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Box modelling the transfer of sulfur on Mars using Earth as a geochemical analogue

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ABSTRACT

Volcanism was once the primary source of sulfur transport on Mars, and its present-day surface preserves a geological record of these mineralogical processes. Sulfur plays a key part in the eruption process, forming sulfides, and less commonly sulfates in the magma chamber, and being expelled as sulfur dioxide-rich gas. However, there is a mismatch between the location of existing volcanic provinces and detections of high sulfur abundances measured through satellite instruments such as the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and the Gamma Ray Spectrometer (GRS). Despite similarly hosting a basaltic surface, the sulfur content in Martian meteorites (408–2700 ppm) and by Martian dust measured by rovers (2 wt% S) exceeds Earth's basalts by almost an order of magnitude. This study attempts to account for the observed abundance of sulfur through applying comparative planetology using Earth's volcanoes, including both eruptive and quiescent degassing rates and solid leachate particles. The study successfully provided order-of-magnitude estimates of the mass of sulfur produced in volcanism over the Noachian-Hesperian periods of >3.7 to 3.1 Ga and it provided values similar to previous studies. However, it was not possible to confirm mass balance due to large uncertainties in the mass of sulfur in the sedimentary reservoir.

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YASJ Editors' Note: This study applies comparative planetology and box modelling to investigate the Martian sulfur cycle at a planetary scale. The use of terrestrial volcanic data, including eruptive and quiescent degassing, provides a creative basis for estimating sulfur fluxes over geological time. Readers should note that the model relies on assumptions about eruption duration, volcanic surface area and sulfur reservoirs, while the unknown depth of the sedimentary reservoir prevents a complete mass balance. Within these limitations, the study provides a useful framework for further investigation.

INTRODUCTION

Understanding the sulfur budget on Mars is critical for reconstructing its volcanic history and early climate evolution. Unlike Earth, Mars has no current active volcanism or plate tectonics, hence hosting many rocks older than 3.6 Ga (Tanaka et al., 2014) that preserve a historical record for its mineralogical processes and planet formation (Ehlmann & Edwards, 2014). Mars' geologic history is divided into the Noachian (>3.7 Ga), Hesperian (3.7–3.1 Ga), and Amazonian (<3.1 Ga) periods (Figure 1), and has been continuously constructed through insights from orbital infrared spectroscopy and in situ chemical measurements from rovers and landers. Its volcanic rock pri-

marily formed during the planet's early formation as a magma ocean 4.48 Ga ago (Moser et al., 2019), and during the Noachian-Hesperian periods (Ehlmann & Edwards, 2014). Like the other terrestrial inner planets, Mars has a dominantly basaltic surface, however the Martian sulfur content exceeds Earth's basalts by almost an order of magnitude (Ojha et al., 2019). Atmospheric SO_2 derived from volcanic activity is highly likely to have influenced the early climate of Mars, providing a greenhouse effect that may have maintained warm, wet conditions in the early Noachian period necessary to account for the observed clay deposits. The widespread availability of sulfur on Mars could have provided an abundant source for energy and nutrients to fuel sulfur-metabolizing microbes. Sulfates also have a high potential to preserve biomarkers and palaeoenvironmental conditions since they can rapidly precipitate from a brine. Thus, understanding the source and transport processes for the abundance of sulfur on Mars can help characterise its past habitability, potential for life, and climate change that eventuated in its current dry, oxidising environment.

The excess sulfur on Mars suggests that volcanism was the most important geologic process in enriching the Martian bedrock (Szynkiewicz et al., 2022). This is because sulfur is involved in every part of an eruption process; it forms sulfides and sulfates in the magma chamber or becomes supersaturated into sulfur-bearing species that alter the crust in a fluid phase, becoming an SO_2-rich gas that is expelled at low pressure (Casas et al., 2026).

After being released into the atmosphere, S-bearing volcanic gases undergo oxidation-reduction reactions and solid disproportionation to become different sulfur species deposited in S-bearing solids. At shallow depths of the near-surface crust within volcanoes, sulfur may become supersaturated in the melt, forming bubbles of different S-species that either escape as gas or build up and release explosively at a volcanic plume (Casas et al., 2026). When eruptions occur, solid volcanic fragments can be transported and deposited, potentially including sulfur-bearing species. Whilst the ferric oxides that colour Mars' surface red indicate a currently dry, oxidising environment (Bibring et al., 2005), sediment analysis reveals clays older than the mid-Hesperian. These may indicate a previously wet environment (Ehlmann & Edwards, 2014) that allowed sulfuric acid to form and transport S-species. This may have formed some very early sulfates on Mars' surface, suggesting other sulfates formed in a continually drying environment.

Mars' lack of present volcanic activity prevents direct observation, hence geochemical information is derived from rover and satellite missions characterising samples of the sedimentary rock currently on the Martian surface.

As shown in Figure 2, surface materials containing typical SO_3 abundances have concentrations of ~4-7 wt% (1.6-2.8 wt% S) reaching 40 wt% (16 wt% S) for sulfate-rich veins. These sulfur-rich areas mapped by GRS do not appear to correspond with CRISM sulfate-bearing rocks, nor with the volcanic provinces, nor with any particular unit of volcanic rock, further raising questions regarding the transportation and depositional processes that result in high S concentrations and distributions. The only currently observed process for transportation of sedimentary sulfur is aeolian due to the dry Martian environment, however there is evidence of previous fluvial and potentially glacial processes promoting sulfur dissolution. However, these processes only serve to redistribute existing sulfur on the Martian surface, and do not affect how they are sourced, and thus do not explain their abundance. This suggests that key sulfur sources or transport mechanisms remain unidentified.

There have been several attempts to quantify the output and concentration of sulfur on Martian surfaces. Applying the law of uniformitarianism, scientists have used analogue volcanic systems from Earth to better understand Mars' mineralogy. For example, Ende and Szynkiewicz (2021) used chosen terrestrial O_2-depleted acidic hydrothermal vents as a geochemical analogue for the hydrothermal S-rich deposits in Gusev crater on Mars, in order to investigate potential oxidation mechanisms of volcanic S. Whereas Earth's climate and surface chemistry are mostly dependent on the water and carbon cycle, Mars likely hosted a sulfur cycle (Franz & King, 2026; Hynek et al., 2019; Ojha et al., 2019). Gaillard et al. (2013) have attempted to box model this sulfur cycle, concluding from experimental results, thermodynamic models, and the direct measurements of Martian soils that a variety of sulfur reservoirs and sulfur cycling processes are involved.

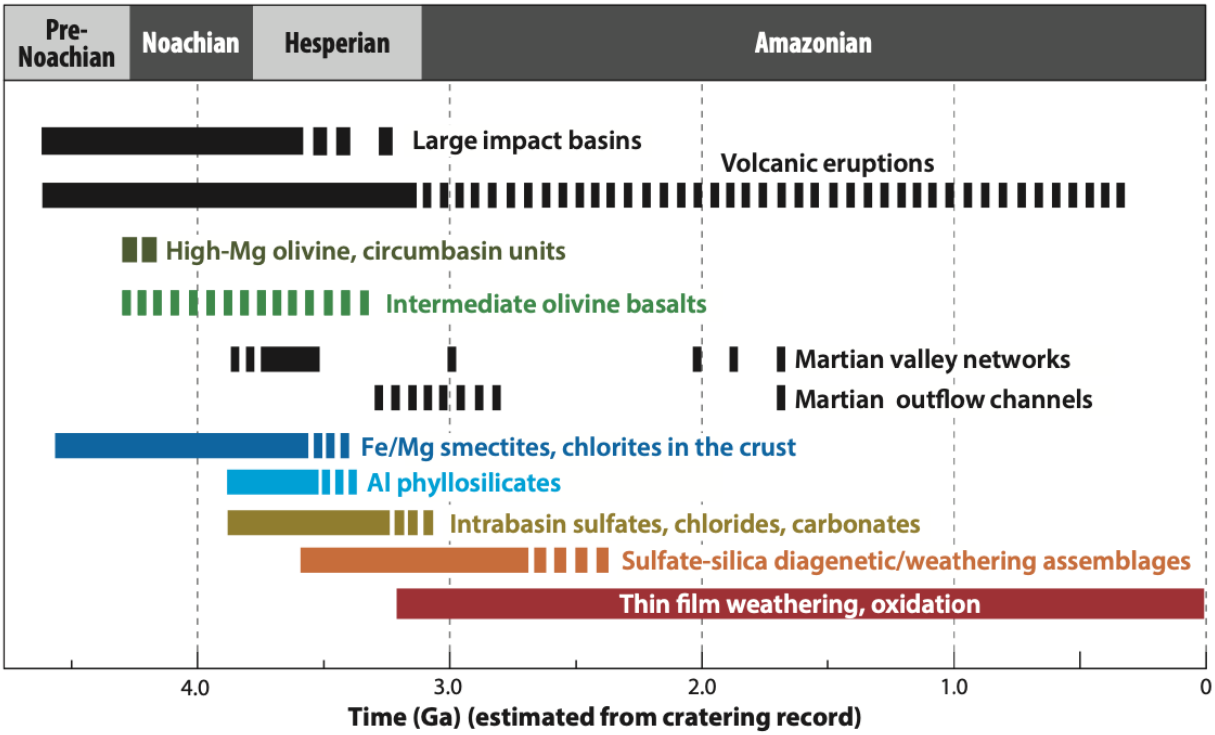


Figure 1. Mars' geologic time scale from Ehlmann and Edwards (2014)

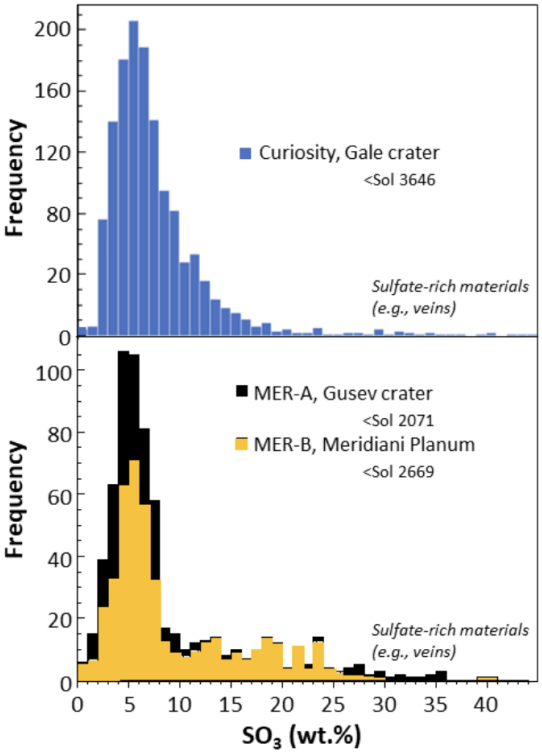


Figure 2. Histograms showing sulfur content as SO_3 wt% from the Alpha-particle X-ray Spectrometer (APXS) using bins of 1 wt%. The trend identifies primarily 5 wt% of SO_3 as the concentration of sulfur content currently observed in three landing sites on Mars, with higher concentrations >30 wt% observed in sulfate-rich veins (Franz and King, 2026)

Figure 3 represents their proposed early Martian sulfur cycle, before major reduction in magmatic rates some time greater than 3 Gyr ago, and outlines the major potential reservoirs and transport processes to be considered for the distribution of sulfur. However, these estimations lack quantitative values, especially fluxes that consider time. This existing model only serves as a visualisation of the many potential interactions of sulfur reservoirs.

Other studies, such as Hynek et al. (2019) and Ojha et al. (2019) have attempted to balance a box model for local, well-studied sites on Mars, specifically Meridiani Planum and the Medusae Fossae Formation (MFF) respectively. Hynek et al. (2019) used mass balancing, by providing relevant volumes and identifying the limitations of individually proposed scenarios of groundwater upwelling, volcanic airfall, atmospheric source and fluvial input. However, these models do not account for the likely possibility of these input scenarios occurring simultaneously and affecting one another. They identified the need for a better constraint of the primary basaltic sediment and sulfate sources in order to justify any further calculations. Ojha et al. (2019) concluded the mass of the S emitted from the MFF-forming event(s) was up to "8 orders of magnitude higher than the mass of S emitted from the largest Quaternary vol-

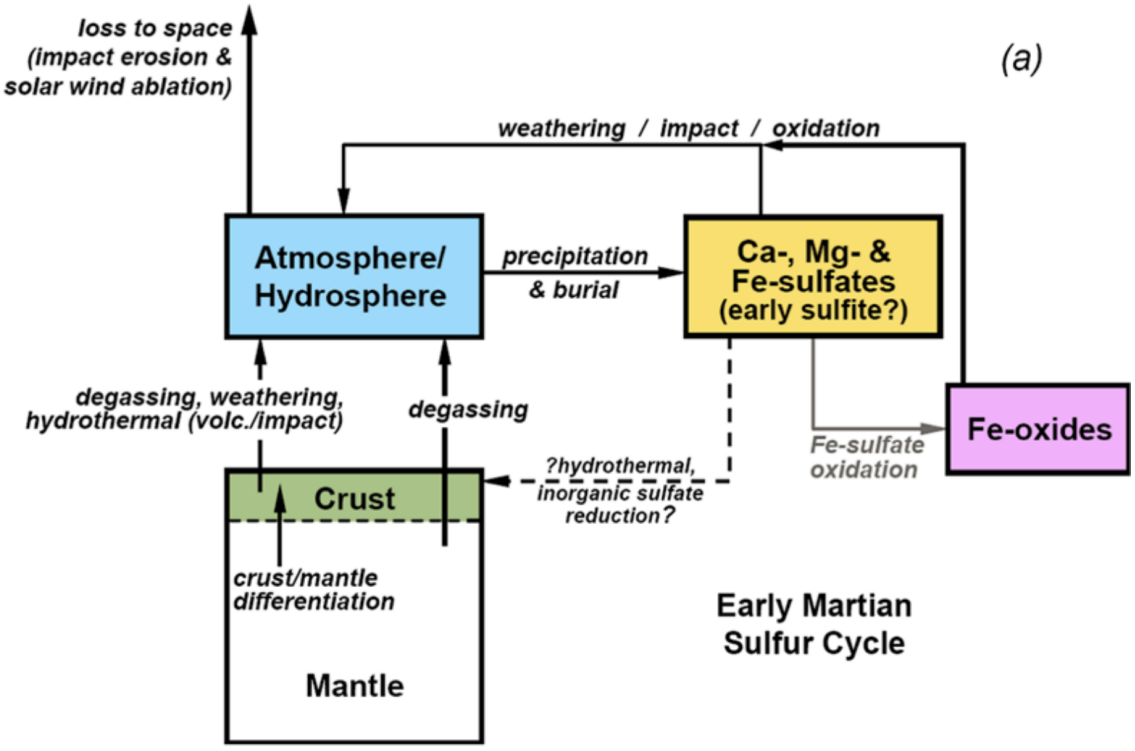


Figure 3. A simplified box model of the early Martian sulfur cycle, with no quantitative values, identifying the primary fluxes between reservoirs (from Gaillard et al., 2013)

canic eruption on Earth", further emphasizing the need to constrain the source of sulfur that would create the observed abundance. Neither of these studies included the effects of time, which significantly limits their reliability as the timescale over which the events they describe occurred would significantly affect the magnitude of final emitted sulfur mass.

All three studies described above have produced models which have remained largely incomplete as their proposed mechanisms for sulfate deposition and formation (e.g. groundwater upwelling and fluvial input) do not explain the abundance of sulfur in the bedrock. Eruptions in Kilauea, an analogue basaltic shield volcano in Hawaii, show that there are other sources of sulfur not considered by these authors. Sulfates can also form during quiescent degassing and also in the eruption plume, as seen at Kilauea (Franz & King, 2026) and these may be sampled in volcanic ash-leachates (the adsorption of volatiles onto ash) that have avoided contact with water, which would actively dissolve the sulfates into groundwater (Casas et al., 2026). Quiescent degassing is the release of gas during a volcano's life outside of sole-eruption events, and can take place over months to decades. From an estimate of ~2.8×10^{12} g of SO_2 per year from Earth's eruption data from 1978-2014, ~43% is contributed by quiescent degassing (Carn et al., 2016) demonstrating that it makes significant contributions to the total amount of sulfur transported into the atmosphere reservoir.

This study attempts to quantitatively constrain the sulfur cycle on Mars by applying comparative planetology using data from Earth's volcanoes, including both eruptive and quiescent degassing rates and incorporating the effects of eruption duration through flux rates. Box modelling was used to assess whether incorporating quiescent degassing alongside eruptive degassing can better account for the sulfur output by volcanic reservoirs on Mars during the Noachian-Hesperian periods. By doing so, I provide useful estimates that can be used in future research to help scientists further characterise the primary chemical cycle on Mars and its broader effect on Martian climate change. Additionally, this comparative planetology methodology could be developed and eventually applied to other rocky planets with basaltic magma systems to understand their planetary evolution.

METHODOLOGY

Earth's SO_2 gas output flux rate

The dataset was chosen from four review papers which collated multidecadal measurements of ter-

restrial volcanic eruptive and quiescent degassing (i.e. Carn et al., 2003; Carn et al., 2016; Carn et al., 2017; Shinohara, 2008). The volcanoes chosen had to satisfy the following list of parameters in order to best replicate Martian volcanic conditions:

- Primarily basaltic (Ehlmann & Edwards, 2014)
- Must originate from intraplate volcanism or intercontinental rift zones, as Mars has no plate tectonics
- Measurements avoid contact with water to ensure the sulfur has not been dissolved

The last condition removed mid-ocean ridge formations from consideration; despite contributing a large amount of basalt production on Earth, the presence of seawater would render measurements inaccurate for comparison with Mars. This decreased the sample size to 16 volcanoes, a list of which can be found in Supplementary Material (Appendix V).

These mass values were collated and converted to kilotonnes (kT). Their respective flux values (mass/time) were determined through dividing this mass with the respective period of eruption the sulfur was released over, sourced from the Smithsonian Natural History Global Volcanism Program. These volcanoes were further classified by magma type (including alkali-basalts and basalt-rhyolitic), tectonic environment and type of eruption (active or quiescent). In order to be able to apply these fluxes directly to Martian volcanic sources for which only the surface area is known, the approximate surface area for each terrestrial volcano was found through satellite imagery. To do this, a spherical map projection was used and simplified into 2D of a circle's area, with variable radius. The centre of the circle was placed in the centre of the volcanic vent, whilst the radius was adjusted to extend to where volcano elevation reaches zero.

Thus, each flux was calculated using the following formula:

$$\text{Flux}_{\text{output}} = \frac{V}{t \cdot SA}$$

where (V) = volume of extruded S, (t) = eruption period, SA = surface area of Earth volcano.

Volcanoes at rift zone boundaries and of slightly altered basaltic compositions were also included to identify any different trends in flux. Due to the large order of magnitude difference in range between active volcanic eruptions output flux and quiescent degassing rates, a logarithmic scale was applied to the data. Flux was then grouped through the Past4 program, creating a histogram frequency distribution graph. The bin size varied with integer intervals. When observing for a peak, there was no difference in the highest value between the histograms of 5, 6 and 7 bins for the same range, and hence the primary flux value was derived by observing the highest frequency value.

Volcanic reservoir sizes

To quantify the Martian volcanic reservoir, a total surface area was calculated to apply the terrestrial SO_2 flux to and this was applied to predict the mass of sulfur released during the Noachian-Hesperian periods. A mass representing the current size of the reservoir was also calculated using known sulfur concentrations from Martian meteorites representing the Martian source region for volcanic rocks.

The total surface area for volcanic Martian reservoirs was determined through using the United States Geological Survey (USGS) Geologic Map of Mars (Tanaka et al., 2014). The same map projection process applied for Earth's volcanoes in the Earth's SO_2 Gas Output Flux Rate section was employed for each volcanic unit, using a different shape maintained by approximating the projection of the map as two circles attached to the central rectangle (Figure 9). This shape was then resized to contain all individual Noachian to Hesperian volcanic units within it, matching the scale to calculate the surface area of the volcanics (Figure 10).

The sum of the surface area of these shapes was multiplied with the Earth SO_2 sulfur output flux to create an equivalent output flux for Martian volcanism.

In addition, the amount of sulfur in the mantle reservoir was estimated using the volatile content of undegassed Martian meteorites such as shergottites and nakhlites with S contents of <0.27 wt% and <0.2865 wt% respectively (Franz & King, 2026). The maximum values of the indicated range were taken as they represent the least degassed S contents of the meteorite that was measured. The assumption was made that the highest sulfur contents of the meteorites can be used as an estimate for mantle volatile content, as there would

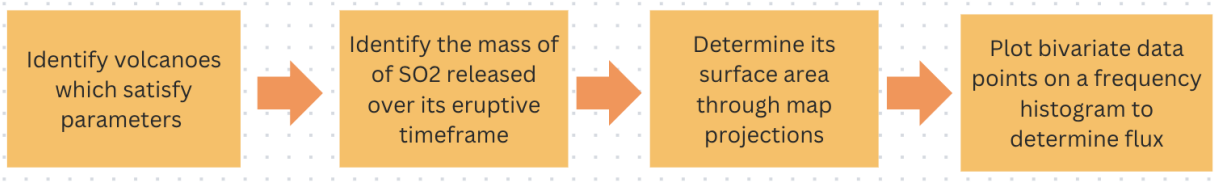


Figure 4. Overview of methodology to calculate the Earth SO_2 gas output flux

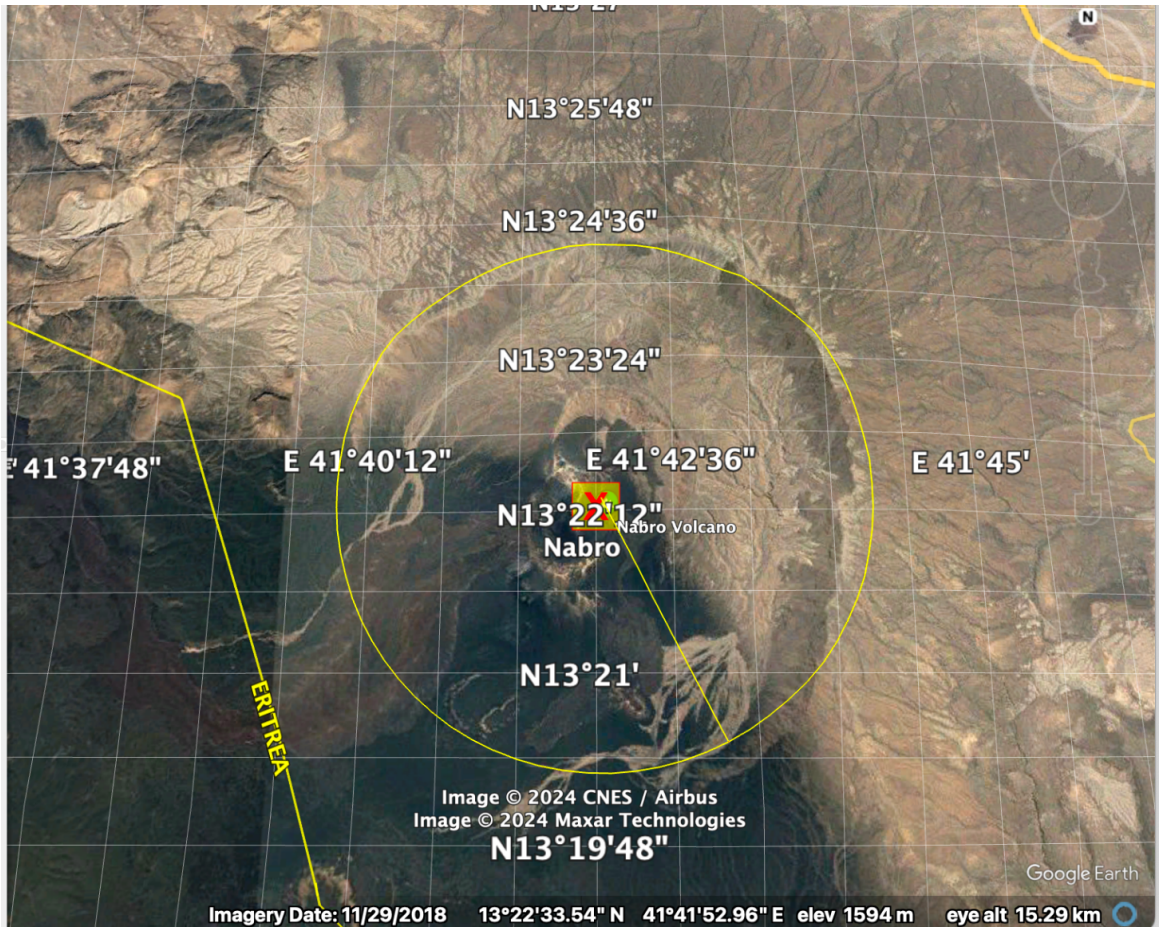


Figure 5. Google Earth circle measurement tool used to create surface area estimates. Radius extends to the edge of the volcano's elevation

be no other new sources of S in the meteorite. This assumes that the mantle has an approximate uniform distribution of sulfur near the crust. Although likely not precise, this method provides a range for source regions (i.e. the magma chamber) and surface rocks (Jakosky & Treiman, 2023). The size of the volcanic reservoir in kt of sulfur was also calculated through estimates of the total mass of extruded Martian volcanic materials

with an assumed constant density of 3.3 g cm^{-3} from Craddock & Greeley (2009). Only the values from the Noachian-Hesperian periods were considered, hence creating an estimate for the size of the reservoirs through the chosen time frame.

Sedimentary reservoir sizes

The sedimentary reservoir surface area was calculated through further map projections over a Mercator projection of the USGS Geological Map for Mars (Franz & King, 2026).

Using a similar approach to calculating the volcanic reservoir sizes, shapes of the CRISM sulfate-bearing rocks were outlined in rectangles and circles in Microsoft PowerPoint, with the surface area calculated. The changing scale of a Mercator projection was accommodated for through identifying the different scales at different latitudes throughout the test. However, the average depth and thus volume is indeterminable with the limited measurements on Mars, and the dramatic differences in elevation between the Northern lowlands and

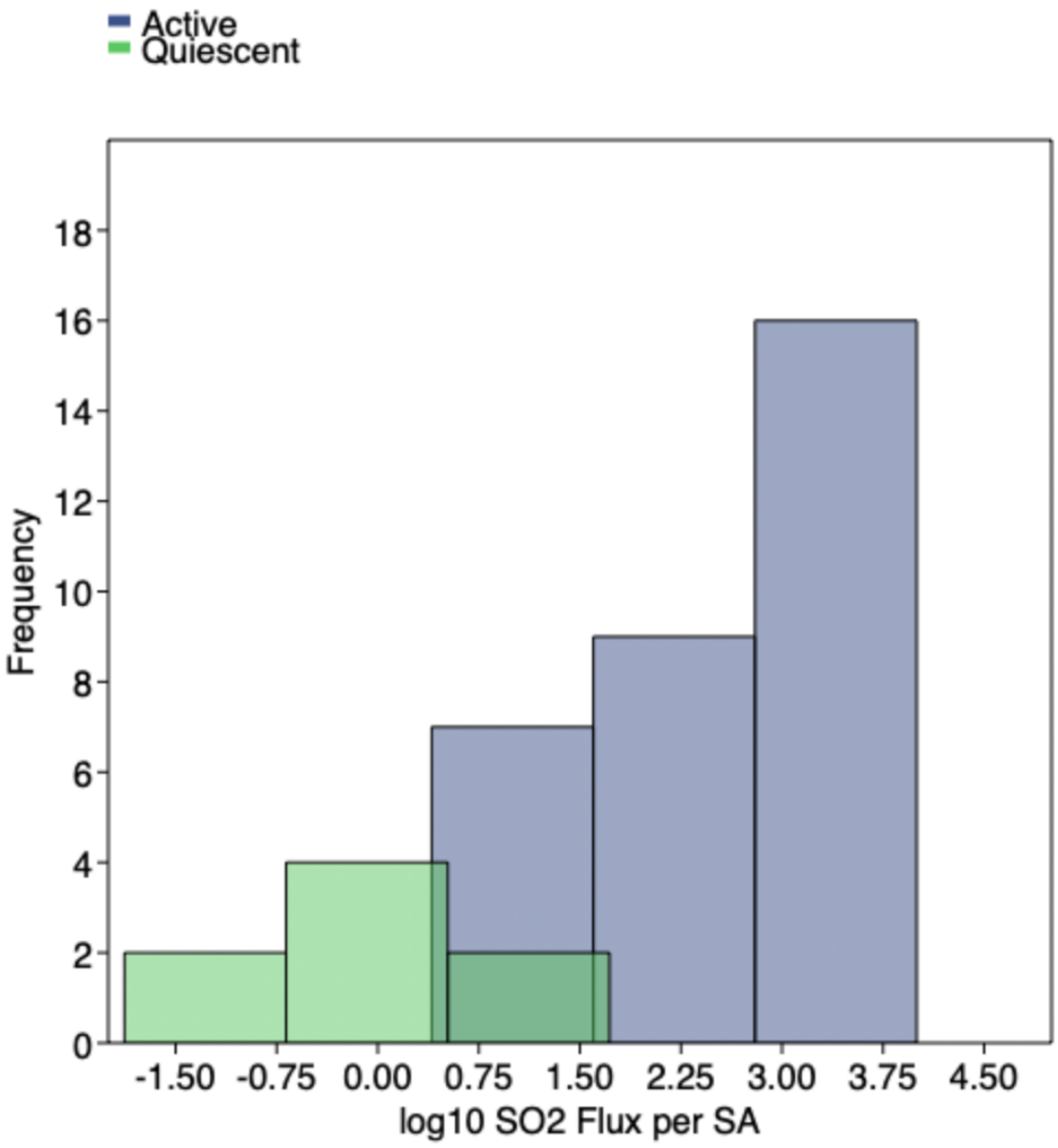


Figure 6. Frequency histogram showing a $\log_{10}$ scale in the x-axis of the SO_2 flux per surface area (SA) in kt yr^{-1} km^{-2}, ranging from -2 to 4 with 5 bins. The peak for Quiescent is from -0.75 to 0.5, whilst the peak for Active volcanism is from 3 to 4

Southern highlands. Hence, it was not possible to calculate a valid volume, density, or mass of its total sulfur. The model only used the surface area of the sedimentary reservoir to predict the total flux, as the mass of this reservoir could not be determined.

RESULTS AND DISCUSSION

Quantifying sulfur release from Noachian to Hesperian volcanism

By assuming an average duration of eruption of 2 Myr (Jiang et al., 2021), the model indicates that 5.8×10^{15} to 5.8×10^{16} kt of sulfur was released into the atmosphere from active degassing (flux of 5×10^{2}–5×10^{3} kt yr^{-1} km^{-2}) and quiescent degassing (flux of 0.5 kt yr^{-1} km^{-2}) from the Noachian-Hesperian periods. Once the sulfur has been released into the atmosphere, it can be deposited and redistributed in a multitude of different ways, however this would not affect the total amount of sulfur present on the surface of Mars. This is because the model assumes a closed system, and hence unlike Gaillard's qualitative model, assumes there are no additional inputs or outputs of sulfur on a planetary scale. Impact events and meteorites would not reintroduce significant amounts of any new material, rather only redistributing on the surface of Mars. This is a valid approach, as the orders of magnitude of

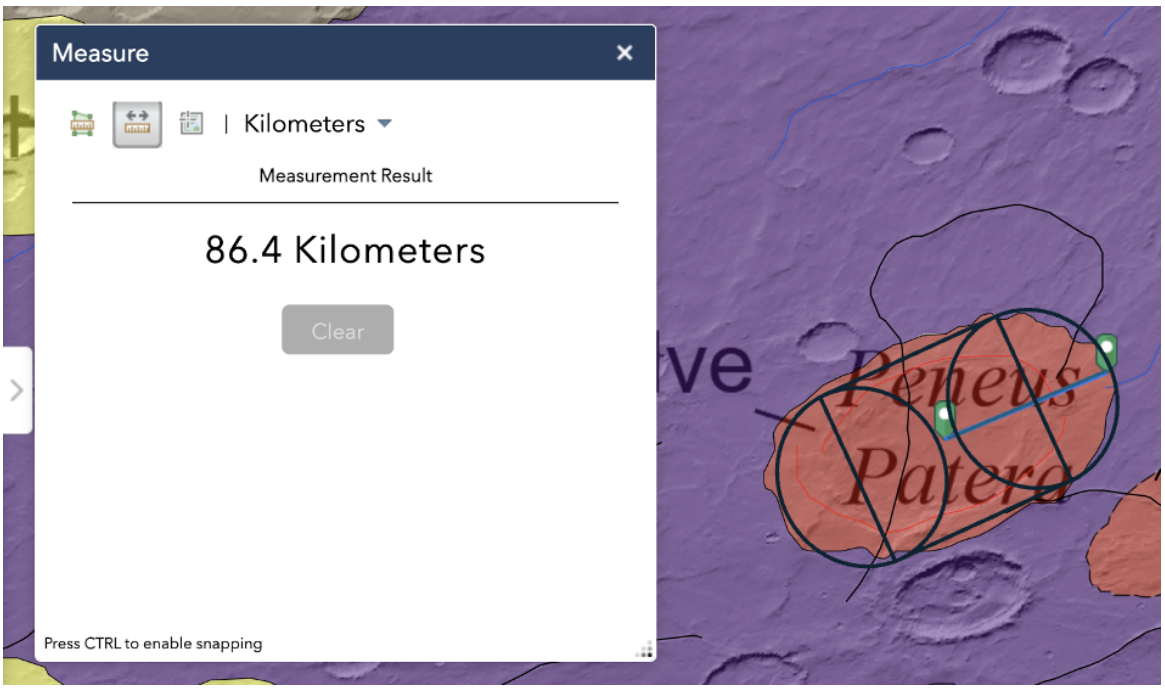


Figure 7. Demonstrating how an image of USGS Interactive Map Measurement tool can be annotated in PowerPoint to produce an area using the map projection shape for a Noachian volcanic unit

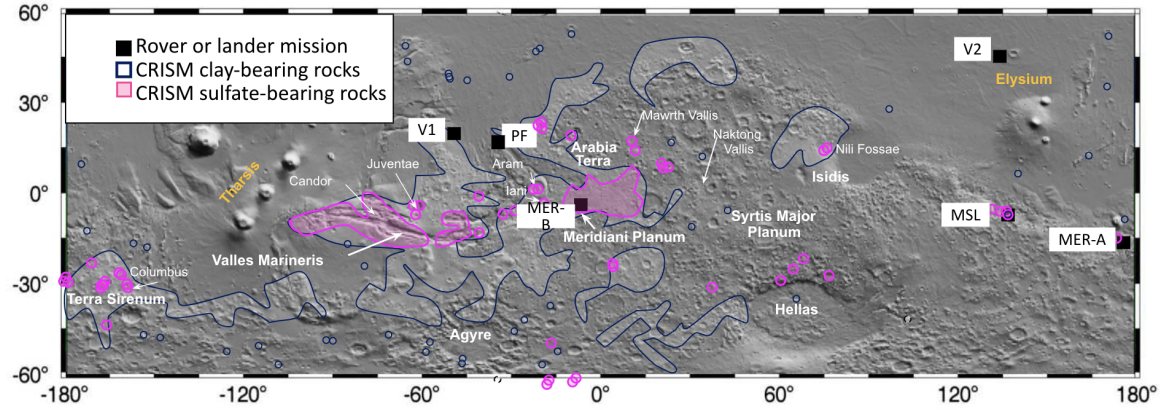


Figure 8. Sulfur and sulfate concentrations and locations on the surface of Mars, overlying a map of Noachian rocks. Sulfate-bearing rocks and phyllosilicate-bearing rocks are based on data from CRISM (Ehlmann and Edwards, 2014). Map from Franz and King 2026

sulfur in consideration as produced by the box model (10^15-10^16 kt) would not be drastically disturbed by the small sulfur content supplied by scattered meteorites. The study also does not consider the effects of hydrothermal transfer between the reservoirs, and only considers volatile output, as it primarily focuses on degassing. This is again a valid approach, as acid and water soluble sulfur species would only be mobilised if infiltrated by groundwater, and would not be sourced from the groundwater itself. The source of S would have to result from volcanic processes.

The assumed duration eruption period of 2 myr, which is the average between 1-5 myr as commonly cited in Jiang et al. (2021), is based on Earth's large igneous provinces; intraplate, mafic igneous volcanic systems. These are intentionally very similar to Martian volcanic conditions. It does not consider the possibility of 32 Myr in magnitude, the maximum cited volcano eruption length, which would shift results by an order of magnitude.

However, since the duration of Martian eruptions is unable to be determined, it is in the best interest to accommodate for a wide range of possibilities for the eruptive time frame.

The final perceived order of magnitude is in agreement with current literature such as Ojha et al. (2019), which found $>10^{14}$ kt (10^{17} kg) of S was delivered to the atmosphere. Similarly, the map

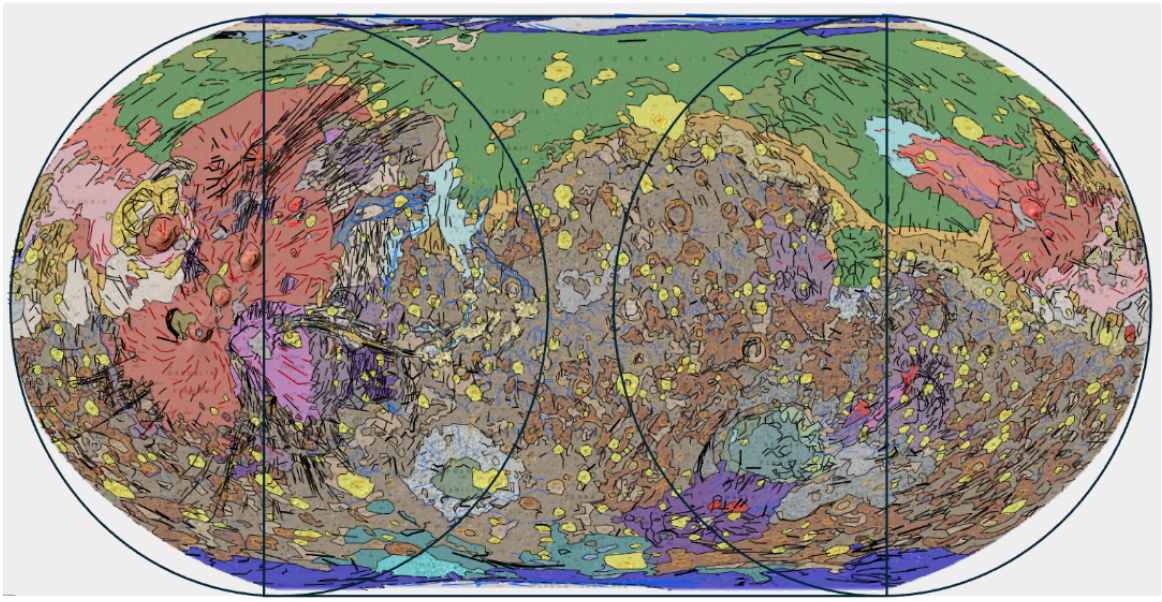


Figure 9. USGS Geologic Map of Mars, modified from Tanaka et al. (2014) with shapes overlain above through PowerPoint package. This model is limited as the irregularity of the shape of volcanic units compared indicates it may overestimate the size of the units

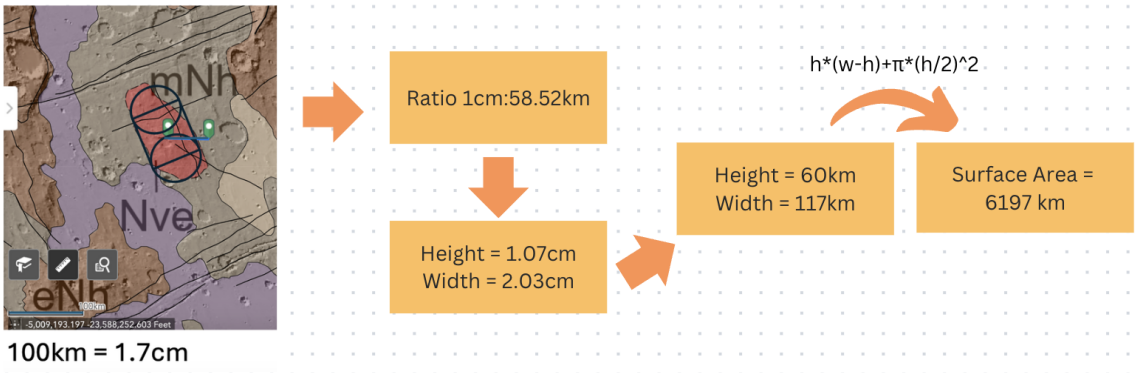


Figure 10. Calculations of one sample of Volcanic Surface Area. When repeated for all samples of Noachian-Hesperian surface area, the final value is 1.1×10^7 km^2. All calculated values can be found in Supplementary Material (Appendix II)

projection method in calculating volume of volcanic rock is consistent with Craddock & Greeley (2009), which estimated a total volume of 4.244×10^7 km^3 of S. The total surface area from map projections of 1.1×10^7 km^2 multiplied with average thickness of 5 km in the Middle Noachian era (Jakosky & Treiman, 2023), provides 5.5×10^7 km^3, which is in the same order of magnitude.

Key limitations

The first key limitation to address is the use of surface areas in order to relate the calculated Earth sulfur output flux to Martian volcanoes. Volcanoes, especially the shield volcanoes mainly observed on Mars, have a gradually decreasing thickness further away from the volcano. This variation in slope also determines the volume of volcanic rock present, and thus provides separate insight into the size of the volcano and its magma chamber.

However, due to the lack of precise depth measurements on Mars, it would be impractical to attempt to account for thickness differences in order to use volume of volcanic rock to relate the two planets. Hence, the assumption was made such that the surface area of a volcano is directly proportional to the rate of sulfur release. As surface area can be deduced using map projections for both Earth and Mars, this factor allowed the flux rates to be related to each other despite differences in topography.

Another key limitation in deriving the sedimentary reservoir size was the use of a Mercator projection geological map, which was necessary as it fea-

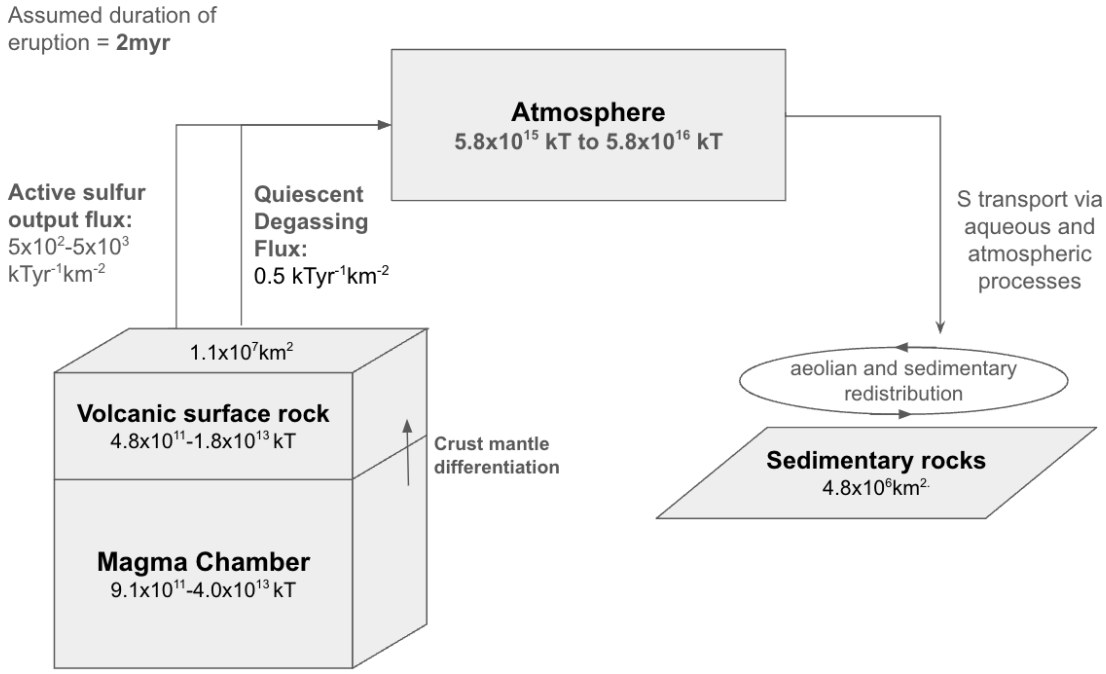


Figure 11. Finalised Box Model, including all relevant values. All values are in elemental S, with reservoir sizes given in kt (10^9 g) of S, as well as surface area of Mars. The total output flux rate (with the addition of quiescent degassing) when multiplied with the eruption period and volcanic surface area produces 5.8×10^{15}–5.8×10^{16} kt of sulfur released into the atmosphere over 2 Myr

tured labelled CRISM sulfur-rich areas. Despite the scale of the map changing with the latitude, each area spans only a small latitudinal range, resulting in minimal error. However, this process would have increased the uncertainty of this method of measurement taking, as there would be an increased number of scales for different latitudes.

Future directions

As this study is the first to attempt to consolidate the total Martian sulfur cycle by using comparative planetology as an estimate of the total sulfur released over time on Mars, more study is necessary to remove confounding variables and address the assumptions made. An immediate next step would be to include the eruption of early-Amazonian volcanoes (Ehlmann & Edwards, 2014; Tanaka et al., 2014) that may have released sulfur. Although difficult to acquire, using more direct data measurements from existing rovers on Mars to calculate a measurement for the average depth of sedimentary soil layers and height of volcanoes would constrain the size of the sedimentary reservoir and find a quantitative mass that could complete the box model. To do this, topographic data, gravitational anomalies, or potentially seismic studies could be used to determine crustal thickness. Such an approach would confirm that the box model is mass balanced if the amount of sulfur released into the atmosphere is comparable with the size of the sedimentary deposit reservoir; further verifying that the methods used in this study are appropriate.

CONCLUSION

This study successfully used Earth analogues and box modelling to provide fluxes for the cycling of sulfur on Mars, notably being the first attempt at applying this concept to the whole planet as a closed system. The principles of comparative planetology were used in selecting a criteria of Earth volcanoes to replicate Martian conditions. Previously overlooked quiescent degassing rates were also considered, increasing the rate of output of sulfur. The final box model approximated $5.8{\times}10^{15}$ to $5.8{\times}10^{16}$ kt of sulfur was released from the Noachian to Hesperian period from volcanism.

A remaining gap is the unknown depth of the sedimentary reservoir, which hinders a calculation of mass balance as current data cannot confirm whether the proposed output sulfur mass

truly matches the observed abundance on Mars. Nonetheless, future studies can consider these calculations and begin to consolidate a sedimentary reservoir size in order to further test the calculated flux rates.

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SUPPLEMENTARY MATERIAL

Supplementary material accompanying this article contains the underlying volcanic sulfur flux data, Martian volcanic surface-area calculations, sulfur reservoir estimates, volcano selection criteria and supporting calculations (Appendices I–VI).

The supplementary PDF is available with the online article at https://doi.org/10.67642/97wtbw66.

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