

Element flux to the environment of the passively degassing crater lake-hosting Kawah Ijen volcano, Indonesia, and implications for estimates of the global volcanic flux

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Abstract: Volcanoes play an important role in the global cycling of elements by providing a pathway from the deep Earth to its surface. Here, we have constrained the flux to the environment for most elements of the periodic table for the passively degassing, crater lake-hosting Kawah Ijen volcano in the Indonesian arc. Our results indicate that emissions of Kawah Ijen are dominated by acid water outflow, especially for the ligands (Cl, F, Br), with active fumaroles contributing significant (semi)metals (e.g. Se, As, Sb, Hg), as well as C and S. The compositional signature of emissions from Kawah Ijen is similar to that of major volcanic emitters such as Etna, but element fluxes are smaller. This result provides the prerequisite foundation for extrapolating a small set of measured volcanic gas emissions to a global volcanic flux estimate. However, the aqueous flux (i.e. seepage of volcanic hydrothermal fluids and volcano-influenced groundwater) is at least as important in terms of element release, and the consideration of the gaseous flux alone thus represents a significant underestimate of the impact of volcanoes on their environment and the contribution of volcanic hydrothermal systems to global element cycling.

Supplementary material: The full datasets of water and fumarole gas chemical analyses are available at <https://doi.org/10.6084/m9.figshare.c.2134359>

To quantify element cycling through the Earth, and to assess the impact of humanity on these cycles, requires precise knowledge of natural fluxes. Volcanoes represent a direct pathway from the Earth's interior to the atmosphere, hydrosphere and crust, and are an important component of this natural flux. They act as point sources, with emissions ranging from persistent passive emissions in degassing and outflow of magmatic hydrothermal waters, to punctuated release of material during periods of eruption. The comprehensive datasets necessary to quantify the output of a volcano are only available for a limited number of terrestrial volcanic centres.

When estimating global terrestrial volcanic gaseous emissions (e.g. Hinkley *et al.* 1999; Allard *et al.* 2000), the flux of a single volcano, or a small compilation of volcanoes, is therefore scaled to a component for which the global volcanic flux is known; commonly SO₂. However, this assumes that these emitters are representative of average global volcanism. Quantification of global volcanic element fluxes has focused on the largest emitters, such as Etna (e.g. Gauthier & Le Cloarec 1998; Aiuppa *et al.* 2008) and Kilauea (Hinkley *et al.* 1999; Mather *et al.* 2012), with almost no information available for the far more common minor

emitters. There is, therefore, a need to establish the compositional signature of minor emitters and to determine if large emitters are indeed compositionally representative of the global volcanic flux.

In this contribution, we estimate the total element flux released into the environment by the comparatively small, passively emitting Kawah Ijen volcano in the Indonesian arc, to emphasize its potential impact on the local environment, and to explore the flux signature of minor emitters in the context of the global volcanic element flux. In particular, we have attempted to constrain the flux for as complete a suite of elements as possible.

Kawah Ijen volcano

Kawah Ijen volcano is an active basaltic to dacitic stratovolcano located within the Ijen Caldera Complex on the eastern tip of Java in Indonesia (Fig. 1). It is part of the Sunda volcanic arc (see Hall 2011). Kawah Ijen is positioned on the intersection of the caldera rim and an inter-caldera lineament, both of which host post-caldera-collapse volcanoes (Kemmerling 1921; Tjia 1967; Handley *et al.* 2007; van Hinsberg *et al.* 2010a). Compositions of the juvenile deposits fall within both of the series defined by the inter-caldera and caldera-rim volcanoes (Handley *et al.* 2007; van Hinsberg *et al.* 2010b) and may, therefore, tap both source reservoirs. Magmatic deposits are dominated by lava flows and scoria falls of basaltic to andesitic composition. Dacite is present as a flow on the volcano's western flank, and as (breadcrust) bombs scattered around the summit area. Towards the crater rim phreatic deposits appear and increase in abundance, commonly with erosional contacts into older deposits. Palaeosol horizons are also observed.

Surface volcanic activity is confined to a mound located in the southern part of the summit area (Fig. 1), and consists of strong fumarolic emissions. This area was also the centre of activity of the 1817 eruption (cf. 'Oudgast' 1820; Junghuhn 1853; Bosch 1858; Caudron *et al.* 2015), which lowered the fumarole plateau (cf. Leschenault de la Tour 1811; 'Oudgast' 1820). The feeder level of older fumaroles, likely destroyed in the 1817 eruption, is exposed in a valley next to the presently active mound. Photographs from the early 1900s (e.g. Kemmerling 1921) show a flat plateau with fumaroles, whereas the fumaroles are presently located on top of a mound approximately 20 m in height. This rapid growth is difficult to reconcile with precipitation from the fumaroles, and in fact, the material of the mound predominantly consists of variously altered rock fragments, including near-pristine rhyolitic glass (see van Hinsberg *et al.* 2010b). We therefore tentatively interpret this

mound as a volcanic dome or plug, likely of dacitic composition (cf. Berlo *et al.* 2014). High-temperature, well-established fumaroles vent from intensely altered bare grey rocks surrounded at a variable distance by a pyrite and alunite precipitate. All surfaces near the vents are coated with native sulphur (see also van Hinsberg *et al.* 2010a, b). Metal pipes, inserted in the fumarole vents, condense native sulphur from these emissions, which is subsequently mined. Fumarole emissions have been on-going at Kawah Ijen since at least 1790 ('Oudgast' 1820).

The summit of Kawah Ijen is presently occupied by a crater lake, 1000 by 600 m in surface area and approximately 200 m deep (Takano *et al.* 2004; Caudron *et al.* 2015). Lake waters are hyperacidic (pH \approx 0), warm ($T \approx 38^\circ\text{C}$) and highly concentrated ($\text{SO}_4 = 5.6 \text{ wt\%}$, $\text{Cl} = 2.8 \text{ wt\%}$, $\text{Al} = 4000 \text{ ppm}$, $\text{F} = 1500 \text{ ppm}$ (e.g. Delmelle & Bernard 1994, 2000; this study). These waters seep through the western flank of the volcano to emerge in springs approximately 250 m downstream from the lake. Gypsum precipitation from these spring waters has built up a terraced slope *c.* 100 m in length. Two further sets of acid springs are found 400 and 1000 m downstream of the seepage outlets, respectively. Waters discharged from the final spring are not sourced from the lake, and have been posited to represent direct outflow from the hydrothermal system (Palmer 2010). This spring has the highest discharge and is the source of the Banyu Pahit river, which flows through the Ijen caldera and subsequently onto its outer slopes (Fig. 1). Before reaching the sea, most of the water is diverted into the irrigation system of the Asambagus Plain, which is resulting in damage to soils and accompanying loss of crop productivity, and harm to the health of the local population and livestock (Heikens *et al.* 2005; Löhner *et al.* 2005; van Rotterdam-Los *et al.* 2008).

The most recent magmatic eruption of Kawah Ijen took place in 1817 and resulted in expulsion of the crater lake and deposition of juvenile material ('Oudgast' 1820; Junghuhn 1853; Bosch 1858; Kemmerling 1921; Caudron *et al.* 2015). Subsequent eruptions have largely been confined to the crater lake, with significant phreatic activity in 1916–17, 1936, 1952, 1993–94, 1999 and 2010–12 (Kemmerling 1921; Caudron *et al.* 2015).

Methods

Approach

To determine the total element flux of a volcano requires the identification and quantification of all of its major emissions. Here, we investigate the flux during quiescence at Kawah Ijen, i.e. passive degassing that has persisted as the characteristic style of activity since its last magmatic eruption

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

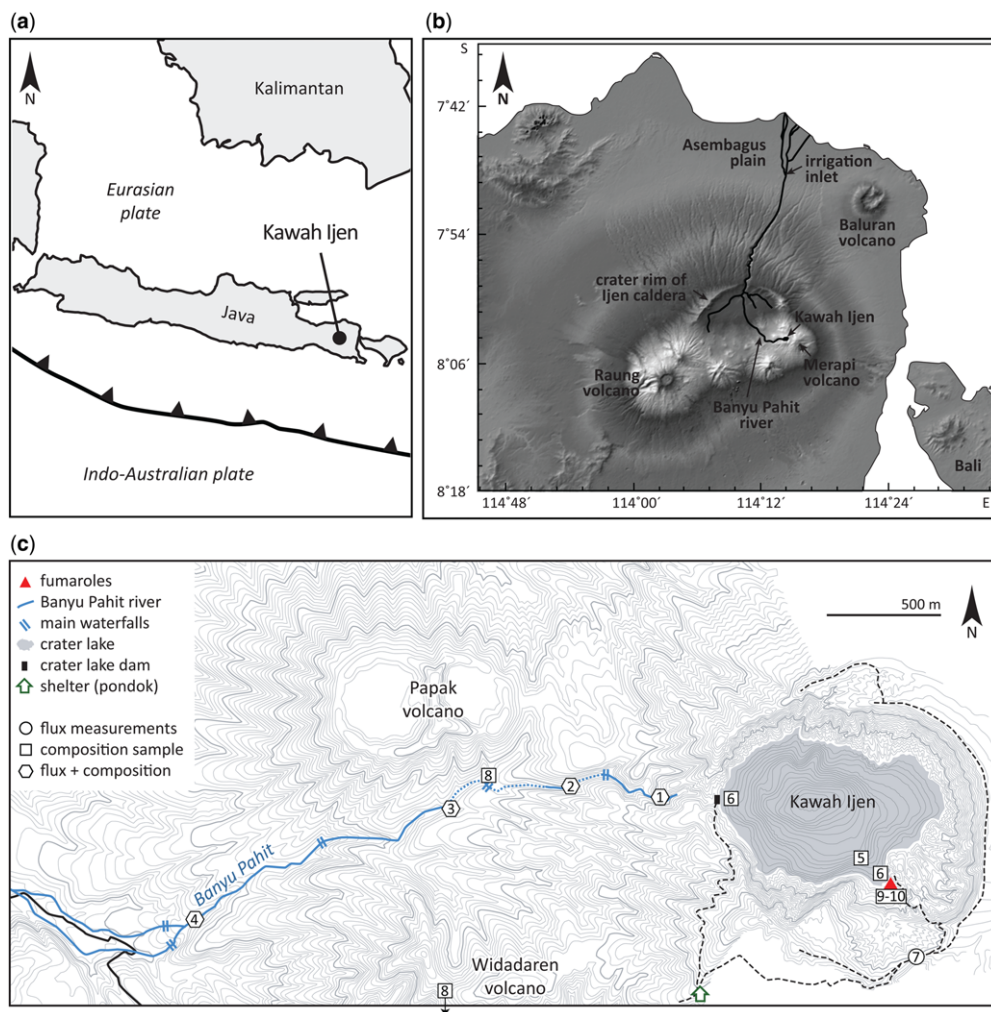


Fig. 1. Overview maps of (a) the Kawah Ijen–Banyu Pahit system on the eastern tip of Java, (b) within the Ijen Caldera Complex and (c) with main sampling locations indicated.

in 1817. Emission pathways can, therefore, be expected to be well established. A schematic model of the element emission pathways at Kawah Ijen is shown in Figure 2, with fumaroles, hydrothermal waters released through the Banyu Pahit river, and diffuse contamination of groundwater postulated to be the main outputs from this system. Depending on whether the crater lake has reached a steady-state, it can be a source or sink of elements, or a (dynamic) reservoir. The ultimate source(s) of the emitted elements will not be discussed here, except to note that a clear magmatic signature is present (Berlo *et al.* 2014).

Representative samples of all components identified in Figure 2 were collected during fieldwork

in July and August 2007 through 2009 (Figs 1 & 2). This time period represents the dry season, and rain was uncommon in the caldera, although there were overcast and rainy days in the 2009 field season. High temperatures and low winds characterized the 2008 field season, which was associated with the highest fumarole temperatures. Discharge and flux measurements of fumaroles and hydrothermal waters were also carried out.

Gas samples

Fumarole emissions were sampled on top of the mound in natural vents characterized by visually high flow, high temperature (>350°C as measured

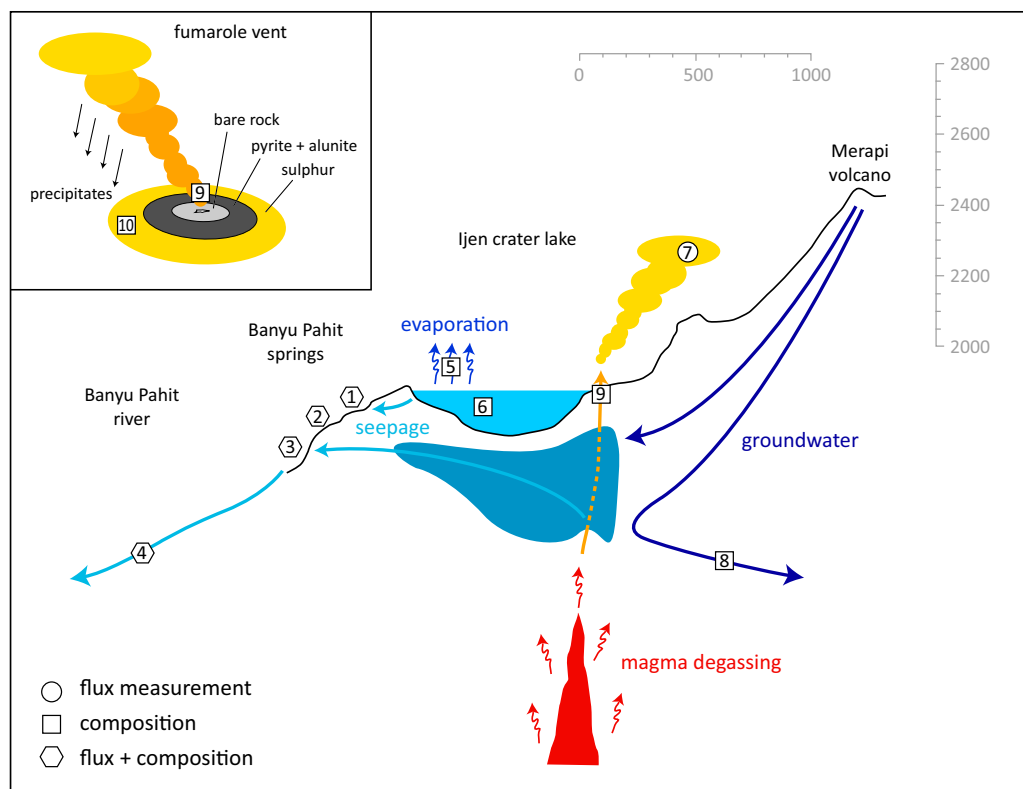


Fig. 2. Schematic model of the Kawah Ijen–Banyu Pahit system identifying all major sources and sinks of elements. Numbers link to sampling locations in Figure 1.

with a type-K thermocouple) and a lack of native sulphur precipitates. Gas was channelled to the sampling equipment using high-purity quartz tubes inserted into the vent, with connections made by Tygon silicone tubing. This sampling train was kept as short as possible to avoid a drop in temperature, and formation of condensate, and was purged with sample gas before sampling. Samples for major gas species were collected in evacuated Giggenbach-style glass bottles (see Giggenbach 1975) filled with a 4 M 99.995% pure NaOH solution. Gas was let into the bottle at a rate lower than the flow rate of the vent to avoid drawing in air, and was stopped when the flow rate decreased sharply. The mass of gas collected was determined by weighing the bottles before and after sampling. Samples for minor and trace element concentrations and stable isotopes were collected by condensing the gas in a glass condenser suspended in a water + ice mixture. The gas was pumped through the condenser using a hand-operated vacuum pump at the outflow end of the condenser. Sampling was conducted with the condenser at a position below that

of the silica tube, so that any condensate developing in the tubing would be collected. Formation of such condensate was minimal, and was absent for the highest temperature vents. Isotope samples were stored in completely filled amber glass vials with a conical seal, and samples for elemental analysis in pre-cleaned HDPE bottles. One charged Giggenbach bottle was not used for sampling to act as a blank in the analytical procedures. No rock particles were observed in the Giggenbach control or condensate samples and the solutions in both were clear. A contribution to element concentrations from particulate matter is thus unlikely.

Vapours can be seen rising from the lake water, especially early in the morning. These vapours were sampled using the same evacuated NaOH-filled Giggenbach-style bottle as used for the fumarole emissions. A small bamboo raft was floated on the lake that captured the vapour in an area below the raft enclosed in an HDPE skirt. The vapour was conducted to shore from this enclosed space by Tygon tubing. The sampling arrangement was left for 30 min prior to sampling to allow for the

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

vapour to purge the air below the raft and in the tubing.

The major gas composition of the 2008 Giggenbach bottle samples was determined at the University of New Mexico following the methodology detailed in Zimmer *et al.* (2004), which uses the approach of Giggenbach & Goguel (1989). CO contents were not corrected for absorption by the NaOH solution (cf. Giggenbach & Matsuo 1991) and thus represent minimum estimates. Condensates and Giggenbach bottle solutions were analysed for major elements by ICP-OES, and trace elements by ICP-MS by Geoscience Laboratories (Sudbury, Canada). A thin film of native sulphur invariably developed on the inside wall of the condensate sample bottles during storage. This sulphur was removed, weighed, and analysed separately (see below) in order to reconstitute the condensate compositions. Giggenbach bottle solutions were converted to a nitric acid matrix for ICP analysis by evaporating the solution to dry at 70°C, and subsequently re-suspended in 5% ultrapure HNO₃.

Stable isotope compositions of H and O were determined at the Queen's University Facility for Isotope Research (2007 samples), and at the University of Waterloo Environmental Isotope Laboratory (2008 samples). For 2008 samples, the O isotopic composition of water and sulphate were determined separately.

Water samples

Water samples were collected from the crater lake, seepage springs, the Banyu Pahit river, local groundwater and rainwater (see Fig. 1 for sample locations). Furthermore, the diurnal variation in Banyu Pahit river composition was assessed using an auto-sampler installed after the confluence of all springs (Fig. 1). All samples were filtered in the field through 0.45 µm disposable filters, and stored in HDPE sample bottles, one for major and trace elements and one for anions. Cation samples of waters with a pH in excess of 2 were acidified with two drops of dilute ultrapure nitric acid. Conductivity and pH were measured in the field using electrodes that were calibrated daily (pH = 1 and 3 standards for the acid solutions, pH = 5 and 7 for the neutral solutions). pH has also been calculated from water compositions (Table 1).

Anion concentrations were determined by ICP-OES at the Geochemical Laboratory of Utrecht University in 2007, and by ion chromatography at McGill University in 2008 and 2009. Samples were analysed for major and trace elements by ICP-OES and ICP-MS; at Utrecht University for 2007 samples and by Geoscience Laboratories (Sudbury, Canada) for all other samples. Blanks of the diluting acid were analysed to check and

quantify the contribution from the acid to element concentrations. The 2007 crater lake sample was re-analysed in each analysis batch to test for reproducibility.

Solid samples

A sample of native sulphur needles coating the fumarole mound and the sulphur precipitates from the condensates were digested for 17 h using 7.5 M trace metal grade nitric acid in sealed Teflon test tubes enclosed in a steel autoclave at 240°C. Gypsum from the uppermost seepage outlets, and yellow Al sulphate precipitates from the banks of the Banyu Pahit river were air-dried, crushed and handpicked for purity, and digested in a hot HF–HNO₃–HClO₄ acid mixture. These solutions were subsequently analysed for major and trace elements with the 2007 water samples.

Flux measurements

The SO₂ flux from Kawah Ijen volcano was determined by FLYSPEC UV spectroscopy (Horton *et al.* 2006). Traverses dissecting the plume were made on the southern crater rim with the plume directly overhead at *c.* 10 m elevation. Wind speed was recorded simultaneously. Full details are given in Vigouroux (2011).

Discharge was measured along the Banyu Pahit river and at the seepage outlets (Fig. 1) by dye-dilution experiments, and measurements of riverbed dimensions combined with flow rate measurements using a rotor flowmeter (Palmer 2010). The dilution and passage time of multiple pulses of red food dye were measured by sampling river water downstream of the injection site every 2 s and analysing these samples with a field photo-spectrometer. For low discharge sites, the time required to fill a known volume was determined.

Results

The compositions of all components identified in Figure 1 are given in Tables 1–4, where water compositions represent the mean + standard deviation of 2007–09 samples. Interlaboratory reproducibility was better than 5% relative for all elements as determined from lake water sample KV07-IJN2. Lake and Banyu Pahit river compositions are similar for 2007–09, with differences reflecting variable dilution by neutral groundwater.

Condensate fluid compositions were combined with the composition of their sulphur precipitates to arrive at the original condensate composition. These compositions were subsequently combined with the major element concentrations in the Giggenbach flasks to obtain the complete gas composition (Table 2); see the discussion for details.

Table 1. Water compositions, with their associated standard deviation (1 s). Calculated pH values were determined by charge balance

Sample	Crater lake		Springs I		Springs II		Springs III		Banyu Pahit		Groundwater	Rainwater
Temperature (°C)	36		22–27		34		22–27		20		14	
pH measured	0.0		0.2		0.2		0.4		0.4		8.2	
pH calculated	0.5		0.7		0.7		1.0		1.0		n.c.	
Conductivity (S m ⁻¹)	32		28		35		19		15		0.01	
discharge (dm ³ s ⁻¹) flm			0.96		0.99		31.3		50.8			
Discharge (dm ³ s ⁻¹) dye			n.a.		n.a.		n.a.		59.4			
<i>Cations</i>	<i>mg kg⁻¹</i>	<i>1 s</i>	<i>mg kg⁻¹</i>	<i>1 s</i>	<i>mg kg⁻¹</i>	<i>1 s</i>	<i>mg kg⁻¹</i>	<i>1 s</i>	<i>mg kg⁻¹</i>	<i>1 s</i>	<i>µg kg⁻¹</i>	<i>µg kg⁻¹</i>
Al	5792	309	4871	1072	4606	668	3692	292	3336	165	64	16
Fe	2384	128	2275	379	2528	200	2087	124	1824	160	34	89
K	1312	49	1042	241	983	145	806	61	780	38	3124	n.d.
Na	1141	104	940	168	882	105	711	33	647	26	18 252	15 290
Ca	807	161	831	157	778	123	776	38	696	15	6346	105
Mg	686	69	594	117	557	92	471	18	404	23	1548	25
Si	56	7	38	6	38.2	0.1	42	1	46	1	n.a.	n.a.
Mn	45	3	41	7	40	6	29	6	28	1	<6	<9
Sr	16	1	15	2	14	1	11	2	11.0	0.2	39.6	0.7
V	11	1	10	2	11	1	7	1	7.5	0.4	10	0.1
Ti	8	1	24	2	46		27		24.5	0.1	0.5	0.4
Zn	5	1	5	2	6		4		3.3	0.1	8.0	n.d.
Pb	4.5	0.3	3.5	0.9	3.1	0.2	2.3	0.5	1.9	0.1	0.003	0.004
Rb	3.8	0.2	3.2	0.8	3.0	0.3	2.1	0.3	2.1	0.1	4.9	0.1
Zr	2.1	0.1	1.7	0.5	1.8	0.1	1.1	0.2	0.74	0.04	<0.2	<0.3
Ce	1.47	0.04	1.3	0.2	1.22	0.09	1.01	0.08	0.89	0.03	0.07	0.04
Sc	1.2	0.1	1.2	0.4	1.2	0.1	0.9	0.1	0.8	0.1	<0.2	0.1
Y	0.95	0.05	0.9	0.1	0.84	0.07	0.66	0.06	0.57	0.03	0.033	0.006
Ga	0.9	0.3	1.0	0.3	1.1	0.1	0.88	0.04	0.7	0.2	0.011	0.004
Li	0.9	0.2	0.7	0.3	0.6	0.2	0.5	0.1	0.5	0.1	0.45	0.01
Nd	0.80	0.05	0.7	0.1	0.69	0.06	0.58	0.04	0.50	0.02	0.03	0.02
Tl	0.77	0.03	0.6	0.2	0.61	0.05	0.46	0.06	0.38	0.03	0.003	0.003
La	0.65	0.03	0.54	0.08	0.52	0.04	0.45	0.03	0.38	0.02	30	39

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

Bi	0.61	0.04	0.66	0.06	0.65	0.05	0.52	0.08	0.42	0.07	0.7	2.3
Co	0.56	0.03	0.59	0.05	0.60	0.05	0.45	0.05	0.38	0.03	0.03	0.02
Ge	0.45		0.39	0.04	0.40	0.03	0.34	0.02	0.31		n.a.	n.a.
Sn	0.39	0.05	0.2	0.1	0.28	0.09	0.18	0.06	0.10	0.01	0.01	0.03
Cu	0.4	0.1	0.3	0.3	0.5	0.1	0.4	0.1	0.5	0.2	14	10
Cr	0.30	0.03	0.31	0.08	0.4	0.2	0.3	0.1	0.21	0.06	0.07	0.05
Th	0.29	0.01	0.25	0.03	0.22	0.02	0.19	0.02	0.17	0.01	0.003	<0.003
Ni	0.28	0.07	0.29	0.05	0.29	0.04	0.3	0.1	0.16	0.04	0.3	0.4
Pr	0.19	0.01	0.17	0.04	0.18		0.12		0.117	0.003	0.008	0.005
Ba	0.19	0.08	0.05	0.01	0.09	0.02	0.05	0.01	0.045	0.004	5.9	0.5
Gd	0.181	0.006	0.16	0.03	0.16	0.01	0.123	0.008	0.114	0.008	0.02	0.01
Sm	0.18	0.01	0.16	0.03	0.16	0.01	0.12	0.01	0.113	0.003	0.009	0.002
Dy	0.17	0.02	0.15	0.03	0.15	0.01	0.11	0.01	0.103	0.002	n.d.	0.004
Cs	0.11	0.00	0.10	0.02	0.09	0.01	0.07	0.01	0.06	0.01	0.05	0.01
Er	0.098	0.009	0.09	0.02	0.090	0.008	0.065	0.004	0.062	0.002	0.006	0.001
Yb	0.093	0.008	0.09	0.02	0.083	0.008	0.061	0.003	0.058	0.002	0.004	>0.003
Be	0.08	0.02	0.07	0.02	0.06	0.01	0.08	0.02	0.04	0.01	<0.02	<0.03
U	0.07	0.02	0.05	0.01	0.05	0.01	0.05	0.01	0.031	0.002	0.013	0.002
Cd	0.05	0.01	0.04	0.01	0.037	0.004	0.030	0.002	0.0264	0.0005	0.01	0.01
Eu	0.050	0.004	0.047	0.009	0.045	0.004	0.034	0.002	0.033	0.001	0.003	0.001
Hf	0.044	0.004	0.03	0.01	0.034	0.005	0.012	0.003	0.006	0.001	0.004	>0.01
Sb	0.04	0.02	0.05	0.03	0.013	0.001	0.003	0.002	0.001	0.001	0.01	0.6
Ho	0.033	0.003	0.031	0.006	0.030	0.003	0.022	0.001	0.0211	0.0004	0.005	0.0004
In	0.030		0.025	0.004	0.024	0.003	0.019	0.001	0.018		n.a.	n.a.
Tb	0.027	0.001	0.025	0.004	0.025	0.002	0.019	0.001	0.017	0.001	0.003	0.0003
Tm	0.015	0.001	0.013	0.004	0.014		0.010		0.0090	0.0001	0.0005	0.0002
Lu	0.014	0.001	0.013	0.003	0.013	0.001	0.0092	0.0004	0.0089	0.0003	0.003	0.0003
Ag	0.005	0.001	0.002		n.a.		n.a.		0.002		<0.001	0.005
Nb	0.0045		0.0008	0.0002	0.00052	0.00003	0.0021	0.0003	0.0002		n.a.	n.a.
Mo	0.003	0.001	0.006	0.001	0.009		0.004		0.003	0.001	0.2	0.01
Ta	0.0020		0.00011	0.00003	0.00016	0.00003	0.0015	0.0002	0.0003		n.a.	n.a.
As	1.8	0.3	2.1	0.2	n.a.		n.a.		1.57	0.04	0.2	3.6
Se	0.52	0.05	0.49	0.03	n.a.		n.a.		0.240	0.001	<0.4	<0.6
<i>Anions</i>	<i>mg kg⁻¹</i>	<i>ls</i>	<i>mg kg⁻¹</i>	<i>ls</i>	<i>mg kg⁻¹</i>	<i>ls</i>	<i>mg kg⁻¹</i>	<i>ls</i>	<i>mg kg⁻¹</i>	<i>ls</i>	<i>mg kg⁻¹</i>	<i>mg kg⁻¹</i>
SO ₄	64 771	4443	48 943	9540	45 389	4807	37 711	2572	31 750	1903	25.38	n.a.
Cl	22 115	1574	16 084	33 53	14 587	1703	11 760	1061	10 318	938	1.8	n.a.
F	1394	109	1002	226	868	101	733	40	640	42	0.38	n.a.
BO ₃	256	11	n.a.		n.a.		n.a.		n.a.		n.a.	n.a.
PO ₄	156	18	139	33	99	61	112	5	111	22	n.a.	n.a.
Br	51		44	8	40	4	39	1	76	35	n.d.	n.a.

Flm, flowmeter; dye, dye dilution; n.d., not detected; n.a., not analysed; n.c., not calculated.

Table 2. Fumarole compositions and our best estimate of the Kawah Ijen gas composition

Sample no. Year	KV07-402 2007	KV07-411 2007	KV07-421 2007	KV08-003 2008	KV08-010 2008	KV08-014 2008	Best estimate 2007–08	Uncertainty	
<i>T</i> (°C)	495	330	335	490	>400	>400			
Gas collected (g)	9.61	13.38	9.88	11.88	12.79	16.96			
<i>Stable isotopes</i>									
δD	−10.30	n.a.	−12.80	−10.57	−8.02	−26.26			
δ ¹⁸ O in H ₂ O	4.80	n.a.	4.60	3.56	5.30	1.86			
δ ¹⁸ O in SO ₄	n.a.	n.a.	n.a.	7.59	15.07	16.97			
<i>Major species</i>									
	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>g kg⁻¹ gas</i>	<i>Is/P−</i>	<i>Is/P+</i>
H ₂ O	n.a.	n.a.	n.a.	755.7	704.9	729.1	717	17	17
CO ₂	n.a.	n.a.	n.a.	183.8	212.1	207.0	210	4	4
SO ₂	n.a.	n.a.	n.a.	25.5	35.7	24.2	30	8	8
H ₂ S	n.a.	n.a.	n.a.	25.8	44.9	38.1	41	5	5
N ₂	n.a.	n.a.	n.a.	8.58	1.47	1.15	1.3	0.2	0.2
<i>Minor and traces</i>									
	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>mg kg⁻¹ gas</i>	<i>Is/P−</i>	<i>Is/P+</i>
HCl	n.a.	n.a.	n.a.	472	902	491	696	291	291
HF	n.a.	n.a.	n.a.	71.4	22.0	3.74	13	13	13
He	n.a.	n.a.	n.a.	0.086	0.079	0.101	0.09	0.02	0.02
H ₂	n.a.	n.a.	n.a.	1.13	1.03	1.29	1.2	0.2	0.2
Ar	n.a.	n.a.	n.a.	71.7	12.8	8.96	11	3	3
O ₂	n.a.	n.a.	n.a.	1.52	0.59	1.79	1.2	0.9	0.9
CH ₄	n.a.	n.a.	n.a.	0.069	0.007	0.105	0.06	0.07	0.07
CO	n.a.	n.a.	n.a.	0.013	0.013	0.209	0.1	0.1	0.1
Si	83.2	165	175	n.a.	n.a.	n.a.	165	55	7
Na	173	49	120	n.a.	n.a.	n.a.	120	47	36
Ca	n.a.	n.a.	51	36	31	52	44	10	8
B	43.2	26	39	n.a.	n.a.	n.a.	39	9	3
Al	52.3	20	39	n.d.	n.d.	23	31	9	15
Fe	n.a.	n.a.	47	17	17	20	18	2	15
P	16.3	6.8	12	n.a.	n.a.	n.a.	12	4	3
K	24.4	4.8	27.5	10	9.6	9.6	10	0.8	15
Mg	n.a.	n.a.	11.3	7	6	7	6.9	0.3	2.2
Se	n.a.	n.a.	3.8	n.a.	n.a.	n.a.	4		
As	8.16	4.4	6.8	2.1	2.1	2.1	3	1	4
Ti	3	3	3	2	2	2	2.8	1.2	0.5
Cu	2.54	2.5	5.8	2	2	<i>n.d.</i>	2.5	0.4	1.1

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

Cr	0.76	0.8	5.5	2.1	2.3	3.1	2	1	1
Ni	1.20	1.2	3.1	1.2	1.3	1.2	1.23	0.03	0.36
Zn	1.27	1.3	2.3	1.0	0.9	1.07	1.2	0.2	0.3
Mn	n.a.	n.a.	1.51	1.5	0.67	0.75	1.1	0.4	0.4
Te	1.15	0.65	1.09	n.a.	n.a.	n.a.	1.09	0.29	0.04
Sc	0.69	0.69	1.26	0.5	0.45	0.49	0.6	0.1	0.2
Ba	0	0	0	0	0	0	0.4	0.1	0.1
V	0.22	0.22	0.47	0.13	n.d.	0.15	0.22	0.07	0.08
Sr	0.22	0.22	0.18	0.09	0.08	0.34	0.20	0.11	0.04
Hg	0	0	0	n.a.	n.a.	n.a.	0.12	0.03	0.07
Pb	0.08	0.08	0.12	0.06	0.05	0.06	0.07	0.01	0.02
<i>Trace elements</i>	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	$\mu\text{g kg}^{-1}$ gas	<i>I</i> _s / <i>P</i> −	<i>I</i> _s / <i>P</i> +
Li	14	14	26	82	81	197	54	39	49
Sb	45	45	74	26	30	29	37	9	13
Mo	54	54	52	22	20	20	37	17	17
Sn	34	34	32	20	16	40	33	14	2
Tl	44	44	36	23	22	28	32	9	12
Rb	30	30	55	28	26	59	30	2	26
Zr	16	16	14	20	31	74	18	2	21
Ce	19	19	15	9	8	20	17	8	2
Be	15	15	33	10	10	12	14	3	5
La	12	12	14	n.a.	n.a.	n.a.	12	0	2
Ga	11	11	15	6	6	13	11	5	2
Bi	n.a.	n.a.	n.a.	38	10	1	10	6	18
Y	10	10	14	6	6	18	10	4	5
Nd	7	7	19	9	8	16	8	2	9
Nb	6.3	6.3	8	3	4	4.4	5	2	1
Ho	n.d.	n.d.	n.d.	3	3	3	3.1	0.01	0.2
Pr	1.9	2	n.d.	0	0	2	1.9	1.5	0.1
Co	n.a.	n.a.	n.a.	0.6	1.6	3.4	1.6	0.7	1.2
Dy	0.9	1	n.d.	0.3	0.2	2.0	0.9	0.6	0.3
Gd	0.9	1	n.d.	0.3	0.2	1.8	0.9	0.7	0.3
Sm	0.9	1	n.d.	0.4	0.2	2.2	0.9	0.6	0.4
Cd	0.9	0.9	n.d.	n.a.	n.a.	n.a.	0.9		
Th	0.9	1	1	0.7	0.6	1.7	0.9	0.2	0.1
Cs	n.d.	n.d.	n.d.	0.9	0.8	1.8	0.9	0.1	0.6
Hf	n.d.	n.d.	n.d.	0.5	0.8	1.1	0.8	0.2	0.2
In	n.a.	n.a.	n.a.	0.4	0.3	1.1	0.36	0.03	0.51
W	n.a.	n.a.	n.a.	0.2	0.6	0.2	0.19	0.02	0.24
Yb	n.d.	n.d.	n.d.	0.1	0.1	0.7	0.14	0.02	0.40

(Continued)

Table 2. *Continued*

Sample no. Year	KV07-402 2007	KV07-411 2007	KV07-421 2007	KV08-003 2008	KV08-010 2008	KV08-014 2008	Best estimate 2007–08	Uncertainty	
	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>μg kg⁻¹ gas</i>	<i>1s/P-</i>	<i>1s/P+</i>
U	n.d.	n.d.	n.d.	0.1	0.1	0.7	0.14	0.003	0.38
Er	n.d.	n.d.	n.d.	0.1	0.1	1.0	0.13	0.01	0.59
Eu	n.d.	n.d.	n.d.	0.1	0.0	0.5	0.07	0.02	0.31
Tb	n.d.	n.d.	n.d.	0.04	0.03	0.3	0.04	0.005	0.19
Lu	n.d.	n.d.	n.d.	0.03	0.02	0.1	0.03	0.003	0.04
Tm	n.d.	n.d.	n.d.	0.02	0.02	0.13	0.020	0.0001	0.073
Ta	n.a.	n.a.	n.a.	0.004	n.d.	n.d.	0.004		
Ag	<3	<2	<4	n.a.	n.a.	n.a.	<3		

The uncertainty reported is 1 standard deviation from the mean, or upper and lower 34 percentile for the median. (n.d., not detected; n.a., not analysed; values in italics denote semi-quantitative data). Data for Ho are inconsistent with the other REE and are likely affected by an analytical artefact (see Fig. 8).

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

Table 3. Compositions of native sulphur precipitates from the plume (KV07-804) and from the condensate solutions (KV07-402 and 411)

Sample Sample no. Element	Needles KV07-804 ppm	Cond. precip. KV07-402 ppm	Cond. precip. KV07-411 ppm
Al	514	535	65
Fe	311	751	102
Si	298	n.d.	1452
Ca	267	649	263
Na	255	1712	450
K	98	245	n.d.
Te	63	12	8
Mg	38	163	32
Ni	n.d.	44	14
Ti	28	24	35
Zn	11	28	12
Ba	7.9	n.d.	4.0
Cu	6	79	28
Sc	4.3	15	7.0
Sb	3.7	0.7	0.3
Sn	1.8	0.2	0.3
Sr	1.8	2.5	0.4
Hg	1.6	1.2	0.8
Li	1.4	n.d.	n.d.
Mo	1.3	0.4	0.6
V	1.3	4.6	1.3
Zr	0.9	n.d.	n.d.
Mn	0.8	14	n.d.
Pb	0.8	1.2	0.4
Rb	0.6	0.7	0.2
Ag	0.5	n.d.	n.d.
Cr	0.5	97	8.5
Tl	0.5	0.2	0.2
Ce	0.3	0.2	0.1
Nb	0.2	n.d.	0.1
Y	0.2	0.2	0.1
Be	0.1	0.4	0.1
Cd	0.1	n.d.	n.d.
Cs	0.1	n.d.	n.d.
Ga	0.1	0.2	0.1
Gd	0.1	n.d.	n.d.
Ho	0.1	n.d.	0.1
La	0.1	0.2	0.1
Lu	0.1	n.d.	n.d.
Nd	0.1	0.2	n.d.
Sm	0.1	n.d.	n.d.
Th	0.1	n.d.	n.d.
Cl	2914	21 966	5868
As	467	67	37
Se	>224	37	32
BO ₃	391	424	141
PO ₄	n.d.	502	207

Component compositions

The Kawah Ijen system did not exhibit significant change during the 2007–09 period. Activity was restricted to passive degassing. Fumarole temperatures were highest in 2008 (up to 450°C) and lowest

in 2009 (most vents <400°C) corresponding to hot, calm weather in 2008 and overcast windy conditions in 2009. Lake temperatures at 80 cm depth were constant at $37 \pm 1^\circ\text{C}$. Banyu Pahit river discharge remained unchanged. Discharge at the first and second seepage areas was higher in 2009 and was accompanied by the appearance of new seepage outlets and persistence of flow beyond the first waterfall. Nonetheless, discharge at these seepage areas is small compared with the Banyu Pahit river discharge, and, therefore, we regard the total element output of the Kawah Ijen system as equivalent for the 2007–09 period.

Major element composition of fumarole gas

Sampling of surface fumarole emissions as a measure of volcanic gas composition is potentially hindered by contamination by near surface processes, including mixing with air and/or shallow groundwater (e.g. Giggenbach & Matsuo 1991). Although the samples are on a trend to humid air (Fig. 3), the low oxygen and nitrogen contents ($\text{O}_2 < 2$ ppm and $\text{N}_2 < 1.5$ wt% for the two best samples) indicate only minimal contamination. Ratios of all gas species are also in agreement with fields for andesite or arc volcanoes (cf. Delmelle & Stix 2000).

Fumarole compositions have been determined previously at Kawah Ijen (Fig. 3 – data in Delmelle *et al.* (2000); Takano *et al.* (2004); and courtesy of the Volcanological Survey of Indonesia). However, these samples were taken at the exit of the pipes used in sulphur mining, which emit significantly lower temperature gases ($T = 189 \pm 21^\circ\text{C}$ for 43 pipes measured in 2008 compared with $>400^\circ\text{C}$ for the natural vents that we sampled). The outflow of liquid sulphur indicates loss of S from the gas by condensation, and the presence of iron-sulphate on the inside of the pipes shows interaction between the gas and the pipe material. A residual enrichment in the non-condensable and non-reactive gases can thus be expected, and a trend to lower S_{total} and higher CO_2 content is indeed observed in these samples (Fig. 3).

To explore whether the measured major element fumarole composition preserves that of a high-temperature gas, we thermodynamically calculated the equilibrium speciation at varying P and T for the median sample, KV08-014 (Fig. 4a). The measured speciation shows good agreement with the thermodynamically predicted speciation, with the exception of CH_4 , which appears to have formed or have been introduced at low temperature. The equilibrium constants for the reactions $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ and $\text{SO}_2 + 3\text{H}_2 = \text{H}_2\text{S} + 2\text{H}_2\text{O}$, which control the CO_2 –CO and SO_2 – H_2S ratios, respectively, are also in mutual agreement (Fig. 4b).

Table 4. Representative compositions of gypsum and yellow Al-sulphate precipitates formed on the terrace of seepage area 1, and the Banyu Pahit riverbed, respectively

Sample no. Element	Gypsum KV07-505 ppm	Al-sulphate KV07-701 ppm
Sr	754	49.1
Al	606	63 715
K	268	44 610
Na	265	5457
Fe	216	17 899
Mg	67.7	4014
Ce	28.8	3.7
Nd	18.4	2.0
Pb	17.7	13.5
Ti	15.4	582
Zn	13.8	43.4
La	7.7	1.7
V	4.7	78.1
Pr	4.3	0.47
Li	3.7	5.4
As	3.5	18.9
Sm	3.2	0.53
Ni	2.6	3.4
Y	2.1	4.2
Gd	1.9	0.7
Mn	1.8	287
Cu	1.7	14.6
Ba	1.5	4.2
Rb	1.09	114
Cr	0.87	3.0
Dy	0.81	0.75
Zr	0.73	7.8
Eu	0.70	0.17
Ag	0.42	0.43
Er	0.30	0.47
Th	0.28	1.06
Sn	0.24	1.03
Tl	0.23	16.6
Tb	0.19	0.12
Yb	0.13	0.47
Ho	0.12	0.16
Te	0.11	n.d.
Ga	0.071	4.6
Be	0.058	0.37
Mo	0.046	0.094
Sb	0.037	0.067
Cs	0.031	3.9
Cd	0.028	0.21
Tm	0.026	0.070
Hf	0.022	0.14
Lu	0.016	0.072
U	0.016	0.26
Sc	n.d.	9.2
Nb	n.d.	0.19
Hg	n.d.	0.02

Moreover, measured and predicted speciation converge at *c.* 400°C and 100 bar (Fig. 4c). We conclude that the sampled fumarole emissions are

representative of the volcanic gas composition and have not been significantly modified.

Trace-element composition of fumarole gas

Giggenbach flasks are closed systems and sample a representative aliquot of gas. In contrast, condensate samples are sampled in an open system with gas pumped through the condenser. In such a sampling arrangement volatile elements will not be trapped efficiently (e.g. CO₂, Hg). However, concentrations for trace elements are commonly too low to be determined accurately in Giggenbach-bottle samples because of the small amount of gas sampled, the large diluting volume of NaOH-solution, and the fluid matrix conversion required to analyse these samples by ICP-techniques. Moreover, our Giggenbach-bottles were made of borosilicate glass, which is not inert and may contribute elements to the solution. Giggenbach-bottle solution compositions are reported in the supplementary data file. However, only condensates are used here to provide minor and trace element concentrations for the fumarole gas.

Gas compositions are given in Table 2. No correlations are observed between composition and fumarole temperature or flow, and the element signature and concentrations are similar for all fumaroles and for both years. To obtain a characteristic gas composition, we averaged the concentrations of the major elements in our best samples (KV08-010 and KV08-014), which represent high temperature, high flow fumaroles, with the lowest N₂ and water contents, and with a preserved equilibrium gas speciation (see above). For minor and trace elements we report the median and associated 68-percentile window of all samples.

The crater lake

Kawah Ijen crater lake water is made up of three main sources: water from rain; anions and acidity from volcanic gas; and cations from alteration of rocks added in rock falls (Delmelle & Bernard 1994; van Hinsberg *et al.* 2010b). van Hinsberg *et al.* (2010b) suggest that the lake is a distinct reservoir, separate from the underlying hydrothermal system, and which has persisted in its present form since at least the 1840s (Bosch 1858; Kemmerling 1921). The lake shows a persistent concentration increase from the earliest quantitative analysis in 1847 (Flückiger 1862) to a present-day plateau (Fig. 5). We acknowledge an inherent uncertainty in the oldest analyses. However, total dissolved solid (TDS) values, determined by drying and weighing, can be regarded as reliable, and these show

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

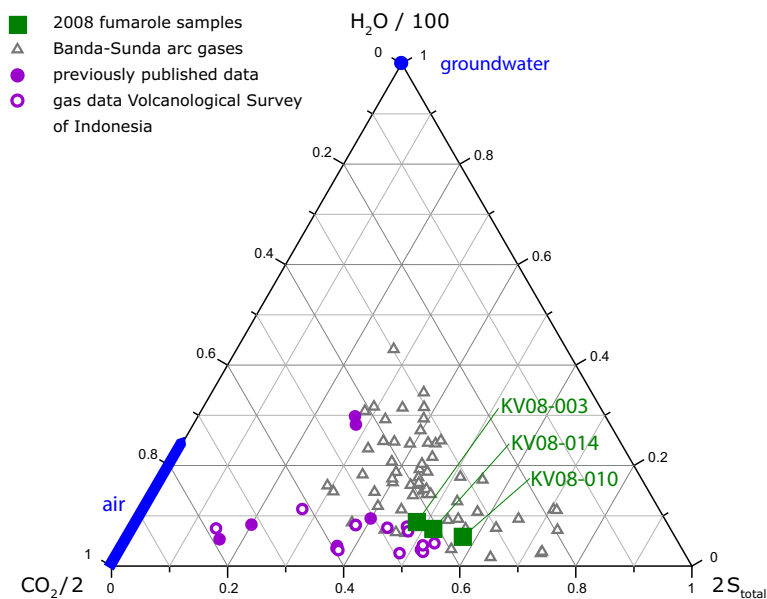


Fig. 3. Fumarole gas compositions of Kawah Ijen volcano compared with those of other Banda and Sunda arc volcanoes. Our data represent compositions of high-temperature vents, whereas previous samples were taken at the sulphur-mining pipe exits and represent modified and cooled gas.

the same behaviour. We interpret this trend as a progressive build-up of the element load after the lake re-established itself following the 1817 eruption and lake expulsion, and that the present lake has reached a compositional steady-state. In this case, the flux-in equals the flux-out, and the lake becomes a dynamic reservoir that need not be considered in constraining the element output of the volcano. A similar TDS value for the pre-1817 lake, calculated from measured density (Leschenault de la Tour 1811), suggests that this lake had reached a similar steady-state composition.

The fluxes out of the lake are evaporation, seepage and precipitation. Of these, evaporation and seepage have been sampled directly, although concentrations of all elements in the evaporative vapour were below the detection limit and this flux can, therefore, not be constrained quantitatively. Delmelle & Bernard (1994, 2000) and Delmelle *et al.* (2000) calculated that the lake is saturated in silica, barite, covellite, native sulphur and gypsum, and a distinct deficit in their constituent elements is observed when lake composition is plotted against that of Kawah Ijen andesite (fig. 7 in van Hinsberg *et al.* 2010b). Moreover, the S/Cl ratio in the fumarole gas is higher than that observed in the lake water, indicating deposition of sulphur. The presence of native sulphur at the bottom of the lake is further evidenced by the occurrence of sulphur 'spherules' (Delmelle *et al.* 2000; Takano *et al.*

2004). Lake sediments, enriched in Si, Ba and S are present at Kawah Ijen (Takano *et al.* 2004). However, these sediments are not pure chemical precipitates, and lack the predicted Cu enrichment. It is therefore not possible to constrain the precipitate sink from these. Precipitates do represent part of the flux from the Kawah Ijen system, albeit one that will only be emitted in a violent eruption (e.g. the lake expulsion in the 1817 eruption).

Seepage springs and Banyu Pahit river water composition

The compositions of individual springs in each seepage area vary in absolute element concentrations, especially for the smaller seepage outlets just below the dam. However, element ratios are similar, and we therefore conclude that the compositional variations are due to variable dilution by neutral groundwater. Representative compositions of each seepage area were calculated as the average of all samples and its associated 1 standard deviation (Table 1).

River water composition is near identical from 2007 to 2009, and is furthermore similar to that of the dry season in 1993 (Delmelle & Bernard 1994), 1996 (Delmelle *et al.* 2000) and 1999 (van Hinsberg *et al.* 2010b). Element ratios are identical within error, indicating that the differences reflect variations in dilution by neutral groundwater.

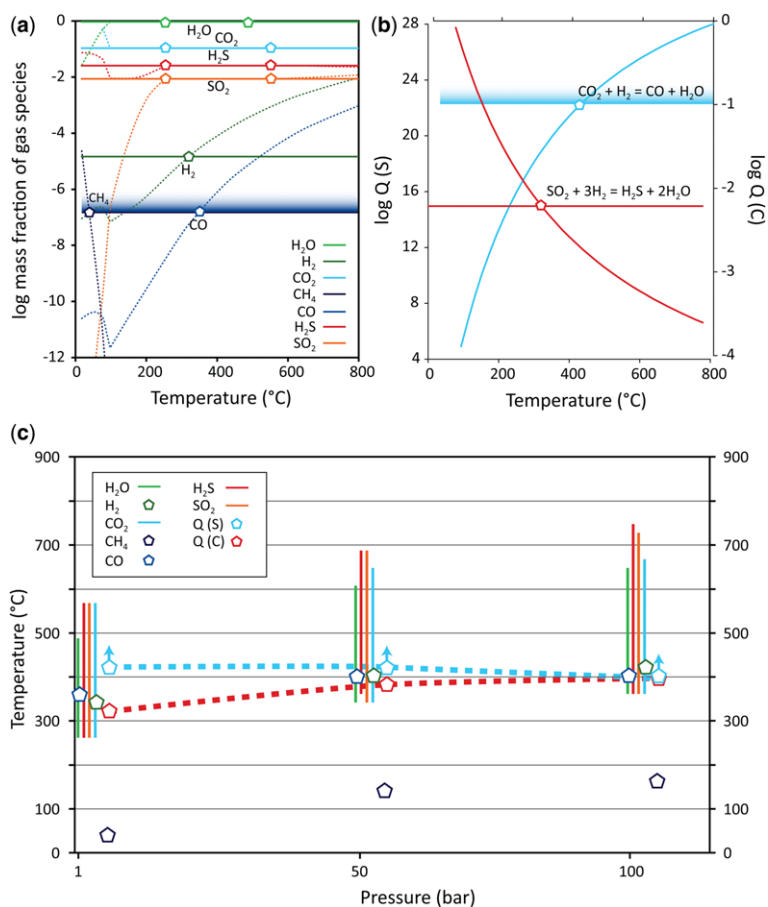


Fig. 4. (a) Thermodynamic predictions of gas speciation with changing temperature at 1 bar (dashed lines) compared with the measured speciation for sample KV08-014 (solid lines). Symbols indicate the temperature, or minimum and maximum of the temperature range, where measured and predicted speciation agree. (b) Thermodynamically predicted C- and S-system equilibrium constants with changing temperature at 1 bar compared with the measured value. (c) Compilation of temperature estimates from speciation and C + S equilibria against pressure shows convergence to c. 400°C and 100 bar. Only CH₄ deviates suggesting that it formed or was added to the gas at low temperature. Thermodynamic calculations were performed with FactSage and the Fact 5.3 database of gas species (see Bale *et al.* 2002). No gas species were excluded from the calculation. Measured CO concentrations represent minimum estimates.

No systematic diurnal variations were observed, and element ratios are indistinguishable within error (Fig. 6a, b). Therefore, the Banyu Pahit river water composition is taken as constant over the studied period.

Precipitates are present in the Banyu Pahit valley in several locations, including precipitation of gypsum at the seepage outlets, barite and Al-sulphate precipitation in altered rocks of the seepage springs and Banyu Pahit riverbed and yellow Al-sulphate precipitates on the banks of the river. Gypsum precipitates form a terraced deposit at the uppermost seepage outlets that is up to 30 cm thick and actively

growing. However, this deposit was already observed in the early 19th century (Bosch 1858; Kemmerling 1921) indicating that growth is slow. This is confirmed by water compositions, which show within error conservative behaviour for SO₄ (van Hinsberg *et al.* 2010b). Similarly, evidence of precipitation of barite and Al-sulphates cannot be recognized in Ba, Al or SO₄ contents, although it does remove Pb (van Hinsberg *et al.* 2010b). The yellow Al-sulphate deposits form from evaporation of spray, and generally dissolve in the morning dew, whereupon these are added back to the river. We therefore limited correction for the impact of

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

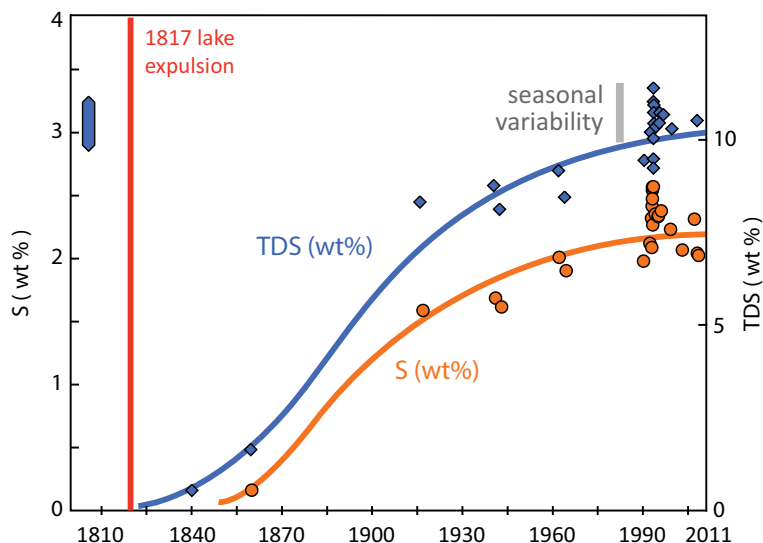


Fig. 5. Change in lake water composition over time. The lake was expelled in 1817, and shows a consistent increase in element concentrations to a current plateau. Composition data are from Leschenault de la Tour (1811), Flückiger (1862), Woudstra (1921), Tazieff *et al.* (1966), Zelenov (1969), Delmelle & Bernard (1994), Sumarti (1998), Delmelle *et al.* (2000), Takano *et al.* (2004), van Hinsberg *et al.* (2010b) and Palmer (2010).

precipitates on the element output to Pb concentrations, using the rock dissolution relationships discussed in van Hinsberg *et al.* (2010b).

Groundwater

Groundwater from the Banyu Pahit river valley (1 km downstream of the lake, and 300 m downstream of surface river flow) and a spring on the flank of Widadaren volcano (1.5 km from the lake) lacks a hyperacid water signature. Rather, it is characterized by a pH of ~ 8 and high Ca and Mg concentrations, typical of groundwater that has interacted with basaltic and andesitic deposits (e.g. Aiuppa *et al.* 2000). This complete lack of a hydrothermal signature suggests that the impact of the acid waters is localized. Indeed, acid springs are only present in the Banyu Pahit river valley (Fig. 1). It appears that the acid waters are channelled into this valley, possibly by strong groundwater flow to the SW from Merapi volcano, the summit of which is 600 m above that of Kawah Ijen (Fig. 1). Although contamination of groundwater cannot be excluded, it would appear to be insignificant.

Component flux

Volcanogenic emissions of Kawah Ijen are dominated by the fumarole flux and the Banyu Pahit river water discharge. There is no evidence for

release of material into the groundwater away from the volcano, and the steady-state composition of the crater lake indicates that it is neither a sink nor a source of material. Precipitation of material in the subsurface is likely, but this cannot be quantified, nor can the trace element sink by precipitation in the lake. Both represent emissions from the system into its environment and our estimates will therefore be an underestimate of the total flux.

Seepage water flux

Discharge at each seepage area was measured after the confluence of all constituent springs, and is approximately 11 s^{-1} at each of seepage areas 1 and 2, and 31 l s^{-1} at seepage area 3 (locations in Fig. 1). The latter area is, therefore, the main source of the Banyu Pahit river. Springs in the first seepage area represent direct outflow of the crater lake, based on similar anion ratios (anions act as conservative elements in the Kawah Ijen – Banyu Pahit system and their ratios are therefore a source indicator, see Palmer 2010). Compositions of the springs in the third area indicate a source for these waters distinct from the crater lake, which has been interpreted to be the underlying hydrothermal system (Palmer 2010).

Water flow is continuous downstream from seepage area 3, whereas the outflow of both the first and second seepage areas disappears into the sediment (Fig. 1). It is therefore unclear whether the three

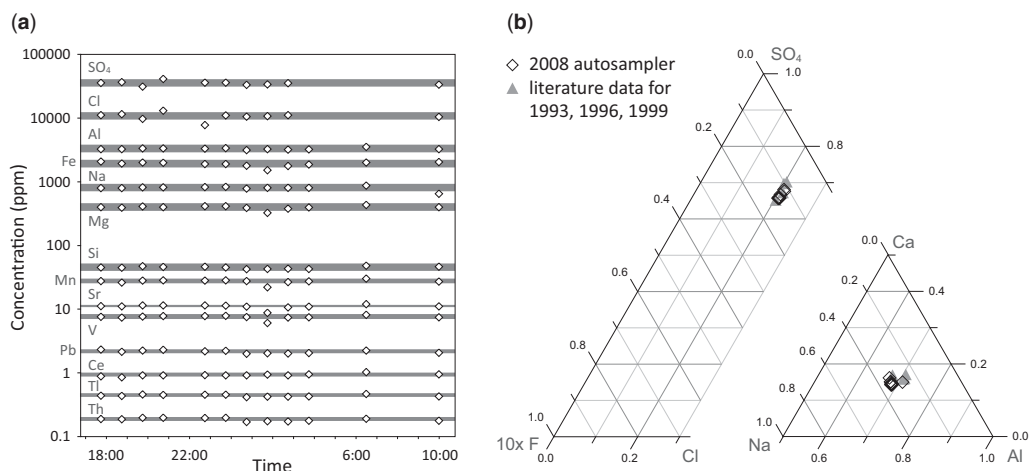


Fig. 6. Diurnal variations in the composition of the Banyu Pahit river at sample locality 4. (a) No systematic variations in element concentration are observed and (b) anion and cation ratios remain constant. The ratios are furthermore identical, within error, to literature values for 1993–99.

seepage areas represent a continuous flow of water through the Banyu Pahit valley. In fact, discharge measurements and field observations suggest that these three seepage emissions are additive. Discharge at area 2 is only marginally larger than that at area 1 (Table 1), but the anion ratios indicate that only up to 50% of the water emitted at area 2 could have been derived from area 1 (Palmer 2010). At least half of the outflow from seepage area 1 is therefore unaccounted for at the second seepage area. The Banyu Pahit river valley is dry at its confluence with the outflow of the third springs area, and no water appears from the riverbed despite it being cut by a c. 20 m high cliff cutting across the riverbed. Moreover, the third seepage area is located in a valley separated from that of the Banyu Pahit. Therefore, we regard the seepage outflow in areas 1 and 2 as an emission in addition to the waters released at the third seepage area, rather than re-appearance of previously emitted waters.

River water flux

The Banyu Pahit river has continuous water flow from its appearance at seepage area 3. Rather than using the spring compositions and their discharge, we have quantified the flux of this component downstream. Apart from easier access, the river flows on top of a lavaflow at this locality, which provides for more accurate discharge determination than at the springs where it flows on top, and partially through coarse-grained sediment. Furthermore, this site was sampled each year, was used to check for diurnal variations, and was sampled as part of previous studies (e.g. Delmelle & Bernard 1994, 2000;

Sumarti 1998). Negligible compositional variability is observed, resulting in a robust river flux estimate.

Discharge at this sample site is 55 l s^{-1} owing to addition of groundwater, and the composition has been further modified from that of the springs by water–rock interaction. Previous work on the Banyu Pahit river (van Hinsberg *et al.* 2010a, b) indicates that water–rock interaction acts mainly as a source of elements, owing to intense leaching by these fluids. Only Pb, Sb and Sn are significantly removed from the river water, in the case of Pb as a result of barite precipitation. This was corrected for using SO₄, Cl and F as conservative tracers and the water–rock interaction systematics as presented in van Hinsberg *et al.* (2010b), resulting in the corrected Banyu Pahit river flux of Table 5.

Fumarole emissions

FLYSPEC measurements of the fumarole plume give a 3-year consistent and constant flux of SO₂ of $2.2 \pm 0.8 \text{ kg s}^{-1}$ (c. 190 tonnes day⁻¹), although this value may be overestimated as the lateral motion of the plume affected our traverses over the rim (Vigouroux 2011; see also discussion in Gunawan *et al.* 2016). This value is similar to the SO₂ flux obtained by various methods in September 2014 (Gunawan *et al.* 2016). Combined with the fumarole gas composition, this provides an estimate of the gas flux from Kawah Ijen. However, the SO₂ content of the gas likely changes from the vent to the location of its measurement in the plume approximately 150 m from the fumarole mound. Needles of native sulphur precipitate from the plume as it cools and mixes with air. Moreover, sulphur



ELEMENT FLUX FROM KAWAH IJEN VOLCANO

condenses in the pipes used in sulphur mining. And, finally, H_2S and SO_2 will oxidize in the plume to form sulphate, among others, and aerosols (Oppenheimer *et al.* 1998; Mather *et al.* 2004; Martin *et al.* 2006). The FLYSPEC SO_2 flux will thus underestimate the total gaseous emissions.

Conversion of SO_2 to sulphate and aerosols cannot be quantified with the current dataset, but the loss to native sulphur precipitation can be estimated from the amount of sulphur that is mined (0.16 kg s^{-1} , see below), and which dominates over sulphur needle precipitation. The correlation between H_2S and SO_2 contents in gas samples taken at the exits of the pipes, which are affected by sulphur condensation (see above and Fig. 3), suggests sulphur formation by the reaction:



A mined native sulphur flux of 0.16 kg s^{-1} would, therefore, correspond to an underestimate of SO_2 emissions of 0.11 kg s^{-1} . This has been added to the FLYSPEC measurement to arrive at a total SO_2 flux of 2.3 kg s^{-1} . The resulting element flux from the fumaroles is given in Table 5.

Sulphur mining flux

The flux of mined material is not an independent flux from Kawah Ijen, because it condensed out of the fumarole emissions. However, it is of direct interest, because this sulphur is removed from the immediate surroundings of Kawah Ijen volcano, and is eventually used in industrial processes (including the bleaching of cane sugar). It, therefore, represents a direct and concentrated flux into the environment, similar to the channelled flux of the Banyu Pahit river water and its use in irrigation. Our best estimate for the amount of sulphur mined per day is 14 000 kg, based on reports from the miners that approximately 100 miners work each day, they make two trips to the crater and carry on average 70 kg of sulphur per trip. Table 5 compares the mined flux to total element emissions, indicating that sulphur mining removes a significant percentage of toxic elements including Sb, As and Se.

Kawah Ijen flux in a global context

Kawah Ijen flux estimates compared with those of other volcanoes

The fumarolic, aqueous and total element fluxes into the environment from the Kawah Ijen system are listed in Table 5, and presented in Figure 7a together with flux estimates reported in the literature for other volcanoes. The gaseous volcanic flux varies

by up to six orders of magnitude among the different volcanoes, and Kawah Ijen generally resides at the lower end of this range. In a global context, the gaseous flux of Kawah Ijen is small. The element pattern for Kawah Ijen's fumarole emissions is similar to that of the other volcanoes, but not identical, with Kawah Ijen's emissions relatively low in Cl and F or, vice versa, relatively rich in S and C, and low in the heavy metals, especially Pb and Cd. Berlo *et al.* (2014) show that the fumarole emissions of Kawah Ijen are composed of a degassing component from a deep mafic magma undergoing sulphide breakdown, which interacts shallowly with a dacitic magma. The contribution from this mafic magma could potentially cause the higher C and S relative to Cl and F.

The element pattern, and even the absolute flux values, is remarkably similar to those for Kilauea (data from Mather *et al.* 2012), despite their very different geotectonic setting and magma compositions. In fact, apart from differences in absolute flux, the various volcanoes are highly similar in the element signature of their gaseous emissions and there are no apparent differences, for example, between minor and major emitters. This similarity validates the approach of extrapolating a limited set of measured volcanic emissions to an estimate of the global volcanic flux (cf. Lambert *et al.* 1988; Gauthier & Le Cloarec 1998; Hinkley *et al.* 1999; Fischer 2008).

Flux estimates for aqueous volcanic emissions are sparse. For Etna, an estimate of the aqueous flux is available from the groundwater flux (Aiuppa *et al.* 2000), and Varekamp (2008) reports flux estimates for the Rio Agrio associated with Copahue volcano. These aqueous emissions are internally consistent in element signature but markedly different from that of the gaseous emissions (discussed in more detail below). The fluids are important carriers of (earth) alkali elements and ligands, and commonly exceed the gaseous flux for these elements. They also represent a significant emission of metals, although less so in the case of Etna groundwater. This likely reflects the lower transporting capacity of Etna groundwater compared with the acidic and ligand-rich fluids of Kawah Ijen and the Rio Agrio.

Fumarole v. water flux

It is evident from Figure 7a that the Kawah Ijen fumarole flux is dwarfed for most elements by that of the Banyu Pahit river, with the exception of volatile metals and semi-metals including Cu, As, Se, Te, Sb, Hg and Mo, but not Tl. The flux of Ba and Si is also higher in the fumaroles, but this is an artefact owing to saturation of the waters in barite and silica. The fluid flux completely dominates the major and minor 'rock-forming' elements,

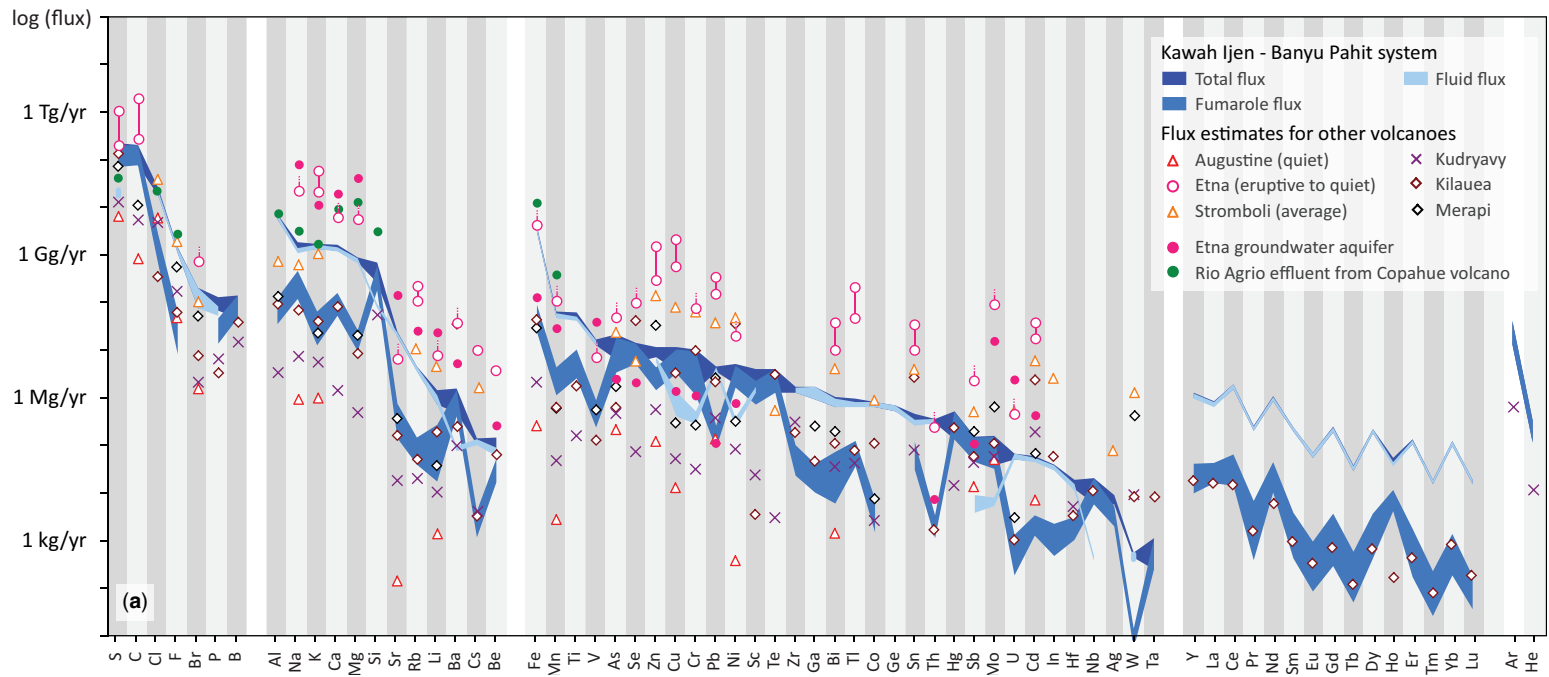
Table 5. Fumarole, aqueous and total element flux of the Kawah Ijen–Banyu Pahit system in $Mg\ a^{-1}$, and the proportion of elements removed in sulphur mining

Element	Ijen total	16 perc.	84 perc.	Ijen aqueous	1 s	Ijen gaseous	16 perc.	84 perc.	Mined	% of total
S _{total}	151 777	66 121	66 121	20 337	2471	131 440	63 650	63 650	–	–
C _{total}	139 094	63 659	63 659	–	–	139 094	63 659	63 659	–	–
Cl	20 963	3687	3687	19 316	2667	1647	1020	1020	15	0.07
F	1226	181	181	1197	148	30	33	33	–	–
Br	138	65	65	138	65	–	–	–	–	–
P	97	32	31	67	15	30	16	15	–	–
B	94	48	44	–	–	94	48	44	0.4	0.39
Al	6305	765	775	6231	725	74	41	50	2.6	0.04
K	1475	179	207	1452	168	23	11	39	0.5	0.03
Ca	1394	191	189	1288	137	106	55	52	1.4	0.10
Na	1499	310	293	1209	135	291	175	159	1.3	0.09
Mg	771	98	100	755	90	17	8	9	0.2	0.03
Si	484	235	192	84	9	401	226	184	1.5	0.32
Sr	21	2	2	21	2	0.5	0.3	0.2	0.009	0.04
Rb	4.0	0.5	0.5	3.9	0.4	0.07	0.03	0.07	0.003	0.08
Li	1.0	0.3	0.3	0.9	0.2	0.1	0.1	0.1	0.007	0.70
Ba	1.0	0.6	0.5	0.08	0.01	0.96	0.56	0.48	0.04	3.88
Cs	0.12	0.02	0.02	0.12	0.02	0.002	0.001	0.002	0.0004	0.36
Be	0.11	0.03	0.03	0.07	0.02	0.03	0.02	0.02	0.0004	0.40
Fe	3440	477	498	3396	456	45	21	42	1.6	0.05
Mn	55	8	8	52	6	3	2	2	0.004	0.01
Ti	53	9	8	46	5	7	4	3	0.1	0.27
V	14	2	2	14	2	1	0	0	0.006	0.04
As	11	5	10	2.9	–	8	5	10	2.4	22.3
Zn	9	2	2	6.2	0.7	3	1	1	0.1	0.60
Cu	7	3	4	0.8	0.4	6	3	4	0.03	0.45
Cr	6	4	4	0.4	0.1	5	4	4	0.003	0.04
Se	10	4	4	0.4	–	9	4	4	1.2	11.9
Pb	4.0	0.5	0.5	3.8	0.5	0.2	0.1	0.1	0.004	0.10
Ni	3	1	2	0.3	0.1	3	1	2	–	–
Sc	2.9	1.0	1.0	1.5	0.2	1.4	0.7	0.8	0.02	0.75
Te	3	1	1	–	–	3	1	1	0.32	12.2
Zr	1.5	0.2	0.2	1.4	0.2	0.04	0.02	0.05	0.005	0.32

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

Ga	1.3	0.4	0.4	1.3	0.4	0.03	0.02	0.01	0.0004	0.03
Bi	0.8	0.2	0.2	0.8	0.2	0.02	0.02	0.05		
Tl	0.8	0.1	0.1	0.7	0.1	0.08	0.04	0.05	0.003	0.33
Co	0.71	0.09	0.09	0.71	0.09	0.004	0.002	0.003		
Ge	0.58	0.08	0.08	0.58	0.08					
Sn	0.38	0.09	0.08	0.30	0.04	0.08	0.05	0.04	0.009	2.40
Th	0.32	0.03	0.03	0.316	0.034	0.002	0.001	0.001	0.0004	0.13
Hg	0.3	0.2	0.2			0.3	0.2	0.2	0.008	2.84
Sb	0.10	0.05	0.05	0.006	0.003	0.09	0.05	0.05	0.02	19.5
Cd	0.05	0.01	0.01	0.049	0.005	0.002	0.001	0.001	0.0004	0.83
Mo	0.10	0.06	0.06	0.007	0.001	0.09	0.06	0.06	0.006	6.70
U	0.058	0.008	0.008	0.058	0.008	0.0003	0.0002	0.0009		
In	0.034	0.004	0.005	0.033	0.003	0.0009	0.0004	0.0013		
Hf	0.015	0.003	0.003	0.013	0.002	0.002	0.001	0.001		
Nb	0.01	0.01	0.01	0.0004	0.0000	0.01	0.01	0.01	0.0009	6.40
Ag	0.007	0.002	0.002	0.00362		0.004	0.002	0.002	0.003	35.5
W	0.0005	0.0002	0.0006			0.0005	0.0002	0.0006		
Ta	0.0005	0.0001	0.0001	0.00048	0.00005	0.000009	0.000004	0.000004		
Y	1.1	0.1	0.1	1.1	0.1	0.024	0.015	0.016	0.0009	0.08
La	0.7	0.1	0.1	0.7	0.1	0.029	0.013	0.014	0.0004	0.06
Ce	1.70	0.21	0.20	1.7	0.2	0.042	0.028	0.020	0.001	0.08
Pr	0.22	0.03	0.03	0.22	0.02	0.005	0.004	0.002		
Nd	1.0	0.1	0.1	0.9	0.1	0.02	0.01	0.02	0.0004	0.05
Sm	0.21	0.02	0.02	0.21	0.02	0.002	0.002	0.002	0.0004	0.20
Eu	0.06	0.01	0.01	0.06	0.01	0.0002	0.0001	0.0008		
Gd	0.21	0.03	0.03	0.21	0.03	0.002	0.002	0.001	0.0004	0.20
Tb	0.032	0.004	0.005	0.032	0.004	0.00009	0.00005	0.00047		
Dy	0.195	0.022	0.02	0.19	0.02	0.0023	0.0019	0.001		
Ho	0.05	0.01	0.01	0.039	0.004	0.008	0.003	0.004	0.0004	0.91
Er	0.12	0.01	0.01	0.12	0.01	0.0003	0.0001	0.0014		
Tm	0.017	0.002	0.002	0.017	0.002	0.00005	0.00002	0.00018		
Yb	0.108	0.012	0.013	0.11	0.01	0.0003	0.0002	0.001		
Lu	0.017	0.002	0.002	0.017	0.002	0.00007	0.00003	0.00011	0.0004	2.56
Ar	27	14	14			27	14	14		
He	0.2	0.1	0.1			0.2	0.1	0.1		

Data for Ho are inconsistent with the other REE and its flux is an overestimate (see Fig. 8).



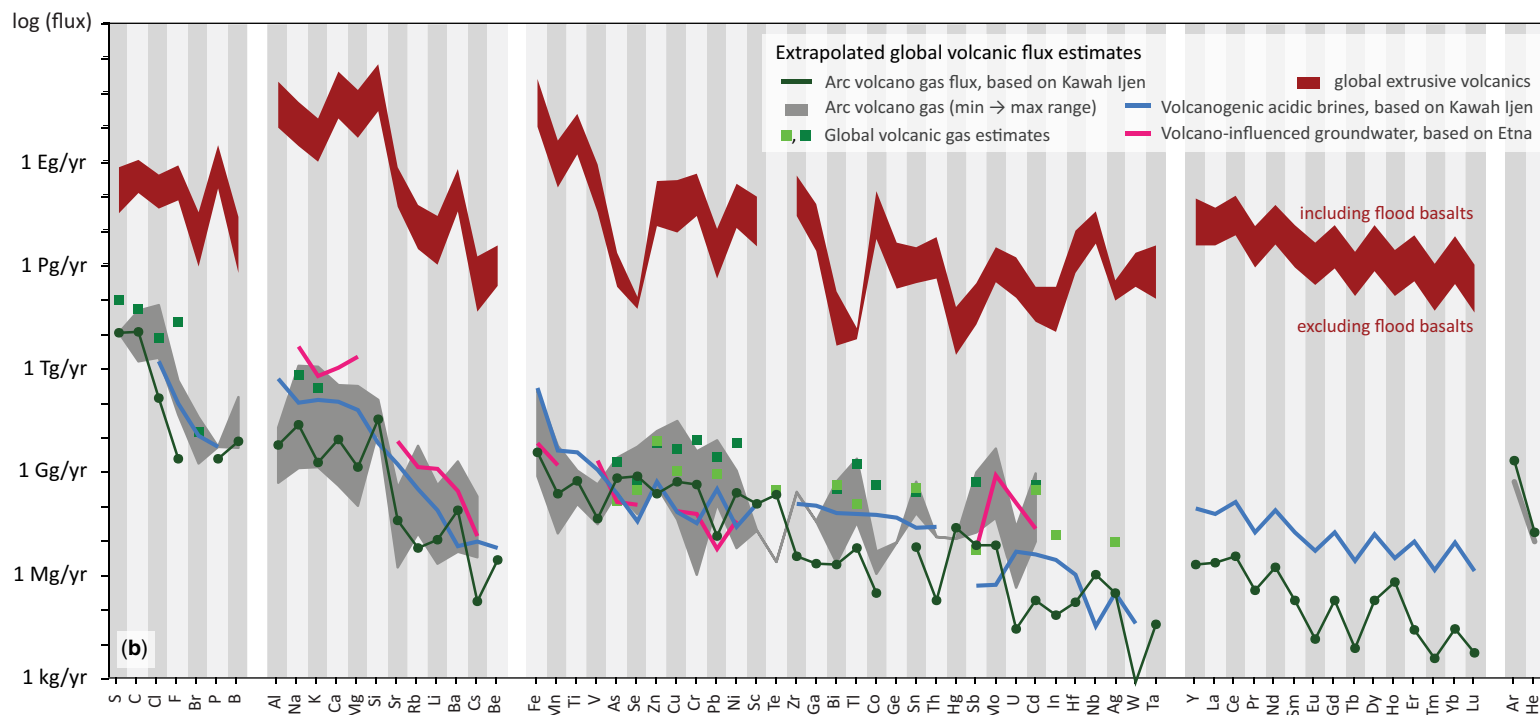


Fig. 7. (a) Gaseous, aqueous and total element flux of Kawah Ijen volcano compared with that of other volcanoes, both during quiescence and eruption, and (b) extrapolated estimates of the global gaseous, aqueous and solid volcanic flux. Values for Kawah Ijen emissions are shown as the 68% range around the mean (major anions) or median (other elements). Data for other volcanoes: Augustine volcano during quiescence – Symonds *et al.* (1992); Kilauea – Hinkley *et al.* (1999), Mather *et al.* (2012); Etna eruptive and during quiescence – Lambert *et al.* 1988, Gauthier & Le Cloarec (1998), Aiuppa *et al.* (2008); Etna groundwater – Aiuppa *et al.* 2000; Stromboli (average of reported data) – Allard *et al.* (2000); Kudryavy high temperature vents – Taran *et al.* (1995), Fischer *et al.* (1998); Merapi – Symonds *et al.* (1987); global volcanic gaseous emissions, light green squares – Lambert *et al.* (1988), Gauthier & Le Cloarec (1998), Allard *et al.* (2000), Aiuppa *et al.* (2005), Fischer (2008); dark green squares – Hinkley *et al.* (1999); Rio Agrio – Varekamp (2008). The range for arc volcanic gaseous emissions is based on the arc volcanoes presented in (a), with additional gas compositions for Momotombo and Colima taken from Quisefit *et al.* (1989) and Taran *et al.* (2000). The extrusive flux is calculated by combining volumetric flux estimates for the various settings and styles of volcanic activity from White *et al.* (2006) with bulk rock compositions for these settings from the GeoRoc archive, with the upper bound including flood basalts, whereas the lower bound excludes these.

including Ca, Mg, Fe, Al, Na, K and Sr, as well as the rare earth elements (REE) and the ligands, with the exception of S. Although it is at present still unclear whether the pathway for the fumaroles could represent a dry conduit, we regard this as unlikely, and rather expect interaction at depth between the hydrothermal aqueous reservoir and the gases that are eventually emitted at the fumaroles (see Fig. 2). In this case, the distinct differences in composition between the gaseous and aqueous emissions reflect the partitioning of elements between these.

Comparison with Etna gaseous and groundwater emissions shows identical partitioning behaviour to that observed at Kawah Ijen; Etna groundwater is characterized by a high flux of rock-forming elements, and a relatively low metal flux. This is especially striking when comparing Fe + Mn to Cu → Pb in Figure 7a. Although no corresponding gaseous flux is available for Copahue, the Rio Agrio data are consistent with those for Etna and Kawah Ijen.

Volcanic acidic brines are commonly regarded to arise from ‘scrubbing’ of volcanic gas by shallow waters (including groundwater and lakes), resulting in acidification of these waters and subsequent wall-rock leaching and build-up of their element load (Symonds *et al.* 2001). The efficiency of scrubbing, and hence the proportion of elements emitted in fumaroles compared with those deposited in shallow waters, varies strongly among volcanoes and with the activity level of a given volcanic system (Symonds *et al.* 2001; Varekamp *et al.* 2001). The strong compositional differences in Kawah Ijen fluid and fumarole emissions indicate that variations in scrubbing efficiency will directly influence the element signature of volcanic emissions: If a given aliquot of deep volcanic gas is directly emitted, these emissions will be characterized by volatile metals, whereas when it enters shallow water and is emitted as a fluid, it will be characterized by high concentrations of the rock-forming elements.

Global volcanic flux estimates

The global volcanic flux consists of three components: (1) A gaseous flux, emitted locally in vents, as well as diffusely, during activity and/or quiescence; (2) aqueous emissions in the form of (acid) rivers, lakes and modified groundwater; and (3) solid emissions. The actual term ‘global volcanic flux’ is commonly limited to the gaseous flux, but this is unfortunate. Not only does this underestimate the total flux of volcanoes onto the surface of the Earth, but it also misrepresents the total contribution of volcanoes to global element cycling. Furthermore, such a separation is commonly untenable due to the presence of ash particles in gaseous

emissions (e.g. Mather *et al.* 2012), and the potential for a significant proportion of gaseous element load to be captured into shallow water by scrubbing (cf. Symonds *et al.* 2001). For example, Varekamp *et al.* (2001) show that Copahue volcano has S emissions typical for a passively degassing volcano. However, efficient scrubbing at Copahue results in a complete lack of gaseous emission of this S. Finally, a significant proportion of the gaseous element load is ultimately derived from degassing of magma, indicating that erupted solid products are depleted relative to the undegassed magma.

To compare the element signatures of these three components, their relative importance, and to evaluate the atmophile, hydrophile and lithophile behaviour of the elements in a volcanic–hydrothermal environment, we calculated global flux estimates for the gaseous, aqueous and solid components emitted by volcanoes. Global estimates were derived as follows:

- (1) Gaseous global emissions were calculated by scaling gas flux values to the estimated global arc volcanic flux of SO₂ (2×10^7 Mg a⁻¹; Fischer 2008), e.g. for Ca;

$$Ca_{\text{global}} = \frac{SO_2^{\text{global}}}{SO_2^{\text{Kawah Ijen}}} \cdot Ca_{\text{Kawah Ijen}}, \quad (2)$$

all values in Mg a⁻¹.

- (2) The aqueous flux estimates were derived by assuming that the ratio between aqueous and gaseous emissions at Kawah Ijen and Etna is representative. We have no evidence for or against this and it therefore only represents a very preliminary estimate. The scaling factors in this case are the gaseous arc volcanic SO₂ flux from Fischer (2008) divided by the gaseous SO₂ flux of Kawah Ijen and Etna, respectively.
- (3) For the estimate of the extrusive volcanic element flux (i.e. in lavas, pyroclastics, scoria, etc.), we combined the flux estimates for the various styles of volcanic activity from White *et al.* (2006) with bulk rock compositions in the GeoRoc database (<http://georoc.mpch-mainz.gwdg.de/>). Rather than screening these compositions, we used the median of several thousand analyses for each category to obtain a representative composition. To convert the volumetric estimates of White *et al.* (2006) to mass flux, we calculated a density for each averaged composition using the partial molar volumes of Bottinga *et al.* (1982). By far the largest flux contribution is from flood basalts (c. 90% of the long-term averaged global volcanic activity – White

ELEMENT FLUX FROM KAWAH IJEN VOLCANO

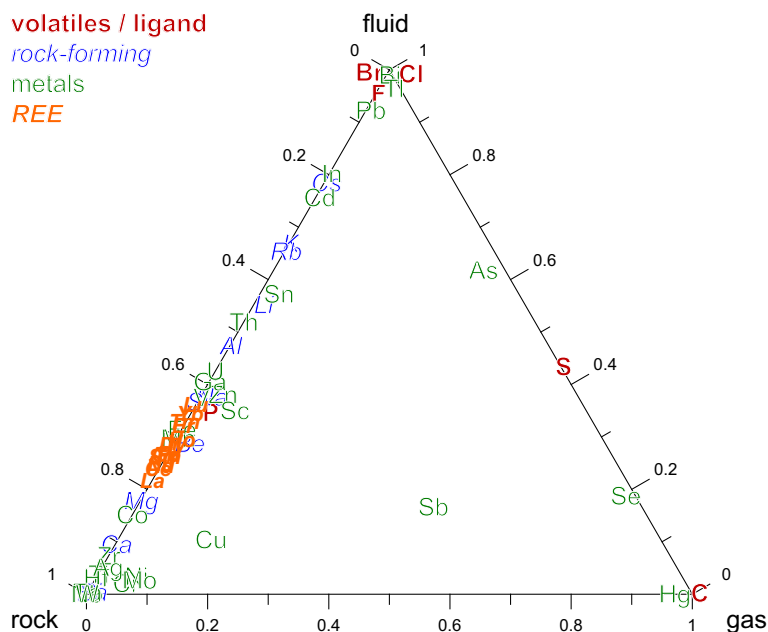


Fig. 8. Ternary diagram comparing the element preferences for gaseous, aqueous and solid volcanic emissions. Based on extrapolated Kawah Ijen and global extrusive data of Figure 7b.

et al. 2006). Given the paucity of flood basalts in recent activity, we have also calculated this estimate excluding flood basalts.

The resulting estimates show that the volcanic flux to the surface of the Earth is, unsurprisingly, dominated by the extrusive volcanic element flux, even when flood basalts are excluded (Fig. 7b). The dominance of the extrusive flux is most pronounced for the REE where it is 9 orders of magnitude larger than that of gaseous emissions. Literature estimates of the global volcanic gaseous flux (green squares in Fig. 7b) are in good overall agreement, although they do underestimate metal emissions, especially Se. The aqueous element flux is only rarely accounted for when assessing volcanic emissions, because surface expressions of this flux are uncommon, and quantification of the subsurface flux is non-trivial. However, it is a significant flux, equivalent in magnitude to the gaseous flux, and its exclusion will thus strongly underestimate emissions to the environment.

Comparing these three volcanic flux components shows a characteristic partitioning of elements among them, largely following their expected geochemical preferences (Fig. 8). The gaseous flux is characterized by enrichment in C and S, and the volatile (semi)metals As, Se, Sb and Hg, and Cu to a lesser extent. The ligands Cl, F and Br prefer the fluid, as do Pb, Tl, Bi, In, Cd, and the labile

alkalis Cs, Rb, K and Li, whereas Si, Mg, Ca and the REE follow their lithophilic behaviour and are enriched in the rock flux. This characteristic distribution means that changes in emission style will have a direct and profound impact on the signature of the volcanic emission. Vice versa, this allows the composition of surface emissions to be used as a probe of the volcano–hydrothermal system at depth, with, for example, the S/Cl and S/F ratios acting as a monitor of scrubbing efficiency (cf. Symonds *et al.* 2001).

Conclusions

The emissions calculated here provide a representative estimate for the total element output of a passively degassing arc volcano. On a local scale, the impact of the Kawah Ijen–Banyu Pahit system on its surrounding environment is substantial, with most of its total element output transported to the Asambagus coastal plain where these elements are subsequently transferred to soil and crops in irrigation (van Rotterdam-Los *et al.* 2008). In a global context, the gaseous flux from Kawah Ijen is significant, despite its small size, being similar to Merapi for many elements and exceeding emissions from Augustine and Kudryavy, all of which are much larger volcanic centres.

Kawah Ijen is representative of many small passively degassing arc volcanoes. Its acid river is not a common occurrence, but such hydrothermal fluids are an inseparable companion to this style of volcanic activity (cf. gas scrubbing – Symonds *et al.* 2001). We consider that the presence of the Banyu Pahit river reflects a topographical intersection of the hydrothermal system, which allows for these waters to escape by surface flow, rather than to be restricted to the subsurface. Accordingly, we view this river as the equivalent of subsurface hydrothermal element emissions in volcanoes that lack observable aqueous outflow, and these fluids to be an integral part of arc volcanic emissions globally. Even when such acidic brines do not develop, volcano-influenced groundwater represents an important flux of elements, as evidenced by Etna groundwater.

The global volcanic element flux on to the surface of the Earth is completely dominated by the extrusive flux, and it is this flux that is most important in global element cycling. However, these materials are solid and will take time to release their element load into the environment. On shorter timescales, the gaseous and aqueous emissions are more important, both in element flux and in potential environmental impact. These are also selectively enriched in metals, semi-metals and ligands, which are potentially toxic, and their environmental impact is thus disproportionately large. Measurements of the aqueous flux at Kawah Ijen and Etna indicate that this flux is similar, or exceeds the gaseous flux, and estimates restricted to gaseous emissions thus strongly underestimate the total emissions from volcanic-hydrothermal systems and their contribution to global element cycling.

This work represents the synthesis of a multi-year collaborative project between McGill University and Simon Fraser University. We thank all field assistants and locals who have helped us over the years to do fieldwork at Kawah Ijen; Marcus Burnham, Bill Minarik and Glenna Keating for their analytical expertise that allowed us to analyse these complicated samples; and our colleagues at the Institut Teknologi Bandung, Asnawir Nasution and Arif Susanto for technical assistance. Financial support has been provided by NSERC, FRQNT, and the European Union Seventh Framework Program (FP7/2007-2013) under grant agreement nos 254015 and 254216. Suggestions by two anonymous reviewers are greatly appreciated.

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ELEMENT FLUX FROM KAWAH IJEN VOLCANO

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