<sup>b</sup>Significant digits on emission rates have been retained to eliminate rounding errors when calculating cumulative loss of S to brine, and to be consistent with Werner et al. (submitted manuscript, 2012). Uncertainties for emission rates are estimated at ±20%, see text for details.

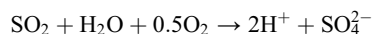
<sup>c</sup>October and November 2008 SO<sub>2</sub> emission rates determined by Interscan contouring, COSPEC was below detection limits.

<sup>d</sup>Calculated from the 6.6 × 10<sup>6</sup> m<sup>3</sup> of ice melt over 30 days in February 2009.

<sup>e</sup>There was no estimation of CO<sub>2</sub> emission rate on Feb 27th; this value is estimated to be the same as Feb. 21, 2009.

Photo documentation of increased glacial melting (Figure 2d), the decline in the already-low SO<sub>2</sub> emissions while CO<sub>2</sub> remained high (Figure 3a), and increasing concentrations of SO<sub>4</sub><sup>2-</sup> and decreasing pH in stream waters (Figure 3c) all support this hypothesis. The increased melting is thought to be a direct consequence of increased steam upflow through the volcanic edifice (Bleick et al., submitted manuscript, 2012), possibly due to clearing of flow paths as the result of a significant throughput of gas starting in late January, and not to conductive heating due to shallowing of magma (Bleick et al., submitted manuscript, 2012). In this regard it is important to note that ice-melt rates increased dramatically (up to nearly 60 m<sup>3</sup>/s) following the onset of eruption in mid-March when magma was present near the surface.

[27] Scrubbing by the stream water was calculated assuming quantitative conversion of SO<sub>2</sub> into dissolved SO<sub>4</sub><sup>2-</sup>:



For the average stream SO<sub>4</sub><sup>2-</sup> concentration during February of ~1.5 g/l, a streamflow of 1 m<sup>3</sup>/s would correspond to 86 t/d of scrubbed SO<sub>2</sub>; 197 t/d for the average meltwater production rates of 2.3 m<sup>3</sup>/s (or 197 × 10<sup>6</sup> L/d, Table 3) for February 2009 (this would increase to 329 t/d for the 3.8 m<sup>3</sup>/s in March, 2009). The estimates of SO<sub>2</sub> scrubbed by stream/meltwaters are similar to the decline in plume SO<sub>2</sub> emissions from late January to late February (~150 t/d) and support a direct correlation. The maximum estimated flow rates (10 m<sup>3</sup>/s) accompanied with the observed SO<sub>4</sub><sup>2-</sup> load would have had the capability to scrub 860 t/d had this flow rate

been steady over long time periods, yet this is not thought to be the case until perhaps late February 2009.

[28] The amount of SO<sub>2</sub> scrubbed is significantly less than the expected SO<sub>2</sub> emission based on CO<sub>2</sub> emissions and expected C/S ratios (Figure 3a and Table 3). The C/S ratio was estimated based on past degassing sequences at Redoubt and other Cook Inlet volcanoes, all of which converged on similar molar C/S ratios between 0.5 to 2 [Werner et al., 2011]. In retrospect, this assumption was reasonable as the syn- and post-eruptive C/S ratio was near the range originally expected (average of 2.4 as compared to 2 originally assumed). Assuming a molar C/S of 2.4 the expected SO<sub>2</sub> emission ranged from 740 to 5470 t/d in the pre-eruptive period (Table 3). The difference is much more than can apparently be attributed to increased meltwater scrubbing according to stream chemistry and our estimates above (Table 3). According to our calculations, surficial scrubbing into meltwater only accounted for up to 8% of the mismatch between the expected and observed SO<sub>2</sub> (Table 3).

[29] Calculations utilizing Henry's law solubility, however, suggest that the influx of meltwater near the summit in the precursory period was sufficient to dissolve more than the expected SO<sub>2</sub>. However, we argue that removing the amount of SO<sub>2</sub> needed to maintain a relatively constant C/S ratio between 30 to 60 over period of months (from October 2008 to early February 2009) while CO<sub>2</sub> emission rates increased by a factor of four seems somewhat unlikely. We therefore suggest that during this initial period of relatively stable C/S and greatly increasing emission rates, scrubbing of SO<sub>2</sub> into

meltwater near the surface had a minimal effect on the gas composition, which was largely controlled by deeper processes.

### 5.2.2. Scrubbing Deep Within or Below the Volcanic Edifice

[30] High C/S ratios could alternatively reflect scrubbing (through reaction with fluids or mineralization) of SO<sub>2</sub> in a deep magmatic-hydrothermal system, which would lie at >1 to ~3.5 km depth below the summit and above the mid-crustal magma storage region based on other systems within the Cascades and Aleutians [Symonds *et al.*, 2003]. Evidence for such fluid is that seismic tremor during the month preceding the eruption had a ‘hydrothermal’ character, consistent with the growth and collapse of bubbles (H. Buurman *et al.*, The seismicity of the 2009 Redoubt eruption, submitted to *Journal of Volcanology and Geothermal Research*, 2012). However, additional evidence suggests that such fluids were not significantly affecting gas emissions.

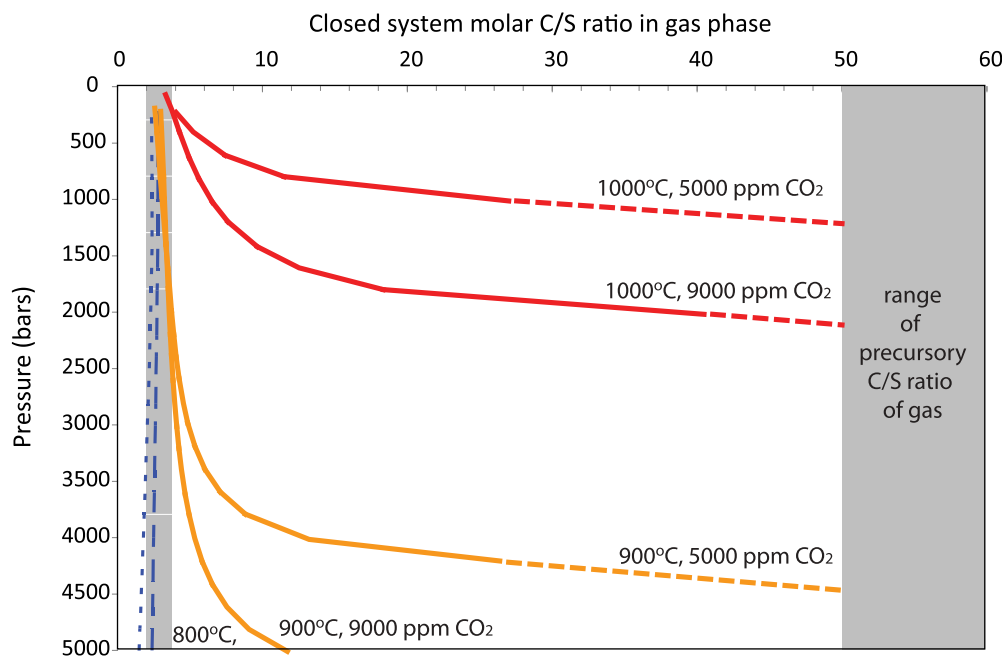
[31] As noted earlier, no thermal manifestations exist around Redoubt apart from in the central crater near the dome complex, and alteration in this region is minimal, whereas neighboring volcanoes and other glaciated volcanoes in the Cook Inlet and the Cascades do show evidence of active hydrothermal systems, mostly in the form of hot springs, persistent boiling point fumaroles, and large altered regions at the surface [Motyka *et al.*, 1993; Symonds *et al.*, 2003]. The quantity of magmatic-hydrothermal brine within or below the edifice is unknown, but was apparently not very efficient at removing sulfur when low emissions were measured in 2005 (molar C/S of 8 at a CO<sub>2</sub> emission rate of ~50 t/d [Doukas and McGee, 2007]. As gas emissions increase, the SO<sub>2</sub> scrubbing efficiency of a magmatic-hydrothermal system is expected to decline, as noted by Symonds *et al.* [2003]. Thus, molar C/S ratios should have decreased below 8 in October–November 2008, when a minimum of 1220 t/d of CO<sub>2</sub> was measured.

[32] In volcanoes with obvious hydrothermal systems, such as Mount Lassen and Mount Baker, hydrothermal gases like CO<sub>2</sub> and H<sub>2</sub>S [McGee *et al.*, 2001; Symonds *et al.*, 2003; Werner *et al.*, 2009] are prevalent, and sometimes emissions of over 100 t/d CO<sub>2</sub> are measured. If such a hydrothermal system boils off during a period of unrest, increases in CO<sub>2</sub> and H<sub>2</sub>S emissions are expected [Giggenbach, 1980], as was pointed out by Gerlach *et al.* [1994]. While speculative, the pilot reports

of strong H<sub>2</sub>S odors at ~35–110 km downwind of the volcano during September 2008, suggests that plume concentrations of H<sub>2</sub>S were high, perhaps over 10 ppmv at 35 km downwind (the concentration that is reported to give headaches, see [http://www.health.state.ny.us/environmental/chemicals/hydrogen\\_sulfide/docs/sulfide.pdf](http://www.health.state.ny.us/environmental/chemicals/hydrogen_sulfide/docs/sulfide.pdf)). In comparison, with our highest H<sub>2</sub>S emission rate measured (1230 t/d) (Werner *et al.*, submitted manuscript, 2012), concentrations of H<sub>2</sub>S reached approximately 2.5 ppmv at 6 km distance from the volcano. Therefore, if a magmatic-hydrothermal system existed within Redoubt, perhaps the initial reports of strong H<sub>2</sub>S odors point to its drying out in the earliest stages of unrest prior to the first airborne measurements.

[33] Symonds *et al.* [2003] also differentiate between volcanoes that emit SO<sub>2</sub> regularly and those that do not. The volcanoes discussed in Symonds *et al.* [2003], some of which support hydrothermal systems up to 3 km deep beneath the summit and have superheated fumaroles (Mount Baker, Mount Mageik, and Mount Griggs volcanoes), do not emit SO<sub>2</sub> according to Doukas and McGee [2007]. The fact that SO<sub>2</sub> was observed at Redoubt from the onset of measurements, even at relatively low emission rates, suggests that a dry pathway for ‘high temperature magmatic gases’ existed between the gas source and the surface.

[34] It is also worth considering the amount of sulfur scavenging needed to produce C/S ratios of 30–190 from the average value of 2.4. Subtracting the measured SO<sub>2</sub> emission rate and the amount scrubbed into the outflow stream from the expected SO<sub>2</sub> emission rate implies (on average) scrubbing of 1800 t/d S in the 30 days leading up to the eruption (Table 3). Cumulative S scavenged in the 5 months leading up to the eruption would have been on the order of 164 kt, or an average of 1220 t/d. These rates of sulfur scavenging are significantly higher than estimates from other volcanoes. For instance at Ruapehu volcano, 1.5 Mt of S was estimated to have been deposited in the hydrothermal system between the 1945 and 1995 eruptions [Christenson, 2000], which yields 82 t/d S on average. At Mount Baker, between 10 and 84 t/d are thought to be scrubbed on average [Symonds *et al.*, 2003]. It is unclear why a magmatic-hydrothermal system at Redoubt could be 2 orders of magnitude more efficient at scrubbing during a period of high gas flow rates. In fact, Symonds *et al.* [2001, 2003] clearly demonstrate that scrubbing efficiency declines as the gas/water ratio increases and, as pointed out by Shinohara [2008], scrubbing is thought to be minimal at



**Figure 8.** Modeled C/S ratios of the volatile phase accompanying the low-silica andesite during decompression. Solubility of CO<sub>2</sub> and S in the melt (see text) were calculated in 200 bar increments, and subtracted from estimated primary values to yield the composition of the coexisting volatile phase. Primary bulk volatile contents were estimated at either 5000 ppm CO<sub>2</sub> and 1600 ppm S (low estimate) or 9000 ppm CO<sub>2</sub> and 2400 ppm S (high estimate) (Werner et al., submitted manuscript, 2012). The dashed part of the lines indicate where the S solubility of the melt was greater than the primary bulk S content (i.e., all S could be dissolved in the melt), giving an infinitely high C/S value for the 200 bar interval. See text for further details.

volcanoes with high emission rates. Nevertheless, evidence for rapid deposition of alunite in equilibrium with magmatic SO<sub>2</sub> in the open fractures above the brittle-ductile transition have been found in fossil hydrothermal systems [Landis and Rye, 2005]. Thus, without further investigation, we cannot rule out the possibility that a magmatic-hydrothermal system could have scavenged sulfur in large quantities prior to the Redoubt eruption.

### 5.3. Primitive Magma Degassing

[35] An alternate hypothesis to scrubbing is that the high C/S ratios reflect the initial degassing of primitive CO<sub>2</sub>-rich magmas that intruded the mid-crust in the 5 months prior to eruption. Petrologic analysis of the erupted products showed that three magma types were erupted: a low silica andesite (LSA, 910 ± 31°C based on Fe-Ti oxides), an intermediate (ISA), and a high silica andesite (HSA, 799 ± 24°C based on Fe-Ti oxides, glass SiO<sub>2</sub> > 76 wt. %). The preferred model is that the LSA was the primary magma for the eruption, that it rose from an unknown depth, mixed with the HSA, and formed the ISA [Coombs et al., 2012]. The oxygen fugacity of the melts were ~NNO + 1.4 [Coombs et al., 2012].

[36] We calculated simple bulk C/S degassing trends by combining the results of CO<sub>2</sub> and S solubility models by Newman and Lowenstern [2002] and Baker and Moretti [2011], respectively, with changing pressure and temperature (Figure 8). Both a rhyolite and basalt were modeled for CO<sub>2</sub> solubility, and the composition of the LSA was used with the S solubility model. The models were relatively insensitive to composition as compared to temperature and pressure. Primary contents of CO<sub>2</sub> and S were assumed as 5000–9000 ppm and 1600–2400 ppm, respectively, and were calculated from bulk degassing and magma volumes erupted (Werner et al., submitted manuscript, 2012). At each step, any excess CO<sub>2</sub> or S that could not be dissolved in the melt was assumed to be present in a coexisting gas phase. The amount of S that could be dissolved in the LSA melt was determined using the sulfur content at anhydrite saturation (SCAS) model of Baker and Moretti [2011] which required setting  $fO_2$  to NNO + 1.5. Initial petrologic analysis suggests that anhydrite was not present in the 2009 samples [Coombs et al., 2012] although small anhydrite crystals were found in samples from the 1989–90 eruption [Swanson and Kearney, 2008]. Coombs et al. [2012] observed small blebs of an



immiscible Cu-Fe-S phase, though modeling of a sulfide saturated melt resulted in very low S solubility in the melt [Baker and Moretti, 2011], and thus uniformly low C/S ratios in the vapor phase. For simplicity, the model presented does not incorporate the effects of crystallization, which drives up primary volatile contents in the melt phase, and tends to shift C/S degassing curves to greater pressures. In addition, the crystallization or breakdown of S-bearing minerals would alter the sulfur budget and are not accounted for. We stress that the model results are limited in scope and should be taken only as a first-order parameterization of the effects of decompression and cooling on C/S ratios in the gas phase.

[37] The simple model shows the striking sensitivity to small changes in temperature of the melt. The initially high C/S gas ratios measured in the precursory period could have accompanied a high temperature LSA melt (1000°C) at relatively low pressures (up to ~1600 bars or 3.5 to 6 km depth, similar to the final equilibration depth determined by melt-plagioclase hygrometry [Coombs *et al.*, 2012]). However, at 900°C (i.e., the minimum estimated for the LSA), the curves shift to much greater pressure. Thus the results cannot be used to estimate a depth from which magma rose. Geophysical methods (both seismicity and deformation) suggested magma movement in the months prior to eruption between 18 and 32 km below the edifice, which would support deep magma involvement. The model shows good agreement with the final measured bulk C/S in gases for all temperature ranges, and demonstrates that if the hot LSA mixed with a cooler HSA (800°C) as suggested by petrologic data, the measured average gas composition of ~2.4 would quickly be obtained. Following this mixing process, the majority of CO<sub>2</sub> and S would be present in the vapor phase. Indeed this and the previous Redoubt eruption were thought to have been vapor-saturated with a sulfur-rich exsolved phase [Gerlach *et al.*, 1994; Werner *et al.*, submitted manuscript, 2012] throughout the eruption.

## 6. Conclusions

[38] We present here a pre-eruptive sequence of gas emissions from an arc volcano, including direct airborne measurements of CO<sub>2</sub> emissions starting six months prior to the 2009 Redoubt eruption. CO<sub>2</sub> emission rates up to 9018 t/d and C/S ratios  $\geq 30$  were measured in the months prior to the eruption, making these measurements critical for setting volcano alert levels. In addition, observations of

ice-melt rates and water discharge in the vent region and water chemistry were used together to evaluate the role of SO<sub>2</sub> scrubbing by meltwater near the surface. These data suggest that all or almost all of the streamflow represented drainage from a surficial, perched reservoir of condensed magmatic steam and glacial meltwater that had a residence time just long enough to allow pH neutralization (to ~5) and react with local rocks. The surficial perched reservoir scrubbed a few hundred tonnes/day of SO<sub>2</sub>, even though the waters had the capacity to scrub many thousands of t/d SO<sub>2</sub>, implying that high pre-eruptive C/S ratios in gas emissions reflected deeper processes.

[39] While we cannot rule out the possibility that sulfur was scavenged at least in part in a magmatic-hydrothermal system overlying the mid-crustal storage region, the strongest evidence against this hypothesis includes (1) the lack of thermal manifestations and of a hydrothermal water component in the stream water at Redoubt, (2) a low C/S ratio was measured in 2005 during a period of low emission, and hydrothermal scrubbing should have affected that measurement more than the measurements in this study, and (3) the large pre-eruptive emission rates observed (over 9000 t/d CO<sub>2</sub>) would result in a very high gas/water ratio which would argue against significant scrubbing, or would imply that scavenging happened at a very high average rate of 1220 t/d S over 5 months leading up to eruption, which is perhaps not reasonable. The high C/S in gas data can also be explained by decompressional degassing of an S-saturated low silica andesite that intruded into the mid-crust in the 6 months prior to the eruption, though the depth cannot be resolved from simple modeling. Mixing of this low silica andesite with high silica andesites in the mid-crust would have resulted in the average C/S composition observed during the eruption.

## Acknowledgments

[40] This work was supported by the USGS Volcano Science Center. The authors would like to thank Mark Huebner for water analyses, and Christoph Kern and Sandro Aiuppa for helpful reviews.

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