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Helium, carbon and nitrogen isotope evidence for slab influence on volcanic gas emissions at Rabaul caldera, Papua New Guinea

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Abstract

The chemical and isotopic composition of the gases emitted by subduction zone volcanoes can provide insights into the origin of magmatic volatiles. In volcanic arcs, magmatic volatiles and therefore emitted gases can be supplied from the mantle, the subducting slab, or the rocks of the arc crust. Determining the relative contributions of these distinct sources is important for understanding the transfer of volatiles between Earth's interior and exterior reservoirs, which has implications for the physical and chemical evolution of both the mantle and the atmosphere. Each subduction zone is a different experiment in recycling efficiency according to the composition of the slab and the pressure-temperature path it experiences on subduction, and accordingly all volcanic arc emissions can be characterised by their particular chemical and isotopic compositions. In this study, we analyse the composition of volcanic gases from Rabaul caldera in the New Britain subduction zone, Papua New Guinea, and show that the emissions are substantially influenced by slab recycling of carbon and nitrogen. We find helium emissions are dominated by a mantle contribution, with little influence from the arc crust. Carbon isotopes point to a mixture of mantle, carbonate and organic sediment-derived contributions, with carbonate dominant. This may be of sedimentary origin, seafloor calcareous muds, or altered basalts of the subducting oceanic crust. Nitrogen isotopes also indicate a significant influence of organic sediments. Our study is the first comprehensive investigation of volatile sources in this subduction and our results and interpretation are consistent with previous studies of element recycling based on New Britain arc lavas.

1. Introduction

Rabaul is a restless caldera volcano in East New Britain province, Papua New Guinea (PNG, Figure 1). Since the last caldera forming eruption (667-699 CE), there have been numerous eruptions, of diverse styles, from multiple intra-caldera vents (Bernard and Bouvet de Maisonneuve, 2020; Fabbro et al., 2020; Heming, 1974; McKee et al., 2015; Patia et al., 2017; Wood et al., 1995). The most recent eruptions (1994-2014) were accompanied by substantial outgassing from the caldera's most active cone, Tavurvur (Carn et al., 2016; Global Volcanism Program, 2013; McCormick et al., 2012). Rabaul has been cited as among the highest emitters of volcanic gas into the atmosphere over the past two decades, the active cone of Tavurvur, where outgassing has been focussed, ranked seventh worldwide for both SO_2 and CO_2 flux in 2005-2015 (Aiuppa et al., 2019; Carn et al., 2017). Following the cessation of eruptive activity, unrest at Rabaul has dwindled to significantly lower levels, in terms of the intensity of seismicity or ground deformation, vigour of gas emissions, and the temperature and overall abundance of hot springs and fumaroles across the caldera. It remains unclear whether prodigious gas emissions from Rabaul are an inherent characteristic of the volcanic system or a transient feature, given the short history of instrumented monitoring. The chemical and isotopic composition of gas emissions at Rabaul have been little studied and we do not know whether, or to what extent, volatiles are supplied to the volcanic system from (i) the nearby subducting Solomon Sea plate or (ii) crustal rocks of the New Britain volcanic arc. Magmatic volatiles play a key role in modulating eruption style and intensity at Rabaul and understanding their origin and abundance is therefore critically important for hazard assessment and risk mitigation (Bernard et al., 2022).

In this contribution, we present geochemical and isotopic data from volcanic gases at Rabaul, collected from Tavurvur crater fumaroles and nearby hot springs in 2016 and 2019. We report the composition of gases in terms of the relative abundance of major (H_2O, CO_2, sulfur) and trace (He, Ar, N_2) chemical species, as well as helium, carbon, nitrogen and argon isotopes. These are valuable tracers for determining the relative proportion of volatiles supplied from the mantle and the crust (Barry et al., 2022; Hilton et al., 2002) as well as for assessing the influence of recycled subducting slab phases (Fischer et al., 2002; Halldórsson et al., 2013; Mitchell et al., 2010; Sano and Marty, 1995). On the scale of individual volcanic systems, such information is valuable for understanding magmatic volatile budgets and for interpreting the chemistry of gas emissions. Considering a group of volcanoes, whether within the same arc or in different arcs, we can learn about the variable efficiency of volatile recycling during subduction according to differences in the phases present on the slab and the pressure-temperature path experienced by the slab as it sinks (Aiuppa et al., 2019; Hilton et al., 2002; Plank and Manning, 2019). Taken globally, these insights into volatile recycling efficiency during subduction contribute to our understanding of the secular evolution of mantle and atmospheric composition, plate tectonics, environmental change, and planetary habitability (Bekaert et al., 2021; Hilton et al., 2002; Jambon, 1994).

Our understanding of magmatic volatile budgets at Rabaul and of volatile recycling in the wider New Britain subduction zone is at an early stage. In this study, we have characterised the isotopic and chemical of fumaroles on the active cone Tavurvur and hot springs around Rabaul caldera for the first time. Many of our samples are affected by air contamination, potentially due to shallow seawater intrusion or air circulation in the hydrothermal system within the poorly consolidated rocks of the volcanic edifice. Nonetheless, by combining a range of complementary chemical and isotopic tracers, along with a compilation of the available geochemical and isotopic data from whole rock analyses, we have determined the provenance of volatiles at Rabaul. We find a strong mantle influence, based on high $^3He/^4He$ values, and evidence from $\delta^{13}C$ and $\delta^{15}N$ for slab-derived carbonate and organic sediment contributions.

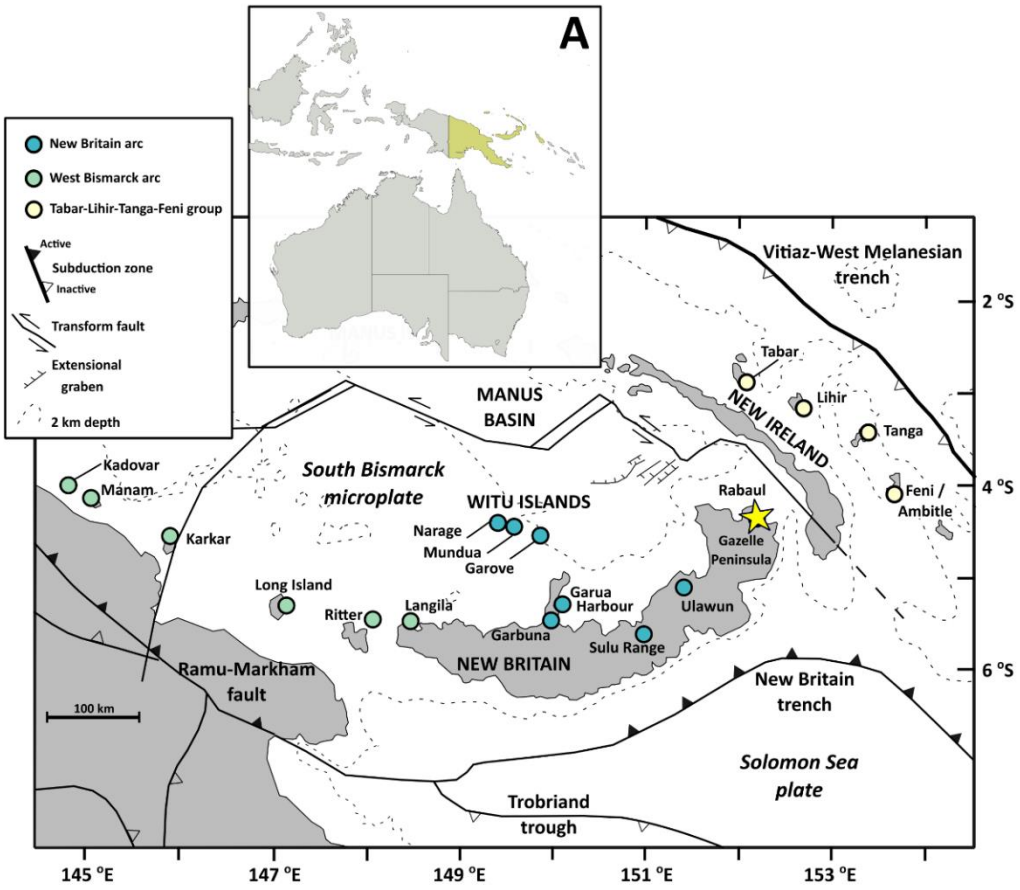


Figure 1. A. Map of New Britain, highlighting tectonic or geographic features mentioned in the text and selected volcanoes of the West Bismarck, New Britain, and Tabar-Lihir-Tanga-Feni groups. Of the volcanoes shown, all except Tabar, Tanga and Narage have reported Holocene activity (Global Volcanism Program, 2013). Map modified from (Holm et al., 2016; Macpherson et al., 1998). Inset shows location of PNG within Oceania. **B.** Google Earth image showing Rabaul caldera with major features (urban areas, volcanic edifices, our sampling sites) highlighted.

2. Geological Context

2.1 Tectonic Setting

Rabaul is located on the Gazelle Peninsula of New Britain in a complex tectonic setting between the converging Pacific and Australian plates (Holm et al., 2016; Woodhead et al., 1998). The island is built of Eocene-Oligocene volcanic rocks and intrusives, with overlying Miocene limestones and younger volcanics. Modern convergence is accommodated by microplate rotation and subduction of the Solomon Sea beneath the Bismarck Sea (Figure 1). The convergence rate at the New Britain trench is ~9-13 cm yr^{-1} (Holm et al., 2016; Tregoning et al., 2000, 1998). New Britain's Paleogene volcanic and igneous rocks are related to an earlier period of subduction, when the Pacific plate was subducted along the now inactive Vitiaz-West Melanesian trench to the northeast of modern New Ireland (Figure 1). Subduction along this margin ended around 26-20 Ma, possibly caused by the docking of the Ontong-Java plateau with the trench. The pause between these two phases of arc magmatism permitted the development of platform carbonates, in the Gazelle Peninsula represented by the Yalam Formation (Lindley, 2006; Madsen and Lindley, 1994).

The Solomon Sea slab dips ~70° northwards beneath the Gazelle Peninsula, steepening to subvertical towards its western end at 149° E (Zhang et al., 2023). Rabaul is ~148 km above the slab (Syracuse and Abers, 2006). The subducting crust age is 24-44 Ma based on heat flow measurements (Joshima and Honza, 1986) and 28-34 Ma based on magnetic lineations (Joshima et al., 1986). There are no ocean drill cores of the Solomon Sea but samples of seafloor sediments and basalts obtained by dredges and freefall grabs from the R.V. *Natsushima* in 1983-4 may represent the subducting slab lithologies. The sediments are hemipelagic lower bathyal deposits comprising claystones and tuffaceous calcareous muds (Crook, 1986). The volcanic samples are variably altered ferrobasalts, both quench-textured lavas and devitrified hyaloclastites (Davies and Price, 1986). The major and trace element chemistry and Sr-Nd-Pb isotopic composition of these rocks was reported by Woodhead et al. (1998). Sediments sampled from the upper New Britain trench wall comprise a complex suite of limestones, glauconite-bearing sediments, and arenites and rudites derived from both volcanic rocks and carbonates (Crook, 1986). At the western end of the trench, there is a 2.5 km-thick accretionary prism which is absent at the eastern end, closest to Rabaul (Honza et al., 1989). It remains unclear whether the uneven distribution of sediment in the New Britain trench is a consequence of lateral sediment transport caused by oblique plate convergence, greater debris infill at the western end due to proximity to the Western Bismarck arc and Australian continent collision zone, efficient subduction of sediment at the eastern end of the trench, or an eastward increase in tectonic erosion of the forearc crust (Bernstein-Taylor et al., 1992; Galewsky and Silver, 1997; Honza et al., 1989; Malatesta et al., 2013).

2.2 Eruptive History of Rabaul

Volcanism on the Gazelle Peninsula dates from the Lower to Middle Pleistocene and is distributed across four major centres, the Varzin Depression, the Vanakunau Basin, the submarine Tavui caldera and Rabaul, the most active (Hohl et al., 2022; Nairn et al., 1995). The oldest dated deposits at Rabaul (~0.5 Ma) are associated with three basaltic stratovolcanoes, Tovanumbatir, Kombiu and Turangunan, adjacent to the modern caldera. Since 0.125 Ma, nine ignimbrite-forming eruptions have occurred, most recently the Rabaul Pyroclastics event in 667-699 CE, which deposited an 11 km^3 ignimbrite and formed a 6×8 km caldera (McKee et al., 2015; Nairn et al., 1995). Historical eruptions have occurred at multiple vents within the caldera (Tavurvur, Vulcan, Rabalanakaia, Sulfur Creek, Palangiagia), including events (1878, 1937, 1994) where Vulcan and Tavurvur erupted simultaneously. The post-caldera eruptions exhibit lava flows, violent Strombolian behaviour, and Vulcanian to sub-Plinian blasts, with the diversity in eruption dynamics attributed to variations in magma ascent rate (Bernard and Bouvet de Maisonneuve, 2020). Caldera-forming eruptions are of dacitic composition while post-

caldera eruption products range from basaltic andesite to trachydacite (58-64 wt% SiO_2) (Bernard and Bouvet de Maisonneuve, 2020; Fabbro et al., 2020; Nairn et al., 1995). Intermediate magmas at Rabaul apparently result from the mingling and mixing of recharging basalts and resident dacites (Bouvet de Maisonneuve et al., 2015; Patia et al., 2017). There has been no eruption at Rabaul since August 2014.

2.3 Previous Work on Magma and Volatile Sources

The mantle wedge beneath New Britain, of Indian MORB affinity based on whole-rock Pb isotopes, is exceptionally depleted in high field strength elements (HFSE), a consequence of prior melting in the back arc, i.e. Manus Basin (Woodhead et al., 1998). Post-Miocene New Britain volcanics are enriched in fluid mobile elements (e.g. Ba/La, Sr/Nd), resulting from slab fluids infiltrating the mantle wedge (DePaolo and Johnson, 1979; Johnson, 1979). Based on Sr-Nd-Pb isotopes, high Sr/Nd and low Th/Yb, Woodhead et al. (1998) described New Britain volcanics as an end-member suite among global arcs, bearing a strong influence of hydrous fluids derived from altered basaltic crust with relatively minor influence of recycled sediments. This interpretation was previously advanced on the basis of lava B/Be ratios (Morris et al., 1990). New Britain arc volcanoes lie over a remarkably wide range in depth to the slab, from ~100 km at the volcanic front to ~600 km at the Witu Islands (Johnson, 1979; Woodhead and Johnson, 1993). Tracers of slab fluid in the erupted lavas (e.g. Ba/La, Sr/Nd, $^{206}Pb/^{204}Pb$, Eu anomaly) diminish from south to north across the arc, suggesting a decrease in fluid influence with increasing depth to slab. This trend is convolved with increasing HFSE concentration, reflecting a decrease in partial melting, also correlated with depth to slab (DePaolo and Johnson, 1979; Woodhead et al., 1998; Woodhead and Johnson, 1993). Rabaul is not included in the Woodhead et al. (1998) study, though the authors note that limited Sr-Pb isotopic analyses of 1994 Vulcan and Tavurvur andesites are notably more radiogenic than other New Britain rocks (Johnson et al., 1995) and that this may be a consequence of 'paleo-enrichment' of the mantle wedge, related to the earlier subduction of the Pacific plate (see section 2.1). More recent work (Hohl et al., 2022), argues for the influence of both slab-derived fluids and slab sediment-derived melts on the mantle beneath Rabaul, based on trace element and Sr-Nd-Hf isotope analyses of 'inner caldera' (post-1400 B.P. eruptions of Tavurvur, Vulcan, Rabalanakaia, Sulphur Creek) and outer caldera (undated rocks from neighbouring mafic stratovolcanoes, e.g. Kombiu) deposits.

Studies of gas emissions from Rabaul and other PNG volcanoes have largely focussed on determining SO_2 and CO_2 flux, using drone-based sensing (Galle et al., 2021; Liu et al., 2020; McCormick Kilbride et al., 2023), ground-based remote sensing (Andres and Kasgnoc, 1998; McGonigle et al., 2004) or satellite observations (Carn et al., 2017; McCormick et al., 2012). These data show that PNG volcanoes (specifically Rabaul, Manam and Bagana) are globally important sources of both SO_2 and CO_2 (Aiuppa et al., 2019; Carn et al., 2017; Fischer et al., 2019). Analyses of gas chemistry are more restricted. Soil CO_2 emissions at Rabaul were sporadically monitored in the 1990s (Global Volcanism Program, 1997a, 1997b, 1995). Otherwise, there are two measurements of helium isotopes in hot spring gases (Farley et al., 1995) and two measurements of helium and carbon isotopes in gas samples from Tavurvur and Rabalanakaia (Sano and Williams, 1996). The helium isotopes range from 5.7-8.6 R/R_A, indicating a predominantly mantle-derived helium with little crustal input. The carbon isotopes ($\delta^{13}C$) range from -2.55 to -2.80 ‰, consistent with mixing between carbonate and mantle-derived carbon. Recent global compilations of arc outgassing have suggested that the high carbon fluxes from PNG volcanoes are due to efficient recycling of subducted carbon, though no distinction is made between the tectonically and geochemically distinct West Bismarck, New Britain and Bougainville arcs in these studies (Aiuppa et al., 2019, 2017; Plank and Manning, 2019). In contrast, other work argued for remobilized crustal carbonate as the main source of volcanic CO2 in PNG (Mason et al., 2017). Here, our aim is to discriminate between these scenarios, and moreover to determine the influence of sediment recycling on Rabaul gas emissions.

3. Methods

3.1 Sampling Methods

We sampled multiple sites of gas emissions at Rabaul across two field expeditions, in September 2016 and May 2019. In 2016, we collected gas samples from a fumarole at the base of Tavurvur crater, from hot springs on the beach north of Tavurvur towards Sulfur Point, and from hot springs at Rababa (Figure 1b). In 2019, we sampled fumaroles on the northeast rim of Tavurvur and re-sampled Rababa hot springs (Figure 1b).

We collected fumarolic gases by inserting a titanium tube into the fumarole and connected this tube to our sampling line, composed of a Giggenbach bottle and multiple copper tubes connected in series using silicon tubing. The 2019 Giggenbach bottle was an evacuated glass flask containing 5M NaOH solution (Broadley et al., 2020; Giggenbach, 1975; Giggenbach and Goguel, 1989). In 2016, the Giggenbach bottle was evacuated, but did not contain any NaOH solution.

We collected hot spring samples by placing an inverted plastic funnel over a persistent bubbling area, securely immersing the funnel in the hot spring pool, and connecting it to the Giggenbach bottle and copper tubes with silicon tubing (Barry et al., 2022). At all sites, we allowed the line to be flushed with gas for at least 30 minutes prior to collecting our samples. At the fumarole site and the bubbling springs we also collected gas samples into Tedlar bags for carbon isotopic analyses.

We sampled gases from the Tavurvur crater floor fumaroles in 2019 by means of an uncrewed aerial system (UAS), comprised of a multi-rotor DJI Phantom airframe equipped with a Tedlar gas bag sampling apparatus (Galle et al., 2021; Liu et al., 2020). We determined that the aircraft was in the plume by visual observations and triggered sample capture by means of a set timer.

3.2 Analytical Methods

Our samples have been analysed in multiple laboratories in several institutions: the University of Oxford (UO), the University of Manchester (UM, both UK), Woods Hole Oceanographic Institution (WHOI) and the University of New Mexico (UNM, both USA).

Gas chemistry. We analysed headspace gases from the Giggenbach bottles using a combination of gas chromatography and quadrupole mass spectrometry. Dissolved gases from the Giggenbach bottles were analysed using wet chemical techniques and ion chromatography. The analytical procedures have been recently described (Ilanko et al., 2019; Lee et al., 2017). In short, the gas chromatograph with a Discharge Ionization Detector and helium carrier gas was used to determine N_2, Ar+O_2, CO_2, CO, CH_4 and H_2 and the quadrupole was used to quantify Ar, O_2, He, and N_2. The NaOH solution was analysed for CO_2 by alkalinity titration. Sulfur species were analysed by ion chromatography and alkaline iodine titration. Chlorine and fluorine were analysed by ion chromatography.

Helium isotopes. Our noble gas analyses followed similar procedures between labs, whether at UO, UM or WHOI (Barry et al., 2022, 2016). At UO, the instruments were an SFT and an ARGUS, at UM a modified VG5400 with upgraded electronics, and at WHOI a Nu Noblesse. We connected copper tubes to the respective extraction lines using an O-ring connection, and released small volumes (*2*-20 cm^3) of gas sample into the sample clean-up lines. We removed reactive gases using a chemical procedure, exposing the sample to a heated titanium sponge, and then passed the gases through (hot and cold) getters. We then passed a small aliquot of cleaned gas into a cryogenic trap, which allowed separation of each noble gas. The noble gases measured varied between labs. At UO, we measured all stable noble gas isotopes, whereas at WHOI, we only measured He isotopes and $^4He/^{20}Ne$. We were unable

to measure Ne isotopes at UM, hence the lack of $^{4}He/^{20}Ne$ data for these samples. Given the $^{40}Ar/^{36}Ar$ is very close to air, we could assume an air $^{20}Ne/^{22}Ne$ and $^{4}He/^{20}Ne$ for most samples. We estimate uncertainties of ≤5% for helium isotopes and ≤3% for neon and argon isotopes.

Carbon isotopes. We analysed the Tedlar bag samples using a Delta-Ray Infrared Isotope analyser (Fischer and Lopez, 2016; Galle et al., 2021; Liu et al., 2020). We set up the Delta Ray instrument at Rabaul Hotel, in Rabaul Town (Figure 1b). The CO_2-free air carrier gas was produced on-site by passing air, pressurized in a tank, through Sulfulime absorbent. The calibration gas was pure CO_2 obtained from a company in PNG. We did not know the $\delta^{13}C$ value of the calibration gas at the time of our analyses in Rabaul, so we collected a sample of this gas and analysed it on the Delta Ray at the University of New Mexico after our return and then retroactively corrected the values obtained during the fieldwork.

Nitrogen isotopes. We performed nitrogen isotope measurements on gas splits from copper tubes. In brief, our fumarole and hot spring gas samples were purified on a specially designed N gas extraction vacuum line (Barry et al., 2012) and analysed for nitrogen isotopes on the Nu Noblesse at WHOI (Bekaert et al., 2023). We placed a third stainless steel clamp on each tube approximately one-half inch from one of the original clamps to subsample an aliquot of the gas in each tube. We connected copper tubes to the extraction line with VCR fittings and pumped down to $<1 \times 10^{-7}$ Torr. Once sufficient vacuum was achieved, we removed the exterior clamp to inlet the aliquot of gas. We froze out condensable gases (mainly CO_2 and H_2O) on a cold finger using liquid nitrogen. The non-condensable gases were expanded into the extraction line and diluted until the sample pressure was low enough to be measured. We then exposed the gas to a Pt furnace at 1000 °C and a CuO furnace that was heated from 450 °C to 850 °C, held for 15 minutes to covert CO to CO_2, and step cooled back to 450 °C over 30 minutes. A second cold finger with liquid nitrogen was used to freeze down the CO_2. Once the CuO furnace had cooled to its initial temperatures and CO conversion was complete, we passed an aliquot of the gas into the mass spectrometer for analysis and typically performed each analysis in triplicate. We ran line blanks prior to the analysis to use for correction and an air standard following the analysis; the size of the standard is calibrated to match the size of the sample. We applied a linearity correction to the samples using the line blanks and air standards (Bekaert et al., 2023).

4. Results

The gas compositions (Figure 2) of our fumarole and hot spring gas samples are reported in Table 1. The helium (Figure 3) and carbon (Figure 4) isotopic composition and relative abundance ratios (Figure 5) are reported in Table 2, along with our estimates of mantle- and slab-derived influences (after Sano & Marty, 1995). In Table 3, we report the nitrogen isotopic composition (Figure 6) of our samples and independent estimates of mantle- and slab-derived influences (after Sano et al., 2001).

4.1 Gas chemistry

The abundance of major and minor gas species in Rabaul samples are reported in Table 1, with relative N_2, He and Ar abundance shown in Figure 2. Samples from the 2016 field expedition were collected without NaOH solution in the Giggenbach bottles, so we could not measure H_2O, sulfur or halogen species in these gases. Samples collected in 2019 were dominated by H_2O (678 to 967 mmol/mol in Tavurvur fumaroles, 773 mmol/mol in Rababa hot spring gases) with minor CO_2 (13 to 18 mmol/mol in fumaroles and 222 mmol/mol in hot spring gases), and total S (S_t) (0.33 to 2.1 mmol/mol SO_2 and 0.33 to 2.10 mmol/mol H_2S in fumaroles, 0.06 mmol/mol SO_2 and 1.06 mmol/mol H_2S in hot spring gases). CO_2/S_t in the fumarole gases collected in 2019 range from 5.7 to 6.1, slightly higher than what was measured by a 2016 measurement by MultiGAS in Tavurvur's crater (2.6 - 2.8, Galle et al., 2021).

These gas compositions exhibit the high N_2/He ratios characteristic of volcanic arc gases worldwide, and a wide range in He/Ar and N_2/Ar because of variable mixing between magmatic gases and air or air-saturated water (ASW), in common with low-temperature arc emissions elsewhere (e.g., Fischer et al., 2021). Air and ASW have N_2/Ar of 83 and 40 respectively (Fischer et al., 1998). The influence of ASW is also consistent with the higher CO_2/S_t ratios measured in our Giggenbach bottle samples compared to ratios based on MultiGAS measurements made on the crater floor (Galle et al., 2021). Our samples exhibit high degrees of air or ASW contamination, evidenced by $N_2/Ar < 100$ and $He/Ar < 0.01$. Arc gases of pristine magmatic composition (e.g., Fischer et al., 1998) tend to have $N_2/Ar > 100$, higher He/Ar, and lower N_2/He; both N_2 and Ar excesses in volcanic gases can be attributed to air contamination during sampling (Giggenbach, 1980).

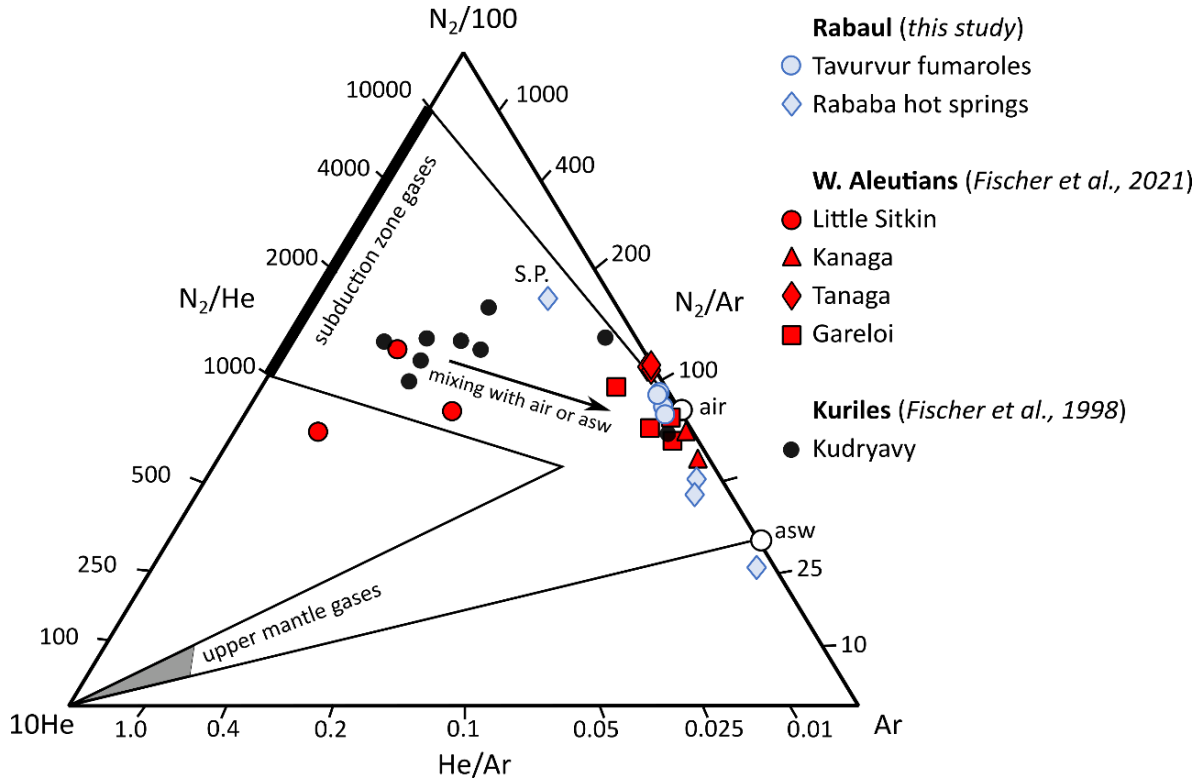


Figure 2. Ternary diagram showing relative molecular nitrogen, helium and argon (N_2-He-Ar) compositions of fumarole and hot spring gas samples from this study, to highlight magmatic versus air and ASW contributions (Giggenbach, 1980). Also shown are gas data from two other Pacific rim subduction zones (Fischer et al., 2021, 1998).

Site	Sample ID	T (°C)	H_2O	CO_2	St	SO_2	H_2S	HCl	HF	He	H_2	Ar	O_2	N_2	CH_4	CO	N_2/Ar	N_2/He	He/Ar
2019																			
Tavurvur rim fumarole	RB-19-1b	97	967	18.3	3.02	1.99	1.02	0.13	nd	0.00020	0.217	0.181	0.001	11.3	0.00070	nd	62	55780	0.001
Tavurvur rim fumarole	RB-19-6a	98	678	13.8	2.43	2.1	0.33	0.06	nd	0.00007	0.165	0.085	<0.001	5.35	0.00051	nd	63	77835	0.001
Rababa hot spring	RB-19-3a	75	773	222.0	1.13	0.06	1.06	0.43	0.07	0.00037	0.001	0.129	0.029	3.57	0.02741	nd	28	9596	0.003
2016																			
Tavurvur floor fumarole	Tav-2B	100		0.33						0.0014	nd	0.850	19.2	79.6	nd	nd	94	56872	0.002
Tavurvur floor fumarole	Tav-2A	140		0.45						0.0018	0.017	0.868	19.97	78.7	nd	nd	91	43720	0.002
Rababa hot spring	RB-HS-1	78		86.6						0.0011	nd	0.219	0.41	12.3	0.521	nd	56	11155	0.005
Rababa hot spring	RB-HS-3	78		72.9						0.0035	nd	0.497	1.03	25.4	0.083	nd	51	7267	0.007
Hot spring near Sulfur Pt.	RB-HS-2	82		71.60						0.0034	nd	0.128	1.07	27.2	0.046	nd	213	7986	0.026
MORB																	152 ± 58	48 ± 6	2
ASW																	40	150,000	0.0005

Table 1. Gas chemistry from fumarole and hot spring gases sampled at Rabaul. Data from 2019 campaign are reported as mmol/mol since we sampled with caustic solution in Giggenbach bottle and could isolate H_2O. Data from 2016 are reported as molar percent dry gas. Concentrations cannot be directly compared across these two campaigns, though N_2/Ar, N_2/He and He/Ar ratios can be. 'nd' signifies not detected.

Site	Sample ID	Lab	T (°C)	R/R_A	R_C/R_A	$^4He/^{20}Ne$	X-value	$^{40}Ar/^{36}Ar$	$^{84}Kr/^{36}Ar$ ($\times10^{-2}$)	$^{132}Xe/^{36}Ar$ ($\times10^{-2}$)	$\delta^{13}C$	$CO_2/^3He$	% mantle He	% M	% L	% S
2019																
Tavurvur rim fumarole	RB-19-1b‡	WHOI	97	1.9	5.7	0.40	1.3	na	na	Na	-5.39	1.14×10^{10}	71	17.5	67.4	15.0
Tavurvur rim fumarole	RB-19-1b_dup‡	WHOI	97	2.2	6.5	0.41	1.3	na	na	Na	na		81			
Tavurvur rim fumarole	RB-19-1b	UM	97	2.1		n.a.		300.7	3.83	2.02	na					
Tavurvur rim fumarole	RB-19-1b_dup	UM	97	2.3		n.a.		299.4	2.29	1.15	na					
Tavurvur rim fumarole	RB-19-1b2	UM	98	0.9		n.a.		298.9	2.00	1.00	na					
Tavurvur rim fumarole	RB-19-6a‡	WHOI	98	2.7	6.0	0.48	1.5	na	na	na	-4.61	2.39×10^{10}	75	8.4	77.7	14.0
Rababa hot spring	RB-19-3a‡	WHOI	75	5.8	6.3	3.23	10.1	na	na	na	-3.67	6.71×10^{10}	79	3.0	85.3	11.7
Rababa hot spring	RB-19-3a_dup‡	WHOI	75	6.1	6.7	2.78	8.7	na	na	na	-3.67		84			
Rababa hot spring	RB-19-3a1	UM	75	5.6		na		306.3	5.36	3.06	na					
Rababa hot spring	RB-19-3a2	UM	75	6.5		na		303.7	4.84	4.63	na					
Rababa hot spring	RB-19-3a2_dup	UM	75	6.5		na		303.9	5.69	3.48	na					
2016																
Tavurvur floor fumarole	Tav-2A	UO	140	1.0	n.d.	0.31	1.0	309.7	1.99	0.72	na	2.27×10^8	9			
Rababa hot spring	RB-HS-1	UO	78	6.4	6.9	3.16	9.9	320.1	4.42	3.37	-4.5	8.04×10^9	87	24.9	64.3	10.9
Hot spring near Sulfur Pt.	RB-HS-2	UO	82	3.3	6.2	0.46	1.5	318.6	1.68	2.31	-9.2	2.47×10^9	77	81.1	1.8	17.2
Garbuna crater fumarole	Gar-F-343	UO	97	7.5	7.5	36.01	113.0	307.6	3.12	2.6	na		94			
Garbuna crater fumarole	Gar-F-344	UO	89	7.1	7.2	30.71	796.4	310.0	3.82	3.53	na		90			
Silanga village hot spring	Sil-HS-345	UO	76	5.3	5.4	20.03	62.9	314.3	3.51	2.35	na		67			
Pangalu hot spring	Pan-HS-1A	UO	87	6.3	6.6	5.41	17.0	313.5	na	na	na	6.75×10^8	82			
Pangalu hot spring	Pan-HS-2	UO	100	2.3	6.7	3.51	11.0	312.3	3.18	2.03	-9.6	1.79×10^9	84			

Table 2. Helium and carbon isotopes, relative abundance ratios, and estimates of mantle helium (Barry et al., 2013) and mantle (%M) and slab (limestone, %L, or sedimentary, %S) carbon (Sano and Marty, 1995) contributions from fumarole and hot spring gases sampled at Rabaul. Different noble gas isotope ratios were measured between laboratories and not all samples were analysed for $\delta^{13}C$ ('na' signifies not analysed). ‡Samples were splits from Giggenbach bottles, all others were copper tubes. Suffix "_dup" indicates duplicate analyses of the same copper tube or Giggenbach bottle split.

4.2 Helium isotopes

We have determined the helium isotope composition of 14 fumarole and hot spring gas samples from Rabaul (Figure 3, Table 2), reported as R/R_A values ($R = {}^3He/{}^4He$ in sample, R_A = atmospheric ${}^3He/{}^4He = 1.39 \times 10^{-6}$). Fumarole gases collected from Tavurvur's crater floor and rim range from 0.92 to 2.70 R_A, while hot spring gases collected from Rababa range from 5.62 to 6.47 R_A, and hot spring gases collected near to Sulfur Point were 3.3 R_A. Figure 3 also shows helium isotope measurements from volcanic and geothermal gases we sampled elsewhere in New Britain during a reconnaissance survey in 2016: from fumaroles at the summit of Garbuna volcano, hot springs near Silanga village close to the Sulu Range, and hot springs from Pangalu village close to the Garua Harbour/Talasea volcanic field. We also plot helium isotope data from hot springs in Rabaul caldera, fumaroles from the Witu Islands, and various geothermal and fumarolic gases sampled across the nearby Tabar-Lihir-Tanga-Feni group (Craig and Poreda, 1987; Farley et al., 1995). Our helium isotope data from Rabaul hot springs overlap with those of Farley et al. (1995) and Sano & Williams (1996), excepting the Tavurvur sample from the latter study which has R/R_A of 8.6. Our samples from elsewhere in New Britain (Sulu, Garua Harbour, Garbuna) record slightly higher He isotope values with respect to Rabaul. Many of the TLTF gases and the Witu Islands gases approach the MORB range, i.e. ~8 ± 1 R_A (Hilton et al., 2002).

For seven of our samples (Table 2), we use the ${}^4He/{}^{20}Ne$ value to apply an atmospheric correction, assuming that ${}^{20}Ne$ is derived from air (${}^4He/{}^{20}Ne = 0.32$) or air saturated water (ASW, ${}^4He/{}^{20}Ne = 0.26$ at 15 °C) (Hilton, 1996; Ozima and Podosek, 2002). This allows us to calculate an atmospheric He value and subtract it from our measured ${}^3He/{}^4He$. Our sample collected on the floor of Tavurvur crater has ${}^4He/{}^{20}Ne$ very close to ASW, suggesting substantial atmospheric contamination, while our remaining samples (Sulfur Point and Rababa hot springs at Rabaul, plus our samples from elsewhere in New Britain) have significantly higher ${}^4He/{}^{20}Ne$ suggesting lesser atmospheric contributions (Figure 3b). Our correction is based on the methods of (Hilton, 1996), using 'X-values' to correct helium isotope ratios for atmospheric influence. The X-value of a gas sample is defined as:

$$(X)_{gas} = ({}^4He/{}^{20}Ne)_{measured} / ({}^4He/{}^{20}Ne)_{air}$$

where $({}^4He/{}^{20}Ne)_{measured}$ is the measured ratio and $({}^4He/{}^{20}Ne)_{air}$ is the value of air, 0.32.

We can then combine our X-values with measured helium isotope values (R/R_A) to calculate atmospheric corrected values (R_C/R_A):

$$R_C/R_A = ((R/R_A \times X) - 1) / (X - 1)$$

where R_C/R_A is reported relative to air ($= 1.39 \times 10^{-6}$). Our samples from Tavurvur rim fumaroles and Rababa and Sulfur Point hot springs show air-corrected He isotope (R_C/R_A) values ranging from 5.7 to 6.9 (Table 2, Figure 3c). Tavurvur samples show greater air contamination than the hot spring samples. We consider the least air contaminated sample of Rababa hot spring, R_C/R_A of 6.7, as the most representative value of the Rabaul magmatic system. These helium isotope values are below the canonical range for upper mantle helium (8 ± 1 R_A) and high above the range associated with radiogenic (i.e., crustal) helium, 0.05 R_A (Andrews, 1985), suggesting that all samples are a mixture of mantle and radiogenic sources. With regards to helium isotope values in volcanic arcs globally, our samples are consistent with the average high temperature fumaroles in volcanic arcs globally of 6.8 R_A (Kagoshima et al., 2015) and within the overall average range of gases emitted from fumaroles and hot springs of arc volcanoes of 5.4 ± 1.9 R_A (Hilton et al., 2002) (Figure 3c).

We measured the isotopic composition of heavy noble gases in a subset of our samples, shown in Supplementary Figure 1. Most cluster around the composition of air and air-saturated water, though there is evidence for higher ${}^{84}Kr/{}^{36}Ar$ and ${}^{132}Xe/{}^{36}Ar$ in all samples from Rababa hot springs.

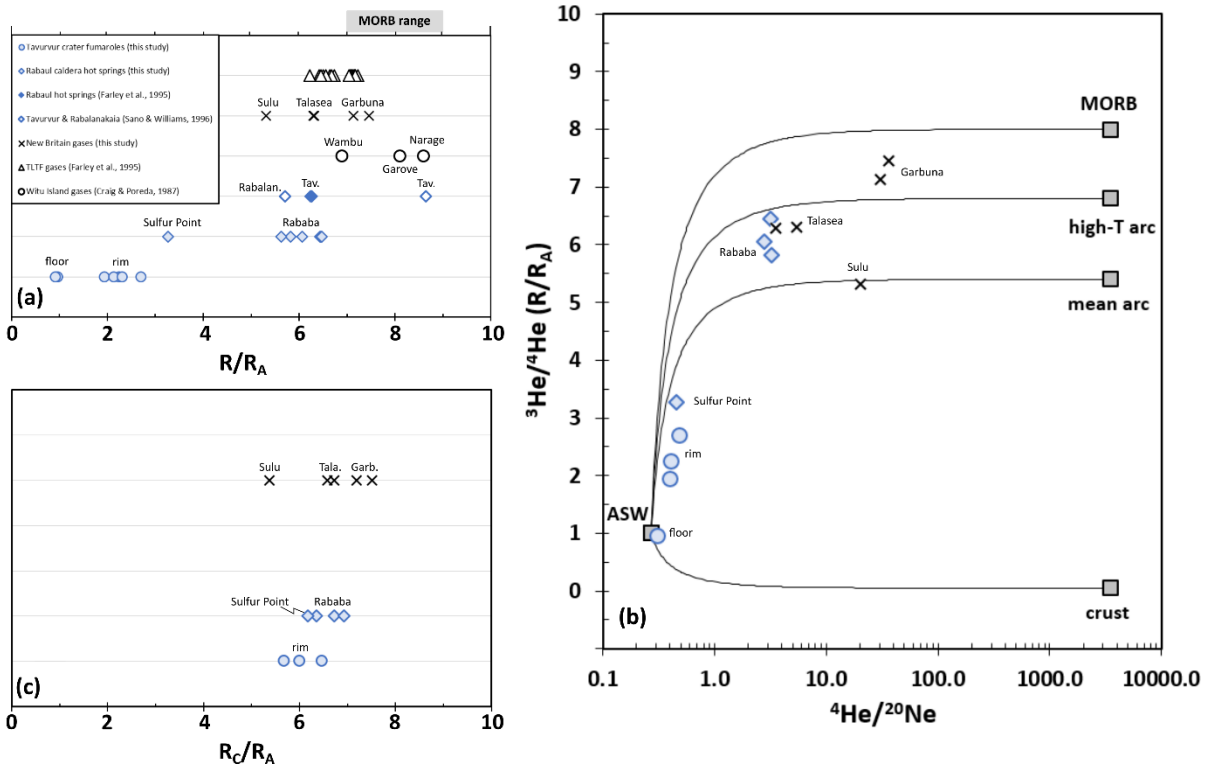


Figure 3. (a) Helium isotopes measured in fumarole and hot spring gases from Rabaul (this study, Farley et al., 1995; Sano & Williams, 1996), and other volcanoes on New Britain and neighbouring islands (Craig and Poreda, 1987; Farley et al., 1995); (b) the same data plotted versus $^{4}He/^{20}Ne$ along with calculated binary mixing lines between air saturated water (ASW) and crustal and mantle endmember compositions (Barry et al., 2021; Hilton et al., 2002; Kagoshima et al., 2015); (c) air-corrected helium isotopes for our new Rabaul and New Britain samples.

4.3 Carbon isotopes

Gases emitted from a vent in the floor of Tavurvur crater, and sampled by our UAS, range in CO_2 concentration from 432 to 555 ppm, with $\delta^{13}C$ varying from -6.48 ± 0.17 to -8.95 ± 0.03 ‰, with respect to the Pee Dee Belemnite (PDB) reference standard (Table 3, Figure 4). We measured higher CO_2 concentrations and more positive carbon isotope compositions in fumarole gases collected on the crater rim (709 to 949 ppm CO2, -4.61 ± 0.55 to -5.39 ± 0.07 ‰ $\delta^{13}C$) and in Rababa hot spring gases (2506 to 2646 ppm CO_2, -3.67 ± 0.06 ‰ $\delta^{13}C$). Over the course of our one-week campaign, there was no significant temporal variation in $\delta^{13}C$ at each site. Clean air collected on a beach away from volcanic plume influence had a CO_2 concentration of 430 ppm and $\delta^{13}C$ of -7.70 ± 0.05. On a Keeling plot (Keeling, 1958), our data fall along a linear regression and the extrapolated $\delta^{13}C$ value of the pure source CO_2 is estimated to be -2.6 ± 0.62 ‰ (Figure 4).

4.4 $CO_2/^3He$ values

Our samples span a range in $CO_2/^3He$ over an order of magnitude from ~2.5×10^9 to 6.7×10^{10} (Figure 5). The minimum value is in the hot spring gases collected near Sulfur Point and lies within the MORB range of $CO_2/^3He$, 1-6 x 10^9 (Marty et al., 2020). Our samples from both Rababa hot springs and the Tavurvur crater rim fumarole are consistent with the addition of carbon from subducted or crustal limestones. Our sample from Rababa collected in 2019 has higher $CO_2/^3He$ than the sample collected in 2016, 6.7×10^{10} compared to 8.0×10^9. All our samples lie in a region of $CO_2/^3He$ space bounded by mixing curves between MORB, subducted organic sediment and marine limestone end-members, suggesting that the carbon emitted in volcanic gases at Rabaul is partly supplied by all three of these sources.

4.5 Nitrogen isotopes

We report nitrogen isotope data in delta notation, where $\delta^{15}N$ is the per mil (‰) deviation of the measured $^{15}N/^{14}N$ from that of air, which has $\delta^{15}N = 0$ ‰. Measured $\delta^{15}N$ (± 1-σ errors) range from -0.75 ± 0.50 to 1.99 ± 0.80 ‰ in Tavurvur crater rim fumarole samples and from 0.16 ± 0.18 to 4.56 ± 0.63 ‰ in Rababa hot spring samples (Table 4, Figure 6). N_2/He ranged from 55780 to 77835 in Tavurvur crater gases and from 9596 to 11155 in Rababa hot spring gases. Our samples from Tavurvur crater are likely to be air contaminated (see Section 5.3). The positive enrichment in N isotopes observed in the Rababa hot springs samples is comparable to that seen in volcanic gases in other circum-Pacific arcs where nitrogen is supplied both from the mantle and from sediments carried on the subducting slab (Clor et al., 2005; Fischer et al., 2005, 2002; Mitchell et al., 2010).

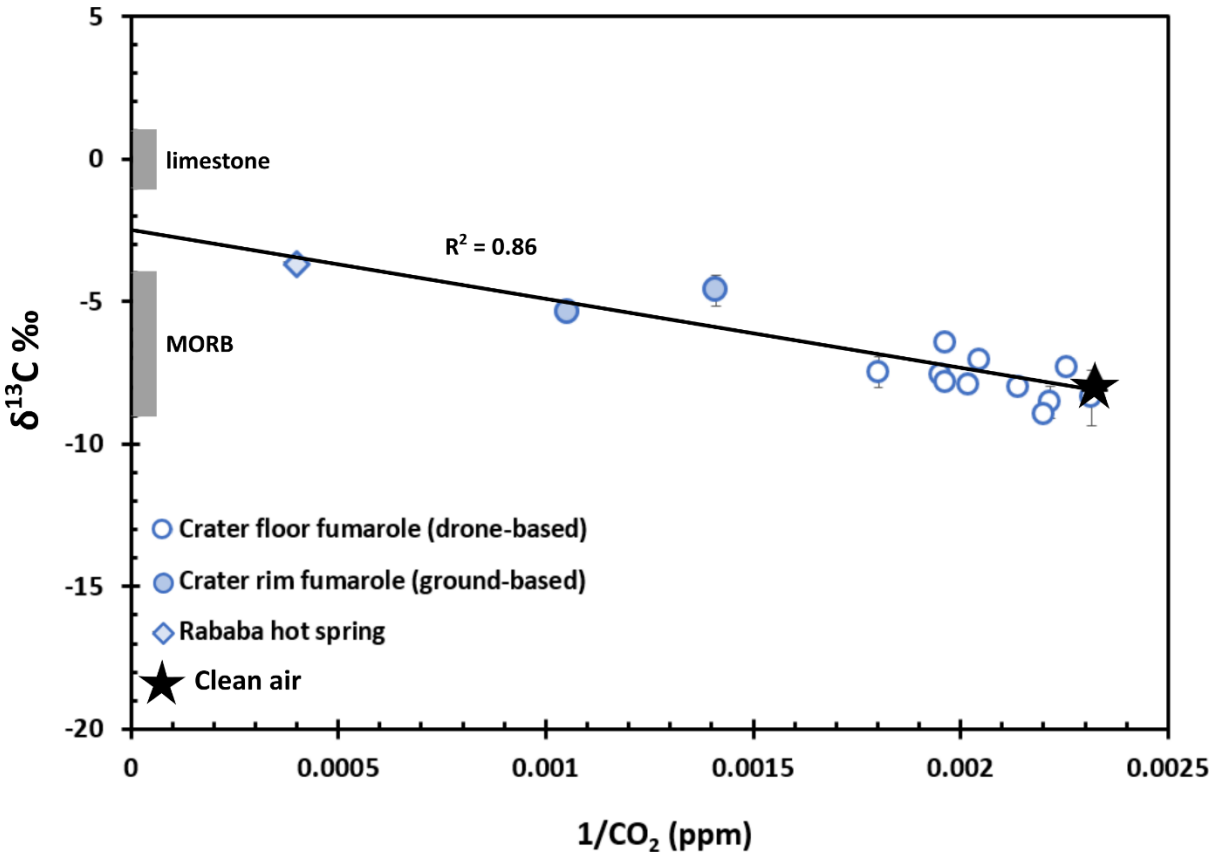
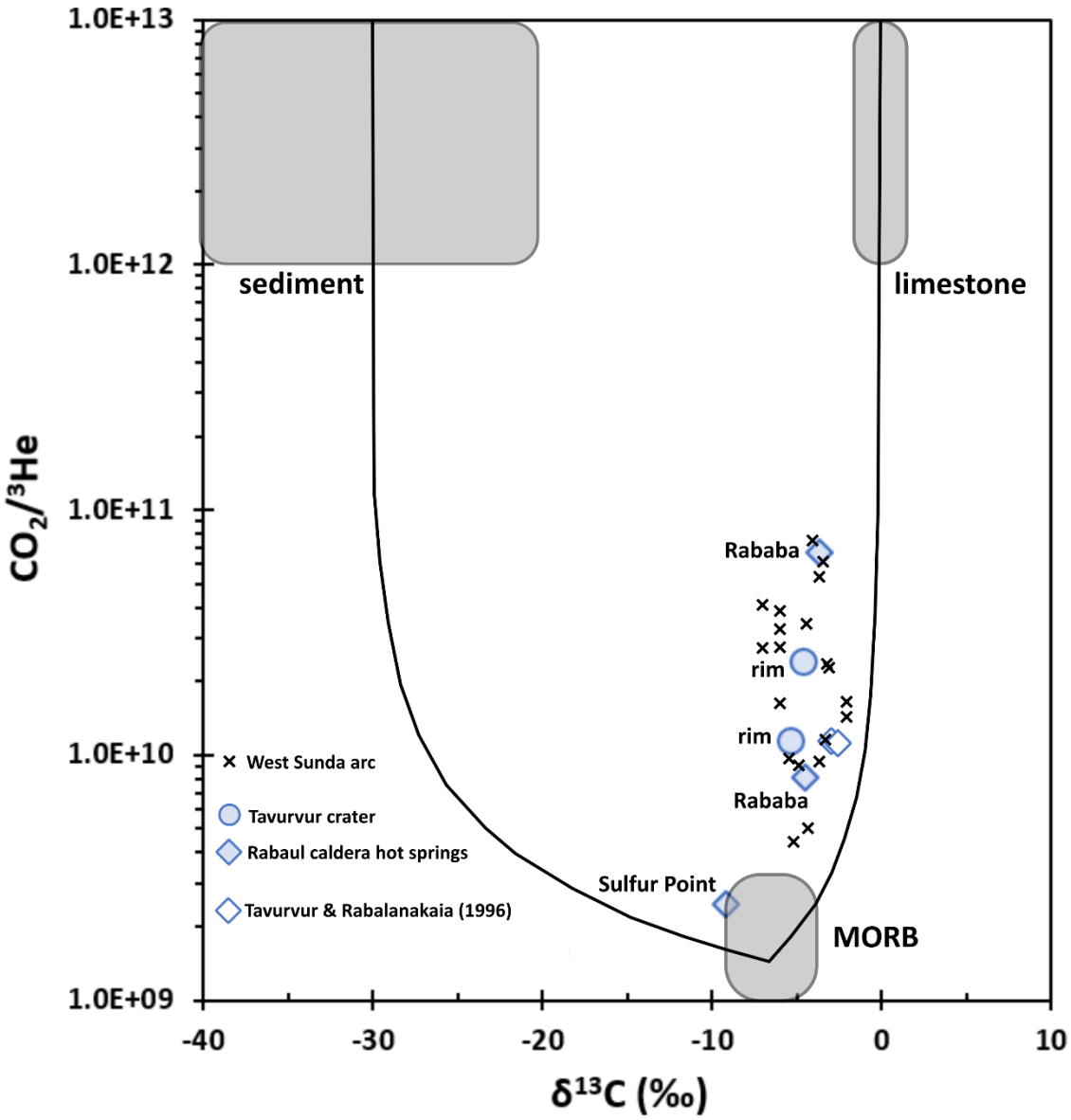


Figure 4. Relationship between carbon concentration and $\delta^{13}C$ for fumarole and hot spring gases at Rabaul. The typical $\delta^{13}C$ range for reference endmembers are also shown: limestone (subducted marine carbonate, $\delta^{13}C$ ~0 ‰) and MORB (upper mantle material, $\delta^{13}C$ ~-6.5 ± 2.5). The black line indicates a mixing line projected from ambient air through the composition of gases sampled from Tavurvur crater floor and rim fumaroles and Rababa hot springs.

Sample ID	Date	Sampling Site	CO_2 (ppm)	$\delta^{13}C$	+/-
TAV-CRF_1401	14/05/21	crater floor	467	-8.02	0.11
TAV-CRF_1402	14/05/21	crater floor	489	-7.06	0.07
TAV-CRF_1403	14/05/21	crater floor	432	-8.38	0.96
TAV-CRF_1404	14/05/21	crater floor	451	-8.54	0.58
TAV-CRF_1405	14/05/21	crater floor	443	-7.34	0.09
TAV-CRF_1601	16/05/21	crater floor	512	-7.60	0.16
TAV-CRF_1602	16/05/21	crater floor	509	-7.86	0.09
TAV-CRF_1603	16/05/21	crater floor	495	-7.94	0.06
TAV-CRF_1604	16/05/21	crater floor	454	-8.95	0.03
TAV-CRF_1605	16/05/21	crater floor	555	-7.48	0.54
TAV-CRF_1606	16/05/21	crater floor	509	-6.48	0.17
TAV-CRR_1601	16/05/21	crater rim	709	-4.61	0.55
TAV-CRR_1601	16/05/21	crater rim	949	-5.39	0.07
RAB-HS1_1701	17/05/21	Rababa hot spring	2646	-3.67	0.06
RAB-HS1_1702	17/05/21	Rababa hot spring	2506	-3.67	0.03
RAB-AIR_1701	17/05/21	clean air	430	-7.70	0.05

Table 3. Carbon isotopes and measured CO_2 concentration in fumarole and hot spring gases. Crater floor fumaroles and clean air were sampled using a Tedlar bag onboard our multirotor UAS and analysed by Delta Ray during the fieldwork. The remaining samples were collected using Giggenbach bottles and analysed by IRMS at UNM.



414

415 **Figure 5.** Three component mixing diagram between $CO_2/^3He$ and $\delta^{13}C$ (CO_2), after (Sano and Marty,
416 1995). We show new data from Rabaul (Table 2), comprising caldera hot springs and Tavurvur crater
417 fumaroles, previous measurements from Rabaul (Tavurvur and Rabalanakaia) made in 1996 (Sano and
418 Williams, 1996) and published data from thirteen volcanic centres in Sumatra (Halldórsson et al.,
419 2013). Model end-members of mid-ocean ridge basalt (MORB), marine limestone (including slab
420 carbonate) and organic sediment are also shown, as grey boxes (Sano and Marty, 1995; Sano and
421 Williams, 1996). Black lines show mixing among the end-members.

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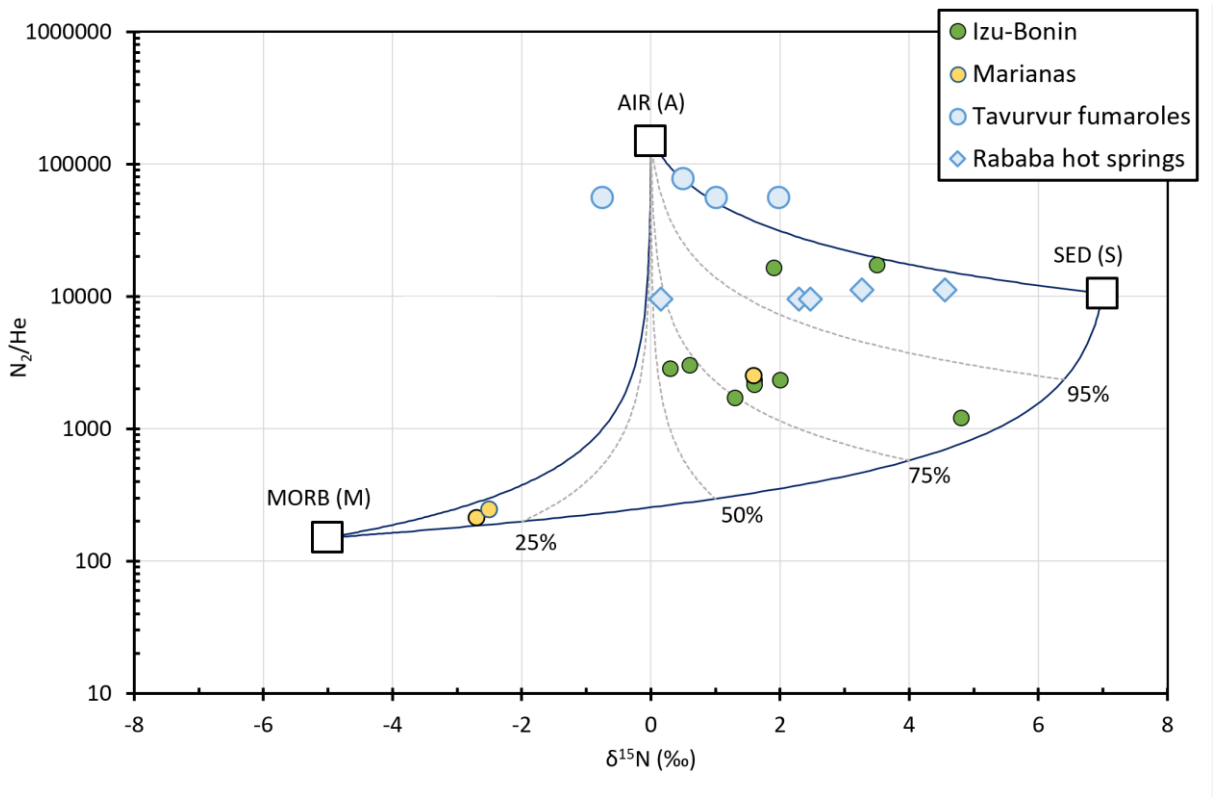

424

425 **Figure 6.** N_2/He vs. δ^{15}N, with mixing lines between air, sediment and mantle end members. Labelled
426 dashed lines represent mixing (% sediment) between mantle and sediment. We also show data from
427 the Izu-Bonin and Northern Marianas arcs (Mitchell et al., 2010).

Site	Sample ID	Mean $\delta^{15}N$	N_2/He	% M	% A	% S	% M_C	% S_C	$\delta^{15}N_c$
2019									
Tavurvur rim fumarole	RB-19-1 A	1.02 ± 0.33	55780	0.3	85.0	14.7	1.8	98.2	6.79
Tavurvur rim fumarole	RB-19-1 C	1.99 ± 0.80	55780	0.3	71.1	28.6	0.9	99.1	6.89
Tavurvur rim fumarole	RB-19-1b C	-0.75 ± 0.50	55780	0.3	-10.6	110.3	-2.6	102.6	7.31
Tavurvur rim fumarole	RB-19-6a A	0.50 ± 0.53	77835	0.2	92.6	7.2	2.6	97.4	6.69
Rababa hot spring	RB-19-3a B	0.16 ± 0.18	9596	1.6	95.0	3.4	31.6	68.4	3.21
Rababa hot spring	RB-19-3a B_dup	2.29 ± 0.42	9596	1.6	64.5	33.9	4.4	95.6	6.47
Rababa hot spring	RB-19-3a C	2.47 ± 0.56	9596	1.6	62.1	36.3	4.1	95.9	6.51
2016									
Rababa hot spring	RAB HS 1 A	4.56 ± 0.63	11155	1.3	32.6	66.1	2.0	98.0	6.76
Rababa hot spring	RAB HS 1 B	3.27 ± 0.65	11155	1.3	51.1	47.6	2.8	97.2	6.67

Table 4. Nitrogen isotopes and estimated mantle (M), atmospheric (A) and sediment (A) percentage contributions from fumarole and hot spring gases sampled at Rabaul. M_C and S_C are percentage contributions of mantle versus sediment influence on air-corrected nitrogen isotope values, $\delta^{15}N_c$. Capital letter suffixes (A, B, C) in the sample ID column refer to separate copper tube splits of our Giggenbach bottle samples. Where present, 'dup' refers to a duplicate. Each line in the table represents the mean and standard deviation of a triplicate analysis of each copper tube split.

5. Discussion

5.1 Atmospheric contamination

Before determining volatile provenance at Rabaul, we must first evaluate sample integrity, specifically potential contamination by atmospheric components such as air or air-saturated water. Key indicators of substantial air contamination can include high N_2/He (43720-56872), low He/Ar (0.002) and high O_2 (19.2-20.0 mol%), typified by our samples from Tavurvur crater floor (Table 1). Atmospheric contamination may be introduced during sample collection or, more likely, via abundant air-saturated steam circulating in the poorly consolidated Tavurvur cone. Tavurvur rim fumarole samples, are less air contaminated, i.e., have O_2 of < 0.002. All our samples fall close to either air or air-saturated water (N_2/Ar = 80 and 43 respectively) in a N_2-He-Ar ternary diagram (Figure 2), indicating that all are subject to variable degrees of atmospheric contamination. This is further suggested by a range in $^{40}Ar/^{36}Ar$ of 298.9-320.1, only slightly above the atmospheric value of 295.6 ± 0.5, (Lee et al., 2006). Rababa hot spring samples exhibit lower N_2/He (7267-9596) and higher $^{40}Ar/^{36}Ar$ (303.7-320.1) than Tavurvur crater floor or rim samples (Table 1).

Helium isotopes and $^4He/^{20}Ne$ (Table 2, Figure 3) allow us a further means of evaluating variable degrees of atmospheric contamination. Tavurvur samples, both crater floor and rim, have low He isotope values (0.9-2.7 R_A) and $^4He/^{20}Ne$ (0.3-0.4), indicating a strong atmospheric influence. Conversely, Rababa hot spring samples have higher R/R_A (5.6-6.5) and $^4He/^{20}Ne$ (2.78-3.23), indicating less contamination. Helium isotopes can be corrected for air contamination using X-values as described in Section 4.3.

Overall, on the basis of gas chemistry and He-Ne-Ar isotopes, we judge our Tavurvur (and Sulphur Point) samples to be heavily overprinted by atmospheric influence. This atmospheric contamination significantly affects gas species that are abundant in air, i.e. primarily nitrogen and therefore makes the determination of nitrogen sources in Tavurvur and Sulphur Point gases challenging. Our Rababa hot spring gases indicate a mixture of magmatic and atmospheric influence and can be used, with care, to evaluate deep volatile inputs to the Rabaul volcanic-hydrothermal system, as described below. Likewise, $\delta^{13}C$ values of our gas samples from all localities extrapolate to values that are characteristic of magmatic arc fumaroles and provide information on CO_2 sources at Tavurvur.

5.2 Mantle versus crustal helium

We can use the air-corrected helium isotope composition of our samples to estimate the fraction of helium derived from the mantle beneath Rabaul rather than the crust, assuming a binary mixture of mantle and crustal end-members (Barry et al., 2013):

$$\% \text{ mantle helium} = (R_C/R_A - {}^3He/{}^4He_{crust}) / ({}^3He/{}^4He_{mantle} - {}^3He/{}^4He_{crust})$$

where $^3He/^4He_{mantle} = 8\ R_A$ (Graham, 2002) and $^3He/^4He_{crust} = 0.05\ R_A$ (Morrison and Pine, 1955).

Most of our Rabaul gases are characterised by 71 to 87 % mantle helium (13 to 29 % crustal helium), with the exception of the highly air contaminated sample from the Tavurvur crater floor, which has only 10 % mantle-derived helium (Table 2). The mean (± standard deviation) of 79 ± 5 % mantle helium for our non-contaminated samples is greater than the value of 67 % mantle helium in our sample from the Sulu Range hot springs at Silanga village, and lower than the values of 82 and 84 % (Garua Harbour) and 90 and 94 % (Garbuna) in our other New Britain volcanic gas samples (Table 2).

Mixing between primordial (mantle) and radiogenic (crustal) helium is typically controlled by crustal thickness (Barry et al., 2022; Hilton et al., 2002; Lages et al., 2021; Mason et al., 2017). Seismic refraction surveys suggest crustal thickness of ~32 km beneath Rabaul and the Gazelle Peninsula and

~25 km under central New Britain and the Williaumez Peninsula (Finlayson et al., 1972). Our data are consistent with a small crustal influence beneath Rabaul and a lesser influence (higher R/R_A) in central New Britain where the crust is slightly thinner, i.e. beneath the Garua Harbour and Garbuna volcanic systems (Figure 3). The high R/R_A of 8.6 reported by Sano & Williams (1996) for Tavurvur was measured in gases emitted in an interval of relatively intense unrest, relative to our sampling periods, which may explain the stronger mantle (/magmatic) signature.

5.3 Sources of carbon

Figure 4 displays the $\delta^{13}C$ of fumarole and hot spring gases plotted against the inverse of CO_2 concentration in each sample. We also show the carbon isotope composition of reference standards, (1) limestone, that is, subducted marine carbonate ($\delta^{13}C$ ~0 ‰) and (2) MORB, representing upper mantle material ($\delta^{13}C$ ~-6.5 ± 2.5) (Sano and Marty, 1995). The majority of our data falls on a mixing line between air and a range in $\delta^{13}C$ that is intermediate between limestone and MORB (linear correlation coefficient of 0.86, y-intercept of -2.56 ± 0.62). The range in CO_2 and $\delta^{13}C$ exhibited by our samples indicates a variable degree of mixing between ambient air and deep fumarolic hot spring gases. A sample of pristine volcanic gas, that is, without any air contamination, would plot at the far left of this mixing line, close to the y-intercept. Thus, we can estimate the carbon isotopic composition of such a gas to be ~-2.6 ± 0.62 ‰. This is isotopically high with respect to the upper mantle reservoir and would be consistent with CO_2 input from carbonate, either on the subducting slab or in the crustal country rocks. It closely matches the $\delta^{13}C$ values of -2.55 to -2.80 ‰ reported for Rabaul by Sano and Williams (1996).

Figure 5 displays the relative abundance of helium and CO_2 in our samples, together with their carbon isotope composition. Previous studies have established that He-CO_2 characteristics can also be used to determine relative mantle and subducted contributions (Halldórsson et al., 2013; Hilton et al., 2002; Mitchell et al., 2010; Sano and Marty, 1995; Sano and Williams, 1996; Snyder et al., 2001; van Soest et al., 1998). The method assumes that there is no crustal input of volatiles and that possible carbon reservoirs feeding volcanic outgassing are the mantle wedge (M), limestone (L) from subducted sediment or carbonate in the altered oceanic lithosphere, and sedimentary organic carbon (S). These reservoirs have distinct $CO_2/^3He$ ($M = 2 \times 10^9$, $L = 1 \times 10^{13}$, $S = 1 \times 10^{13}$) and $\delta^{13}C$ (M = -5 ‰, L = 0 ‰, S = -30 ‰) as shown in Figure 5. Using the following equations (Sano and Marty, 1995), we can calculate the mass fraction of each potential source of carbon:

$$(^{13}C/^{12}C)_O = f_M(^{13}C/^{12}C)_M + f_L(^{13}C/^{12}C)_L + f_S(^{13}C/^{12}C)_S$$

$$1/(^{12}C/^{3}He)_O = f_M/(^{12}C/^{3}He)_M + f_L(^{12}C/^{3}He)_L + f_S(^{12}C/^{3}He)_S$$

$$f_M + f_L + f_S = 1$$

where subscripts M, L, and S correspond to the mantle, limestone and sediment end members and subscript O is the measured or observed sample.

The mean L:S:M ratio we observe in our Rabaul samples is 59:14:27, though this is subject to large standard deviation (33:3:31) owing to our sample from the hot springs near Sulfur Point plotting close to the mantle range of $\delta^{13}C$ while our remaining samples plot close to the mixing line between mantle and limestone (Figure 5). The mean (and standard deviation) L:S:M ratio of the four Rababa hot spring and Tavurvur crater samples is 74:13:13 (10:2:10). The Sulfur Point hot springs sample is difficult to interpret: it has low R/R_A and $^4He/^{20}Ne$ consistent with substantial air contamination, yet higher He/Ar and N_2/Ar than any of our other Rabaul samples. This composition points to a dominance of slab over mantle in supplying carbon to Rabaul and, as above, suggests carbonates are the main carbon source, with a second, more modest input from organic sediments. This is reasonable, if the subducting

assemblage matches the calcareous mudstones and altered basalts sampled by dredging of the Solomon sea floor (Crook, 1986; Davies and Price, 1986).

Sano & Marty (1995)'s approach assumes that only the mantle and the slab supply carbon to volcanic emissions. Several studies have since argued that emissions from many volcanic arcs are subject to substantial additions of carbon via the interaction of rising magmas and crustal carbonates (Barry et al., 2022; Deegan et al., 2010; Lages et al., 2021; Mason et al., 2017; van Soest et al., 1998). Indeed, Mason et al. (2017) identify PNG (not discriminating between New Britain, West Bismarck and Bougainville) as one of a subset of arcs where outgassed carbon is sourced dominantly from crustal limestone, along with Central America, the Aegean, Indonesia, Italy and parts of the Andes. Our data suggests otherwise, with high air-corrected helium isotopes (R_C/R_A) in the majority of gas samples pointing to only minimal crustal influence on outgassing. A minor role for crustal carbon is certainly possible, given widespread growth of carbonate platforms across the region during the Miocene, but we note that these rocks are most prevalent in the western part of the Gazelle Peninsula, separated from Rabaul by major north-south trending fault systems, and may be unlikely as a result to influence the magmatic system (Lindley, 2006; Madsen and Lindley, 1994).

5.4 Sources of nitrogen

Similarly to helium and carbon, we can quantitatively resolve the different contributions to Rabaul's nitrogen output. Equations developed by (Sano et al., 2001, 1998) allow us to calculate how air (A), upper mantle (M) and sediments (S) supply nitrogen to the volcanic system using measured $\delta^{15}N$ and N_2/He values (Table 4, Figure 6):

$$\delta^{15}N_{obs} = (\delta^{15}N_A \times f_A) + (\delta^{15}N_M \times f_M) + (\delta^{15}N_S \times f_S)$$

$$1/(N_2/He)_{obs} = f_A / (N_2/He)_A + f_M / (N_2/He)_M + f_S / (N_2/He)_S$$

$$f_A + f_M + f_S = 1$$

where f_A, f_M, and f_S are the fractions of the measured N_2 derived from air, mantle and sediment respectively and $\delta^{15}N_{A/M/S}$ and $N_2/He_{A/M/S}$ are the respective values of the end members. End member $\delta^{15}N$ values are 0 ‰ for air, -5 ± 2 ‰ for the upper mantle, and +7 ± 4‰ for sediments (Sano et al., 2001). End member N_2/He values are 1.49×10^5, 150, and 1.05×10^4 respectively (Fischer et al., 2002; Sano et al., 2001).

Our samples from Tavurvur are likely to be subject to substantial air contamination, based on air-like $\delta^{15}N$ (-0.75-1.99 ‰) and N_2/He in excess of 50,000. Our samples from Rababa show a range in $\delta^{15}N$ of 0.16-4.56 ‰ and so may provide more reliable insight into nitrogen sources. These isotopic values suggest, a degree of atmospheric influence notwithstanding, that both upper mantle and subducted organic sediments are supplying nitrogen to Rabaul's magma source region. Four of our five Rababa samples appear to be subject to only limited air contamination and contain substantial (34-66%) sediment-derived nitrogen. Following Mitchell et al. (2010), we calculate an air-corrected nitrogen isotope composition, $\delta^{15}N_C$, that is:

$$\delta^{15}N_C = (\delta^{15}N_M \times f_M) + (\delta^{15}N_S \times (1 - f_M))$$

where $\delta^{15}N_M$ = -5‰, $\delta^{15}N_S$ = +7‰ and f_M is the fraction of mantle nitrogen derived above. We can then calculate air-corrected contributions from sediment ($S_C = S/(S+M)$ and mantle ($M_C = 1 - S_C$). For our four Rababa samples (little air contamination), S_C ranges from 96-98%, pointing to a dominantly sedimentary over mantle origin for nitrogen. In summary, our $\delta^{15}N$ data, along with the $\delta^{13}C$ data described above, indicate the influence of organic sediment on Rabaul volatiles. On the basis of high

563 $^{3}He/^{4}He$ in these gases, we judge the organic sediment influence to be sourced from the subducting
564 slab and not the result of assimilation of crustal volatiles.

565 **5.5 Volatile Provenance at Rabaul**

566 Our data allow, for the first time, an evaluation of the origins of magmatic volatiles and therefore
567 volcanic gases at Rabaul. Air-corrected helium isotope ratios, ranging from 5.7-6.9 R_C/R_A, are indicative
568 mantle-dominated helium and only minor crustal input. This is consistent with the relatively thin crust
569 beneath Rabaul and is characteristic of most intra-oceanic arcs (Hilton et al., 2002). Gas chemistry,
570 e.g. N_2/Ar and N_2/He, is also typical of arc volcanoes in low levels of unrest, indicating a mantle source
571 overprinted by slab influence and a degree of atmospheric contamination (Fischer, 2008).

572 Carbon isotopes, with $\delta^{13}C$ of pure magmatic CO_2 (i.e. a putative air-free sample) estimated at ~-2.6 ±
573 0.62 ‰, suggest a mix of mantle, carbonate and organic sediment influences, with carbonate the
574 major source (75% in most samples). Based on our helium data, only minor volatiles can be supplied
575 from crustal rocks and hence we suggest a limited role for decarbonation of the Miocene Yalam
576 Formation limestones in supplying carbon to Rabaul. Instead, we favour the subducting slab as the
577 source of both carbonate- and organic sediment-derived CO_2. The best estimates of the subducting
578 assemblage are provided by seafloor dredging only, and we emphasise caution is required in stating
579 that these unequivocally represent the slab lithologies. The calcareous mudrocks reported by Crook
580 (1986) are plausible sources of both carbonate and sedimentary carbon, and the altered basalts
581 described by Davies & Price (1986) are likely to be carbonate-bearing. Aiuppa et al. (2017) note that
582 the Solomon Sea depth and age make it likely that the seafloor has been above the carbonate
583 compensation depth for its entire history, which would support the idea of substantial carbonate flux
584 into the New Britain trench on the Solomon slab. Our data support the inference made by Aiuppa et
585 al. (2017, 2019) and subsequently by Plank & Manning (2019) that New Britain, and perhaps other arc
586 segments in PNG, are margins where carbon emissions are dominated by recycling of subducted
587 carbon. Further work is required to evaluate the relative importance of sedimentary carbonate versus
588 altered ocean crust or lithosphere. Thermodynamic modelling of the New Britain subduction zone
589 suggests that carbonate dissolution and metamorphic decarbonation of both sediments and altered
590 basalts are necessary to explain the volcanic arc carbon flux (Arzilli et al., 2023).

591 Our nitrogen isotope data, $\delta^{15}N$ of 0.16-4.56 ‰ in our least air-contaminated samples, further indicate
592 an influence of a second slab phase beyond carbonate, namely organic sediment. This fits with our
593 carbon isotope data and also the arguments advanced by Hohl et al. (2022) based on the whole-rock
594 geochemistry and isotope composition of Rabaul lavas. Further evidence for some organic sediment
595 involvement comes from our measurements of elevated $^{84}Kr/^{36}Ar$ and $^{132}Xe/^{36}Ar$ in our Rababa hot
596 springs samples, i.e. those where heavy noble gas signatures deviate from atmospheric composition
597 (Supplementary Figure 1). We note that nitrogen isotopes in arc gases may be significantly influenced
598 by altered ocean crust, though given a lack of constraint on the variation of $\delta^{15}N$ through the Solomon
599 slab crust we have not attempted to evaluate this possibility quantitatively (c.f. Mitchell et al., 2010).

600 In summary, Rabaul volcanic gases are sourced from the mantle wedge with a substantial recycled
601 slab overprint that supplies carbon and nitrogen from carbonates, organic sediments, and potentially
602 altered ocean crust.

603

6. Conclusion

We have analysed the chemical and isotopic (He-C-N-Ne-Ar) composition of fumarole and hot spring gases from Rabaul caldera, known to be among the most threatening and historically active volcanic systems in Papua New Guinea, but one where activity has declined substantially over the last decade. Ours is the first systematic study of gas composition to be undertaken at Rabaul and the first study to explore volatile provenance at this volcano. Our gas samples are subject to variable and in some cases overwhelming atmospheric contamination. Nonetheless, owing to our combination of helium (mantle versus crust), carbon (mantle versus carbonate versus organic sediments) and nitrogen (mantle versus organic sediments versus atmosphere) isotopic tracers we have been able to estimate the balance of mantle, slab, and crustal influence on Rabaul volatiles.

Rabaul gases are comparable to those of other volcanic arcs, being enriched in carbon and nitrogen. Helium isotopes point to a strong mantle rather than crustal influence, with air corrected He isotope values ranging from 5.7-6.9 R_A and 71-87% of helium in Rabaul gases originating from the mantle. Carbon isotopes ($\delta^{13}C$ estimated as -2.6 ± 0.62 ‰ for magmatic gases) indicate a combined mantle, carbonate, and organic sediment influence, with slab carbonate providing the majority of carbon in Rabaul gases. Nitrogen isotopes ($\delta^{15}N$ ~0.16-4.56 ‰ in our least air-contaminated samples) also point to a second sedimentary source, organic sediments. We consider both carbonate and sedimentary influences to originate from the nearby subducting Solomon Sea slab, though minor crustal contributions are plausible, especially of carbonate.

Many characteristics of the Rabaul volcanic system remain little explored and our understanding of volatile provenance in the New Britain arc is at a nascent stage. In this contribution, our focus is to determine the reservoirs feeding outgassing from the Rabaul caldera complex, and we conclude that the nearby subducting slab plays a significant role in augmenting volatile supply from the upper mantle reservoir beneath Rabaul. Future work should investigate whether the high outgassing of the 1994-2014 eruptive interval is characteristic of the long-term behaviour of Rabaul or not, and whether Rabaul magmas are notably volatile-rich. There remain major unknowns in the wider regional geological context, including an absence of core samples of the subducting lithologies and the relative influence of both ongoing (New Britain trench) and earlier (Vitiaz-Melanesian trench) sequences of subduction recycling on the mantle wedge below the Bismarck Sea and Manus Basin.

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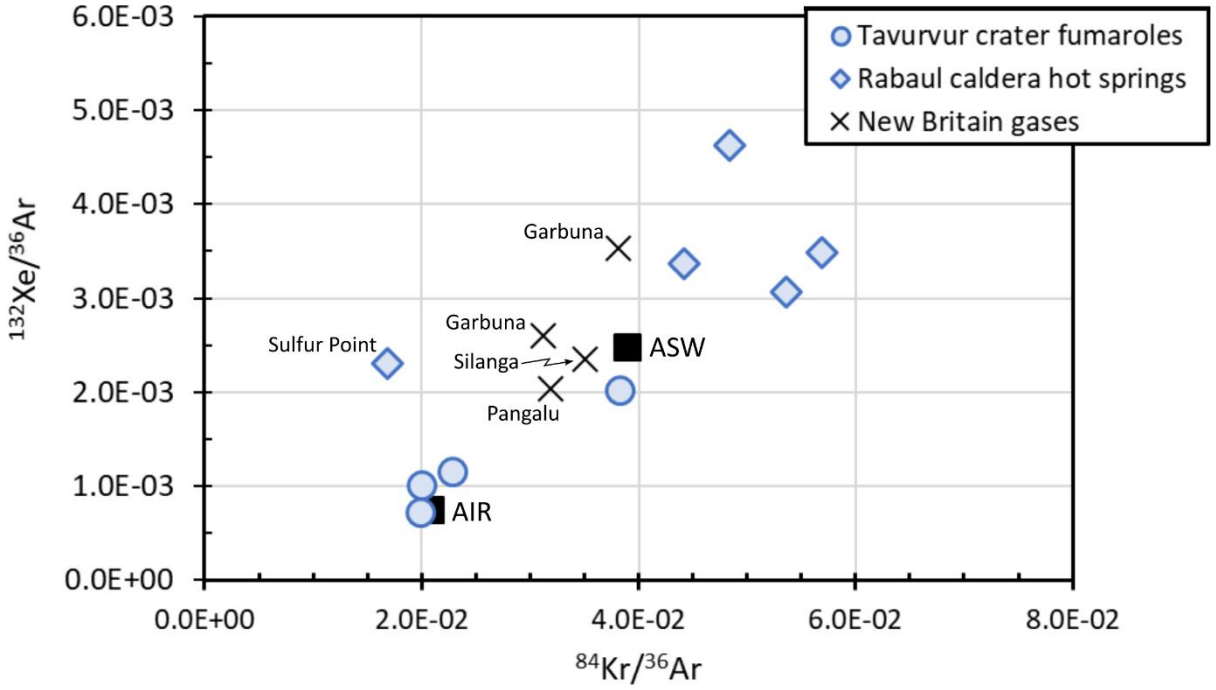
642



643 **Supplementary Figure 1.** Heavy noble gases in a subset of our samples (those analysed at University
644 of Oxford in 2016 and University of Manchester in 2019). $^{84}Kr/^{36}Ar$ and $^{132}Kr/^{36}Ar$ in air and air-
645 saturated water after Ozima and Podisek (2001).

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