

Limited sulfur degassing and muted environmental impact of Ontong Java Plateau lavas

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ABSTRACT

The mainly deep-submarine Ontong Java Plateau (OJP) is the result of the largest outpouring of lava in the geologic record. Volcanic events of this magnitude can have dramatic environmental impacts due to volatile emissions. We report new S measurements in naturally glassy, olivine-hosted melt inclusions and pillow basalt glasses from the OJP. We combined these data with previous S measurements in OJP glasses to quantify S degassing in a suite of OJP glasses. Comparison with an S degassing model suggests OJP lavas that erupted at depths >1500 m did not degas S; OJP lavas that erupted at depths <1500 m degassed up to $\sim 40\%$ initial S, but these lavas likely made up a small fraction of OJP lavas. This result suggests that despite its large volume compared to continental large igneous provinces (LIPs), OJP lavas emitted less S, potentially contributing to its muted environmental impact. The OJP may provide a framework for the temporal evolution of S degassing at oceanic LIPs, with early eruptions at great water depths releasing limited to no S, and later eruptions at shallow water depths releasing larger, but still limited amounts of S. This framework may also have implications for continental LIP magmas, which may release significant amounts of CO₂ but limited amounts of S during intrusive activity, with magmatic S emissions only becoming important during extrusive phases.

INTRODUCTION

Large igneous provinces (LIPs) are the largest volcanic events on Earth, emplacing 10^5 – 10^7 km³ of lava over 1–2 m.y. The largest LIP in the geologic record is the Ontong Java Plateau (OJP) with a total crustal volume of ~ 3 – 6×10^7 km³ (Fig. 1A; Coffin and Eldholm, 1994). Main emplacement occurred ca. 123–121 Ma, with a second, disputed minor phase ca. 90 Ma (Tejada et al., 1996; Chambers et al., 2004); however, a recent study suggests younger dates of 117–108 Ma for the main emplacement of the OJP (Davidson et al., 2023). LIPs emit vast amounts of volatiles with potentially severe environmental consequences, motivating proposed links to multiple mass extinctions (Rampino and Stothers, 1988; Bond and Wignall, 2014).

CO₂ and SO₂ are the volcanic volatiles that exert the strongest controls on climate, with CO₂ driving long-term warming and SO₂ driving short-term cooling (Bond and Wignall, 2014; Schmidt et al., 2016; Black et al., 2018).

Early Cretaceous warming, ocean acidification, and Oceanic Anoxic Events 1a and 1b have been attributed to CO₂ emissions during OJP emplacement (Tejada et al., 2009; Erba et al., 2015; Davidson et al., 2023). It is curious that despite its apparently large CO₂ emission rates, which are suggested to play a role in driving mass extinctions (Clapham and Renne, 2019; Green et al., 2022), and the documented environmental consequences of CO₂ release, OJP emplacement did not coincide with a mass extinction (Erba et al., 2015). Unlike CO₂, submarine pressure (P) may be high enough to suppress S degassing, effectively decoupling S degassing from CO₂ emissions during submarine eruptions (Gaillard et al., 2011; Green et al., 2022). Therefore, limited S emissions from the OJP may be connected to the absence of a coeval mass extinction (Roberge et al., 2004; Reekie et al., 2019)—a link that has been proposed for S-poor continental LIPs (Callegaro et al., 2014).

Previous studies that measured [S] (where [] denotes concentration) in OJP glasses noted high

[S] and suggested limited S degassing (Roberge et al., 2004; Reekie et al., 2019). However, these studies, and a study that included measurements of [S] in recrystallized melt inclusions (Jackson et al., 2015), did not attempt to quantify OJP emissions. Here, we present new measurements of [S] in pillow basalt glasses and the first [S] measurements of naturally glassy, olivine-hosted melt inclusions (MIs) from the OJP. We compared the new measurements of [S] in MIs and pillow basalt glasses to estimates of initial [S] to quantify S emissions during OJP emplacement. We also compared the differences in S emissions between the OJP and continental LIPs to test the hypothesis that limited S emissions at OJP could have played a role in the muted environmental impact of the largest LIP in the geologic record.

SAMPLES AND METHODS

OJP lavas were sampled during Ocean Drilling Program (ODP) Leg 192, at Deep Sea Drilling Program Site 289, and at ODP Sites 803 and 807 (Fig. 1A; Mahoney et al., 2001). Thin sections of exceptionally fresh, glassy pillow basalt rims from Site 1187 (ODP Leg 192) included naturally glassy, bubble-free, olivine-hosted MIs (Fig. 1). Major element, S, and Cl concentrations in glassy rims and olivine-hosted MIs were measured via electron probe micro-analysis on the JEOL JXA-8200 Superprobe at Rutgers University (Tables S1 and S2 in the Supplemental Material¹).

RESULTS

Sulfur concentrations in OJP pillow basalt glasses and MIs (corrected for postentrapment crystallization; see Supplemental Material) from this study, along with previous measurements of [S] in OJP glasses, are shown in Figure 1. Sulfur concentrations in glasses covered a wide range of ~ 600 – 1400 ppm, while sulfur concentrations in MIs covered a smaller range of ~ 800 – 1000 ppm.

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¹Supplemental Material. Detailed methods and spreadsheets with data used in main text. Please visit <https://doi.org/10.1130/G51283.1> to access the supplemental material, and contact editing@geosociety.org with any questions.

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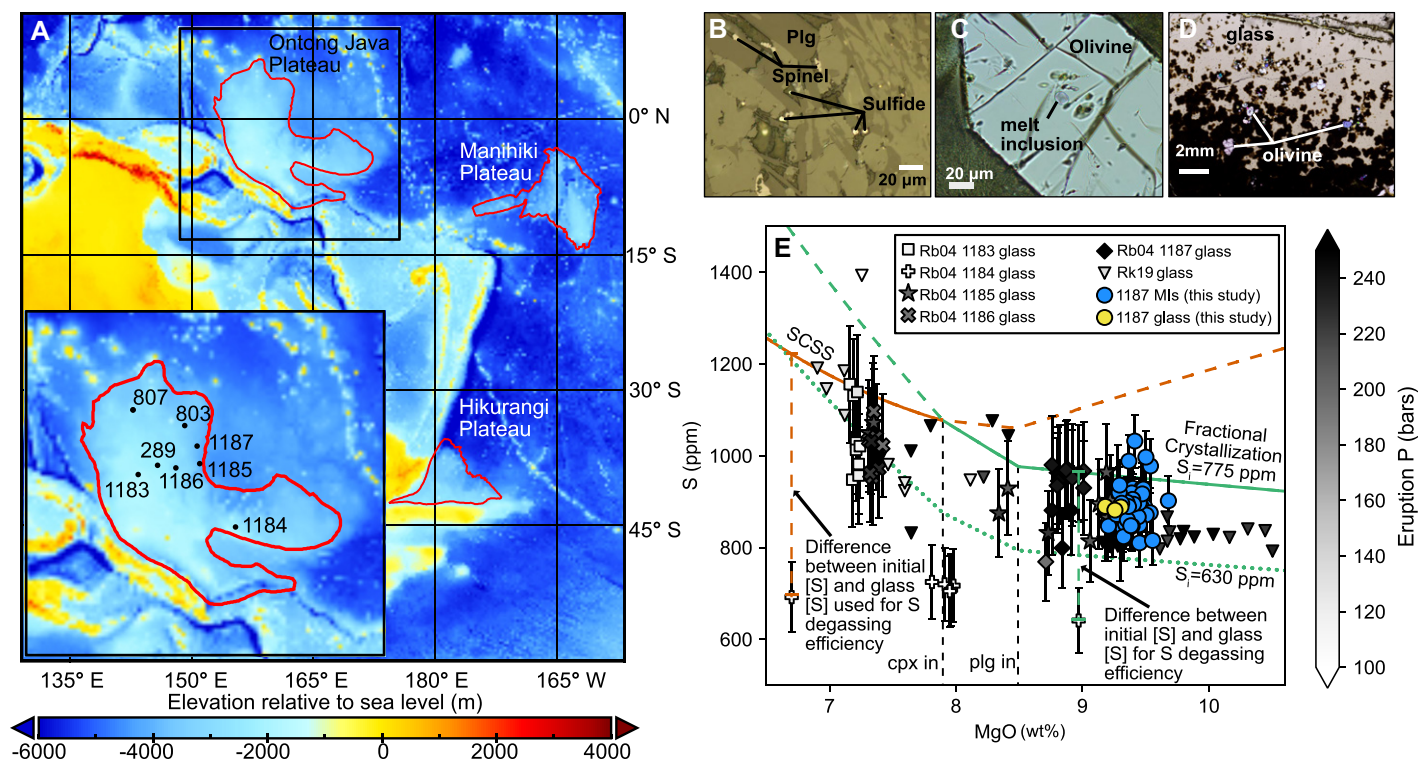


Figure 1. (A) Regional map showing elevation relative to sea level. Plateau delineations are after Chandler et al. (2012). Numbers in inset refer to drill sites (Mahoney et al., 2001). Bathymetric data are from GEBCO Compilation Group (2023). (B) Reflected light image of sulfides with plagioclase (Plg). (C) Plane-polarized image of olivine-hosted melt inclusion (MI). (D) Cross-polarized image of pillow basalt glass (polarizer and analyzer offset $\neq 90^\circ$, so glass is not extinct). (E) [S] in Ontong Java Plateau (OJP) glasses and MIs. Green lines show how [S] varies as a function of [MgO] for two different [S]_i during fractional crystallization. Orange line is calculated [S] at sulfide saturation (SCSS; calculated with PySulfSat [Wieser and Gleeson, 2022]; see Supplemental Material [text footnote 1]) as a function of [MgO]. Orange and green lines are solid at [MgO] where SCSS and fractional crystallization were used as estimates of [S]_{initial} in Equation 1. Gray-scale symbols are shaded for eruption pressure (P). Error bars are 1σ precision from electron probe micro-analysis. Rb04—Roberge et al. (2004); Rk19—Reekie et al. (2019); cpx—clinopyroxene; plg—plagioclase.

Sulfur concentration appears to increase as [MgO] decreases, with a change in slope at ~ 8 wt% MgO. Several processes control [S] in silicate melts, including fractional crystallization, sulfide saturation, and degassing (Reekie et al., 2019). In the following, we discuss how these processes worked in concert to control [S] in the OJP melts.

DISCUSSION

Fractional Crystallization and Sulfide Saturation

To understand S degassing, we first considered fractional crystallization and sulfide saturation. Figure 1 shows [S] in the melt calculated via bulk partition coefficients for S (Callegaro et al., 2020) along the liquid line of descent and calculated [S] at sulfide saturation (SCSS; see Supplemental Material). At [MgO] $> \sim 8$ wt%, [S] in OJP glasses slightly increases with decreasing [MgO] and plots along trends controlled by fractional crystallization, while also being significantly lower than SCSS (Fig. 1). Therefore, it is likely that high-MgO OJP melts were not sulfide saturated, and [S] was controlled by olivine fractionation, consistent with chalcophile systematics (Reekie et al., 2019).

At [MgO] $< \sim 8$ wt%, clinopyroxene and plagioclase began to crystallize (Fig. 1), and a

given decrease in [MgO] required more crystal fractionation, increasing the slope of [S] controlled by fractional crystallization. In contrast to high-MgO glasses, which followed the trend of [S] controlled by fractional crystallization with [S]_i = 775 ppm, no glasses with ≤ 8 wt% MgO reached [S] controlled by fractional crystallization with [S]_i = 775 ppm (Fig. 1). A single low-MgO sample, which we suspect assimilated seawater, exceeded [S] controlled by fractional crystallization with [S]_i = 775 ppm (see Supplemental Material). In glasses with $< \sim 8$ wt% MgO, the highest [S] followed SCSS, suggesting sulfide saturation. Increases in [S] driven by fractionation of plagioclase and clinopyroxene likely drove sulfide saturation at [MgO] $< \sim 8$ wt% (Reekie et al., 2019). In support of this interpretation, we only observed sulfides in samples with abundant plagioclase (Fig. 1B).

Sulfur Degassing

To quantify S degassing, we compared [S] of OJP glasses to S degassing curves modeled with Sulfur_X (Supplemental Material; Ding et al., 2023) to determine the samples that likely degassed S. For both high- and low-MgO samples, Sulfur_X predicted the onset of significant S degassing at $P \sim 150$ bars and tracked [S] in

OJP glasses with low eruption P (assumed to equal saturation P calculated with [CO₂] and [H₂O] using the model of Dixon [1997] implemented in VESICAL [Iacovino et al., 2021]; Fig. 2). At $P \geq 150$ bars, Sulfur_X predicted minimal S degassing, and the observed spread in [S] was likely controlled by fractional crystallization and sulfide saturation, as illustrated by increasing [S] with decreasing [MgO] (see Fig. 1). Thus, we considered samples with eruption $P > 150$ bars to be undegassed and samples with eruption $P < 150$ bars to be degassed with respect to S. Our new MI data also support minimal S degassing at Site 1187. If S degassing was important at Site 1187, we would expect pillow basalt glasses to have significantly lower [S] values compared to MIs from Site 1187, which they do not (Fig. 1).

To quantify S degassing, we calculated the difference between [S] in OJP glass and inferred initial [S]. We treated initial [S] as a function of [MgO], set by fractional crystallization at high MgO and SCSS at low MgO (Fig. 1). S degassing efficiency was defined as:

$$\text{S degassing efficiency} = \frac{([S]_{\text{initial}} - [S]_{\text{glass}})}{[S]_{\text{initial}}} \times 100\% \quad (1)$$

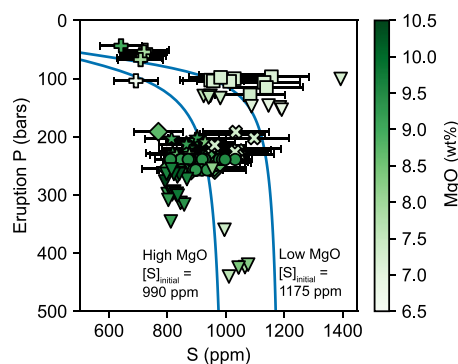


Figure 2. Sulfur concentration in Ontong Java Plateau (OJP) glasses as a function of eruption pressure (P). Eruption P of melt inclusions (MIs) from this study were assumed to equal eruption P of host glass. Color scale is for [MgO]. Blue lines are modeled [S] from Sulfur_X (Ding et al., 2023) (see Supplemental Material [text footnote 1]). Two degassing curves are presented to show both high- and low-MgO lavas with different [S]_{initial} (see Fig. 1), which predict onset of significant S degassing at $P \sim 150$ bars. Eruption P values calculated for OJP samples are considered a minimum because some samples may be $\text{CO}_2/\text{H}_2\text{O}$ undersaturated (Reekie et al., 2019). Symbols are same as in Figure 1.

Assuming S degassing efficiencies = 0% for glasses with eruption $P > 150$ bars, the average S degassing efficiency of OJP glasses = 5% (Fig. 3), i.e., an order of magnitude less than the 75%–90% estimated for continental flood basalts (Black et al., 2012). If this assumption is ignored, average degassing efficiency increases to only 10% (Fig. S4). In support of our interpretation of minimal S degassing at $P > 150$ bars, increasing S degassing efficiency with decreasing eruption P was only observed in sample sets emplaced at $P < 150$ bars (Fig. S3).

It remains important to consider whether the large volume of the OJP could have resulted in S emissions similar to continental LIPs. If the OJP released a similar mass of S as the Siberian Traps, which has been implicated as a trigger for Earth's largest mass extinction (Dal Corso et al., 2022), it would suggest that differences in S emissions alone cannot explain the differences in environmental impact between the two LIPs. Volume estimates of OJP extrusive products are $\sim 1 \times 10^7 \text{ km}^3$, while total crustal volume of the greater OJP is estimated at $\sim 1 \times 10^8 \text{ km}^3$ (i.e., including coeval Manihiki and Hikurangi Plateau and Nauru and East Mariana Basins; Fig. 1A; Coffin and Eldholm, 1994; Chandler et al., 2012). In the following, we explore the range of volume estimates for OJP; however, it is likely that only the extrusive products (i.e., $1 \times 10^7 \text{ km}^3$) released appreciable amounts of S, due to the high lithostatic P of intrusive magmas ($>> 150$ bars). With volume $\approx 1\text{--}10 \times 10^7 \text{ km}^3$, initial [S] = 1000 ppm, and S degassing efficiency = 5%, the OJP would have emitted

1400–14,000 Gt S, as compared to the 6300–7800 Gt of magmatic S emissions estimated for the Siberian Traps (Black et al., 2012). However, we interpret the average S degassing efficiency (5%) to be a maximum value, with the true value being much lower. This is because high S degassing efficiencies of samples with eruption $P < 150$ bar are weighted equally in calculating an average S degassing efficiency of 5%, when they may have contributed only a small fraction to the total volume of the OJP. It is suggested that the volcanoclastic sequence at Site 1184 may have been on the order of $10^1\text{--}10^2 \text{ km}^3$ (Thordarson, 2004), which would make its contribution to S degassing negligible. Additionally, over a depth interval of $< 100 \text{ m}$ near the crest of the OJP edifice, S degassing efficiencies at Site 1183 decrease from ~ 20 to $\sim 0\%$ (Fig. S3). This may imply that OJP lavas emplaced at depths $> 100 \text{ m}$ from the crest of the edifice had S degassing efficiencies of $\sim 0\%$. Thus, we interpret 5% as a maximum S degassing efficiency for OJP and infer the true value is closer to 0%.

Our preferred interpretation (that OJP degassed $<< 5\%$ S) implies S emissions $<< 1400\text{--}14,000 \text{ Gt}$. For example, if 10% of the OJP's volume was emplaced at < 150 bars, which is likely an overestimate, and we weigh its contribution accordingly, average S degassing efficiency = 0.5%, which would suggest the OJP emitted 140–1400 Gt S. This illustrates that even when the total volume of the greater OJP is considered, and surely when only the extrusive products are considered, OJP released significantly less S relative to continental LIPs like the Siberian Traps. Therefore, suppressed S emissions may have played a role in the muted environmental impact of the OJP, considering S emissions have been shown to cause rapid and drastic transitions in climate and ocean circulation when combined with CO_2 emissions (Black et al., 2018).

Evolving Sulfur Emissions

Results suggest a spatiotemporal evolution in degassing behavior during OJP emplacement. Early OJP eruptions emplaced at water depths $> \sim 1500 \text{ m}$ (150 bars) (Figs. 2 and 4) erupted at high enough P to suppress S degassing while allowing significant CO_2 degassing. Growth of the volcanic edifice caused later OJP lavas to erupt at shallower water depths and lower P , allowing increased S degassing efficiencies of $\sim 20\%\text{--}30\%$ (Figs. 3 and 4). It is also possible that some late-stage eruptions occurred on the flanks of the plateau, resulting in high eruption pressures and low S degassing efficiencies. Crustal thickening via sill emplacement and dynamic uplift from a plume may have also decreased eruption P of later OJP lavas, though the existence of a plume at OJP has been questioned (Korenaga, 2005).

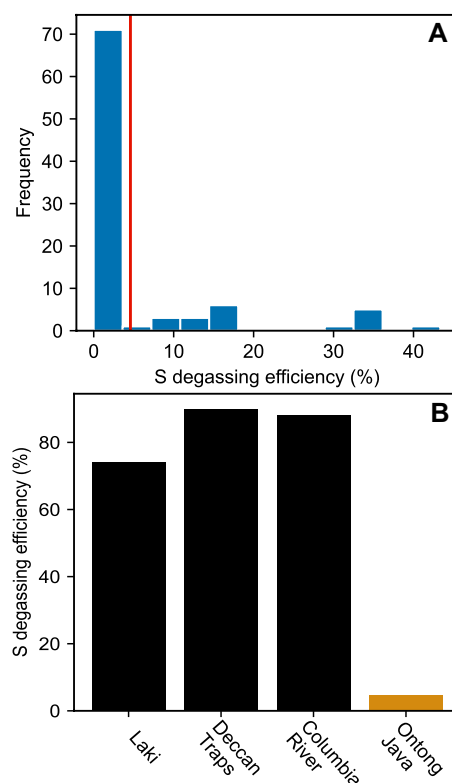


Figure 3. (A) Histogram of S degassing efficiencies for Ontong Java Plateau (OJP) glasses. Red line is average of all values (5%). (B) Bar chart of average S degassing efficiency at OJP compared to continental flood basalts (Black et al., 2012).

Shallow-water OJP eruptions were likely explosive, as evidenced by volcanoclastic sequences at Site 1184 (Thordarson, 2004). Eruption column heights associated with flood basalt phreatomagmatic activity are uncertain (Ross et al., 2008), and SO_2 scrubbing in H_2O -rich volcanic plumes produced during submarine eruptions may decrease SO_2 delivery to the atmosphere (Carn et al., 2022). If, however, volcanoclastic sequences at Site 1184 resulted from vigorous explosive activity, then these eruptions may represent a narrow window where OJP magmas could have injected S higher in the troposphere, where its climatic impact would have been greater (Schmidt et al., 2016). However, delivery of S to the upper troposphere may have been impeded due to OJP emplacement at paleolatitudes of $\sim 25^\circ\text{--}50^\circ\text{S}$ (Chandler et al., 2012) because of higher tropopause altitudes in mid- to low latitudes.

The temporal evolution in degassing behavior proposed for the OJP may provide insights into volatile release at other oceanic plateaus, and even some continental LIPs. Continental LIPs have been proposed to degas significant CO_2 during crustal intrusion, decoupling CO_2 emissions from rates of surface volcanism (Hernandez Nava et al., 2021; Tian and Buck, 2022). Due to the high lithostatic P of

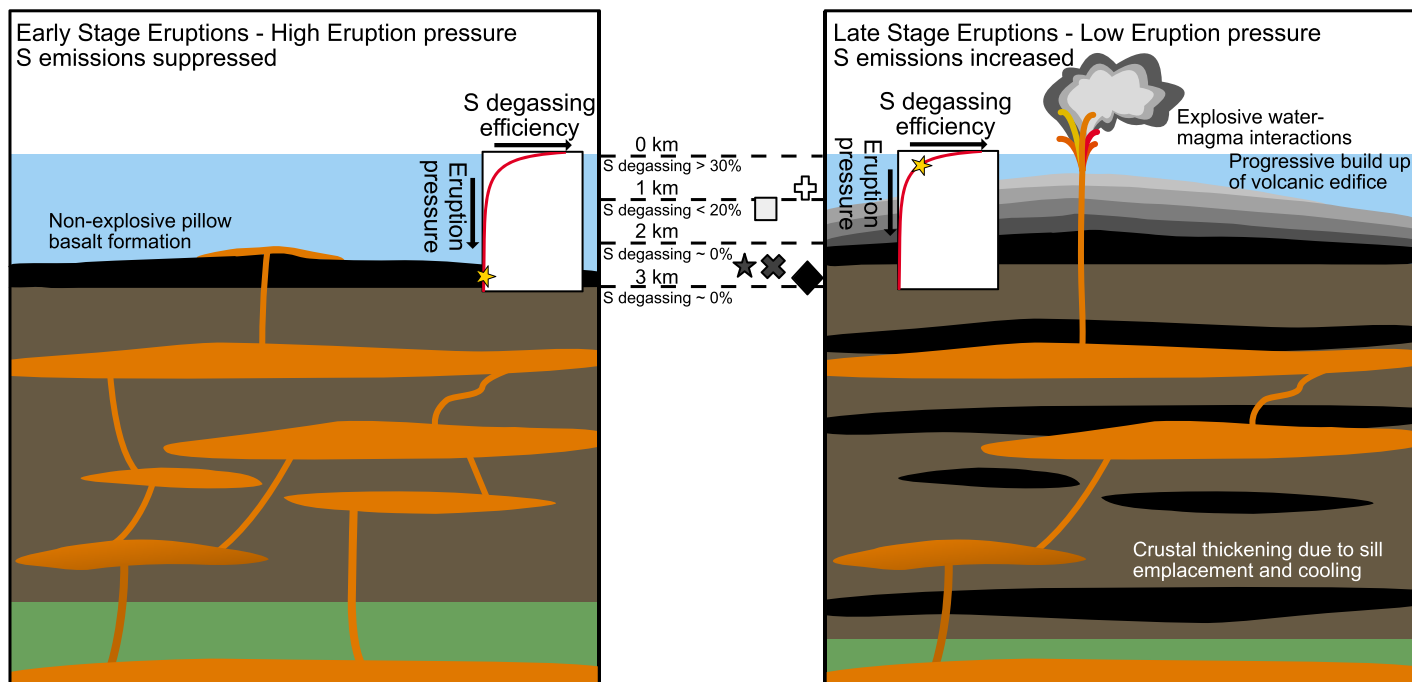


Figure 4. Schematic diagram illustrating temporal shift of S degassing behavior at Ontong Java Plateau (OJP) from limited/no S degassing during early stages to more efficient, yet still limited, S degassing at later stages. Symbols (as in Figure 1) are included to show approximate emplacement depth for each site based on average eruption pressure (P).

crustal intrusions ($>>150$ bars), S degassing may be minimal, like the early OJP eruptions. This comes with the caveat that the intrusive phase of continental LIPs may devolatilize surrounding S-rich sediments (Yallup et al., 2013), though explosive diatremes (Polozov et al., 2016) may be required for this process to have significant climatic effects. Magmatic S degassing would only become important during extrusive phases of continental LIP volcanism due to emplacement at atmospheric P . Shifts between high CO_2 plus low S degassing during intrusive volcanism and high CO_2 plus high S degassing during extrusive phases may have important implications for the tempo of environmental impacts of continental LIP volcanism (Green et al., 2022).

CONCLUSIONS

We interpret [S] in OJP MIs and pillow basalt glasses to result from fractional crystallization at [MgO] $>\sim 8$ wt% and sulfide saturation at [MgO] $<\sim 8$ wt%. We suggest that only OJP lavas that erupted at water depths $<\sim 1500$ m degassed S, and due to the volumetrically minor fraction of OJP lavas emplaced at these depths, total S emissions may have been much lower compared to continental LIPs. Suppressed S degassing of lavas from the OJP may have curtailed its environmental impact compared to smaller continental LIPs, suggesting that a combination of CO_2 and SO_2 emissions may deepen ecological stress. Indeed, freezing temperatures resulting from LIP-derived sulfate aerosols have been implicated in the extinction selectivity of

land animals and the rise of dinosaurs during the end Triassic mass extinction (Olsen et al., 2022). There was likely a temporal evolution in S emissions at the OJP, with early, deep-water eruptions suppressing S degassing and later shallow-water/subaerial eruptions degassing S more efficiently. This P -sensitive evolution in S degassing may be more broadly applicable to other LIPs.

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