

INVITED REVIEW

Fluxes of volatiles (H₂O, CO₂, N₂, Cl, F) from arc volcanoes

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This review gives an overview of the estimates of volatile emissions from arc and mid-ocean ridge volcanoes to the atmosphere and hydrosphere with particular focus on H₂O, CO₂, N₂, Cl and F. The gas compositions of high temperature (>500°C) fumaroles are compiled and used to derive magmatic H₂O/SO₂, CO₂/SO₂, HCl/SO₂ and HF/SO₂ ratios on an arc-by-arc basis to obtain new estimates of major volatile fluxes from arcs globally. The estimate of F flux from arcs is two orders of magnitude smaller than the amount of F released from mid ocean ridges whereas the arc Cl flux exceeds the ridge flux. An important observation is that globally the water budget of subduction zones seems to be balanced and the amount of water degassed through arc volcanism is within the estimates of the amount of water released from the slab below the volcanic front. Recent work that focused on the Central American arc shows that detailed knowledge of the subduction input compositions, coupled with gas emission studies is critical to further constrain the fate of volatiles during the subduction processes.

Keywords: volcanoes, fluxes, water, halogens, sources

INTRODUCTION

Volatiles are transferred from the Earth's mantle to the atmosphere, the hydrosphere and crust through eruptive and non-eruptive subaerial and submarine volcanic activity. Volatiles are also recycled from the surface back to the Earth's mantle via subduction. Quantification of volatile degassing through volcanoes and estimation of their source components (mantle vs. surface) bears fundamental information on a number of issues in the Earth sciences ranging from the evolution of the Earth's atmosphere to the potential origin of geochemical heterogeneities in the mantle. Noble gases are a critical part of estimating the fluxes of other volatiles to the atmosphere by combining, for example, the mid-ocean ridge (MOR) ³He flux of Craig *et al.* (1975) with the CO₂/³He ratio of oceanic basalt to arrive at MOR CO₂ flux (Marty and Jambon, 1987). The application of noble gases to constraining the sources and fluxes of volatiles from subduction zones has recently been reviewed by Hilton *et al.* (2002). Deriving subduction volatile fluxes from melt inclusion studies combined with magma emplacement rates has recently been reviewed by Wallace (2005) and Kerrick (2001) reviewed the present and past nonanthropogenic CO₂ flux from the solid Earth.

Although a large number of SO₂ flux measurements using the Correlation Spectrometer (COSPEC) have been made since the instrument was first pointed at a volcano (Mt. Mihara, Japan) by Moffat *et al.* (1972) and Stoiber's first estimate of global volcanic SO₂ (Stoiber and Jepsen, 1973), there are still large data gaps particularly for volcanoes in remote areas. This is certainly improving with better satellite remote sensing technology (Bluth *et al.*, 1993; Khokhar *et al.*, 2005) and smaller, cheaper ground-based instruments such as the mini DOAS (Galle *et al.*, 2002). Because SO₂ is the easiest gas to measure remotely (high abundance in the plume, low atmospheric background and strong absorption in the UV), its global volcanic flux has been comparatively well constrained. This is also true for CO₂ where recent estimates generally fall within the range of earlier ones. The flux estimates of other major volatiles, still vary by several orders of magnitude (H₂O) or have not received much attention (HCl, HF).

The purpose of this review is to provide the reader with an overview of the work that has been done in the field of volatile flux estimates from volcanoes. Gas chemistry from high temperature (>500°C), magmatic fumaroles world-wide (1970's to 2002) is compiled to determine representative, magmatic H₂O/SO₂, CO₂/SO₂, N₂/SO₂, HCl/SO₂ and HF/SO₂ ratios on an arc-by-arc basis for new estimates of H₂O, CO₂, N₂, HCl and HF fluxes. The water flux, in particular, is discussed in more detail with implications for the water cycle in subduction

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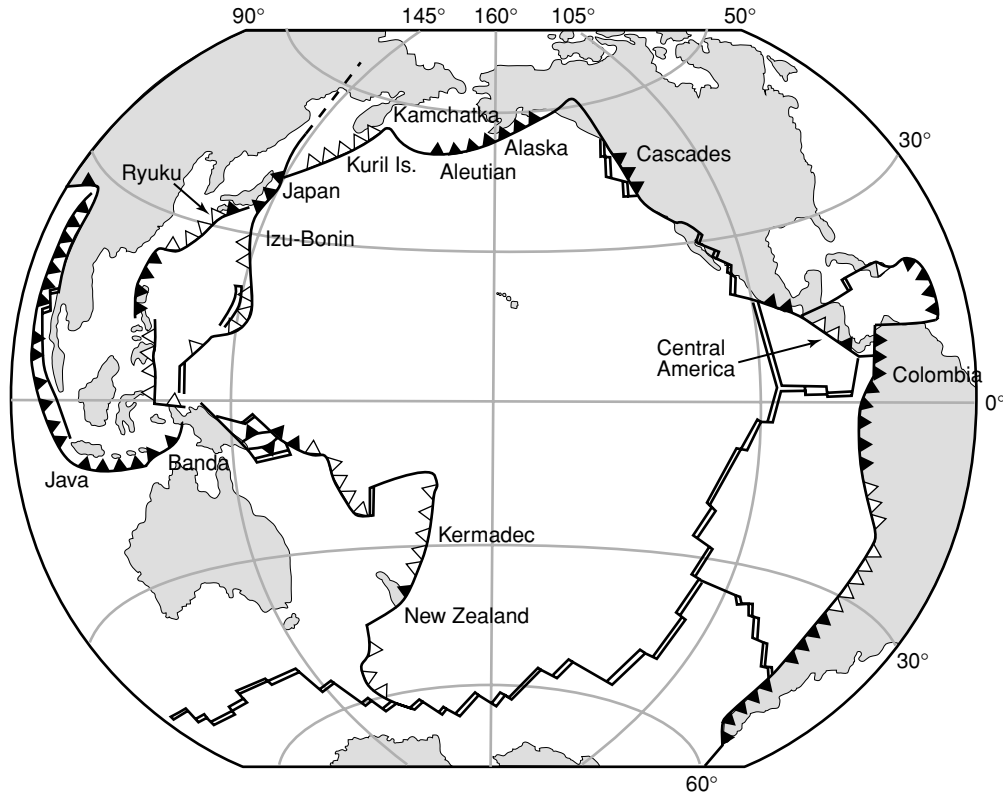


Fig. 1. Arcs that have high temperature (>400°) fumaroles with data compiled in Table 1. Italy is not shown. Modified from Hilton et al. (2002).

zones. After discussing global volatile emissions, the review focuses on some recent studies done in the Central American arc, that provide tighter constraints on both the input into the subduction zone and the output through volcanoes.

GLOBAL VOLCANIC VOLATILE FLUXES

Quantifying volcanic volatile fluxes, in particular for greenhouse gases such as CO₂, is critical for studies that are concerned with global element cycles. Berner and Lasaga, (1989) note that calculating the rate of degassing of CO₂ due to igneous and metamorphic process is a major problem when modeling the global carbon cycle. Although CO₂ degassing from volcanic arcs, mid-ocean ridges and to a lesser extent plumes is now relatively well constrained (within a factor of about two), the CO₂ flux from continental rifts remains largely unknown. Most global volcanic volatile flux estimates rely a) on magma emplacement rates, degrees of melting coupled with known or estimated volatile abundances in the source region of the melts or b) on sporadic point measurements of gas emissions rates (SO₂) from erupting or passively degassing volcanoes coupled with measured or estimated

volatile ratios to arrive at fluxes of gases other than SO₂. Extrapolation of both types of estimates to global emissions is still burdened with large uncertainties and accounting for extreme point source emissions, such as the 18 × 10⁶ tons emitted from Miyakejima volcano, Japan from 2000 to 2003 (Kazahaya et al., 2004) remains a challenge. This is true particularly for species other than SO₂, CO₂ and ³He which are affected by hydrothermal or seawater contributions (H₂O, Cl and F), air contamination (N₂, Ar, Ne), or are extremely variable in volcanic emissions (H₂, CH₄ and CO). Despite these uncertainties, current knowledge of volcanic volatile emissions allows for careful incorporation of these data into global element cycles.

Volatile fluxes from volcanic arcs

Correlation spectrometers (COSPEC) are the standard instruments used to measure volcanic SO₂ fluxes from volcanoes. These instruments were first developed in the 1960s to measure pollution emitted from industrial and chemical plants (as SO₂ and NO₂), but their utility for volcanic flux measurements was recognised shortly thereafter. The COSPEC was first used at Mt. Mihara volcano, Japan, in April 1971. Today, COSPEC measurements re-

Table 1. Gas chemistry of high temperature fumaroles world-wide (mol% total gas) and gas ratios used in flux calculations

Volcano Arc T (°C)	Mount St Helens Cascades 710	Augustine Aleutians 870	Momotombo C. America 844	Momotombo C. America 747	Poas C. America 940	Galeras N. South Am. 358	Galeras N. South Am. 642
Date	Symonds <i>et al.</i> , 1994	Symonds <i>et al.</i> , 1990	Giggenbach, 1996	Elkins <i>et al.</i> , 2006	Rowe <i>et al.</i> , 1992	Feb-1993	Giggenbach, 1996
Ref.							
H ₂ O (%)	98.9	84.77	95.05	96.25	95	89.6	91.5
CO ₂	0.88	2.27	2.38	2.53234906	1.35	7.8312	5.98
SO ₂	0.27	6.98	0.7	0.2334981	2.83	1.2792	0.8415
H ₂ S			0.49			0.53976	0.5725
HCl	0.15	1.01	0.35	0.52757577	0.38	0.3848	0.716
HF	0.03	0.086	0.029	0.03838822	0.015	0.038064	0.062
H ₂	0.4	0.54	0.87	0.35167164	0.9	0.23712	0.285
CH ₄	0.00003			<0.00003	0.0004	0	
CO	0.003	0.016	0.025	0.01121797	0.012		0.0136
NH ₃				7.2133E-05		0.0029744	
N ₂	0.12	0.11	0.08	0.05528918	0.1	0.047944	0.041
Ar	0.000025	0.0025		0.00010983		9.36E-05	
O ₂				<0.00005		0	
He				0.00005		0.000156	0.0003
Total	100.75	95.78	99.97	100.00	100.58	99.96	100.01
CO ₂ /SO ₂	3.259	0.325	3.400	10.845	0.477	6.122	7.106
median	3.250	0.320	3.400			6.614	
mean	3.250		4.907			6.614	
STD			3.086			0.492	
HCl/SO ₂	0.556	0.145	0.500	2.259	0.134	0.301	0.851
median			1.197			0.576	
mean	3.250		0.965			0.576	
STD			0.656			0.275	
N _{2,exc} /SO ₂	0.441	0.001	0.114	0.218	0.035	0.035	0.049
median			0.127			0.042	
mean	0.441		0.123			0.042	
STD			0.053			0.007	
H ₂ O/SO ₂	366.3	12.1	135.8	412.2	33.6	70.0	108.7
median		0.320	135.7			89.3	
mean			193.8			89.4	
STD			113.1			19.3	
HF/SO ₂	0.111	0.012	0.041	0.164	0.005	0.029	0.073
median		0.320	0.041			0.052	
mean			0.070			0.052	
STD			0.048			0.022	

Table 1. (continued)

Volcano	Satsuma Iwojima	Satsuma Iwojima	Usu	Showa Shinzan	Tokachi	Unzen
Arc	Japan	Japan	Japan	Japan	Japan	Japan
T (°C)	885	880	690	800	505	818
Date	Nov-93					1992
Ref.	Goff and McMurtry, 2000	Giggenbach, 1996	Giggenbach, 1996	Giggenbach, 1996	Giggenbach, 1996	Ohba <i>et al.</i> , 1994
H ₂ O (%)	97.8	97.3	99.3	98	93.1	95.5
CO ₂	0.3432	0.51	0.36	1.2	1.152	2.7
SO ₂	0.8712	0.818	0.032	0.043	3.257	0.7
H ₂ S	0.03476	0.164	0.018	0.0004	2.146	
HCl	0.3916	0.5306	0.034	0.053	0.276	0.26
HF	0.08954	0.0277	0.006	0.024	0.0345	
H ₂	0.451	0.607	0.2	0.63	0.012	0.78
CH ₄	0	0.0004	0.00057	0.00071	0.00001	
CO	0	0.00172	0.00005	0.00033	0.00011	0.028
NH ₃	0	0.00013	0.0003			
N ₂	0.011396	0.008	0.0104	0.057	0.0224	0.046
Ar	0.00005	0.000058	0.0001	0.00025	0.00007	
O ₂	0.00005	<0.0005	<0.0001			
He	0.000008	0.000006	0.000002		0.000017	
Total	99.99	99.96	99.96	100.01	100.00	100.01
CO ₂ /SO ₂	0.394	0.623	11.250	27.907	0.354	3.857
median	2.240					
mean	7.398					
STD	4.444					
HCl/SO ₂	0.449	0.649	1.063	1.233	0.085	0.371
median	0.549					
mean	0.642					
STD	0.178					
N _{2,es} /SO ₂	0.011	0.007	0.200	1.093	0.006	0.066
median	0.038					
mean	0.230					
STD	0.175					
H ₂ O/SO ₂	112.3	118.9	3103.1	2279.1	28.6	136.4
median	127.7					
mean	963.1					
STD	556.9					
HF/SO ₂	0.103	0.034	0.187	0.558	0.011	0.000
median	0.068					
mean	0.149					
STD	0.087					

Volcano	Volcano Arc	Volcano Aeolian	Volcano Aeolian	Volcano Aeolian	Volcano Aeolian	Volcano Aeolian	Volcano Aeolian	Kudryavy Kurile	Kudryavy Kurile	Alaid Kurile
<i>T</i> (°C)	546	620	858	858	858	858	858	940	920	700
Date	May-95		1991	1991	1991	1991	1991	Feb-92	Aug-95	
Ref.	Goff and McMurtry, 2000	Giggenbach, 1996	Giggenbach and Matsuo, 1991	Giggenbach and Matsuo, 1991	Giggenbach and Matsuo, 1991	Giggenbach and Matsuo, 1991	Giggenbach and Matsuo, 1991	Taran <i>et al.</i> , 1995	Fischer <i>et al.</i> , 1998	Menyailov <i>et al.</i> , 1986
H ₂ O (%)	92.6	86.1	85.8	85.8	85.8	85.8	85.8	94.4	95.3	97.16
CO ₂	7.0744	11.9	12.4	12.4	12.4	12.4	12.4	1.7976	1.15	1.61
SO ₂	0.048914	0.68	0.68	0.68	0.68	0.68	0.68	1.7976	2.05	0.2
H ₂ S	0.12136	0.48	0.53	0.53	0.53	0.53	0.53	0.1792	0.39	
HCl	0.042772	0.453	0.4331	0.4331	0.4331	0.4331	0.4331	0.4592	0.74	0.042
HF	0.010434	0.101	0.1207	0.1207	0.1207	0.1207	0.1207	0.0252	0.096	0.014
H ₂	0.040478	0.151	0.20022	0.20022	0.20022	0.20022	0.20022	1.1816	0.775	0.94
CH ₄	0	0.00001	0.00001136	0.00001136	0.00001136	0.00001136	0.00001136	<0.000112	<0.000005	<0.00042
CO	0.011	0.011	0.011218	0.011218	0.011218	0.011218	0.011218	0.00065	0.00084	0.018
NH ₃	0.0009028	0.00056	0	0	0	0	0			
N ₂	0.059644	0.1068	0.11076	0.11076	0.11076	0.11076	0.11076	0.13328	0.025	0.18
Ar	0.0003182	0.000112	0.0001136	0.0001136	0.0001136	0.0001136	0.0001136	0.001008	0.00009	0.00057
O ₂	0.0017834	<0.0002	0	0	0	0	0	0.0224	0.0176	
He	0.0000518	0.000115	0.00011928	0.00011928	0.00011928	0.00011928	0.00011928		0.000014	0.0000065
Total	100.00	99.98	100.29	100.29	100.29	100.29	100.29	100.00	100.54	100.16
CO ₂ /SO ₂	144.629	17.500	18.235	18.235	18.235	18.235	18.235	1.000	0.561	8.050
median	17.868							0.915		
mean	17.868							2.096		
STD	0.368							1.195		
HCl/SO ₂	0.874	0.666	0.637	0.637	0.637	0.637	0.637	0.255	0.361	0.210
median	0.666							0.308		
mean	0.652							6.311		
STD	0.015							3.914		
N _{2,exc} /SO ₂	0.959	0.150	0.156	0.156	0.156	0.156	0.156	0.052	0.010	0.786
median	0.156							0.033		
mean	0.153							0.152		
STD	0.003							0.127		
H ₂ O/SO ₂	1893.1	126.6	126.2	126.2	126.2	126.2	126.2	52.5	46.5	485.8
median	126.4							269.2		
mean	126.4							610.9		
STD	0.221							317.5		
HF/SO ₂	0.213	0.149	0.178	0.178	0.178	0.178	0.178	0.014	0.047	0.070
median	0.163							0.058		
mean	0.163							1.418		
STD	0.014							0.949		

Table 1. (continued)

Volcano	Kluichevskoi Kamchatka	Tolbachik Kamchatka	Avacha Kamchatka	Papandayan Java	Merapi Java	Merapi Java	Levotolo Banda
Arc	1100	1020	473	400	803	575	490
T (°C)		1976	1994		1994		1984
Date	Giggenbach, 1996	Taran <i>et al.</i> , 1987	Taran <i>et al.</i> , 1995	Giggenbach, 1996	Giggenbach <i>et al.</i> , 2001	Giggenbach <i>et al.</i> , 2001	Poorter <i>et al.</i> , 1993
Ref.							
H ₂ O (%)	97.73	98	94.8	96	88.7	93.4	76.6
CO ₂	0.12	0.04	2.26	2.94	5.56	4.74	12
SO ₂	0.09	0.05	2.72	0.675	0.98	0.51	8.69
H ₂ S	0.002			0.29	0.134	0.59	
HCl	1.42	1.06	0.17	0.125	0.60794	0.19998	0.61
HF	0.25	0.28	0.003	0.0033	0	0.02772	0.037
H ₂	0.59	0.55	0.05	0.014	0.50059	0.16566	0.54
CH ₄	<0.0001	0.0000004	0.0003	0.00006	0	0.0005775	0.0002
CO		0.0001	0.0002	0.00003	0.023504	0.00462	0.36
NH ₃				0.00049	0	0.001584	
N ₂	0.004		0.112	0.055	3.6047	0.3894	
Ar	0.000032		0.00043	0.000039	0.048477	0.007524	
O ₂				<0.0002	0.017967	0.0033	
He		0.00012	0.0000076	0.000025	0.00004746	0.00001914	0.00003
Total	100.21	99.98	100.12	100.10	100.18	100.04	98.84
CO ₂ /SO ₂	1.333	0.800	0.831	4.356	5.673	9.294	1.381
median				5.015			
mean				5.176			
STD				1.640			
HCl/SO ₂	15.778	21.200	0.063	0.185	0.620	0.392	0.070
median				0.289			
mean				0.317			
STD				0.121			
N _{2,exc} /SO ₂	0.030	0.000	0.035	0.079	1.700	0.173	0.000
median				0.126			
mean				0.488			
STD				0.405			
H ₂ O/SO ₂	1085.9	1960.0	34.9	142.2	90.5	183.1	8.8
median				116.4			
mean				106.2			
STD				37.6			
HF/SO ₂	2.778	5.600	0.001	0.005	0.000	0.054	0.004
median				0.005			
mean				0.016			
STD				0.013			

Volcano Arc	White Island Kermadec	Ngauruhoe Kermadec	Erta Ale African Rift	Kilauea Hawaii
<i>T</i> (°C)	495	640	1131	307
Date	1990		1974	1997
Ref.	Giggenbach, 1996	Giggenbach, 1996	Giggenbach, 1996	Fischer, unpubl.
H ₂ O (%)	92.0	96.0	79.4	92.1
CO ₂	6.0100	1.6050	9.9	6.25
SO ₂	1.0000	1.0200	7.8	1.57
H ₂ S	0.6000	0.6800		
HCl	0.2400	0.2500	0.7	0.8
HF	0.0028			0.00269
H ₂	0.0400	0.1420	0.75	0.00439
CH ₄	0.0014	0.0000		<0.00003
CO		0.0042	0.27	<0.00004
NH ₃	0.0064			
N ₂	0.0390	0.1500	0.18	0.0026
Ar	0.000056	0.001050	0.001	0.00001
O ₂	<0.0001	<0.0030		0.0003
He	0.000021	0.000022		0.000135
Total	99.94	99.86		100.73
CO ₂ /SO ₂	6.010	1.574	1.269	3.981
median	3.792			
mean	3.792			
STD	2.218			
HCl/SO ₂	0.240	0.245	0.090	0.510
median	0.243			
mean	0.243			
STD	0.003			
N _{2,exc} /SO ₂	0.037	0.106	0.018	0.001
median	0.071			
mean	0.071			
STD	0.035			
H ₂ O/SO ₂	92.0	94.1	10.2	58.7
median	93.06			
mean	93.06			
STD	1.059			
HF/SO ₂	0.003	0	0	0.002
median	0.001			
mean	0.001			
STD	0.001			

Notes: Gas ratios, medians, means and STD are calculated for each arc with the all data available for the arc. If more than one sample is available for one volcano, each is weighed equally for calculating the arc compositions. For each arc, the median, mean and STD is shown in the left-most column of each arc heading. For example six gas samples are available for the Japan arc and the median, mean and STD of all these samples are shown in the first column on Table 2.2. High temperature gases from rift and hot spot are also shown for comparison.

Table 2. Volatile emissions from arcs ($\times 10^9$ mol/yr), calculated using ratios of high T fumaroles (Table 1) and arc-by-arc SO_2 flux (Hilton *et al.*, 2002)

	Andes	Aleutians	Central America	Indonesia	Italy	Japan	Kamchatka-Kuriles	Kermadec	PNG	Philippines	Antilles	Total Arcs	Global (+20.6%)
SO_2	47.30	0.34	21.30	1.88	27.00	23.30	1.67	15.30	100.90	18.20	4.41	262	315
CO_2	312.85	0.11	72.42	9.43	482.43	52.20	1.53	58.01	505.96	91.26	14.99	1601	1931
HCl	27.24	0.05	25.49	0.54	17.99	12.79	0.51	3.71	29.12	5.25	5.28	128	154
N_2	1.97	0.0005	2.70	0.24	4.22	0.89	0.05	1.09	12.74	2.30	0.56	27	32
H_2O	4228.10	0.11	2892.24	218.77	3412.72	2975.14	449.49	1423.80	11741.35	2117.87	598.82	30058	36250
HF	2.45	0.11	0.88	0.01	4.40	1.59	0.10	0.02	0.46	0.08	0.18	10	12

Note: because not all arcs have volatile flux data and additional 20.6% is added to the estimates to arrive at a global flux (Hilton *et al.*, 2002). For PNG and Philippines no high T gas data are available and the Indonesian arc values were used for flux calculations. For the Antilles no high T gas data are available and the Central America arc values were used for flux calculations.

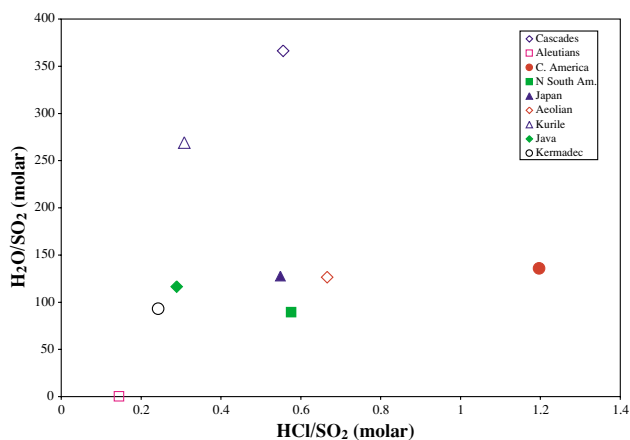


Fig. 2. Median molar $\text{H}_2\text{O}/\text{SO}_2$ and HCl/SO_2 ratios of high temperature fumarole emissions from Table 1.

main the basis for the majority of global volcanic volatile flux estimates (Hilton *et al.*, 2002) and provide the most extensive data set regarding volcanic gas fluxes (Andres and Kasgnoc, 1998).

The first global estimate of the annual contribution of SO_2 to the atmosphere by non-erupting volcanoes was exclusively based on measurements of Central American volcanoes (Stoiber and Jepsen, 1973). Their estimate of 10×10^{12} g/yr (1.6×10^{11} mol/yr) is very similar to much later estimates of 15.2×10^{12} g/yr (Berresheim and Jaeschke, 1983), 18.7×10^{12} g/yr (Stoiber *et al.*, 1987), 20×10^{12} g/yr (Graf *et al.*, 1997), $15\text{--}21 \times 10^{12}$ g/yr (Halmer *et al.*, 2002) and 13.4×10^{12} g/yr by Andres and Kasgnoc (1998). Andres and Kasgnoc (1998) compiled SO_2 flux data measured by COSPEC (9.7×10^{12} g/yr) and by TOMS (3.7×10^{12} g/yr). Considering the COSPEC SO_2 flux alone, more than 99% of the total flux is emitted from passively degassing volcanoes. Including the TOMS SO_2 flux, 71% of the total SO_2 flux is emitted by passively degassing volcanoes.

SO_2 flux data measured at individual volcanoes can be combined with measurements of elemental ratios (SO_2/x where $x = \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{He}$ etc.) to provide flux data for species which cannot be measured directly (see Hilton *et al.* (2002)). A potentially serious caveat of this approach is that in arcs where measurements of elemental ratios are sparse or absent, the resulting fluxes may be burdened with significant errors. The use of median ratios, may alleviate this problem to some extent (Hilton *et al.*, 2002; Fischer and Marty, 2005) but only if a large number of samples are available. An alternative approach is to use only samples from high temperature (>400 and preferably $>700^\circ\text{C}$) fumaroles for each arc system, rather than all available data from low temperature emissions and hot springs. Due to the magmatic temperatures of the emis-

Table 3. Compilation of volatile fluxes from arcs (10^9 mol/yr)

SO ₂	CO ₂	HCl	N ₂	H ₂ O	HF	Reference
292						Stoiber and Jepsen, 1973
240						Berrensheim and Jaeschke, 1983
203						Andres and Kasgnoc, 1998
	2500					Marty and Tolstikhin, 1998
	700					Allard, 1992
	3100					Sano and Williams, 1996
	1500					Varecamp <i>et al.</i> , 1992
226		25–3500			26–320	Halmer <i>et al.</i> , 2002
315	1600		20	81200		Hilton <i>et al.</i> , 2002
		127		5560		Ito <i>et al.</i> , 1983
563		197		17000		Wallace, 2005
			0.64			Sano <i>et al.</i> , 2001
315	1931	154	32	36250	12	This study

Note: the values of the Halmer study consider 75% of the global flux to be arc related and only consider HCl and HF released to the atmosphere, not stratosphere.

sions, processes such as interaction with a shallow hydrothermal system that would cause precipitation of S species and partitioning of HCl and HF into the liquid phase before reaching the surface, are likely to be negligible (Gerlach and Doukas, 1994; Giggenbach, 1996). The compositions of such high temperature fumarole emissions world-wide are shown in Table 1. The arcs that have high temperature fumarole data available are shown in Fig. 1. Although there are still significant variations in gas ratios within an arc system, the variations are generally smaller and considered more representative of the volatiles that are exsolving from the magma. Figure 2 shows the median values for each arc. A similar approach of using high temperature fumarole gas emissions in combination with SO₂ flux estimates has been used by Halmer *et al.* (2002) to calculate global volcanic emissions of H₂S, HCl, HF, HBr, OCS and CS₂ for the period of 1972 to 2000. These authors suggest that 70–80% of the global SO₂ flux, or 186 to 266 × 10⁹ mol/yr is from arc volcanoes.

Using the median ratios of Table 1, the fluxes of the major volatile species from the individual arcs are summarized in Table 2. As discussed in Hilton *et al.* (2002), not all arcs have flux measurements and to extrapolate to a global arc flux 20.6% is added to the sum of the individual arc fluxes. Previous estimates of arc volatile emissions are summarized in Table 3 and it can be seen that the CO₂, SO₂ and HCl fluxes are consistent within a factor of two. The N₂ flux of this study is within a factor of two of Hilton *et al.* (2002) but almost two orders of magnitude higher than that of Sano *et al.* (2001), the only other estimate of N₂ flux from arcs. The arc volcanic fluxes of HCl and HF calculated by Halmer *et al.* (2002) show a higher maximum value for HCl (25–3500 × 10⁹ mol/yr) and for HF (26–320 × 10⁹ mol/yr). The lower end

Table 4. Global volatile fluxes from arc and MORB and the composition of the depleted upper mantle

Volatile	F _{arc} (mol/yr)	F _{MORB} (mol/yr)	Depleted upper mantle (ppm)
H ₂ O	3.25 × 10 ¹³	2.90 × 10 ¹³	142 ± 85
SO ₂	3.15 × 10 ¹¹	2.67 × 10 ¹²	146 ± 35 (S)
CO ₂	1.93 × 10 ¹²	2.20 × 10 ¹²	72 ± 19
N ₂	3.50 × 10 ¹⁰	2.20 × 10 ⁹	2.8 ± 1 (N)
Cl	1.54 × 10 ¹¹	3.90 × 10 ¹⁰	1 ± 0.5
F	1.20 × 10 ¹⁰	1.13 × 10 ¹²	16 ± 3

F_{arc}: total global flux of volatile species from subduction zones. Calculated by summing up the volatile fluxes from individual arcs (Table 2).

F_{MORB}: flux of volatiles from the mantle, approximated by MORB flux.

H₂O: from Jambon and Zimmermann (1990).

SO₂: from Alt *et al.* (1985).

CO₂: from Marty and Tolstikhin (1998).

N₂: from Marty (1995).

HCl: from CO₂ flux and Cl/CO₂ of 0.017 molar from Saal *et al.* (2002).

HF: from CO₂ flux and F/CO₂ of 0.51 molar from Saal *et al.* (2002).

Upper Mantle: all values from Saal *et al.*, 2002; except N from Marty (1995).

of their estimates is similar to the HCl and HF arc fluxes calculated here.

Volatile fluxes from ridges and plumes

Volatile flux estimates from mid-ocean ridges (MOR) fall into two categories 1) using the ³He flux from MOR as derived from the measured ³He concentration in the water column and volatile ratios relative to ³He (i.e., CO₂/³He) or 2) using the global mid ocean ridge basalt production rate and volatile concentrations of the MORB source and a degree of melting. For the ³He flux of MOR,

the value of 1000 mol/yr of Craig *et al.* (1975) has been well established and widely used over the past 30 years. A somewhat smaller estimate for ^3He flux from MOR of 422 ± 181 mol/yr has been made using a global MORB magma flux of $21 \text{ km}^3/\text{yr}$ (Crisp, 1984), a CO_2 mantle source abundance of 72 ± 19 ppm and the $\text{CO}_2/{}^3\text{He}$ ratio of $2.2 \pm 0.7 \times 10^9$ (Saal *et al.*, 2002). The knowledge of the MORB source mantle volatile contents (CO_2 , S, Cl, F) allows for a new estimate of MORB CO_2 flux ($9.3 \pm 2.8 \times 10^{11}$ mol/yr). This value is close to the previous estimate of 2.2×10^{12} mol/yr (Marty and Tolstikhin, 1998) which has been obtained in a similar fashion. Mid ocean ridge Cl and F fluxes calculated using the MOR CO_2 flux of Marty and Tolstikhin (1998) and Cl/ CO_2 and F/ CO_2 ratios from Saal *et al.* (2002) are shown in Table 4. Marty and Tolstikhin (1998) report a nitrogen flux from MOR of $2.2 \pm 1.0 \times 10^9$, similar to the estimate of $1.6\text{--}6.4 \times 10^9$ mol/yr by Zhang and Zindler (1993). Table 4 shows that for H_2O and CO_2 , the arc fluxes are comparable to the MOR fluxes, whereas for N_2 and Cl, the arc flux exceeds the MOR flux. It is interesting to note that MOR flux exceeds the arc flux by factor of about ten for SO_2 and by a factor of about 100 for F.

Because MOR fluxes are calculated using the CO_2 flux from ridges and volatile ratios estimated for the upper mantle it assumes complete degassing of mantle magma for all volatile species. The lower solubility of CO_2 compared to other species (i.e., Cl and F) in the source magmas results in incomplete degassing of the more soluble species. This is evident from the lower CO_2/Cl contents of MORB host glasses compared to MORB melt inclusions, indicating CO_2 degassing and/or Cl contamination in MORBs (Saal *et al.*, 2002). Therefore, the MOR flux estimates for Cl and F in Table 5 represent maxima.

Volatile fluxes from plumes are poorly constrained. Allard (1992) estimates a non-arc subaerial volcanic ^3He flux of 160–240 mol/yr. This estimate includes Etna (which does not show plume-type ^3He) with ~ 58 mol $^3\text{He}/\text{yr}$. Therefore, the plume ^3He flux is about one order of magnitude lower than the ridge flux. Marty and Tolstikhin (1998) estimate a plume CO_2 flux of 3×10^{12} mol/yr which is similar to that from ridges. The N_2 flux from plumes is estimated at 4.1×10^6 mol/yr by Sano *et al.* (2001) and significantly lower than the arc and MOR fluxes. Chlorine flux from plumes is estimated at approximately 3.8×10^{10} mol/yr by Ito *et al.* (1983), which is similar to the MOR flux.

THE IMPORTANCE OF WATER

Water is the most dominant volatile component (by mass) in arc magmas and is the transport medium for all other volatile components during magmatic degassing (Sisson and Layne, 1993; Sobolev and Chaussidon, 1996;

Roggensack *et al.*, 1997), though a notable exception exists for water-poor arc magmas (Sisson and Bronto, 1998). High H_2O contents of arc magmas along with high SiO_2 are also responsible for the explosive and hazardous nature of arc volcanoes. Water also has a profound impact on melt properties such as melting point, viscosity and melt compositions.

Mass imbalance for water

The amount of water in the ocean amounts to 1.4×10^{24} g and that in the continents to 0.2×10^{24} g. Because the oceanic crust is altered by interaction with sea water at the ridge axis, the average oceanic crust (6.5 km thick) contains about 1.5 ± 0.5 wt% H_2O which amounts to $8.8 \pm 2.9 \times 10^{14}$ g (4.9×10^{13} mol) $\text{H}_2\text{O}/\text{yr}$ for $3.0 \text{ km}^2/\text{yr}$ of subducted oceanic crust. This value increases to 1.05×10^{15} g (5.8×10^{13} mol) including oceanic sediments with 6.3 wt% H_2O (Ito *et al.*, 1983). Studies by Ito *et al.* (1983), Peacock (1990) and Bebout (1996) have concluded that there is a significant imbalance between the amount of H_2O subducted into the mantle and the amount returned to the surface by arc magmatism. This imbalance has implications for the permanence of oceans because the total amount of H_2O currently in the oceans would be subducted back into the mantle in about 1 Ga (Fyfe and McBirney, 1975). While the return flux of these studies relies on conservative estimates of the average amount of H_2O in arc magmas and likely underestimates the amount of water returned to the atmosphere; more recent work by Hilton *et al.* (2002) suggests that more water is returned to the surface through volcanic degassing than what is subducted. These authors explain this imbalance by non-magmatic water incorporated into volcanic gases resulting in an overestimate of the average $\text{H}_2\text{O}/\text{CO}_2$ ratio of 50 which is used to calculate the arc H_2O flux.

Towards a mass balance for water

A more recent estimate by Wallace (2005) uses the range of H_2O contents measured in arc melt inclusions (3–6 wt%) and an estimate for the primary, non-degassed CO_2 contents of these magmas. Because all melt inclusions are likely to have been trapped after significant loss of CO_2 by degassing (Fischer and Marty, 2005; Wallace, 2005), the primary CO_2 content of arc magmas is estimated by combining the CO_2 flux from arcs with a maximum magma flux to arcs of $8.5 \text{ km}^3/\text{yr}$ (Crisp, 1984). This method yields a minimum of 3000 ppm CO_2 . A more likely arc magma flux of 2–4 km^3/yr (Crisp, 1984; Carmichael, 2002; Dimalanta *et al.*, 2002) results in a primary CO_2 content of arc magmas of about 0.6–1.3 wt% (Wallace, 2005). These estimates are consistent with the work of Fischer and Marty (2005) who estimate 0.35–0.76 wt% CO_2 for undegassed arc magmas based on arc CO_2 fluxes and magma emplacement rates. Therefore, a primary $\text{H}_2\text{O}/$

CO₂ ratio for arc magmas of ~4 may be more appropriate which would result in a H₂O flux from arc magmas of about 3×10^{14} g/yr (1.7×10^{13} mol/yr) (Wallace, 2005). This amount is comparable to the 4.9×10^{13} mol/yr of H₂O subducted in the altered oceanic crust estimated by Ito *et al.* (1983). However, the global subduction rates of H₂O are still poorly constrained and range from 91.1 to 194×10^{13} g H₂O/yr (5×10^{12} to 1×10^{14} mol H₂O/yr) (see review by Bebout (1996)). Therefore, a maximum of about 1×10^{14} mol H₂O/yr could be subducted globally, which is one order of magnitude higher than the H₂O flux from arc magmas estimated by Wallace (2005).

Certainly, not all H₂O stored in subducted sediments and oceanic crust will make it to the depths of magma generation due to shallow level dehydration and forearc flux back to the ocean. Using phase relationships of oceanic crustal rocks and sediments, Schmidt and Poli (1998) calculate that the oceanic lithosphere contains about $0.71\text{--}1.08 \times 10^9$ g H₂O/m² in a 7 km column of the crust at 20 km depth and that 18 to 37% of that amount (0.124 to 0.4×10^9 g H₂O/m²) are available for the generation of arc magmas. The remainder is lost into shallow, cold corner of the mantle wedge where serpentine is stable (Schmidt and Poli, 1998), alternatively, it could also be returned to the ocean in the fore-arc (but this flux is currently unknown). These estimates result in 1.8 to 5.7×10^4 g H₂O/m³ of crust available for arc magma generation. At an oceanic crust density of 2.9×10^6 g/m³ about 0.6 to 2 wt% of H₂O stored in the subducting crust is available for arc magma generation. Estimates of the global subduction rate of oceanic sediments range from 1.33 to 3.5×10^{15} g/yr and the subduction rate for oceanic crust is well constrained at 60×10^{15} g/yr (see summary by Bebout (1996)). Therefore, about 0.4 to 1.3×10^{15} g H₂O/yr ($2\text{--}7 \times 10^{13}$ mol H₂O/yr) would be available for arc magma generation. The arc H₂O flux by Wallace (2005) (1.7×10^{13} mol/yr) is at the low end of this estimate. Considering the uncertainties, it follows that the amount of H₂O that is globally available for the generation of arc magmas and originates in the subducting oceanic lithosphere is efficiently recycled back to the atmosphere through arc volcanism.

An important observation is that the H₂O flux seems to be balanced with the subduction input when using the estimate of Wallace (2005) which relies on magmatic H₂O/CO₂ ratios derived from melt inclusions and the primary CO₂ content of the mantle below arcs (which in turn depends on arc CO₂ flux and magma production rates). Alternatively, the H₂O flux can be calculated more directly using the H₂O/SO₂ ratios of high temperature arc fumaroles and the global SO₂ flux (Table 2) which results in an arc H₂O flux of 3.6×10^{13} mol/yr, which is also within the range of the flux that is available for arc magma generation based on Schmidt and Poli (1998) and

only a factor of about two higher than the estimate of Wallace (2005). The important implication of this observation is that most of the H₂O discharging from high temperature fumaroles is of mantle origin, without significant meteoric (surficial) contribution. This is also consistent with δD and $\delta^{18}O$ systematics of high temperature arc fumaroles that show compositions close to the “andesitic” or “arc-type” water end-member of Taran *et al.* (1987) and Giggenbach (1992), whereas lower temperature discharges have higher H₂O contents (generally > 97%) and show isotopic compositions similar to meteoric waters (see Goff and McMurtry (2000)).

In summary, a flux of magmatic/mantle (non meteoric) H₂O from arc volcanoes to the atmosphere of 2 to 4×10^{13} mol/yr is currently the best estimate because it is consistent with 1) melt inclusion data and magma emplacement rates 2) high temperature global fumarole data and time averaged arc SO₂ fluxes and 3) the amount of H₂O subducted and available for arc magma generation that implies a balance between the input and the output of H₂O at arcs.

REGIONAL STUDIES: THE CENTRAL AMERICAN ARC

Studies on volatile systematics that focus on one arc where subduction parameters (slab dip, convergence rate, composition of the incoming plate, etc.) as well as output characteristics (trace and isotopic composition of the lavas, crustal composition and thickness) are well constrained provide natural laboratories to study element cycles in greater detail. The Central American Volcanic Arc (CAVA) has recently received much attention because it meets many of the criteria that make it an ideal site to investigate the tectonic, geophysical and geochemical processes operating in subduction zones.

The CAVA is the result of eastward subduction of the Cocos Plate beneath the Caribbean Plate. Figure 3 shows the locations and names of the active volcanoes in the Central American arc. The subducting plate comprises 170 m of hemipelagic sediments overlying 400 m of limestone which, in turn, overlies oceanic basalt basement (von Huene *et al.*, 1980). The crustal basement ranges in age from ~13–17 Ma at the trench adjacent to Costa Rica to ~25–30 Ma off Nicaragua. The dip of the slab is steepest off Nicaragua (up to 84°) and this is relatively constant throughout the country despite abrupt changes in the surface orientation of the volcanic front (Protti *et al.*, 1995). Convergence direction is nearly orthogonal to the volcanic front in Nicaragua, with convergence rates currently proceeding at about 90 mm/a (Minister and Jordan, 1978). Crustal thickness is less than 35 km in Nicaragua whereas it is greater in both Guatemala (~50 km) and Costa Rica (42 km) (Carr *et al.*, 1990).

Western Nicaraguan volcanic rocks are characterized

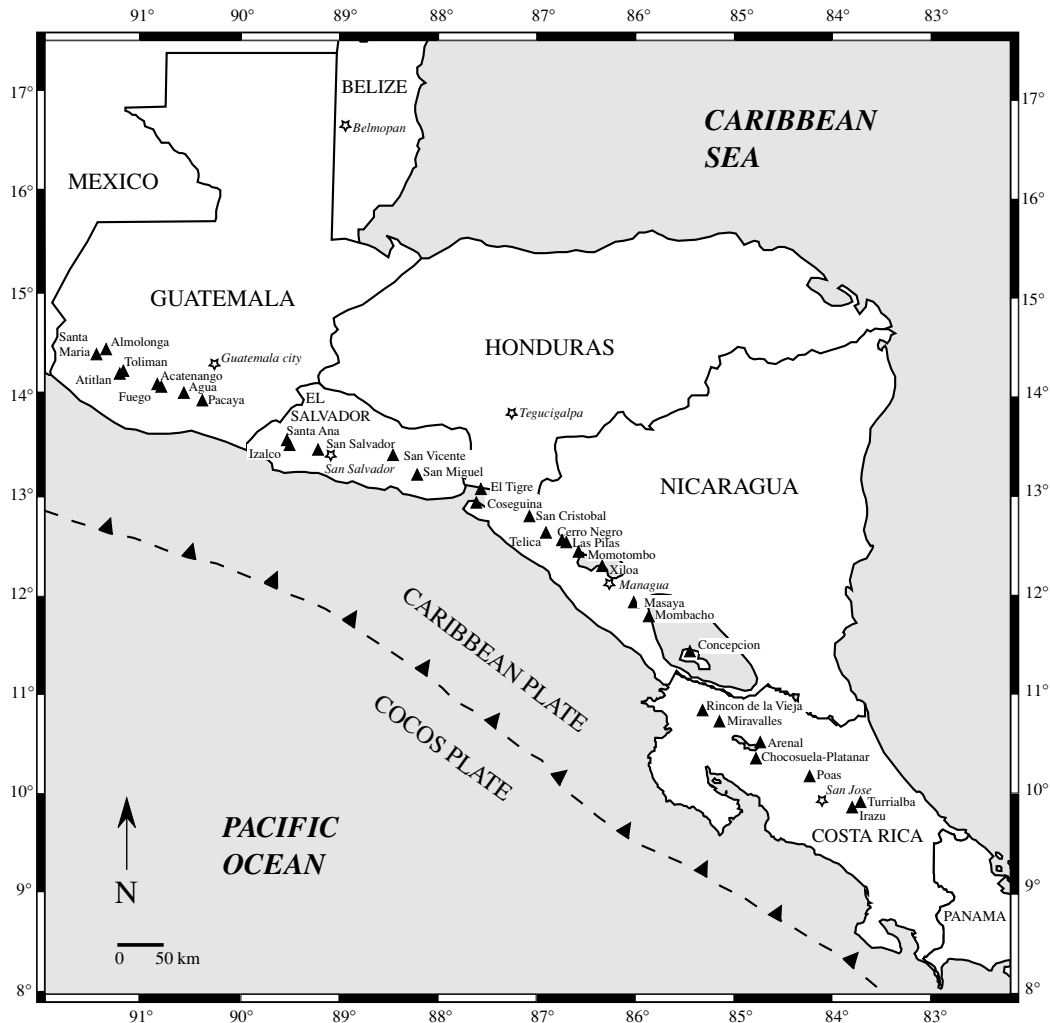


Fig. 3. The Central American Volcanic Arc. Shown are the volcanoes that are associated with gas emissions through fumaroles, bubbling springs, geothermal wells or mud-pots (from Fischer *et al.*, 2007).

by high Ba/La, B/La, and $^{10}\text{Be}/^9\text{Be}$ ratios (Carr *et al.*, 1990; Morris *et al.*, 1990; Leeman and Carr, 1995). These features indicate high degrees of partial melting in the mantle beneath Nicaragua, with addition of fluid mobile elements from the uppermost part of the subducting sediment column. These same ratios are low in Costa Rica and intermediate in eastern Nicaragua, Guatemala, and El Salvador (Carr *et al.*, 1990; Leeman *et al.*, 1994; Patino *et al.*, 2000).

A proposed explanation for these observations is that due to the steep subduction angle beneath Nicaragua, volatiles are released into only a small volume of mantle wedge above the slab (Carr *et al.*, 1990). Consequently, the release of fluids generates a high degree of partial melting but an overall small melt volume. Conversely, the shallow dip of the slab beneath Costa Rica explains

the generation of large volumes of small-degree melts and consequent dilution of the recycled beryllium signature (Carr, 1984; Carr *et al.*, 1990). However, more recent estimates based on extensive age dating reveal that the volcanic fluxes in both arc segments are equal within errors (Carr *et al.*, 2007). Underplating of the uppermost part of the sediment column beneath the overriding crust also has been proposed to explain low cosmogenic ^{10}Be signatures in Costa Rica lavas (Morris *et al.*, 1990; Leeman *et al.*, 1994).

Volatile flux studies: recent constrains on mass balance

Volcanic gas measurements have been an integral part of geochemical and volcanological studies in the Central American arc since the 1960's, starting with Stoiber's pioneering work on gas condensates (Stoiber and Rose,

1970) and have recently been summarized by Fischer *et al.* (2007). With regards to volatile sources and fluxes, gas discharges have been examined for helium, carbon, and nitrogen in Guatemala, Nicaragua and Costa Rica (Fischer *et al.*, 2002; Shaw *et al.*, 2003; Zimmer *et al.*, 2004), and for helium and carbon in Nicaragua, El Salvador and Honduras (Shaw *et al.*, 2003; de Leeuw *et al.*, 2007) and along the entire length of the CAVA (Snyder *et al.*, 2001). Snyder *et al.* (2003) investigated the sources of nitrogen and methane in geothermal fluids along the Central American arc. This work focused on geothermal well fluids and concluded that most of the nitrogen discharging in Nicaragua is crustal in origin, based on high $N_2/{}^3\text{He}$, close to MORB-like ${}^3\text{He}/{}^4\text{He}$ ratios, and an inferred relationship between excess nitrogen and an iodine isotopic component that is much older than the subducted sediments.

Recent work by Elkins *et al.* (2006) shows that nitrogen isotope systematics correlate with other geochemical parameters along the arc (Fig. 4). These correlations support the notion that nitrogen originates from subducted hemipelagic sediments which have $\delta^{15}\text{N}$ values of around +6‰ and high nitrogen contents (Li and Bebout, 2005). Below Costa Rica, the upper-most hemipelagic sediment layer is off-scraped and the resulting $\delta^{15}\text{N}$ values of the gas discharges become mantle or MORB-like ($-5 \pm 3\text{‰}$). Approximation of the end-member compositions of air, mantle and sediments allows for the calculation of the relative contribution of these end-members to the total nitrogen discharge (Sano *et al.*, 1998). For example for Nicaragua, the average contribution of sediment derived nitrogen to the discharging volatiles is 85%. Significantly higher than for Costa Rica to the south (Zimmer *et al.*, 2004). Table 5 tabulates the recent estimates of nitrogen input and output in the Central American subduction zone system. For example considering the Nicaragua N output flux of sedimentary N (85% of total N) of 8.8×10^8 mol/yr (last column) and comparing that value with the estimated N input stored in subducted sediments (9.3×10^8 mol/yr) for Nicaragua, shows that the input is only slightly higher than the output through arc volcanoes. Considering the uncertainties, the volcanic N flux that originates from subducted sediments is approximately balanced by the input of nitrogen stored in the sedimentary sequences of the subducting oceanic crust. Clearly, more work is needed to further constrain the inputs and outputs of volatiles and their recycling efficiency through subduction zones. An important observation of this study is (and shown in Table 5), that the amount of nitrogen stored in the oceanic basement (5 to 50 ppm (Li and Bebout, 2005)) significantly adds to the amount of subducted N. When including the basement N, the subducted N greatly exceeds the amount released through arc volcanism and could likely be subducted into the deeper mantle.

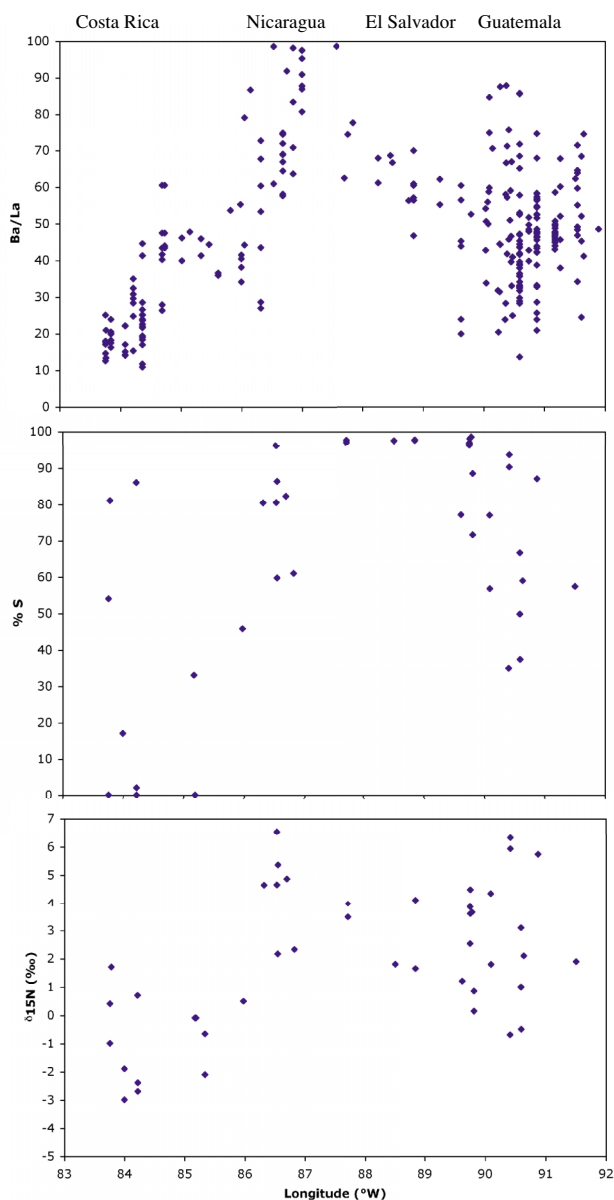


Fig. 4. Variation of geochemical parameters along the Central American arc. Ba/La is from recently erupted lavas (Patino *et al.*, 2000 and Carr *et al.*, 2003). Nitrogen data is from Elkins *et al.* (2006) and %S represents the amount of N_2 that originates from subducted sediments.

The notion that significant amounts of N are subducted into the mantle is also supported by a recent study of carbon systematics of the CAVA. The work by Shaw *et al.* (2003) showed that only about 14–18% of the CO_2 that originates from subducted sediments and the altered oceanic crust is recycled back to the atmosphere through arc volcanism, the remainder is either returned into the deep mantle or lost in the fore-arc, prior to subduction.

Table 5. Calculated nitrogen fluxes for the Nicaraguan volcanic front, in 10^8 mol/yr from (Elkins *et al.*, 2006)

	Nicaragua N flux	Sediment-derived N flux (%S = 71%)			
		Nicaragua	CAVA	Global arcs	(%S = 85%) Nicaragua
N flux (Elkins <i>et al.</i> , 2006)	11	7.8	28		9.4
Calculated from ^3He	9.7	6.9	25		8.2
Calculated from SO_2	2.9	2.1	7.4		2.5
Calculated from CO_2 , ^3He	18	12.8	46		15.3
Calculated from CO_2 , SO_2	10.4	7.4	27	1800	8.8
N inputs					
Fischer <i>et al.</i> (2002)			2.3		
Hilton <i>et al.</i> (2002)			5.5	69	
Li and Bebout (2005)			7.1		
Snyder <i>et al.</i> (2003)				92	
Zimmer <i>et al.</i> (2004):					
Minimum			0.49		
Maximum			1.05		
Li and Bebout (2005):					
Subducted sediment		9.3			
+ Altered ocean crust	14				
[N] = 5 ppm					
[N] = 50 ppm	62				

Note: %S represents the percentage of N derived from subducted sediments. This is calculated using N–He systematic. 71% is the average for Central America, 85% is for Nicaragua only. See Elkins *et al.* (2006) for details on the flux calculations.

Volatile emissions from arc to back-arc: constraining the fate of CO_2

A more recent study of the C–He systematics of El Salvador and Honduras (back-arc) gas emissions has revisited the processes of CO_2 recycling in Central America (de Leeuw *et al.*, 2007). This study takes advantage of the now much more detailed knowledge regarding the C content as well as isotopic composition in the subducted oceanic plate. Li and Bebout (2005) identified three units in the subducting plate: U1 and U2 are clay rich and underlain by U3, a carbonate rich unit. The source of C is characterized by a distinct C-isotopic composition and $\text{CO}_2/{}^3\text{He}$ ratio that allows for the calculation of the contribution of C from a carbonate component (L) and an organic sediment component (S). Each subducted unit has a distinct ratio of C derived from carbonate and from organic C (the L/S ratio) that can be calculated from its C-isotopes and appropriate endmembers following Sano and Marty (1995). Additionally, the amount of C delivered by each unit to the subduction zone has been estimated by Li and Bebout (2005). By knowing the L/S ratio of gas emissions and the flux of CO_2 out of the arc, de Leeuw *et al.* (2007) are able to make a more robust estimate of how much C is contributed from each unit to satisfy the output flux and L/S ratios measured at the volcanic arc. A major finding of this work is that, based on the L/S ratio of the subducting units, no C is contributed from the oceanic basement to satisfy the output in El Sal-

vador or any other part of the volcanic front. Using this new approach, about 29% of the CO_2 stored in the sedimentary pile of the incoming plate is released through arc volcanism, the remainder (about 70%) is either lost in the fore-arc or subducted past the zones of arc magma generation. In Costa Rica, the recycling efficiency is even lower, with only about 12% of the sediment hosted CO_2 released through arc volcanism (de Leeuw *et al.*, 2007). This study shows that as for N_2 (Zimmer *et al.*, 2004; Elkins *et al.*, 2006) the efficiency of CO_2 recycling varies along strike of the Central American arc. Another important aspect of this work is that for the first time, the volatile emissions of a back-arc region (Honduras) are investigated with respect to CO_2 subduction. Although gas discharges in Honduras are exclusively low temperature (boiling) and geothermal in nature with significant amount of crustal contamination in most sites, helium isotope ratios up to 6 R_A are found in the Sula graben (Kennedy *et al.*, 1991) and allow for an evaluation of the CO_2 –He systematics of the mantle beneath the back-arc. Honduras has a lower slab (L + S) versus mantle (M) contribution than El Salvador. The (L + S)/M = 5.7 in Honduras compared to 9.4 in El Salvador. The L/S ratio of both Honduras and El Salvador is comparable and suggests that at least some CO_2 in the back-arc is ultimately slab-derived (de Leeuw *et al.*, 2007). This slab signature behind the volcanic front seems to be unique to CO_2 as other geochemical indicators (Ba/La, $^{87}\text{Sr}/^{86}\text{Sr}$ (Patino *et*

al., 1997; Walker *et al.*, 2000)) show MORB-like signatures. There are two possibilities to explain the arc-like signature in Honduras 1) the slab continues to release CO₂ at >200 km depth after by-passing the zone of arc magma generation or 2) the slab signature reflects either entrainment of a CO₂ charged mantle wedge from the volcanic front or represents a signature from prior subduction fluxing of the mantle wedge. Based on the L/S ratio and mass balance constraints, de Leeuw *et al.* (2007) conclude that the CO₂ discharging in the back-arc, indeed has a slab sedimentary provenance that has been released into the mantle wedge at conditions to maintain the L/S ratio. The current data, however, do not allow to distinguish between a contemporary slab signature due to entrainment of mantle wedge material from above the volcanic front, or the signature of ancient subduction fluxing of this part of the mantle wedge (de Leeuw *et al.*, 2007). Future work on the evolution of the arc system through time should help to better distinguish between these two possibilities. In summary, this across-arc study shows that the fate of volatiles in a subduction zone system can be well constrained when detailed information on the input and output parameters is available.

CONCLUDING REMARKS AND FUTURE DIRECTIONS

This review has focused on the fluxes of major volatiles from volcanic arcs and mid ocean ridges to the atmosphere and hydrosphere. Although a considerable database has been accumulated both on the gas compositions as well as the fluxes of gases from volcanoes, there are still numerous issues that warrant further attention in future studies. The following is a list of topics where significant progress could be made:

1. Although it is encouraging that the fluxes of H₂O, SO₂ and HCl from arc volcanoes are consistent using various approaches of estimating these fluxes (melt inclusions, magma emplacement rates and SO₂ flux coupled with gas chemistry), the estimates of HCl and HF fluxes are still few. Future melt inclusion work should include measurements of F in addition to Cl to better constrain the Cl/F ratio of arc volatiles. The recent work by Saal *et al.* (2002) on MORBs is an example of the amount of information that can be obtained by such complete volatile studies.

2. The number of SO₂ flux measurements is seriously skewed towards volcanoes that are easily accessible and already have been studied for decades (i.e., Masaya, Nicaragua and Etna, Italy). There still remain a number of arcs that have only a couple of measurements during non-eruptive periods (i.e., Papua New Guinea, Northern Marianas, Aleutians, Chile). Recent satellite remote sensing techniques should focus on these remote areas to better quantify passive degassing fluxes and variations

through time and level of volcanic activity.

3. The number of data (volatile abundances and fluxes) from arcs and MORs vastly exceeds those from back-arcs and fore-arcs. Knowledge of the fore-arc and back-arc degassing fluxes is important for the assessment of volatile mass balances between the Earth's surface and interior. In particular for H₂O such information is critical in order to investigate if up 70% of the subducted water is transferred from the oceanic crust to the cool part of the mantle wedge to form serpentinite (Schmidt and Poli, 1998) and how much of the remaining H₂O is not released in the back-arc but subducted into the deep mantle.

4. Studies that focus on one well-constrained arc system are invaluable to correlate volatiles with other parameters (geochemical, geophysical and petrological). A vast amount of data has accumulated for the Central American arc since the first volatile studies in the 1960's and we are now making significant progress towards incorporating volatile studies into the broader framework of the subduction zone. Such focused studies also provide better constraints on the input composition and rates (Li and Bebout, 2005).

5. More data are required on the elemental and isotopic fractionation during the subduction process. Expansion of the work of Schmidt and Poli (1998) for H₂O and CO₂ (Kerrick and Connolly, 2001) to N, S, Cl and F would provide important constraints on the efficiency of volatile release during subduction which could then be related to the emissions through arc volcanism.

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