



RESEARCH LETTER

10.1002/2014GL060653

Key Points:

- Gas output from the Central Volcanic Zone of northern Chile
- Identification of a common magmatic end-member of Chilean volcanism
- Comparison between measured and petrologically estimated carbon/sulfur fluxes

Supporting Information:

- Readme
- Table S1
- Table S2
- Table S3

Correspondence to:

G. Tamburello,
giancarlo.tamburello@unipa.it

Citation:

Tamburello, G., T. H. Hansteen, S. Bredemeyer, A. Aiuppa, and F. Tassi (2014), Gas emissions from five volcanoes in northern Chile and implications for the volatiles budget of the Central Volcanic Zone, *Geophys. Res. Lett.*, *41*, doi:10.1002/2014GL060653.

Received 5 JUN 2014

Accepted 11 JUL 2014

Accepted article online 15 JUL 2014

Gas emissions from five volcanoes in northern Chile and implications for the volatiles budget of the Central Volcanic Zone

G. Tamburello¹, T. H. Hansteen², S. Bredemeyer², A. Aiuppa^{1,3}, and F. Tassi⁴

¹DiSTeM, Università di Palermo, Palermo, Italy, ²GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany, ³INGV, Sezione di Palermo, Palermo, Italy, ⁴Dipartimento di Scienze della Terra, Università di Firenze, Florence, Italy

Abstract This study performed the first assessment of the volcanic gas output from the Central Volcanic Zone (CVZ) of northern Chile. We present the fluxes and compositions of volcanic gases (H₂O, CO₂, H₂, HCl, HF, and HBr) from five of the most actively degassing volcanoes in this region—Láscar, Lastarria, Putana, Ollagüe, and San Pedro—obtained during field campaigns in 2012 and 2013. The inferred gas plume compositions for Láscar and Lastarria (CO₂/S_{tot} = 0.9–2.2; S_{tot}/HCl = 1.4–3.4) are similar to those obtained in the Southern Volcanic Zone of Chile, suggesting uniform magmatic gas fingerprint throughout the Chilean arc. Combining these compositions with our own UV spectroscopy measurements of the SO₂ output (summing to ~1800 t d⁻¹ for the CVZ), we calculate a cumulative CO₂ output of 1743–1988 t d⁻¹ and a total volatiles output of >20,200 t d⁻¹.

1. Introduction

The Chilean Andes is a 4500 km long segment of the Andean Cordillera, extending from the Arica and Parinacota regions to Cape Horn (16°S to 56°S), with more than 200 active (Quaternary) volcanoes distributed into four distinct zones [Stern, 2004; Thorpe and Francis, 1979; Thorpe, 1984].

The Chilean segment of the Central Volcanic Zone (CVZ; 17°S to 26°S, Figure 1) comprises a ~600 km long volcanic district and contains ~34 active volcanoes [Stern, 2004]. Farther to the south, the Southern Volcanic Zone (SVZ; 34°S to 46°30'S) includes at least 60 historically active volcanoes [Stern, 2004] which volcanism is associated with a 70 km thick crust and high degrees of magma differentiation [Hidreth and Moor bath, 1988; Davidson et al., 1990].

Despite the presence of several persistently degassing volcanoes, the present-day volcanic gas output of the CVZ remains poorly known. Gas composition data have been reported for several volcanoes [Tassi et al., 2009, 2011; Capaccioni et al., 2011; Aguilera et al., 2012], but fluxes of major volcanic gas species (H₂O and CO₂) have not been reported. Compared to other, better-characterized arc segments (e.g., Central American Volcanic Arc (CAVA) [Mather et al., 2006; Freundt et al., 2014] and SVZ [Voelker et al., 2014]), the paucity of gas flux measurements and poor knowledge of subducted sediment composition [Plank and Langmuir, 1998] result into an inadequate understanding of the recycling of volatiles along this sector of the Chilean volcanic front.

Here we report on the first combined assessment of volatiles emissions from five of the most active volcanoes of the CVZ in northern Chile. Using rapid deployment scanning Mini-DOAS (differential optical absorption spectroscopy) instruments [Galle et al., 2010] and a dual UV camera system [Kantzas et al., 2010], we obtained new data of the SO₂ output from the Putana, Láscar, Lastarria, Ollagüe, and San Pedro volcanoes (Figure 1 and Table S1 in the supporting information). These results were integrated with plume compositional data obtained using the INGV-type (Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy) Multicomponent Gas Analyzer System (MultiGAS), filter packs, and direct fumarolic gas sampling (Tables S2 and S3 in the supporting information) to indirectly calculate—for the first time—the fluxes of the following other volcanic species: H₂O, CO₂, H₂, HCl, HF, and HBr. Comparison of our results with gas composition data from other Chilean volcanoes (e.g., Villarrica [Shinohara and Witter, 2005; Sawyer et al., 2011]) suggests the presence of a common magmatic gas fingerprint across several thousands of kilometers of the arc. We further propose the first estimate of the total volcanic gas output from the CVZ in northern Chile.

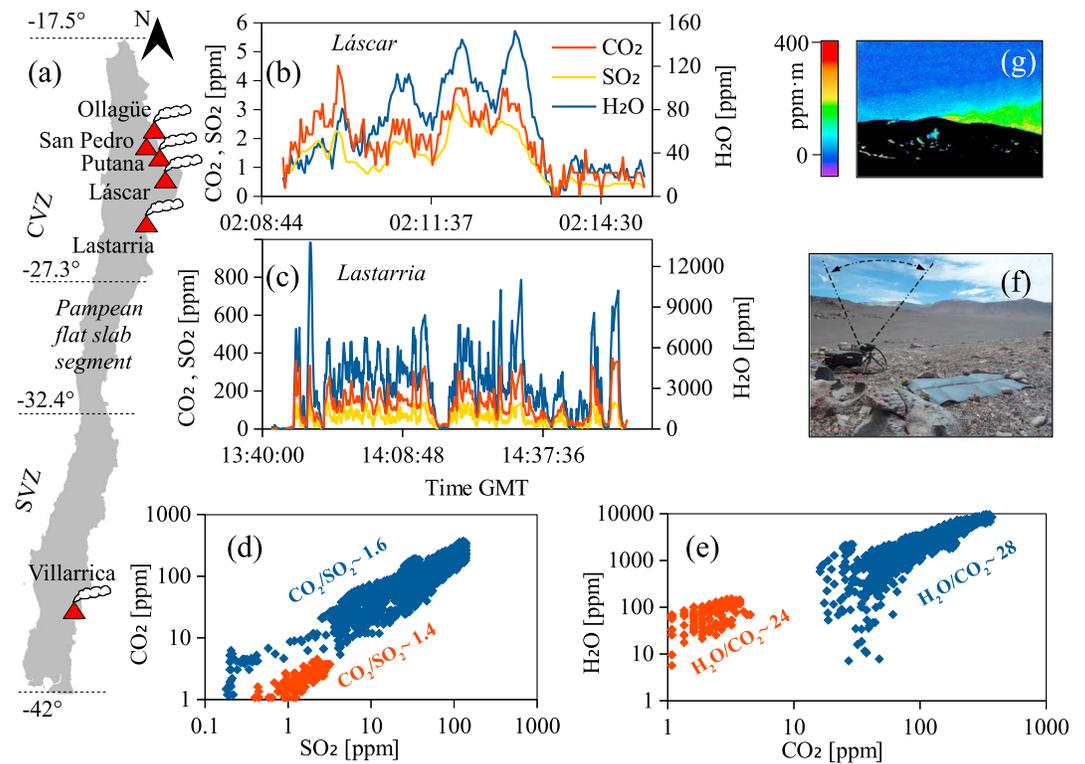


Figure 1. (a) Map of Chile showing the volcanoes of the CVZ and the SVZ targeted in this study. (b, c) Time series of CO₂, SO₂, and H₂O background-subtracted concentrations measured with the Multicomponent Gas Analyzer System (MultiGAS) at Láscar (Figure 1b) and Lastarria (Figure 1c). (d, e) Despite the significant temporal and spatial variabilities of concentrations, remarkably constant molar ratios were obtained at both Láscar (red) and Lastarria (blue). (f) Mobile scanning Mini-differential optical absorption spectroscopy (DOAS) instrument deployed at Lastarria. (g) SO₂ column densities measured at Putana volcano with an SO₂ camera on 5 December 2012.

2. Volcanic Activity

Láscar is a calc-alkaline stratovolcano located east of Salar de Atacama (23.37°S, 67.73°W) and is the most active volcano of the Chilean segment of the central Andes [Oppenheimer *et al.*, 1993]. Several small-to-moderate vulcanian eruptions have been recorded from Láscar since the midnineteenth century (some recently registered eruptions occurred in 2013, 2006–2007, 2005, 2002, 2000, 1994–1995, 1994, 1993–1994, 1993, and 1991–1992), most of which created ash columns with heights of up to a few kilometers above the summit. The activity of Láscar has been cyclic since 1984 [Matthews *et al.*, 1997]; in each cycle a lava dome is extruded into the active crater, accompanied by vigorous degassing through high-temperature fumaroles distributed on and around the dome. The Quaternary Lastarria volcano is located on the Chile-Argentina border at 25.17°S, 68.50°W and rises to 5706 m above sea level (asl). The north-northwest-trending edifice contains five nested summit craters. The youngest (<0.3 Myr) volcanic feature is a lava dome on the northern crater rim [Naranjo, 1986]. Although no historic eruption has been recorded, the youthful morphology of deposits and the ongoing uplift (~2.5 cm yr⁻¹) that began in 1996 [Pritchard and Simons, 2002; Froger *et al.*, 2007] support the active nature of Lastarria. Putana volcano is a 600 km² cone of andesitic-basaltic to dacitic lavas with a summit crater that is ~0.5 km in diameter at 5890 m asl. It has been characterized since the nineteenth century by persistent active degassing from four main summit fumarole fields, which feed a sustained steam plume [Casertano, 1963]. San Pedro (21.88°S, 68.14°W) is a composite basaltic andesite-to-dacitic volcano with several recorded historic eruptions, most recently in 1960 [e.g., O’Callaghan and Francis, 1986]. Steady fumarole activity on the upper western volcano flank has been documented from at least 2012 (Observatorio volcanológico de los Andes del Sur Monthly Reports). Ollagüe (21.30°S, 68.18°W) is also a composite volcano, consisting of high-K calc-alkaline rocks of dominantly andesitic to dacitic composition, but also comprises basaltic andesites [Feeley *et al.*, 1993]. The last eruption occurred in 1903, and the present-day persistent fumarole activity is associated with a summit lava dome.

Table 1. Summary Table of Derived Volatiles Output

Volcano	H ₂ O	CO ₂	SO ₂	H ₂ S	HCl	HF	HBr	Total (t d ⁻¹)	
Putana (t d ⁻¹)			68.5					68.5	
Lastarria (t d ⁻¹)	11,059	973	884	174	385	5.8	0.6	13,480	
Láscar (t d ⁻¹)	5,192	534	554	30	199	9.4	0.15	6,517	
Ollagüe (t d ⁻¹)			150					76	
San Pedro (t d ⁻¹)			161					81	
Total ^a	(t d ⁻¹)	16,251	1,506	1,818	204	604	15.2	0.76	>20,220
	(tyr ⁻¹)	6 × 10 ⁶	5.5 × 10 ⁵	6.7 × 10 ⁵					
Total CVZ ^b	(t d ⁻¹)	2.2–3.3 × 10 ⁴	1,743–1,988	1,818					
	(tyr ⁻¹)	8–12 × 10 ⁶	6.4–7.3 × 10 ⁵	6.7 × 10 ⁵					
Extrusive + Intrusive ^c	(tyr ⁻¹)		3.3–8.1 × 10 ⁵	5.3 × 10 ⁵					

^aCalculated from measured gas compositions and fluxes.

^bH₂O and CO₂ fluxes calculated using molar H₂O/CO₂ = 30–40 and CO₂/SO₂ = 0.9–2.2 for Putana, Ollagüe, and San Pedro volcanoes.

^cCalculated petrological volatiles output.

3. Results

3.1. Láscar

At the time of our field survey of Láscar in 2012 (during 4–7 December), a sustained steam plume was produced by the persistent fumarole field, which is located ~200 m below the rim of its active central crater. The MultiGAS was deployed on the crater's rim in order to measure the bulk plume composition. We detected a dilute plume with strongly correlated volcanic H₂O, CO₂, and SO₂ mixing ratios (Figure 1b). The CO₂/SO₂ and H₂O/CO₂ molar ratios ranged from ~1 to ~1.7 and from ~12 to ~34, respectively, during our monitoring period (Figure 1d). Sets of base-treated filter packs were simultaneously collected to derive the in-plume halogen/SO₂ ratios. Our 2012 results (HCl/SO₂ ~ 0.7, HF/SO₂ ~ 0.06, and HBr/SO₂ = 2.2 × 10⁻⁴) indicate a more F-poor gas than in 2003 (HCl/SO₂ ~ 0.6 and HF/SO₂ ~ 0.5 [Mather *et al.*, 2004]). The Láscar plume was measured for several hours on 3–7 December 2012 and on 2–4 and 8 December 2013 by placing one or two scanning Mini-DOAS stations at various distances from 2.5 to 11 km downwind of the summit. The overall SO₂ output over the two measurement periods was 554 ± 217 t d⁻¹ (mean ± standard deviation). Although SO₂ emissions from Láscar occasionally peak at ~2300 t d⁻¹ [Andres *et al.*, 1991; Mather *et al.*, 2004], our results agree well with previous results obtained during periods of low degassing [Andres *et al.*, 1991; Matthews *et al.*, 1997; Henney *et al.*, 2012].

3.2. Lastarria

There has been continuous fumarole activity at the summit (upper fields) and northwest flank (bottom field) of Lastarria since the earliest available records. The bottom field is located at ~5000 m asl and is the largest (~0.023 km²) emission area on the volcano. On 27 November 2012, we used the MultiGAS to characterize the chemical structure and heterogeneity of the bottom field. Our analysis reveals that the Lastarria bottom field has a homogeneous composition (see Figure 1c). The mean CO₂/SO₂ molar ratio was 1.6 (Figure 1d; range, 1.1–2.3), and the characteristic H₂O/CO₂ and H₂/H₂O ratios were 27.8 ± 2.8 and 6 ± 2 × 10⁻⁵, respectively. Our filter pack-based halogen/SO₂ molar ratios were HCl/SO₂ ~ 0.8, HF/SO₂ ~ 0.022, and HBr/SO₂ = 5 × 10⁻⁴. The plume was measured downwind of Lastarria for several hours on 27–29 November 2012 with the scanning Mini-DOAS stations placed about 8 km from the plume source. The wind speed at the plume height obtained using the Global Data Assimilation System model fitted well with our own anemometer data. The daily fluxes on these 3 days were 1917 ± 607, 473 ± 188, and 433 ± 314 t d⁻¹, respectively, with an overall value for the 3 days of 884 ± 779 t d⁻¹.

3.3. Putana, San Pedro, and Ollagüe

On 5 December 2012, we performed UV camera measurements at ~4.7 km from Putana crater (Figure 1g), which yielded an SO₂ output from this volcano of 40 ± 11 t d⁻¹ (Table 1). The plume was again measured for several hours on 5, 6, and 9 December 2013 using two scanning Mini-DOAS stations. The daily fluxes on

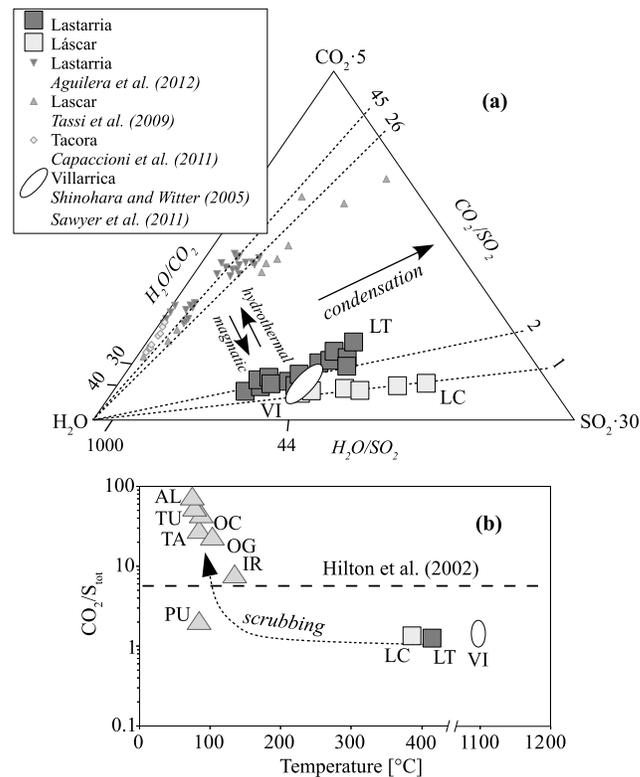


Figure 2. (a) Triangular H₂O-CO₂-SO₂ plot showing the water variability in Lastarria (LT) and Láscar (LC). Compositional data obtained in previous studies (Lastarria, Láscar, and Tacora) show a more hydrothermal nature of the sampled fumarolic gases. Gas compositions converge toward the composition of Villarrica high-temperature gas, which is less affected by water condensation. (b) Temperature dependence of CO₂/S_{tot} molar ratios in gas samples from Alitar (AL), Tupungatito (TU), Olca (OC), Ollagüe (OG), Tacora (TA), Irruputuncu (IR), Putana (PU), Láscar (LC), and Lastarria (LT) in the CVZ within northern Chile, and from Villarrica (VI) in the SVZ. Additional data are from Aguilera *et al.* [2012], Capaccioni *et al.* [2011], Benavente *et al.* [2013], Tassi *et al.* [2011], and Shinohara and Witter [2005].

2011] is typical of residual fluids formed after prolonged gas-water-rock interactions [Symonds *et al.*, 2001] and is therefore taken as representative of the hydrothermal compositional end-member.

Our Láscar and Lastarria results demonstrate considerable fluctuations of water contents (at nearly constant CO₂/S molar ratios) at both volcanoes during the measurement periods (Figure 2a). We ascribe this effect to variable extents of water loss—due to condensation—from the plume prior to the sampling associated with MultiGAS measurements. However, we notice that the more-hydrous and thus possibly less-fractionated compositions of the Lastarria and Láscar gas samples converge in Figure 2a toward the composition of Villarrica gas [Shinohara and Witter, 2005], and cluster at CO₂/SO₂ and H₂O/CO₂ molar ratios of 1–2 and 30–40, respectively. We conclude from Figure 2a that both the Lastarria and Láscar gas samples have a clear magmatic signature. This is in stark contrast with the more S-depleted (Figure 2a) and Cl-depleted (Figure 3) compositions seen in previous direct-sampling studies performed at Láscar (2002–2006 [Tassi *et al.*, 2009]) and Lastarria (2006–2009 [Aguilera *et al.*, 2012]), which supported the presence of gases with a more hydrothermal nature. This difference may merely reflect dissimilar sampling conditions: while the 2012 MultiGAS observations concentrated on the “bulk” plume, the earlier direct sampling studies (2002–2009) concentrated on a small number of easily accessible, low-flux fumaroles. These fumaroles are potentially more affected by secondary processes (e.g., scrubbing), making their composition potentially unrepresentative of bulk gas emissions. Alternatively, the more magmatic signature of the 2012 gases, relative to pre-2009

these 3 days were 55 ± 14, 133 ± 104, and 77 ± 24 t d⁻¹, respectively, with an overall value of 97 ± 78 t d⁻¹. Similarly, the plumes of San Pedro and Ollagüe were measured for several hours using scanning Mini-DOAS instruments on 10 and 12 December 2013 and on 11 and 12 December 2013, respectively; the daily fluxes were 182 ± 188 and 150 ± 140 t d⁻¹ at San Pedro (overall, 161 ± 150 t d⁻¹), and 47 ± 18 and 220 ± 181 t d⁻¹ at Ollagüe (overall, 150 ± 162 t d⁻¹) (Table 1). Unfortunately no MultiGAS or filter pack data are available for these volcanoes.

4. Discussion

4.1. Magmatic Gas End-Member Composition of Chilean Volcanism

Figures 2, 3 compare our Láscar and Lastarria data set with the results of previous observations at Chilean volcanoes, from Tacora in the north (17°43.2'S) to Villarrica in the south (39°25.2'S). To identify the nature (magmatic versus hydrothermal) of the measured gases, we report in Figure 2a two distinct gas end-members: Villarrica gas and Tacora gas. Gas samples from Villarrica, which originate from a persistent lava lake, represent the best available compositional proxy for the magmatic gas end-member in Chile. In contrast, the CO₂-rich (CO₂/SO₂ ~ 27.9) signature of Tacora gas [Capaccioni *et al.*,

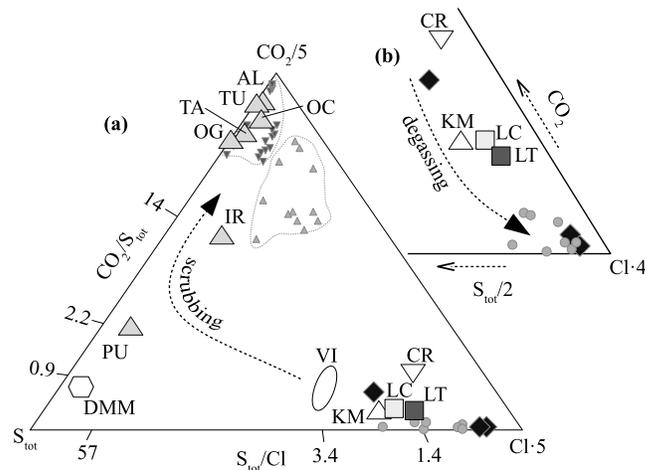


Figure 3. (a) Triangular $\text{CO}_2\text{-S}_{\text{tot}}\text{-HCl}$ plot of the molar gas compositions of northern Chile volcanoes and Villarrica. The compositions of the melt inclusions from Villarrica (dark gray diamonds) and residual glasses from Llaima (small gray circles) are shown. Previous data of Láscar [Tassi *et al.*, 2009] and Lastarria [Aguilera *et al.*, 2012] fumaroles are displayed within the dotted gray lines. For comparison, the Costa Rica magmatic gas (CR, white triangle) from A. Aiuppa *et al.* (The Costa Rica-Nicaragua volcanic segment: along-arc variations in volcanic gas chemistry and an improved CO_2 budget, submitted to *Earth and Planetary Science Letters*, 2014) is also shown. Compositional data of depleted mid-ocean ridge basalt mantle (DMM, white hexagon) are from Saal *et al.* [2002]. (b) Magnification of the lower right part of the triangular plot highlighting a degassing trend from a CO_2 -rich end-member to a Cl-rich end-member.

observations, may indicate a real evolution of the volcanic systems: degassing and seismic activities have only recently resumed at Láscar [Global Volcanism Program, 1994], and ground uplift has intensified at Lastarria in the past few years [Froger *et al.*, 2007].

The plot of $\text{CO}_2/\text{S}_{\text{tot}}$ versus outlet temperature in Figure 2b offers additional evidence for identifying the magmatic versus hydrothermal origin of the 2012 gases. The $\text{CO}_2/\text{S}_{\text{tot}}$ molar ratios in Chilean gas samples vary by 2 orders of magnitude, from ~ 80 in low-temperature gases ($< 150^\circ\text{C}$) down to ~ 1 at magmatic temperatures (Figure 2b). This trend, which has recently been established similarly for the Northwest Pacific Arc Region [Aiuppa *et al.*, 2012], is interpreted to reflect the increasing action of secondary processes at low temperature; under these conditions, the reactive S and Cl species are selectively removed by gas scrubbing [Symonds *et al.*, 2001], masking the pristine magmatic gas signature (Figures 2b and 3). In contrast,

secondary processes exert only marginal effects at the high-temperature conditions of the 2012 Lastarria and Láscar samples. The magmatic signature of these gases is further demonstrated by comparison with the volatile compositions of the melt inclusions and residual glasses from Villarrica [Witter *et al.*, 2004] and Llaima [De Maisonville *et al.*, 2012] (Figure 3). The melt inclusions and residual glasses data record the evolution of volatiles during magma ascent and degassing, from a deep-seated magma with an inferred initial CO_2 content of 2480 ± 1400 ppm (for Villarrica [Witter *et al.*, 2004]) to a more-degassed, Cl-rich magma represented by the residual glasses (Figure 3). The compositions of Lastarria and Láscar gas samples overlap with the compositions of melt inclusions, reinforcing the magmatic nature of the gases, further suggesting that shallow magma degassing is the source of gas emissions at both volcanoes.

In view of the similarity between the SVZ (Villarrica) and CVZ (Lastarria and Láscar) data, we argue that a common magmatic gas end-member—with $\text{H}_2\text{O}/\text{CO}_2 = 30\text{--}40$, $\text{CO}_2/\text{S}_{\text{tot}} = 0.9\text{--}2.2$, and $\text{S}_{\text{tot}}/\text{HCl} = 1.4\text{--}3.4$ —can be considered to be characteristic of the entire Chilean arc. This fits very well with volatile compositions measured or inferred for primitive melt inclusions from the SVZ, which typically have $\text{H}_2\text{O}/\text{CO}_2$ ratios of 30–75 [Watt *et al.*, 2013], and typical S/Cl ratios of 1 to 2 (range: 0.1–3) [Wehrmann *et al.*, 2014a]. Our inferred magmatic $\text{CO}_2/\text{S}_{\text{tot}}$ signature for Chile (0.9–2.2) is approximately fourfold smaller than that proposed by Hilton *et al.* [2002] (Figure 2b), which is probably due to their data set being dominated by low-temperature gases. With our new compositional data, the Chilean arc sits at the CO_2 -poor margin of volcanic arc gas compositions [Fischer, 2008]. Our Chilean gas compositions also match well the accepted range of arc gas $\text{S}_{\text{tot}}/\text{HCl}$ compositions, the majority of which cluster at ~ 2 [Aiuppa, 2009]. The relatively uniform gas composition from the CVZ and the SVZ supports the presence of similar volatile contributions to Chilean magmas from mantle and subduction-derived fluids, and relatively uniform composition of the latter along the entire arc length. Although along-arc variations have been identified in the SVZ in both extent of crustal contamination [Hidreth and Moorbath, 1988], isotopic signature of magmas [Jacques *et al.*, 2014], and S-Cl volatile contents in melt inclusions [Wehrmann *et al.*, 2014a], however, the trace-element proxies (e.g., Ba/La) for slab contribution show far more uniform behavior in SVZ [Wehrmann *et al.*, 2014b] and CVZ [Matthews *et al.*, 1994, 1999; Richards *et al.*, 2013] magmas than in other arc segments (e.g., CAVA [Sadofsky *et al.*, 2008]). Detailed

geochemical studies show that the SVZ slab component is also uniform across the arc [Jacques *et al.*, 2013]. Thus, we interpret the similarly low Ba/La ratios (15–25) in SVZ and CVZ magmas to imply a uniform, more modest (relative to CAVA) contribution from slab-derived fluids, fitting well the low-carbon signature of Chilean volcanic gases seen in this study. We admit, however, that since only three volcanoes with high-T gases were measured, more observations are needed to corroborate our hypothesis.

4.2. Volatiles Output From the CVZ

Given the magmatic nature of the gas samples discussed above, we now attempt to constrain the total output of volatiles from the CVZ. The scanning Mini-DOAS and UV camera measurements made at Lastarria, Láscar, Putana, San Pedro, and Ollagüe lead to a cumulative SO₂ output from the five volcanoes of ~1800 t d⁻¹ (or 6.6 × 10⁵ t yr⁻¹) in 2012–2013 (Table 1). Three additional volcanoes (Irruputuncu, Olca, and Tacora) in this arc segment are reported to comprise high-temperature fumaroles [Capaccioni *et al.*, 2011; Tassi *et al.*, 2011]. The strongest S emitter of the three volcanoes is probably Irruputuncu, a volcano that typically vents S-rich gas [Tassi *et al.*, 2011]. However, even Irruputuncu has regularly failed to produce any statistically significant signal in OMI (Ozone Monitoring Instrument) satellite data sets [Carn *et al.*, 2013], implying an SO₂ flux of ≤190 t d⁻¹ (considering the OMI detection limit quoted by Fioletov *et al.* [2011]). Assuming that each of the three volcanoes emits ~100 t d⁻¹ on average, the cumulative SO₂ output would only rise to a maximum of ~2100 t d⁻¹. We therefore consider the cumulative SO₂ output from Lastarria, Láscar, Putana, San Pedro, and Ollagüe as a good proxy for the total SO₂ output from the CVZ (Table 1). We avoid using extrapolation techniques to quantify unmeasured emissions [e.g., Hilton *et al.*, 2002] because the validity of the power law assumption of Brantley and Koepenick [1995] has recently been questioned [Mori *et al.*, 2013]. However, we argue that if the recently recorded peak (2300 t d⁻¹) SO₂ emissions from Láscar were to be taken into account [Andres *et al.*, 1991; Mather *et al.*, 2004], the cumulative CVZ SO₂ output would increase to ~3500 t d⁻¹ (1.3 × 10⁶ t yr⁻¹). With our assumptions, the total CVZ SO₂ output of 6.6 × 10⁵ to 1.3 × 10⁶ t yr⁻¹ would therefore correspond to 19–40% of the extrapolated annual flux from the Andes (~3 × 10⁶ t yr⁻¹ [Andres and Kasgnoc, 1998; Hilton *et al.*, 2002]), and to 3.3–5.1% of the estimated global SO₂ fluxes from subduction zone volcanoes [Andres and Kasgnoc, 1998; Hilton *et al.*, 2002; Shinohara, 2013]. For comparison, this inferred CVZ SO₂ output is of the same order as the combined SO₂ output from Villarica and Llaima (~3.5 × 10⁵ t yr⁻¹ [Mather *et al.*, 2004; Sawyer *et al.*, 2011]), which are the two most actively degassing volcanoes in the SVZ (a similar rate of quiescent SO₂ degassing (~7.66 × 10⁵ t yr⁻¹) was recently proposed by Voelker *et al.* [2014] for the SVZ). Considering the unknown but potentially additional large contributions from recently erupting volcanoes (e.g., Puyehue-Cordón Caulle and Copahue), SVZ is probably the strongest degassing source in Chile.

The measured SO₂ fluxes combined with the volcanic gas compositions of Láscar and Lastarria provide the basis for quantifying the outputs of other major volatiles. Despite its apparent long inactivity, Lastarria currently represents the most important gas source in the CVZ, with a total volatiles output (~13,500 t d⁻¹) that is twice that of Láscar (~6517 t d⁻¹) (Table 1). These two volcanoes have a combined CO₂ output of ~1500 t d⁻¹. We additionally estimate, based on a total SO₂ output of ~1800 t d⁻¹ and a magmatic CO₂/S_{tot} ratio of 0.9–2.2, that the total CO₂ output from the CVZ is 1743–1988 t d⁻¹. Based on these calculations, northern Chile contributes only a minor fraction (~1%) of the total CO₂ output from subaerial volcanoes worldwide [Burton *et al.*, 2013]. We stress that this CO₂ budget does not take into account the contribution of diffuse soil degassing, which is poorly constrained for Chilean volcanoes, except for Villarica. At this volcano, CO₂ soil degassing was found to be negligible compared to summit crater degassing [Witter *et al.*, 2004].

In an attempt to evaluate how representative our 2012–2013 measurements are of the long-term degassing behavior of the CVZ, we compared the present-day gas fluxes of Table 1 with petrological volatiles output inventories. In the last 12 Myr, the rate of magma extrusion along the ~330 km long Central Andean trench (from 12°30′S to 22°30′S) has been ~2.2 × 10⁻⁶ km³ km⁻¹ yr⁻¹ [Crisp, 1984]. A comparable rate (10–13 × 10⁻⁶ km³ km⁻¹ yr⁻¹) was estimated by Voelker *et al.* [2011] for the SVZ. If we tentatively extend the Central Andean magma extrusion rate to northern Chile and scale it to the total trench length of 1500 km, we then obtain an order of magnitude estimate for the CVZ magma eruption rate of ~3.3 × 10⁻³ km³ yr⁻¹. For a magma density of 2800 kg m⁻³ (andesite) and for preruptive and posteruptive magmatic S contents of ~4100 and ~300 mg kg⁻¹, respectively (as for S in primitive undegassed melt inclusions and

residual glasses of Láscar [Andres *et al.*, 1991]), this would correspond to a time-averaged SO₂ output of $\sim 7.6 \times 10^4 \text{ t yr}^{-1}$ from CVZ volcanism. The proposed (mass) ratio between intrusive and extrusive volcanism for the Andes is $\sim 6/1$ [Crisp, 1984], which leads to a total (intrusive + extrusive) SO₂ output of $\sim 5.3 \times 10^5 \text{ t yr}^{-1}$ (Table 1). Finally, the magmatic gas CO₂/S_{tot} ratio of $\sim 0.9\text{--}2.2$ (molar) converts the SO₂ output into a total CO₂ output of $3.3\text{--}8.1 \times 10^5 \text{ t yr}^{-1}$ (Table 1). The resulting annual SO₂ and CO₂ petrological outputs are in close agreement with our present-day (2012–2013) outputs of $\sim 6.4\text{--}7.3 \times 10^5$ and $6.3 \times 10^5 \text{ t yr}^{-1}$, respectively (Table 1). While our calculations here should be taken as order of magnitude estimates (given the overall uncertainties in the input parameters), the similarity of these values suggests (i) that the present-day fluxes are representative of the long-term CVZ degassing behavior and (ii) that Láscar and Lastarria contribute most of the CVZ gas output. The absence of Deep Sea Drilling Project/Ocean Drilling Program reference sites offshore of northern Chile, and the lack of knowledge about the compositions of subducted materials [Plank and Langmuir, 1998], precludes quantitative comparison between our measured CO₂ output and the CO₂ input flux at the trench (as recently obtained for other arc segments [Freundt *et al.*, 2014; Voelker *et al.*, 2014]).

5. Conclusions

The Láscar and Lastarria volcanoes in northern Chile emitted in 2012–2013 a typically magmatic gas phase whose compositions of major species (H₂O/CO₂ = 30–40, CO₂/S_{tot} = 0.9–2.2; S_{tot}/HCl = 1.4–3.4) resembled those of high-temperature open-vent emissions from Villarrica in the SVZ. This similarity suggests stable magmatic volatiles contents and origin along several thousands of kilometers of the southern Andean trench. We calculate that the CVZ presently emits more than 10^7 t yr^{-1} H₂O-rich volcanic gases into the atmosphere, essentially in a quiescent (noneruptive) form. Our measured CO₂ ($\sim 1500 \text{ t d}^{-1}$) and SO₂ ($\sim 1800 \text{ t d}^{-1}$) outputs in 2012–2013 correspond, respectively, to $\sim 1.3\%$ and $\sim 3.3\text{--}5.1\%$ of the corresponding global gas outputs from arc volcanoes. These present-day fluxes closely match the petrologically estimated long-term outputs obtained from intrusive + extrusive magma fluxes and preeruptive S contents.

Acknowledgments

The authors wish to thank D.M. Pyle and an anonymous reviewer for their very helpful reviews of this paper. This work was supported by the DECADE initiative of the Deep Carbon Observatory. Further funding was obtained from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007/2013)/ERC grant agreement 1305377 (Principal Investigator, Alessandro Aiuppa), and from the Helmholtz Foundation through the "Remote Sensing and Earth System Alliance" (HA-310/IV010). The data for this paper are available in the supporting information and upon request to the corresponding author.

The Editor thanks David Pyle and an anonymous reviewer for their assistance in evaluating this paper.

References

- Aguilera, F., F. Tassi, T. Darrah, S. Moune, and O. Vaselli (2012), Geochemical model of a magmatic-hydrothermal system at the Lastarria volcano, northern Chile, *Bull. Volcanol.*, *74*, 119–134.
- Aiuppa, A. (2009), Degassing of halogens from basaltic volcanism: Insights from volcanic gas observations, *Chem. Geol.*, *263*, 99–109, doi:10.1016/j.chemgeo.2008.08.022.
- Aiuppa, A., G. Giudice, M. Liuzzo, G. Tamburello, P. Allard, S. Calabrese, L. Chaplygin, A. J. S. McGonigle, and Y. Taran (2012), First volatile inventory for Gorely volcano, Kamchatka, *Geophys. Res. Lett.*, *39*, L06307, doi:10.1029/2012GL051177.
- Andres, R. J., and A. D. Kasgnoc (1998), A time-averaged inventory of subaerial volcanic sulfur emissions, *J. Geophys. Res.*, *103*, 25,251–25,262, doi:10.1029/98JD02091.
- Andres, R. J., W. I. Rose, P. R. Kyle, S. de Silva, P. Francis, M. Gardeweg, and H. M. Roa (1991), Excessive sulfur dioxide emissions from Chilean volcanoes, *J. Volcanol. Geotherm. Res.*, *46*, 323–329.
- Benavente, O., F. Tassi, F. Gutiérrez, O. Vaselli, F. Aguilera, and M. Reich (2013), Origin of fumarolic fluids from Tupungatito Volcano (Central Chile): Interplay between magmatic, hydrothermal, and shallow meteoric sources, *Bull. Volcanol.*, *75*, 746, doi:10.1007/s00445-013-0746-x.
- Brantley, S. L., and K. W. Koepnick (1995), Measured carbon emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes, *Geology*, *23*, 933–936.
- Burton, M. R., G. M. Sawyer, and D. Granieri (2013), Deep carbon emissions from volcanoes, *Rev. Mineral. Geochem.*, *75*, 323–354, doi:10.2138/rmg.2013.75.11.
- Capaccioni, B., F. Aguilera, F. Tassi, T. Darrah, R. J. Poreda, and O. Vaselli (2011), Geochemical and isotopic evidences of magmatic inputs in the hydrothermal reservoir feeding the fumarolic discharges of Tacora volcano (northern Chile), *J. Volcanol. Geotherm. Res.*, *208*, 77–85, doi:10.1016/j.jvolgeores.2011.09.015.
- Carn, S., N. A. Krotkov, K. Yang, and A. J. Krueger (2013), Measuring global volcanic degassing with the Ozone Monitoring Instrument (OMI), in *Remote Sensing of Volcanoes and Volcanic Processes: Integrating Observation and Modelling, Spec. Publ.*, vol. 380, edited by D. M. Pyle, T. A. Mather, and J. Biggs, pp. 229–257, Geological Society, London, U. K.
- Casertano, L. (1963), General characteristics of active Andean volcanoes and a summary of their activities during recent centuries, *Bull. Seismol. Soc. Am.*, *53*, 1415–1433.
- Crisp, J. A. (1984), Rates of magma emplacement and volcanic output, *J. Volcanol. Geotherm. Res.*, *20*, 177–211.
- Davidson, J. P., N. J. McMillan, S. Moorbath, G. Woerner, R. S. Harmon, and L. Lopez-Escobar (1990), The Nevados de Payachata volcanic region (18°S/69°W, N. Chile). II. Evidence for widespread crustal involvement in Andean magmatism, *Contrib. Mineral. Petrol.*, *105*, 412–432.
- de Maisonnewe, C., M. A. Bouvet, O. B. Dungan, and A. Burgisser (2012), Insights into shallow magma storage and crystallization at Volcán Llaima (Andean Southern Volcanic Zone, Chile), *J. Volcanol. Geotherm. Res.*, *211*–212, 76–91.
- Feeley, T. C., J. P. Davidson, and A. Armendia (1993), The volcanic and magmatic evolution of Volcan Ollagüe, a high-K, late Quaternary stratovolcano in the Andean Central Volcanic Zone, *J. Volcanol. Geotherm. Res.*, *54*, 221–245.

- Fioletov, V. E., C. A. McLinden, N. Krotkov, M. D. Moran, and K. Yang (2011), Estimation of SO₂ emissions using OMI retrievals, *Geophys. Res. Lett.*, *38*, L21811, doi:10.1029/2011GL049402.
- Fischer, T. P. (2008), Fluxes of volatiles (H₂O, CO₂, N₂, Cl, F) from arc volcanoes, *Geochem. J.*, *42*, 21–38.
- Freundt, A., I. Grevenmeyer, W. Rabbel, T. H. Hansteen, C. Hensen, H. Wehrmann, S. Kutterolf, R. Halama, and M. Frische (2014), Volatile (H₂O, CO₂, Cl, S) budget of the Central American subduction zone, *Int. J. Earth Sci. (Geol. Rundsch.)*, doi:10.1007/s00531-014-1001-1.
- Froger, J. L., D. Remy, S. Bonvalot, and D. Legrand (2007), Two scales of inflation at Lastarria-Cordon del Azufre volcanic complex, central Andes, revealed from ASAR-ENVISAT interferometric data, *Earth Planet. Sci. Lett.*, *255*(1–2), 148–163.
- Galle, B., M. Johansson, C. Rivera, Y. Zhang, M. Kihlman, C. Kern, T. Lehmann, U. Platt, S. Arellano, and S. Hidalgo (2010), Network for Observation of Volcanic and Atmospheric Change (NOVAC)—A global network for volcanic gas monitoring: Network layout and instrument description, *J. Geophys. Res.*, *115*, D05304, doi:10.1029/2009JD011823.
- Global Volcanism Program (1994), Láscaar, volcanic activity reports, BGVN 18:04. [Available at <http://www.volcano.si.edu>.]
- Henney, L., L. Rodríguez, and I. Watson (2012), A comparison of SO₂ retrieval techniques using mini-UV spectrometers and ASTER imagery at Láscaar volcano, Chile, *Bull. Volcanol.*, *74*(2), 589–594, doi:10.1007/s00445-011-0552-2.
- Hidreth, W., and S. Moorbath (1988), Crustal contributions to arc magmatism in the Andes of Central Chile, *Contrib. Mineral. Petrol.*, *98*, 455–489.
- Hilton, D. R., T. P. Fischer, and B. Marty (2002), Noble gases and volatile recycling at subduction zones, *Rev. Mineral. Geochem.*, *47*, 319–370.
- Jacques, G., K. Hoernle, J. Gill, F. Hauff, H. Wehrmann, D. Garbe-Schönberg, P. van den Bogaard, I. Bindeman, and L. E. Lara (2013), Across-arc geochemical variations in the Southern Volcanic Zone, Chile (34.5–38.0°S): Constraints on mantle wedge and slab input compositions, *Chem. Geol.*, *371*, 27–45, doi:10.1016/j.gca.2013.05.016.
- Jacques, G., K. Hoernle, J. Gill, H. Wehrmann, I. Bindeman, and L. E. Lara (2014), Geochemical variations in the Central Southern Volcanic Zone, Chile (38–43°S): The role of fluids in generating arc magmas, *Chem. Geol.*, *371*, 27–45, doi:10.1016/j.chemgeo.2014.01.015.
- Kantzas, E. P., A. J. S. McGonigle, G. Tamburello, A. Aiuppa, and R. G. Bryant (2010), Protocols for UV camera volcanic SO₂ measurements, *J. Volcanol. Geotherm. Res.*, *194*, 55–60, doi:10.1016/j.jvolgeores.2010.05.003.
- Mather, T. A., V. I. Tsanev, D. M. Pyle, A. J. S. McGonigle, C. Oppenheimer, and A. G. Allen (2004), Characterization and evolution of tropospheric plumes from Láscaar and Villarrica volcanoes, Chile, *J. Geophys. Res.*, *109*, D21303, doi:10.1029/2004JD004934.
- Mather, T. A., D. M. Pyle, V. I. Tsanev, A. J. S. McGonigle, C. Oppenheimer, and A. G. Allen (2006), A reassessment of current volcanic emissions from the Central American arc with specific examples from Nicaragua, *J. Volcanol. Geotherm. Res.*, *149*, 97–311, doi:10.1016/j.jvolgeores.2005.07.021.
- Matthews, S. J., A. P. Jones, and M. C. Gardeweg (1994), Láscaar volcano, northern Chile: Evidence for steady-state disequilibrium, *J. Petrol.*, *59*, 72–82.
- Matthews, S. J., M. C. Gardeweg, and R. S. J. Sparks (1997), The 1984 to 1996 cyclic activity of Láscaar volcano, northern Chile: Cycles of dome growth, dome subsidence, degassing and explosive eruptions, *Bull. Volcanol.*, *59*, 72–82.
- Matthews, S. J., R. S. J. Sparks, and M. C. Gardeweg (1999), The piedras grandes—soncor eruptions, Láscaar Volcano, Chile; Evolution of a zoned magma chamber in the Central Andean upper crust, *J. Petrol.*, *40*(12), 1891–1919, doi:10.1093/ptroj/40.12.1891.
- Mori, T., H. Shinohara, K. Kazahaya, J. Hirabayashi, T. Matsushima, T. Mori, M. Ohwada, M. Odoi, H. Iino, and M. Miyashita (2013), Time-averaged SO₂ fluxes of subduction-zone volcanoes: Example of a 32 years exhaustive survey for Japanese volcanoes, *J. Geophys. Res. Atmos.*, *118*, 8662–8674, doi:10.1002/jgrd.50591.
- Naranjo, J. A. (1986), Geology and evolution of the Lastarria volcanic complex, north Chilean Andes, MSc thesis, The Open Univ., Milton Keynes, Bucks., U. K.
- O'Callaghan, L. J., and P. W. Francis (1986), Volcanological and petrological evolution of San Pedro volcano, Provincia El Loa, north Chile, *J. Geol. Soc. London.*, *143*, 275–286.
- Oppenheimer, C., P. W. Francis, D. A. Rothery, and R. W. T. Carlton (1993), Infrared image analysis of volcanic thermal features: Láscaar volcano, Chile 1984–1992, *J. Geophys. Res.*, *98*, 4269–4286, doi:10.1029/92JB02134.
- Plank, T., and T. P. Langmuir (1998), The chemical composition of subducting sediment and its consequences for the crust and mantle, *Chem. Geol.*, *145*, 325–394.
- Pritchard, M. E., and M. Simons (2002), A satellite geodetic survey of large-scale deformation of volcanic centres in the central Andes, *Nature*, *418*, 167–171.
- Richards, J. P., F. Jourdan, R. A. Creaser, G. Maldonado, and S. A. DuFrane (2013), Geology, geochemistry, geochronology, and economic potential of Neogene volcanic rocks in the Laguna Pedernal and Salar de Aguas Calientes segments of the Archibarca lineament, northwest Argentina, *J. Volcanol. Geotherm. Res.*, *268*, 47–73, doi:10.1016/j.jvolgeores.2013.04.004.
- Saal, A. E., E. H. Hauri, C. H. Langmuir, and M. R. Perfit (2002), Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of the Earth's upper mantle, *Nature*, *419*, 451–455, doi:10.1038/nature01073.
- Sadofsky, S. J., M. V. Portnyagin, K. Hoernle, and P. van den Bogaard (2008), Subduction cycling of volatile and trace elements through the Central American volcanic arc: Evidence from melt inclusions, *Contrib. Mineral. Petrol.*, *155*(4), 433–456, doi:10.1007/s00410-007-0251-3.
- Sawyer, G. M., G. G. Salerno, J. S. Le Blond, R. S. Martin, L. Spampinato, T. J. Roberts, T. A. Mather, M. L. I. Witt, V. I. Tsanev, and C. Oppenheimer (2011), Gas and aerosol emissions from Villarrica volcano, Chile, *J. Volcanol. Geotherm. Res.*, *203*, 62–75.
- Shinohara, H. (2013), Volatile flux from subduction zone volcanoes: Insights from a detailed evaluation of the fluxes from volcanoes in Japan, *J. Volcanol. Geotherm. Res.*, doi:10.1016/j.jvolgeores.2013.10.007.
- Shinohara, H., and J. Witter (2005), Volcanic gases emitted during mild Strombolian activity of Villarrica volcano, Chile, *Geophys. Res. Lett.*, *32*, L20308, doi:10.1029/2005GL024131.
- Stern, C. R. (2004), Active Andean volcanism: Its geologic and tectonic setting, *Rev. Geol. Chile*, *31*(2), 161–206.
- Symonds, R. B., T. M. Gerlach, and M. H. Reed (2001), Magmatic gas scrubbing: Implications for volcano monitoring, *J. Volcanol. Geotherm. Res.*, *108*, 303–341.
- Tassi, F., F. Aguilera, O. Vaselli, E. Medina, D. Tedesco, A. Delgado Huertas, R. Poreda, and S. Kojima (2009), The magmatic- and hydrothermal-dominated fumarolic system at the Active Crater of Láscaar volcano, northern Chile, *Bull. Volcanol.*, *71*, 171–183.
- Tassi, F., F. Aguilera, O. Vaselli, T. Darrach, and E. Medina (2011), Gas discharges from four remote volcanoes in northern Chile (Putana, Olca, Irruputuncu and Alitar): A geochemical survey, *Ann. Geophys.*, *54*(2), doi:10.4401/ag-5173.
- Thorpe, R. S. (1984), The tectonic setting of active Andean volcanism, in *Andean Magmatism: Chemical and Isotopic Constraints*, Shiva Geological Series, edited by R. S. Harmon and B. A. Barreiro, pp. 5–8, Shiva Publications, Nantwich, U. K.
- Thorpe, R. S., and P. W. Francis (1979), Variations in Andean andesite compositions and their petrogenetic significance, *Tectonophysics*, *57*, 53–80.

- Voelker, D., S. Kutterolf, and H. Wehrmann (2011), Comparative mass balance of volcanic edifices at the southern volcanic zone of the Andes between 33°S and 46°S, *J. Volcanol. Geotherm. Res.*, *205*, 114–129, doi:10.1016/j.jvolgeores.2011.03.011.
- Voelker, D., H. Wehrmann, S. Kutterolf, K. Iyer, W. Rabbel, J. Geersen, and K. Hoernle (2014), Constraining input and output fluxes of the southern Central Chile Subduction Zone: Water, chlorine, sulfur, *Int. J. Earth Sci.*, doi:10.1007/s00531-014-1002-0.
- Watt, S. F. L., D. M. Pyle, T. A. Mather, and J. A. Naranjo (2013), Arc magma compositions controlled by linked thermal and chemical gradients above the subducting slab, *Geophys. Res. Lett.*, *40*, 2550–2556, doi:10.1002/grl.50513.
- Wehrmann, H., K. Hoernle, G. Jacques, D. Garbe-Schönberg, K. Schumann, J. Mahlke, and L. E. Lara (2014a), Volatile (sulphur and chlorine), major, and trace element geochemistry of mafic to intermediate tephros from the Chilean Southern Volcanic Zone (33–43°S), *Int. J. Earth Sci.*, doi:10.1007/s00531-014-1006-9.
- Wehrmann, H., K. Hoernle, D. Garbe-Schönberg, G. Jacques, J. Mahlke, and K. Schumann (2014b), Insights from trace element geochemistry as to the roles of subduction zone geometry and subduction input on the chemistry of arc magmas, *Int. J. Earth Sci.*, doi:10.1007/s00531-013-0917-1.
- Witter, J. B., C. Victor, P. Kress, J. Delmelle, and J. Stix (2004), Volatile degassing, petrology, and magma dynamics of the Villarrica Lava Lake, Southern Chile, *J. Volcanol. Geotherm. Res.*, *134*, 303–337.