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### ► To cite this version:

Ashwin Braude, Franck Montmessin, Kevin Olsen, Alexander Trokhimovskiy, Oleg Korablev, et al.. Upper limits on volcanic gases in the Martian atmosphere from the ACS MIR instrument. Europlanet Science Congress 2022, Sep 2022, Granada, Spain. pp.EPSC2022-642. insu-03775034

**HAL Id: insu-03775034**

**<https://insu.hal.science/insu-03775034v1>**

Submitted on 12 Sep 2022

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## Upper limits on volcanic gases in the Martian atmosphere from the ACS MIR instrument

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### Abstract

The geological record provides convincing evidence for very recent volcanic activity on Mars (e.g. Horvath et al. 2021, *Icarus* 365, 114499). In this talk we present the results of Braude et al. (2022, *A&A* 658, A86), in which a comprehensive analysis was performed of solar occultation observations from the ACS MIR instrument from MY 34 to 35, in search of three tracers of residual volcanic outgassing from the surface of Mars: SO<sub>2</sub>, H<sub>2</sub>S and OCS. We found no statistically significant detections of either of these three molecules, instead imposing upper limits of 20 ppbv of SO<sub>2</sub>, 15 ppbv of H<sub>2</sub>S, and 0.4 ppbv of OCS. We thereby estimated that volcanic outgassing from the surface of Mars must be below 2 ktons day<sup>-1</sup>.

### Introduction

Several pieces of geological evidence indicate the presence of residual volcanic activity in the Tharsis and Elysium regions dating back only a few million [1] or even hundreds of thousands [2] of years, with the InSight Lander recently confirming present-day seismic activity in the Cerberus Fossae region [3]. On Earth, volcanic emission is dominated by carbon dioxide, water vapour and sulphur species, notably sulphur dioxide (SO<sub>2</sub>) but with smaller amounts of hydrogen sulphide (H<sub>2</sub>S) and the occasional detection of carbonyl sulphide (OCS). Previous ground-based observations of sulphur species on Mars, however, have not resulted in any confirmed detections, instead imposing lowest disc-integrated upper limits of 0.3 ppbv of SO<sub>2</sub> [4,5], 1.5 ppbv of H<sub>2</sub>S [6] and 1.1 ppbv of OCS [7]. In this talk we summarise the results of [8], in which we used solar occultation measurements from the mid-infrared channel of the Atmospheric Chemistry Suite (ACS MIR, [9]) instrument from the start of the ACS science phase in MY 34 to the end of MY 35, in search of SO<sub>2</sub>, H<sub>2</sub>S and OCS in Mars' lower atmosphere.

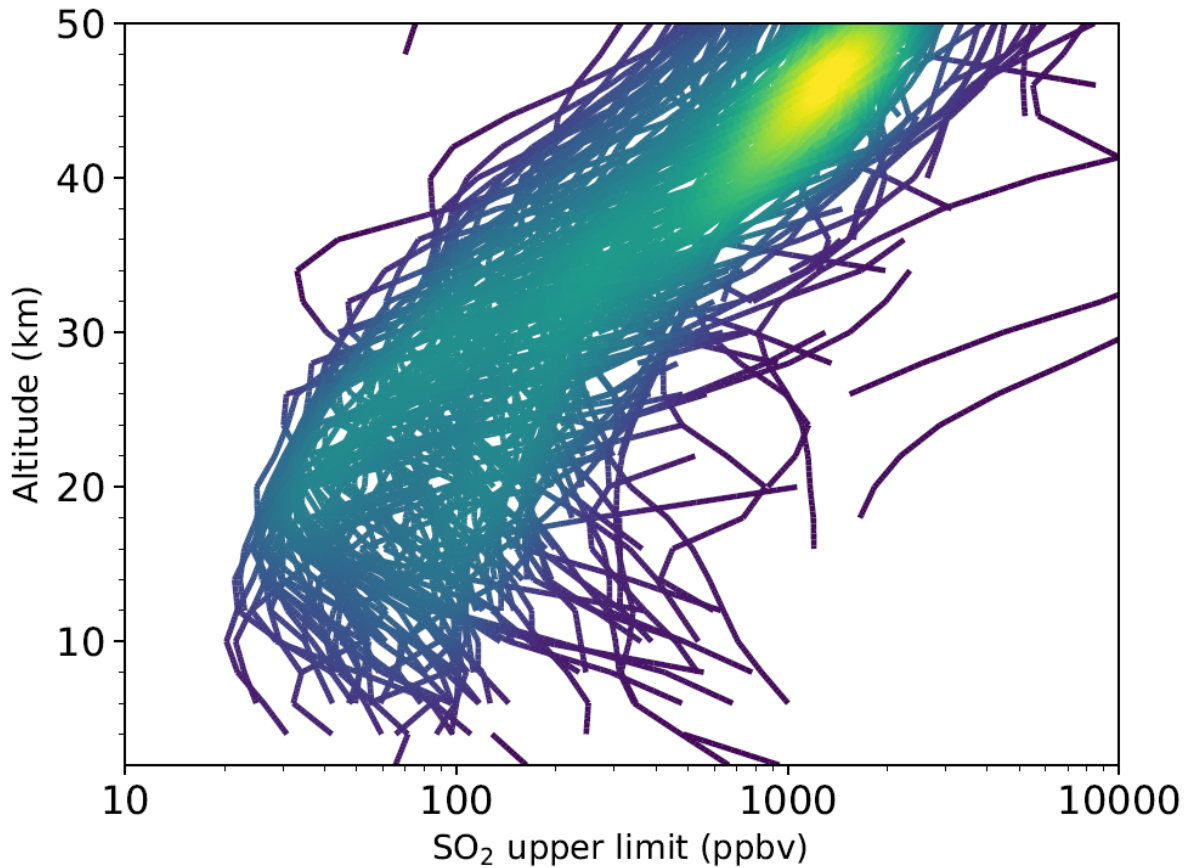


Fig. 1: Retrieved vertical profiles of SO<sub>2</sub> upper limit values from each of the 190 processed solar occultations between  $L_s = 165 - 280^\circ$  of MY 34 and  $L_s = 140 - 350^\circ$  of MY 35. Yellower colours indicate an increased density of retrieved values. (*Reproduced with permission from Fig. 4 of [8]*)

### Method

We made use of three sets of ACS MIR data each obtained using different diffraction grating positions that are sensitive to different wavenumber ranges. 190 individual occultations carried out using grating position 9 were analysed, covering a time period of  $L_s = 165 - 280^\circ$  of MY 34 and  $L_s = 140 - 350^\circ$  of MY 35. This grating position covers the strongest SO<sub>2</sub> absorption features in the wavenumber range covered by ACS MIR. Using the RISOTTO radiative transfer and retrieval code [10], we performed retrievals of this data within a wavenumber range of 2481 and 2492 cm<sup>-1</sup>, which is sensitive to a series of overlapping SO<sub>2</sub> and CO<sub>2</sub> absorption lines, and imposed upper limits by deriving the volume mixing ratio (VMR) of SO<sub>2</sub> that would result in a change in goodness of fit ( $\chi^2/n$ ) to the observed spectra above a given threshold.

Equivalently, we searched for H<sub>2</sub>S in two spectral windows between 3827 and 3833 cm<sup>-1</sup> and around a single absorption line at 3839.2 cm<sup>-1</sup> covered by grating position 5, of which we analysed 86 occultations between  $L_s = 164 - 218^\circ$  and  $L_s = 315 - 354^\circ$  of MY 34. Finally, we searched for OCS in two spectral windows between 2908 - 2912 and 2923 - 2927 cm<sup>-1</sup>, corresponding to the P and R branches respectively of an OCS absorption band in a wavenumber region that is mostly devoid of other gas absorption lines. This region is covered by grating position 11, for which there is almost complete coverage between  $L_s = 163^\circ$  of MY 34 and  $L_s = 355^\circ$  of MY 35. Upper limits for these two molecules were imposed by averaging retrieved vertical VMR profiles from adjacent rows on the MIR detector.

### Results and Perspective

We found no significant detections ( $>3\sigma$ ) of any of these three molecules, instead deriving our best upper limits of 20 ppbv of  $\text{SO}_2$ , 15 ppbv of  $\text{H}_2\text{S}$  and 0.4 ppbv of OCS. The latter value is the lowest reported upper limit of OCS in the Martian atmosphere to date, as opposed to the previous value of 1.1 ppbv reported by [7]. However,  $\text{SO}_2$  is expected to dominate in concentration relative to  $\text{H}_2\text{S}$  and OCS in volcanic emission. We estimate that during the period of observation, no more than 750 kttons of  $\text{SO}_2$  could be present in the entire Martian atmosphere, implying surface outgassing of  $\text{SO}_2$  below 2 kttons/day. Future targeted measurements of sulphur species in regions associated with historic volcanism (e.g. the Tharsis region, Elysium Planitia) could shed greater light on the probability of residual present-day volcanism.

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