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Dukono, the predominant source of volcanic degassing in Indonesia, sustained by a depleted Indian-MORB

Philipson Bani¹, Giancarlo Tamburello², Estelle F. Rose-Koga¹, Marco Liuzzo³, Alessandro Aiuppa⁴, Nicolas Cluzel¹, Iwan Amat⁵, Devy Kamil Syahbana⁵, Hendra Gunawan⁵, Marcello Bitetto⁴

1- Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France

2- Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Via Donato Creti, 12, 40100 Bologna, Italy

3- Istituto Nazionale di Geofisica e Vulcanologia, Sez, Palermo, Via Ugo La Malfa, 153 90146 Palermo - Italy

4- Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università di Palermo via archirafi 36 90123 Palermo

5- Center for Volcanology and Geological Hazard Mitigation, Jl. Diponegoro No. 57, Bandung, Indonesia

Abstract

Located on Halmahera island, Dukono is among the least known volcanoes in Indonesia. A compilation of the rare available reports indicates that this remote and hardly accessible volcano has been regularly in eruption since 1933, and has undergone nearly continuous eruptive manifestation over the last decade. The first study of its gas emissions, presented in this work, highlights a huge magmatic volatile contribution into the atmosphere, with an estimated annual output of about 290 kt of SO₂, 5000 kt of H₂O, 88 kt of CO₂, 5 kt of H₂S and 7 kt of H₂. Assuming these figures are representative of the long-term continuous eruptive activity, then Dukono is the current most prominent volcanic gas discharge point in Indonesia and ranks among the top-ten volcanic SO₂ sources on earth. Combining our findings with other recent volcanic SO₂ flux results, obtained during periodic campaigns at a number of volcanoes with DOAS and UV-Cameras, the SO₂ emission budget for Indonesia is estimated at 540 kt yr⁻¹, representing 2-3% of the global volcanic SO₂ contribution into the atmosphere. This figure should be considered as minimum as gas emissions from numerous other active volcanoes in Indonesia are yet to be evaluated. This voluminous degassing output from Dukono is sustained by a depleted Indian-MORB (I-MORB) mantle source. This latter is currently undergoing lateral pressure from the steepening of the subducted slab, the downward force from the Philippine Sea plate and the westward motion of a continental fragments along the Sorong fault, leading to high fluid fluxes to the surface. Over the course of Dukono eruptive activity, the magma reservoir has changed from a less differentiated source that fed the past voluminous lava flows to a more evolved melt that sustained the current

30 ongoing explosive activity.

Keywords: Dukono Volcano, degassing budget, depleted mantle source, magma source evolution

1. Introduction

35 Dukono is a complex volcano with overlapping craters that culminate at 1230 m above sea level. It is a rather broad and low profile edifice, surrounded by multiple inactive cones. The current activity is hosted in the main central crater of ~700 m in diameter. Located on the northern part of Halmahera island ([Fig. 1](#)), Dukono is the most active volcano in the Maluku region, and perhaps the currently most vigorously active volcano in Indonesia. The historical volcanic activity record, briefly summarized in [Table 1](#), suggests strong eruptive discharges have persisted since 1933. A large eruptive event
40 in 1550 devastated the once known city of Tolo ([Data Dasar, 2011; van Padang, 1983](#)). During our visits in July and September 2015, Dukono exhibited nearly continuous eruptive discharge from its two active vents, forming a persistent dense ashy plume up to 200-300 m above the crater, being dispersed to the north by the prevailing wind. The entire edifice was covered by thick ash deposits (up to a meter at some points) on its flanks.

Despite these remarkable accounts, Dukono is rarely visited, thus very little is known about its manifestations – the main
45 constraints being the remoteness of the edifice and the difficulty of access. We present here the first gas study on Dukono with a focus on the emission budget and the origin of its magma source, using Multicomponent Gas Analyzer System (MultiGAS) and Differential Optical Absorption Spectroscopy (DOAS) measurements, combined with ash-tephra chemistry analysis.

50 2. Geological setting

The geodynamic of the Molucca sea is currently dominated by the collision of the Halmahera and Sangihe arcs ([Fig. 1](#)). The oceanic lithosphere that existed between the two arcs over last 20 million years has been entirely consumed ([Cardwell et al., 1980](#)). According to [Hall and Wilson \(2000\)](#), the Sangihe forearc is presently overriding the Halmahera forearc, while the Halmahera arc itself is thickening by the over-thrusting of its back-arc from the east. The Molucca sea
55 plate that once largely exposed to the surface between Sangihe and Halmahera arcs is now deep in the mantle and sinking further with time ([Hall and Wilson, 2000](#)). The currently active volcanoes are formed along the weak points of the entire forearc-arc-backarc section of Halmahera region ([Hall and Wilson, 2000](#)).

3. Methodology

60 3-1. MultiGAS

The Multi-GAS used in this work is a compact portable instrument from UniPa-INGV (as used by Aiuppa et al., 2015). The system simultaneously acquired concentrations of H₂O, CO₂, SO₂, H₂S and H₂ at 0.1 Hz. H₂O and CO₂ were detected by non-dispersive infrared spectroscopy (LI-COR LI-840A; 0–60,000 ppm range), and SO₂, H₂S and H₂ via specific electrochemical sensors (respectively, models 3ST/F, EZ3H, and EZT3HYT “Easy Cal”; all from City Technology
65 with calibration range of 0–200 ppm). Powered by a (6 Ah) 12 V LiPo battery, this lightweight Multi-GAS was placed on the northern part of Dukono’s crater (Fig. 1), directly in the plume. Nearly 3 hours of continuous recording was achieved. Acquired data were post-processed using the Ratiocalc program (Tamburello, 2015).

3-2. DOAS measurements

70 DOAS measurements were performed from a fixed position about 800 m north of the active crater (Fig. 1) using a scanning system. The plume drifted to the north during DOAS measurements enabling a vertical scanning across the plume. Spectra were collected per scan with a step angle of 1.8°. The spectrometer used was an Ocean Optics USB2000+ with a spectral range of 290–440 nm and a spectral resolution of 0.5 FWHM. The SO₂ column amounts (ppm.m) were retrieved using DOAS calibration and standard analysis procedures (Platt and Stutz, 2008). Reference spectra included in the non-
75 linear fit were obtained by convolving high resolution SO₂ (Bogumil et al. 2003) and O₃ (Voigt et al. 2001) cross sections with the instrument line shape. A Fraunhofer reference spectrum and Ring spectrum, calculated in DOASIS, were also included in the fit. The total column amount of the plume cross section was then multiplied by the wind mean velocity of 5 m s⁻¹, obtained from hand-held anemometer on the crater rim, and assumed representative of the plume dispersion speed, to derive the SO₂ emission rate.

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3-3. Ash-tephra sampling and laboratory analysis

At about 300 m north of the DOAS measurement point, one meter of layered ash-tephra deposits are exposed to the surface (Fig. 1). Each layer was sampled then analyzed for bulk composition using X-ray Fluorescence (XRF) (Johnson et al. 1999) for major elements and compared to fresh ash fall (July and September 2015) samples. To gain further insights into
85 the magmatic processes and source origin, major and trace elements of olivine, pyroxene and plagioclase hosted melt inclusions were analyzed using Electron Probe Micro Analyzer (EMP) (Cameca SX 100) following standard procedure (e.g. Le Voyer et al., 2008; Cabral et al., 2014). Analytical uncertainties on the samples were typically of < 2% for SiO₂, MgO, and Al₂O₃; 3.5% for FeO and CaO; 5% for K₂O, TiO₂, and Na₂O; 10% for P₂O₅; and 30% for MnO (1σ). F, S, and Cl were also measured by EMP with relative uncertainty of 20% for S and 30% for Cl and F. Trace element measurements were

carried out using a laser ablation system (193 nm Excimer Resonetics M-50E) associated with an inductively coupled plasma mass spectrometer (Agilent 7500 cs; LA-ICPMS) (e.g. Rose-Koga et al., 2012). The relative 1σ standard errors are < 3% for Rb, Sr, Y, Zr, Nb, Ba, La, and Ce, < 4% for Nd, < 9% for Th.

4. Results

4-1. Gas composition and emission rate

The position of the Multi-GAS, on the northern part of Dukono's crater rim (Fig. 1), enhanced direct exposure to eruptive gas discharges but also to heavy ash releases that subsequently saturated the filter after about 1h of recording. Results, presented in Figure 2 and Table 2, indicate strong fluctuations in SO₂ concentrations, varying from 0.5 to 32 ppm, with the alternation of 1-3 minutes of strong releases followed by 0.5-1 minutes of low background volcanic gas emission. FFT analysis indicates a degassing periodicity of ~3 minutes. The data-set highlights a H₂O-rich gas composition from Dukono, representing a molar proportion of 97 %. Other gases detected on Dukono are CO₂, H₂S and H₂ with mean recorded values of 362-400 ppmv, 0.2 ppmv (above atmospheric background) and 1-2 ppmv respectively (Table 2). There is no gas composition change between our two observation periods (in July and September, 2015). All these gases exhibit positive correlations with SO₂, implying a common source (Fig. 2).

SO₂ emission from Dukono was also very well characterized on the spectra acquired by DOAS scanning. The SO₂ emission rate, obtained after more than two hours of vertical scanning, fluctuates between 400 and 2000 t d⁻¹ with a mean SO₂ flux of 819 ± 235 t d⁻¹ (Table 3; Fig. 3). The duration of one scan varied between 3 and 6 minutes, depending on the light intensity. The temporal resolution of the DOAS scans is therefore not high enough to resolve the possible degassing periodicity observed with the Multi-GAS. However the difference between the minimum and the maximum emission rates suggests that there are different phases of stronger and lower emissions.

Taking into account the molar ratios of H₂S/SO₂, H₂/SO₂, CO₂/SO₂, H₂O/SO₂ (Table 2) we obtain a daily output of 242 ± 69 t of CO₂, 13 ± 4 t of H₂S, 7 ± 2 t of H₂ and about $14\,000 \pm 4000$ t of H₂O.

4-2. Ash-tephra and melt inclusion composition

Laboratory analyses result of the ash-tephra samples and melt inclusions are provided in Table 4 and 5. Figure 4 displays the composition changes in terms of alkali versus silica, allowing insights into the source composition. The bulk composition of ash-tephra deposits appear in the junction of trackyandesite and andesite whilst the melt inclusion compositions scattered from basalt to dacite with olivine-pyroxene-hosted melt inclusions plotted in the range of basalt and basaltic-andesite while the plagioclase-hosted melt inclusions spread along the transition line between andesite and

trachyandesite and even up to differentiated dacitic composition. The volatile content (S, Cl, F) in the melt inclusions shows a notable drop of S from around 1100 ppm to 200-400 ppm between olivine-pyroxene and plagioclase hosts whilst Cl and F in contrast display relative increase from 600-800 to 1000-1200 ppm and from 200 to 300-700 ppm respectively (Fig.5). Trace elements obtained from melt inclusions show elevated large ion lithophile elements (LILE) and light rare elements (LREE) compare to high-field strength elements (HFSEs). Nb and Ti are below N-MORB concentrations.

5. Discussion

5-1. Prominent volcanic gas contribution into the atmosphere

Due to the remote location and access difficulties, Dukono is one of the least known volcanoes in Indonesia and globally unknown to the scientific community – a paradox since this edifice is among the most active on earth (Table 1) with recurrent eruptive activity since 1933 (GVP Dukono, 2013). In July then in September 2015 (this work), Dukono followed an eruptive manifestation (apparently normal according to local observers) with nearly continuous eruptive discharges from the two active vents in the crater. The mean SO₂ flux released from this activity amounts to 0.8 kt per day, which represents a mean annual SO₂ output into the atmosphere of 292±86 kt. This figure is much lower than the daily 1.7 kt of SO₂ release from Dukono indicated in Carn et al. (2017), based on satellite observations. Although the two SO₂ flux approaches are not exactly equivalent, since we are measuring the emission rates directly whilst satellites output an SO₂ atmospheric burden, the two results should be at least comparable (Bani et al., 2009a; 2009b) or lower for the Ozone Monitoring Instrument (OMI) onboard Aura satellite (McCormick et al., 2012; Bani et al., 2016). This satellite-based high SO₂ flux derived from a longer observation period (several years) but might be biased by over-sampling more vigorous (and most visible) explosive periods (Carn et al., 2016). The OMI estimation for July 13, 2015 is 0.02 kt which is an order of magnitude lower than our DOAS result for that same day (Fig. 3). Other DOAS measurements in the future are required to refine these first estimates, however our finding suggests that Dukono volcanic gas contribution into the atmosphere is higher than any other known persistent volcanic degassing source in Indonesia, measured with modern tools (DOAS and UV-Camera), including Merapi (18 – 160 kt yr⁻¹; Surono et al., 2012), Krakatau (70 kt yr⁻¹; Bani et al., 2015), Kawah Ijen (64 kt yr⁻¹; Gunawan et al., 2016), Bromo (60 kt yr⁻¹; Aiuppa et al., 2015), Semeru (20 – 70 kt yr⁻¹; Smeckens et al., 2015), Sirung (17 kt yr⁻¹; Bani et al. (in press)) and Papandayan (0.5 kt yr⁻¹; Bani et al., 2013). If put in the context of the well known compilation of Andres and Kasgnoc (1998), the Dukono's SO₂ contribution into the atmosphere is comparable to that of Kilauea, in the top ten of the volcanic degassing sources worldwide. Combining together the above SO₂ emission data from 7 Indonesian volcanoes, one obtains a minimum annual volcanic SO₂ output of 540 kt into the atmosphere, representing 2-3 % of the global volcanic emission budget (15-21 Tg; Halmer et al., 2002). This figure is much higher than

the 100 kt of SO₂ emission budget provided by Andres and Kasgnoc (1998) or 120 kt in Fischer (2008) for the whole Indonesian volcanoes. Knowing that there are 127 active volcanoes in Indonesia, it is thus evident that these past figures are strongly underestimating the volcanic degassing budget from this archipelago. Indeed, the most recent estimation provided by Carn et al. (2017) based on satellite observations, indicates a much higher release with an annually SO₂ emission budget of around 2200 kt, representing about 10 % of the global volcanic SO₂ contribution into the atmosphere (23 Tg; Carn et al., 2017). However this figure still requires ground-based validation in Indonesia. Note also that only 16 out of 127 volcanoes are considered in this latter work. .

The daily H₂O flux from Dukono estimated in this work is fairly high and accounts for $\sim 14 \pm 4$ kt (~ 5000 kt yr⁻¹). This figure derives directly from the H₂O-rich signature of volcanic gas vented from Dukono. Indeed, the H₂O molar proportion is 97% (Table 2), which falls in the upper domain for arc volcanic gases (Fischer, 2008) and is comparable, to, e.g., Bromo (H₂O mol. 95%; Aiuppa et al., 2015) or Yasur (H₂O mol. 98%; Metrich et al., 2011). Note that the H₂O flux likely constitutes higher bound estimate since a meteoric water contribution to the Dukono degassing system cannot be ruled out. However the fairly strong correlation between H₂O and the other gases, including CO₂, SO₂, H₂S and H₂ (Fig. 2), suggests a primarily magmatic H₂O source. The high water proportion (4-5 wt%) calculated by weight difference from melt inclusions and its positive correlation with S content (Table 4; Fig.5) supports the magmatic origin of H₂O.

CO₂ is the second most common gas in volcanic exhalations (e.g., Shinohara, 2008). This is also the case on the three better known Indonesian volcanoes, including Bromo, Papandayan and Merapi, where CO₂ represents 3.5 mol. % (Aiuppa et al., 2015), 2.9 mol. % (Giggenbach, 1996) and 4.7-5.6 mol. % (Giggenbach et al., 2001) in their respective volcanic gas. But on Dukono, the CO₂ constitutes the 3rd most abundant gas composition with only 0.7 mol. % behind H₂O and SO₂ (1.6 mol. %). Using the CO₂/SO₂ ratio of (Table 2), we derive an annual CO₂ emission rate of 88 kt from Dukono. Such release represents $\sim 0.03\%$ of the global volcanic CO₂ emission budget (271 Mt yr⁻¹; Burton et al., 2013) into the atmosphere. Further investigations are still required to constrain this low CO₂ signature at Dukono, however, using the CO₂/SO₂ and H₂S/SO₂ ratios of 0.5 and 0.03 respectively (Table 2), one can derive a CO₂/S_T ratio of 0.4, corresponding to group 2 volcanoes in the Aiuppa et al. (2017) classification, suggesting a de-volatilized slab source.

Another gas species quantified in the plume of Dukono is the H₂. It constitutes 0.4 molar % of the emitted gas and a H₂/SO₂ molar ratio of 0.3. Combining this latter ratio with the SO₂ flux, we estimate an annual H₂ emission budget of 2.5 ± 0.7 kt (Table 2). To date, still very few measurements have captured the molecular hydrogen in the plume, thus much is yet required to provide acceptable estimation of global volcanic H₂ output into the atmosphere. In any case, Dukono is a significant source of molecular hydrogen into the atmosphere.

The H₂S, also measured in Dukono plume, has a fairly strong correlation with other gas species (Fig. 2). It

180 constitutes 0.05 molar % of Dukono gas composition. The mean H₂S/SO₂ ratio is 0.03, which gives an annual output estimation of 13±4 kt, representing 0.03-0.8% of the global volcanic H₂S output (1500-37100 kt; Halmer et al., 2002) into the atmosphere.

The quantification of Indonesian volcanic volatile contributions into the atmosphere still remains sparse as the emissions from other volcanoes are yet to be measured. However, Dukono is clearly a strong volcanic volatile contributor
185 into the atmosphere, at the global scale. Taken into account its long eruptive manifestation, as highlighted by Carn et al. (2016), it is plausible that Dukono may constitute the biggest volcanic degassing source in Indonesia.

5-2. A depleted I-MORB source and high fluid fluxing

The trace elements in melt inclusions (this work) normalized to normal mid-ocean ridge basalt (N-MORB) (Sun
190 and McDonough, 1989) point out elevated ratios of large ion lithophile elements (LILEs) and light rare elements (LREEs) to the high-field strength elements (HFSEs) (Fig. 6A). Such patterns observed at Dukono are typical of subduction zones in which the mantle wedge has been contaminated by fluids released from the subduction slab (McCulloch and Gamble, 1991; Davidson, 1996; Macpherson et al., 2003).

It is known that during slab de-volatilization, Nb and Zr are relatively immobile. The MORB sources display a
195 restricted range of Zr/Nb (Fig. 6A) (e.g., Elliott et al., 1997), whilst at subduction zones, Zr/Nb can vary significantly (e.g., McCulloch and Gamble, 1991), as seen at Halmahera (Fig. 6B). A high Zr/Nb cannot be generated by MORB-source (Woodhead et al., 1993). Instead, it characterizes mantle that has previously lost a basaltic melt fraction, leaving behind a source that is more depleted in highly incompatible elements, such as Nb (Macpherson et al., 2003). It is thus likely that this high Zr/Nb on Dukono derived from a depleted mantle wedge (Fig. 6B) in agreement with the changes in Zr/Nb ratios along
200 the Halmahera arc, from N-MORB range (low Zr/Nb) at Obi to an evolved mantle wedge source at Bacan and central Halmahera (Fig.1; Fig. 6A; Macpherson et al., 2003).

A refractory source requires high fluid fluxes to lower the solidus and assist the melting process, therefore a high Zr/Nb ratio suggests important fluid fluxing. Further, given the high mobility of Ba, any incoming fluid into a depleted mantle source will produce a broad correlation between Zr/Nb and Ba/Nb (Fig. 6B) (e.g., Keppler, 1996; Macpherson et al.,
205 2003). The high ratios and strong correlation between Zr/Nb and Ba/Nb obtained at Dukono (Fig.6B) thus support the idea of high fluid fluxes that sustain volcanic activity. The steepening of the subducted slab, the downward force from the Philippine sea plate and the westward motion of a continental fragments along the Sorong fault (Fig.1), are the main tectonic motions that can enhance mantle wedge compression beneath Halmahera (Macpherson et al., 2003; Elliott et al., 1997) leading to high fluid fluxes. These motions were evidenced in the evolution of Zr/Nb and Ba/Nb ratios at Halmahera

210 between Neogene and Quaternary (Macpherson et al., 2003). Indeed the ratios decline and shift toward the enriched I-MORB composition (Fig.6B) (Dosso et al, 1988; Le Roex et al., 1989) suggesting a progressive change from a depleted to enriched mantle source. Further, the steepening of the slab increases the effects of slab rollback in the mantle, leading to an increasing flux of recycled sediment as highlighted by the increase of $^{208}\text{Pb}/^{204}\text{Pb}$ at a given point of $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig.6D, Macpherson et al., 2003). Note here that the scatter plot of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for Halmahera volcanic rocks 215 indicate Indian-MORB source (e.g., Macpherson et al., 2003).

5-3. Evolved magma source

During fractional crystallization, melt inclusions, trapped in series of minerals, behave as closed and isolated systems, retaining much of the original composition of the melt, including their volatile content. Therefore, they constitute 220 an ideal tool to shed light on the source of the magma and on igneous processes (e.g., Schiano, 2003; Cannatelli et al., 2016). In that respect, the melt inclusion results obtained in this work (Fig. 4, Table 4) clearly trace back the fractional crystallization of Dukono magmatic source. The bulk chemistry of the ash-tephra deposits (Table 4), plotted in the total alkali-versus-silica (TAS) and K₂O-silica diagrams (Fig. 4), indicate andesitic to trachyandesitic magma composition with medium to relatively high-K content. Olivine-pyroxene-plagioclase-hosted melt inclusions show a wider range of 225 compositions from basalts to trachyandesites (Fig. 4, Table 4), an indication of a melt composition change in the reservoir. The plagioclase content shows a clear evolution with increasing SiO₂, from Ca-rich to Na-rich composition (Fig. 4). Such change generally reflect the continuous branch of Bowens's reaction series where calcium-rich plagioclase crystallizes first then progressively evolves to sodium-rich with the cooling melt (e.g., Monroe and Wicander, 2014). The melt inclusion volatiles show a progressive increase of Cl and F, from 600 to 1000 ppm and from 200 ppm to >200-700 ppm respectively 230 (Fig. 5), implying incompatible behavior during crystal fractionation (Aiuppa et al., 2009). Fluorine has a high affinity for silicate melts, thus it may progressively enriched in magma through time as magmatic differentiation takes place (Sawyer and Oppenheimer, 2006). Sulfur concentrations in Dukono inclusions show a notable drop from 1100 to ~300 ppm suggesting sulfur lost, likely through open-system degassing. All those observations indicate that the magmatic source beneath Dukono has evolved over time and that the current ongoing explosive activity is sustained by a more differentiated 235 magma, which contrast with the voluminous lava outputs reported in the past (1550 and 1933; Table 1) likely sourced by a less viscous and less differentiated melt source.

6. Conclusion

Dukono is the most active volcano in Maluku and likely the most vigorous edifice in Indonesia with continuous

240 and long eruptive manifestations. But due to its isolation and access difficulties, very little is known about its activity. The first measurements of its magmatic volatile contribution into the atmosphere, presented in this work, indicate that Dukono is the biggest volcanic SO₂ contributor in Indonesia and ranks among the top ten volcanic SO₂ sources on earth. Each year about 290 kt of SO₂ are released into the atmosphere from this volcano, a huge contribution that significantly increases the Indonesia archipelago annual volcanic SO₂ budget from 100 kt (Andres and Kasgnoc, 1998) to 540 kt (including all recent
245 published measurement results). This new Indonesian SO₂ emission budget constitutes 2-3% of the global volcanic SO₂ emission. The CO₂ released from Dukono appears to be much lower than the SO₂ output with 88 kt yr⁻¹, representing 0.03 % of global volcanic CO₂ budget. Dukono also releases annually about 5000 kt of H₂O, 41 kt of H₂S, and 0.4 kt of H₂ into the atmosphere.

The current degassing regime on Dukono is maintained by the ongoing explosive activity, enhanced by a differentiated
250 magmatic source. Indeed, as evidenced in this work, the melt source has changed over the course of Dukono eruptive activity, evolving from a less viscous source that fed the past voluminous lava flows to a silica-rich melt behind the current ongoing explosive activity. In parallel to this differentiated melt source, trace element analyses highlight a depleted Indian-MORB in the mantle wedge beneath Dukono, a paradox behind the high degassing of Dukono. However, as highlighted in this work, the steepening of the subducted slab, the downward force from the Philippine sea plate and the westward motion
255 of a continental fragments along the Sorong fault may develop sufficient pressure on the mantle wedge to enable high fluid fluxes to the surface.

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Captions

Table 1. Brief chronology of Dukono volcanic activity.

Table 2. Dukono gas composition, mean concentrations, gas ratios and fluxes.

Table 3. SO₂ flux results obtained from scanning DOAS.

Table 4. Composition of Dukono bulk ash-tephra deposits and major to trace elements content of olivine-pyroxene-plagioclase-hosted melt inclusion

Figure 1. Dukono volcano located on Halmahera island, east Indonesia. The crater hosts 2 active vents (A). The collision of the Halmahera and Sangihe arcs is highlighted in cross section a-a', adapted from [Hall and Wilson \(2000\)](#) (B). The measurement positions of the scanning DOAS and MutiGAS as well as the ash-tephra sampling points are indicated in (A). Pictures on the right provide an insight into Dukono crater (1), the ashy plume above the crater (2) and a strong eruptive discharge observed 10 km from the crater (3).

Figure 2. Scatter plots of SO₂ vs H₂ (A), CO₂ (B), H₂O (C) and H₂S (D); the correlation between H₂O and CO₂ is displayed (E). The SO₂ fluctuation over the recording period (F) with the corresponding FFT result (G) indicating a degassing periodicity of ~3 minutes.

Figure 3. SO₂ scanning profiles across the plume; the mean profile is in red (above). Fluctuation of SO₂ flux over the DOAS scanning period (below). The sub-image displays the result obtained by OMI (Ozone Monitoring Instrument) for the same date as the DOAS measurement (July 13, 2015). This OMI image was acquired during DOAS measurements. The time difference between Universal Time Coordinated and Halmahera is 9h.

Figure 4. Ash-tephra and melt inclusion samples placed into the total alkali and K₂O versus SiO₂ plots indicate andesite-trachyandesite with medium to high-K bulk composition (red cross), basaltic andesite olivine (blue circle), basalt to basaltic andesite pyroxene (blue asterisk) and andesite-trachyandesite plagioclase (blue square). This latter shows an extend to higher SiO₂. White circles indicate Ibu volcano bulk composition changes for comparison. The subplot (on the K₂O-SiO₂ plot) denotes the evolution of plagioclase composition, from high Ca low Na (anorthite) to high Na low Ca (albite). The pictures on the right are the ash-tephra layer sampled and analyzed. The detail composition of the layers (A, B, C, 1, 2, 3, 4, 5) are provided in Table 3. The white circles denote the melt composition change observed on Ibu, the closest volcano to Dukono ([Saing et al., 2014](#))

Figure 5. Volatile contents in melt inclusions (A). The Cl concentration shows a progressive increase with the increasing SiO₂ (green triangle). F evolved from a relatively stable concentration in low SiO₂ melt (black cross) to higher content with a more differentiated melt. The S highlights a notable drop with the increasing SiO₂, similar to the calculated H₂O. Incompatible element abundance in the olivine-pyroxene-plagioclase-hosted melt inclusions, normalized to N-MORB (B).

Figure 6. (A) Zr/Nb vs MgO of Dukono (this work, red asterisk) compared to Obi, Central Halmahera and Becan (data from [Macpherson et al., 2003](#)) (B); Ba/Nb vs Zr/Nb of Dukono (this work, red asterisk) compared to central Halmahera and I-MORB (data from [Macpherson et al., 2003](#)) (C). Note that [Macpherson et al. \(2003\)](#) observed an evolution in melt composition on Halmahera between Neogene and Quaternary. (C) The Halmahera ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb rocks plotted on Indian MORB. Note the increase in the ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios between Neogene and Quaternary

(data from Mcpherson et al., 2003).

Table 1.

1550	Large eruption spilling out huge amount of lava to the coast, destroying the once known Tolo city (van Padang, 1983).
1719	Eruptive activity on the eastern flank (GVP, 2013)
1861-1869	Eruption at the main crater. Vegetation close to summit was destroyed by fire triggered by the eruption (Data Dasar, 2011).
1901	Eruption occurred at the main crater whilst strong fumarole activity observed on the surrounding cones (Data Dasar, 2011).
Aug. 1933	Strong eruption with large lava flow to the north and ash fall up to 15 km northeast of the volcano (Data Dasar, 2011).
1945	Eruption leading to ash fall on Tobelo city, situated 15 km northeast of the volcano
Jul. 1946	Eruption generating ash fall on Morotai island, 60 km northeast of Dukono. At Tobelo, 1 cm of ash fall was observed (Data Dasar, 2011).
1952	Eruption propelling an ash column up to ~1000 m from the summit. Eruption sound was heard in Tobelo (15 km from volcano) (Data Dasar, 2011).
1969	Eruption building ash column. The explosion was heard at Galela (10 km from summit) (Data Dasar, 2011).
1971	Eruption building up a black column of ash up to 300 m from summit. Ash fall at the summit (Data Dasar, 2011).
1978-1979	Explosions of varying strength occurred about once every 10 seconds, ejecting bombs as large as 4 m up to 200-250 m from the crater rim. Ash emission was nearly continuous, with clouds rising as high as 10 km above the crater. Ash was blown North beyond the Galela, 15 km from the volcano. From Galela incandescent ejecta were visible (GVP, 1978. Report on Dukono (Indonesia)).
Jun. 1991	Eruption generation ash column up to 1500 m above crater rim. Ash fall witnessed on Tobelo, lava glow seen at the summit at night whilst lahar occurred following the eruption (Data Dasar, 2011).
May 1992	Eruption building up ash plume to 400 m above volcano (Data Dasar, 2011).
Nov.-Dec. 1993	Eruption building up ash plume up to 300-600 m above summit (Data Dasar, 2011). The cloud was rising up to 600-1500 m (GVP, 1993. Report on Dukono (Indonesia)).
Jan., Sep. 1995	Eruption generating ash fall but weather condition didn't allow detail observation (Data Dasar, 2011).
Mar. – Dec. 2003	Eruption building up ash plume to 200-500 m above summit. Ash fall witnessed at Tobelo (Data Dasar, 2011).
2004-2005	Continuous ash emission (GVP, 2006. Report on Dukono (Indonesia)).
2006 - present	Intermittent ash emission with variable discharge intensity. In 2007 and 2014 the ash plume was clearly observed by MODIS (GVP, 2007. Report on Dukono (Indonesia))

Table 2.

	13/07/2015	08/09/2015	Average
Gas concentration			
Mean SO ₂ (ppm v)	5.3 ± 1.3	2.0 ± 0.5	3.6 ± 0.9
Mean H ₂ S (ppm v)	0.2 ± 0.05	0.2 ± 0.04	0.2 ± 0.04
Mean CO ₂ (ppm v)	362 ± 90	400 ± 100	381 ± 95
Mean H ₂ (ppm v)	2 ± 0.5	1.0 ± 0.2	1.5 ± 0.7
Mean H ₂ O (ppm v)	9000 ± 2200	8000 ± 2000	8500 ± 2100
H ₂ O/SO ₂	60.5 ± 19.1	61.2 ± 22.1	60.8 ± 20.6
CO ₂ /SO ₂	0.4 ± 0.1	0.6 ± 0.2	0.5 ± 0.1
H ₂ S/SO ₂	0.03 ± 0.01	0.05 ± 0.02	0.03 ± 0.01
H ₂ /SO ₂	0.3 ± 0.1	0.1 ± 0.07	0.2 ± 0.09
Gas composition and flux estimates			
	Composition (mol %)	Flux (t d ⁻¹)	
H ₂ O (mol. %)	97.2 ± 2.7	14000 ± 4000	
SO ₂ (mol. %)	1.6 ± 0.4	819 ± 235	
CO ₂ (mol. %)	0.8 ± 0.2	242 ± 69	
H ₂ S (mol. %)	0.06 ± 0.01	13 ± 4	
H ₂ (mol. %)	0.30 ± 0.07	7 ± 2	

Table 3.

Start Time (LT) (date: Jul. 12, 2015)	End Time (LT)	Number of Spectra	Scanning step (°)	Mean Column Amount (ppm.m)	SO ₂ flux (t/d)
11:11:41	11:14:46	76	1.8	474	756 ± 220
11:14:46	11:16:32	76	1.8	619	992 ± 229
11:17:52	11:22:48	76	1.8	359	778 ± 223
11:24:03	11:28:31	76	1.8	325	1044 ± 289
11:28:41	11:32:57	76	1.8	534	530 ± 162
11:33:10	11:37:58	76	1.8	496	549 ± 170
11:38:08	11:43:20	76	1.8	1059	902 ± 255
11:43:30	11:48:44	76	1.8	1270	834 ± 243
11:51:59	11:57:14	76	1.8	452	1707 ± 470
11:57:27	12:02:28	78	1.8	642	2015 ± 541
12:02:38	12:06:24	76	1.8	589	745 ± 211
12:06:34	12:11:06	76	1.8	613	937 ± 265
12:11:17	12:16:48	76	1.8	332	804 ± 237
12:16:59	12:21:14	76	1.8	347	576 ± 163
12:21:25	12:26:13	76	1.8	392	510 ± 155
12:26:22	12:30:40	76	1.8	564	413 ± 124
12:30:50	12:35:26	76	1.8	362	553 ± 164
12:35:37	12:41:08	76	1.8	446	922 ± 274
12:48:12	12:53:22	76	1.8	446	569 ± 177
13:27:15	13:32:07	76	1.8	465	444 ± 137
					Mean SO₂ flux = 819 ± 235

Table 4.

Bulk composition														
	Fresh ash (Jul 2015)	Fresh ash (Sep 2015)_1	Fresh ash (Sep 2015)_2	Layer A	Layer B	Layer C	Layer D	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
SiO ₂ (wt %)	58.0	59.5	59.3	59.0	58.9	58.9	58.9	59.4	59.2	58.4	59.6	59.0	59.4	58.7
TiO ₂	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.7	0.7	0.7	0.7
Al ₂ O ₃	13.9	15.3	15.8	14.5	14.2	14.1	14.2	14.3	14.3	13.5	14.4	14.2	14.5	15.0
Fe ₂ O ₃	10.5	8.4	8.6	9.4	9.9	10.1	1.0	9.4	9.5	11.2	9.2	9.8	9.1	9.0
MnO	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1
MgO	2.0	2.7	2.3	2.2	2.7	2.6	2.6	2.1	1.9	3.5	2.1	2.6	2.0	1.8
CaO	7.3	5.8	6.0	6.8	6.4	6.6	6.5	6.5	6.7	6.4	6.4	6.5	6.6	7.0
Na ₂ O	3.1	3.4	3.5	3.3	3.3	3.3	3.3	3.3	3.4	3.3	3.4	3.4	3.3	3.5
K ₂ O	3.7	2.5	2.5	3.3	3.1	3.2	3.2	3.4	3.5	3.0	3.3	3.2	3.4	3.3
P ₂ O ₅	0.4	0.3	0.3	0.4	0.4	0.4	0.3	0.4	0.4	0.3	0.4	0.4	0.4	0.3
SO ₃	0.2	-	-	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0
Total	100.1	98.9	99.1	99.7	99.7	100.1	90.9	99.8	99.8	100.7	99.7	100	99.5	99.4
Melt inclusions														
	ol-1	ol-1	cpx-1	cpx-2	plagio-1	plagio-2	plagio-3	plagio-4	plagio-5	plagio-6	plagio-7			
SiO ₂ (wt%)	52.9	52.5	50.8	55.1	59.7	60.0	60.3	61.0	61.9	63.0	64.2			
TiO ₂	0.7	0.6	0.7	0.6	1.0	0.8	0.9	0.9	0.8	0.9	0.8			
Al ₂ O ₃	18.5	18.0	17.2	16.5	14.6	15.1	14.8	14.8	14.5	14.9	14.9			
FeO	6.3	6.6	9.1	5.8	8.0	7.4	7.9	7.4	7.3	7.0	6.1			
MnO	0.0	0.2	0.3	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.1			
MgO	3.1	4.4	4.5	4.1	2.2	2.3	2.1	2.3	2.0	1.4	1.4			
CaO	9.7	9.4	8.9	7.8	4.9	4.8	4.5	4.7	4.3	4.1	3.7			
Na ₂ O	3.2	3.1	2.7	2.8	3.5	3.5	3.8	3.7	3.7	3.8	3.9			
K ₂ O	1.4	1.3	0.7	1.3	3.0	2.9	3.2	3.1	3.4	3.4	3.6			
P ₂ O ₅	0.3	0.2	0.2	0.2	0.7	0.4	0.5	0.7	0.4	0.5	0.4			
Total	96.2	96.4	95.0	94.4	97.9	97.4	98.3	98.8	98.5	99.3	99.0			
H ₂ O (wt%)	3.8	3.6	5.0	5.6	2.1	2.6	1.7	1.2	1.5	0.7	0.9			
Cl (ppm)	741.0	720.0	576.0	780.0	981.0	1178.0	1065.0	960.0	974.0	1230.0	1050.0			
F	200.0	190.0	178.0	173.0	336.0	540.0	626.0	536.0	699.0	359.0	226.0			
S	1120.0	1090.0	1119.0	1100.0	298.0	240.0	307.0	395.0	228.0	289.0	287.0			
Li (ppm)	<4.7	11.2	29.9	49.8	83.4	57.3	21.2	55.7	19.5	24.3	20.8			
V	269.2	259.3	361.7	293.9	180.8	213.0	171.7	157.9	154.5	146.2	93.7			
Cr	41.5	49.9	<8.7	12.5	<7.1	<9.1	<6.9	<6.5	<8.7	<9.2	<6.8			
Co	21.3	21.0	29.8	19.5	22.6	19.5	16.3	18.1	18.5	15.1	11.9			
Ni	14.8	14.1	12.2	10.6	5.8	7.1	3.7	4.8	4.3	5.3	5.6			
Rb	25.2	24.4	9.7	12.3	67.3	40.5	49.6	55.7	52.7	62.8	58.5			
Sr	476.3	469.3	354.1	466.6	293.3	282.7	255.7	283.1	254.1	273.8	234.2			
Y	15.7	15.0	21.5	11.9	40.8	21.1	29.4	31.1	21.3	33.9	34.7			
Zr	60.5	59.9	51.0	47.1	190.0	83.1	117.6	132.5	86.4	152.4	159.2			
Nb	0.9	0.9	0.6	0.7	3.1	1.3	1.8	2.1	1.4	2.4	2.4			
Ba	213.9	214.1	116.3	165.6	462.4	365.5	406.3	432.6	404.0	463.0	534.5			
La	6.7	6.7	8.0	6.7	15.9	8.7	11.6	13.4	10.2	15.1	14.9			
Ce	15.0	14.6	19.5	15.9	37.1	19.3	27.2	30.3	21.7	32.7	33.5			
Nd	9.6	9.4	12.1	9.0	24.2	12.7	18.8	19.8	14.3	21.6	21.4			
Sm	2.3	2.5	2.8	1.9	6.3	3.4	4.3	5.1	3.5	5.8	5.3			
Eu	0.8	0.7	1.0	0.7	1.6	1.0	1.2	1.4	1.2	1.6	1.5			
Gd	2.9	2.6	3.0	1.9	6.8	3.2	4.5	5.5	3.6	6.0	5.9			
Yb	1.6	1.7	2.5	1.5	4.4	2.6	3.2	3.0	2.2	3.6	4.0			
Lu	0.3	0.3	0.4	0.2	0.6	0.4	0.5	0.5	0.3	0.5	0.6			
Pb	6.6	6.4	3.9	4.5	14.8	11.5	11.5	11.7	11.8	15.3	14.0			
Th	1.0	1.0	0.5	0.5	3.1	1.4	2.1	2.3	1.4	2.6	2.6			

Figure 1.

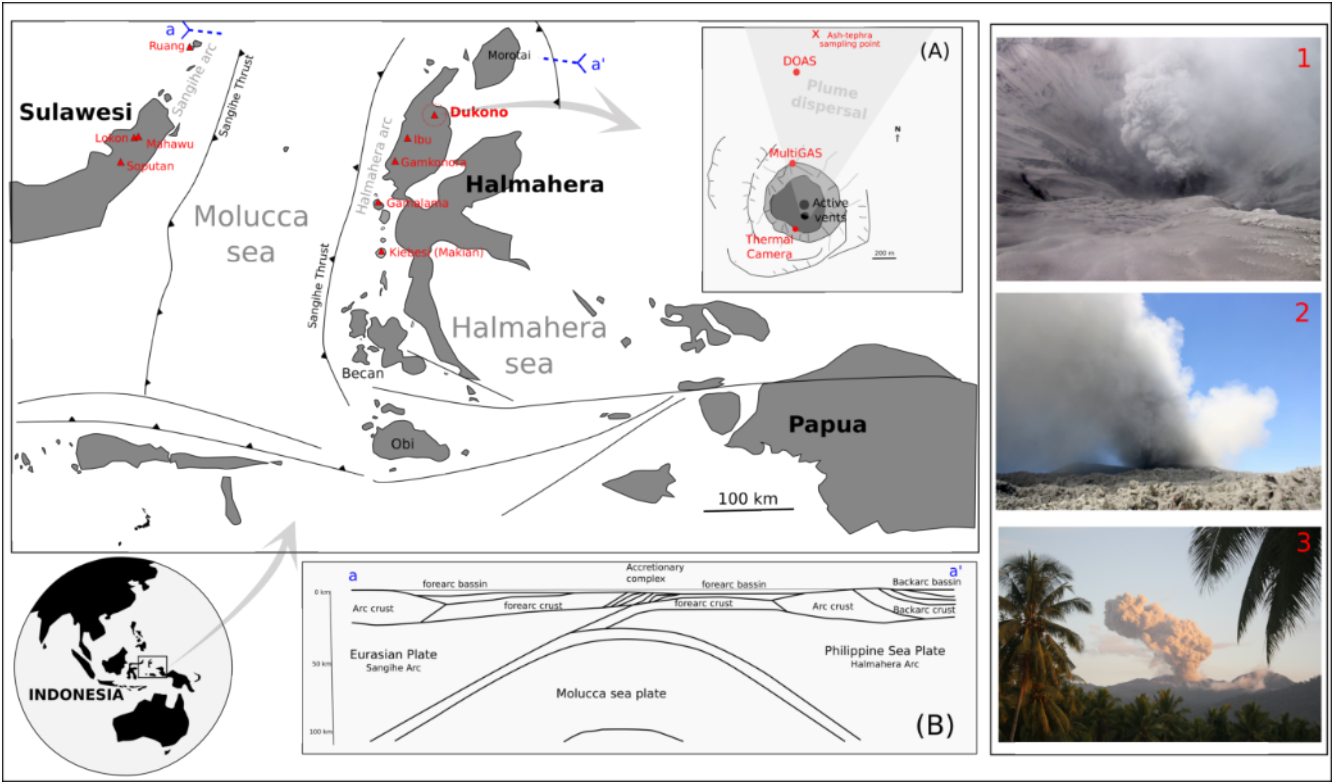


Figure 2.

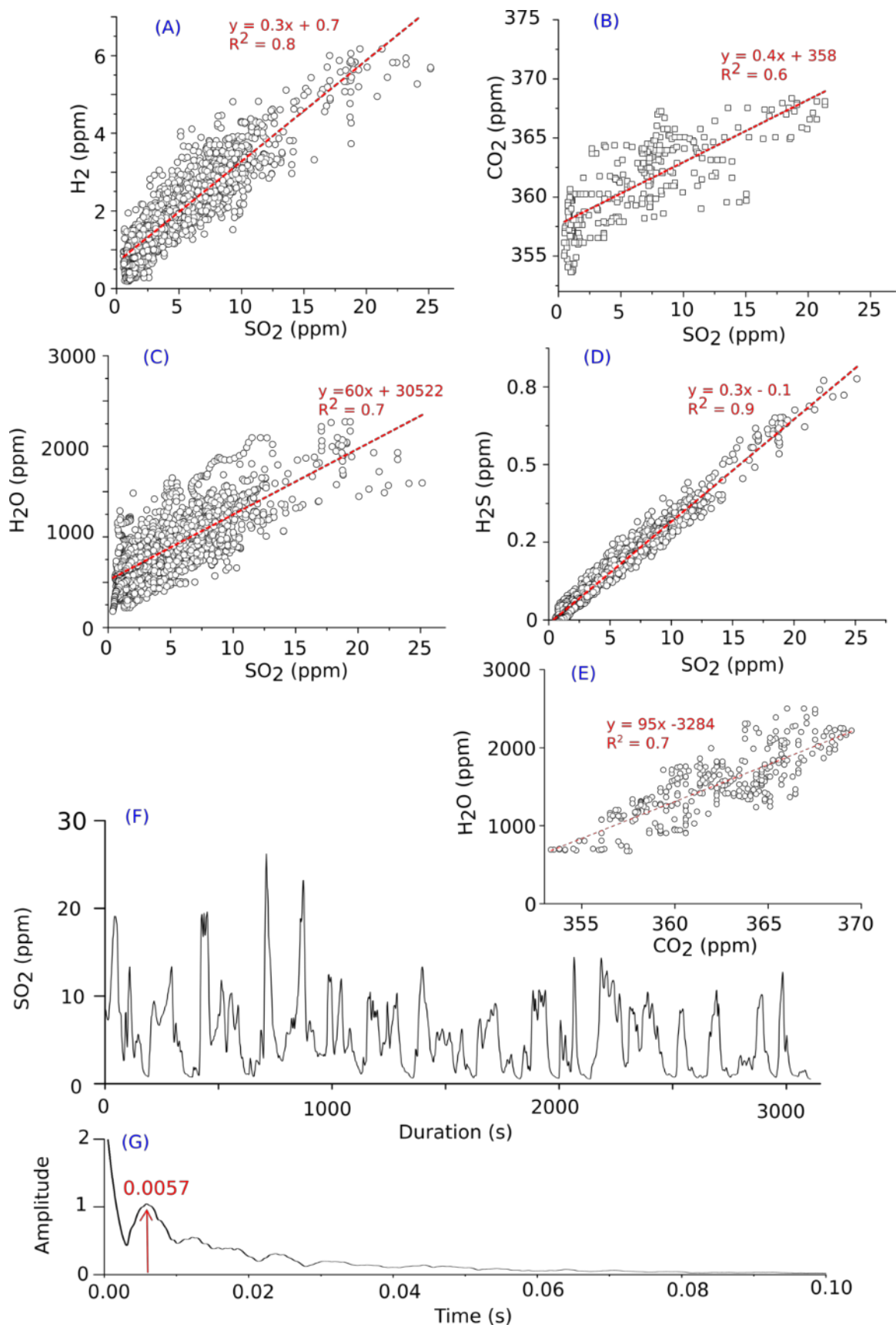


Figure 3.

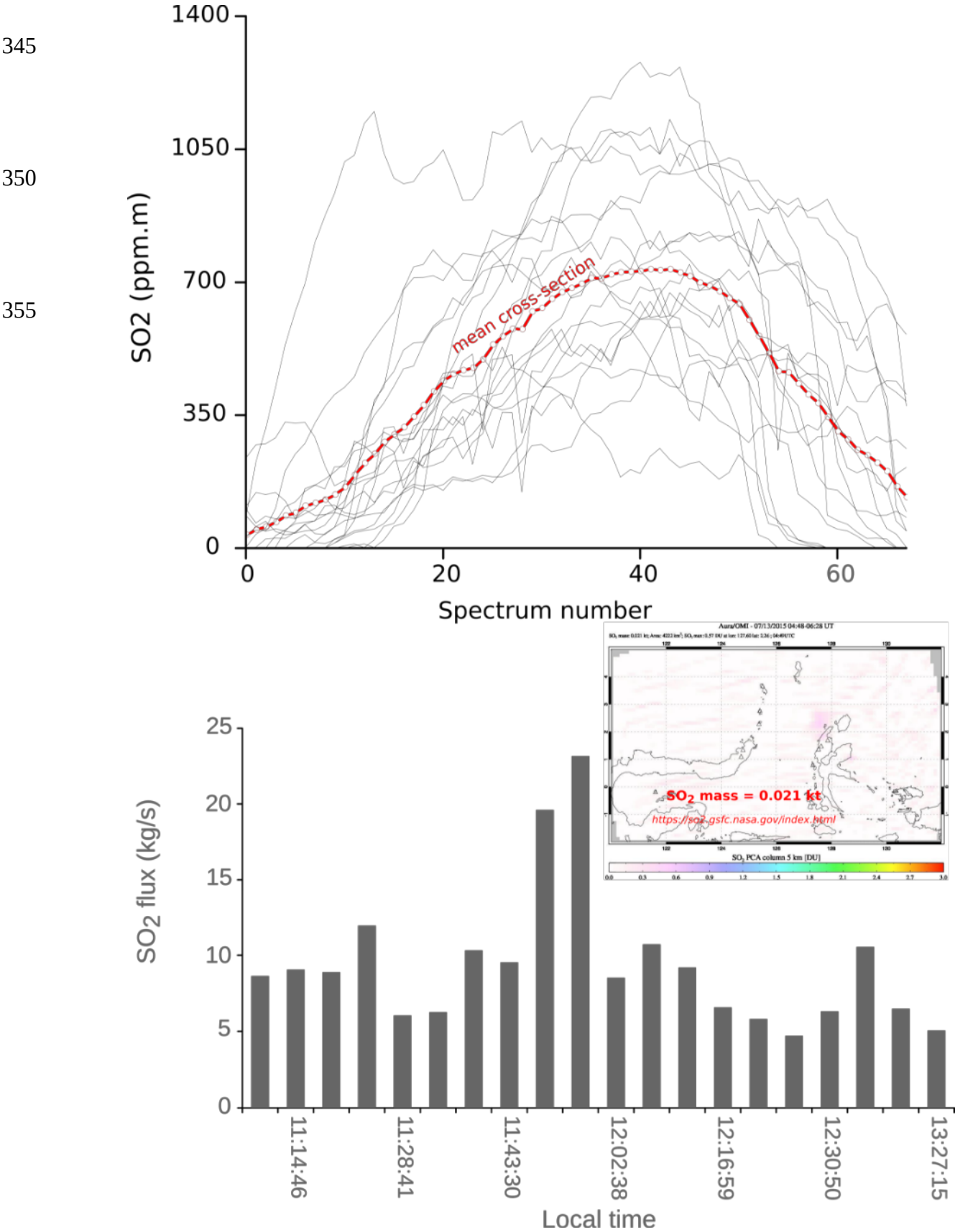


Figure 4.

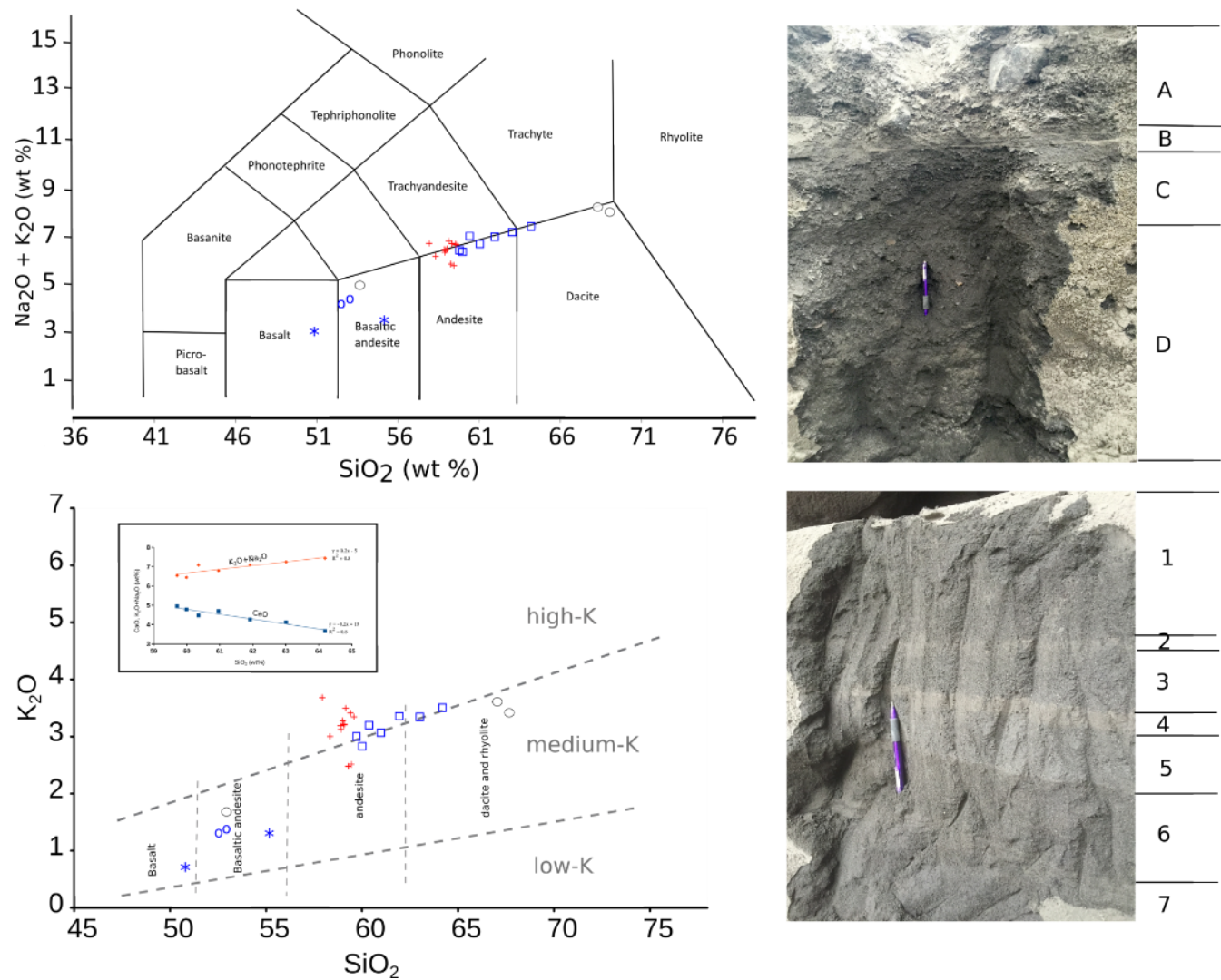


Figure 5.

365

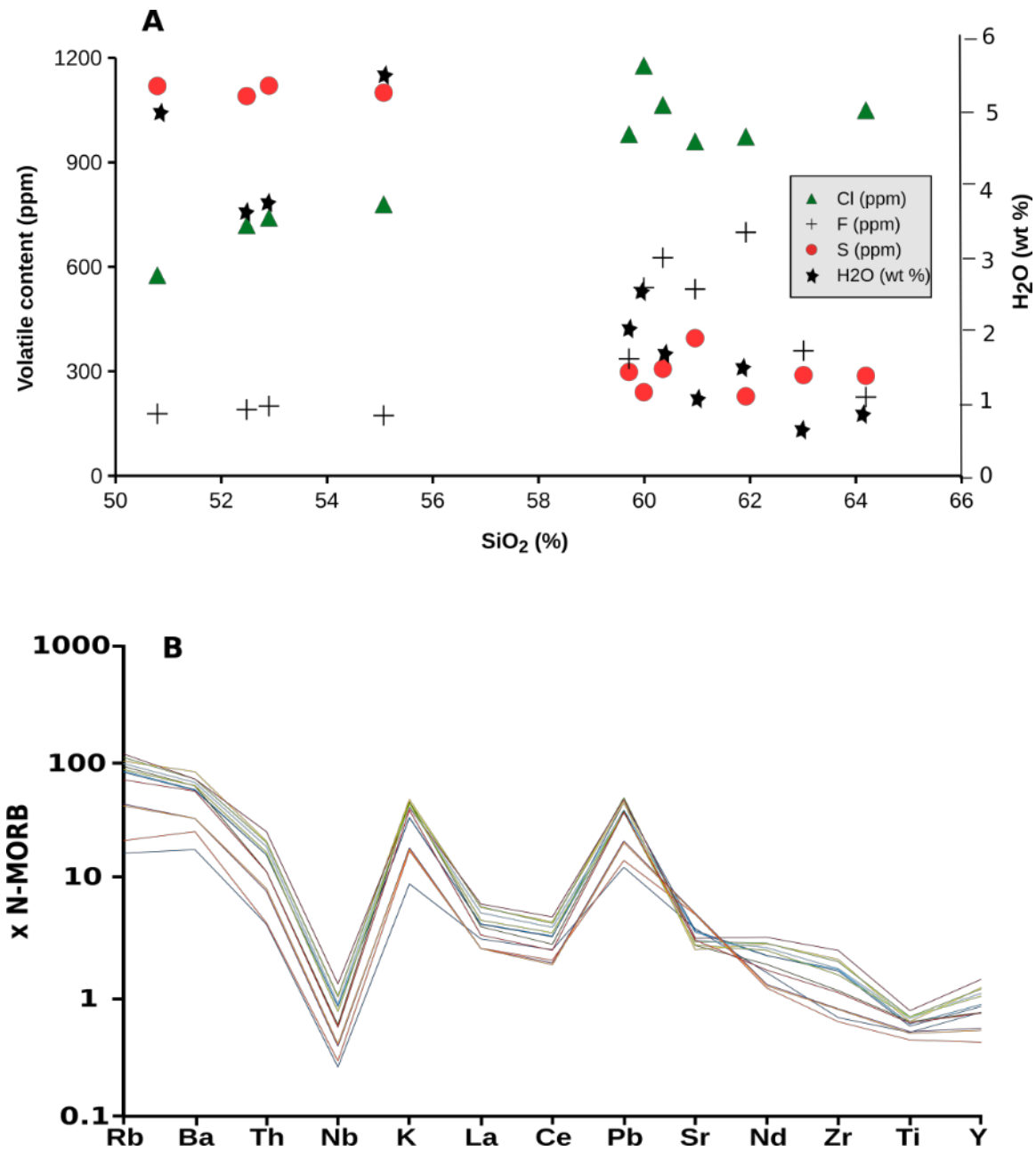


Figure 6.

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