

A new look into the atmospheric composition of WASP-39 b

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ABSTRACT

Being one of the first exoplanets observed by the James Webb Space Telescope (JWST), WASP-39 b has become an iconic target and many transit spectra recorded with different instruments (NIRISS, NIRCAM, NIRSpec G395H, NIRSpec PRISM and MIRI) are currently available, allowing in-depth studies of its atmosphere. We present here a novel approach to interpret WASP-39 b's transit spectroscopic data, consisting of a multi-step process where ab initio equilibrium chemistry models and blind retrievals are used iteratively to find physically robust, optimal solutions. Following this approach, we have identified a new scenario to explain WASP-39 b's atmospheric composition, in which silicon-based chemistry plays a major role. In this scenario, SiO may explain the spectral absorption at 4.1 μm , currently interpreted as being due to SO₂. SiO and the other gas species identified by the retrieval models, i.e. H₂O, CO₂, Na and K, are consistent with an atmosphere in chemical equilibrium with a temperature-pressure profile constrained by H₂O and CO₂ absorption bands. In addition, silicate clouds and hazes can produce the spectral features observed by MIRI in the spectral window 5–12 μm . While we advocate the need for more data, possibly at higher spectral resolution, to confirm our results for WASP-39 b's atmospheric composition, we highlight a refined atmospheric retrieval strategy with pre-selection and post-reconstruction to guide the next generation of transit spectroscopy.

Keywords: Exoplanets(498) — Exoplanet atmospheres(487) — Transmission spectroscopy(2133)

1. INTRODUCTION

1.1. First WASP-39 b observations

WASP-39 b has been among the first exoplanets observed by the James Webb Space Telescope (JWST) shortly after its commissioning phase in 2022 (Rigby et al. 2023). The planet was discovered by the ground-based transit survey SuperWASP (Faedi et al. 2011). Their analysis indicated WASP-39 b to be a highly-inflated Saturn-like exoplanet, with a mass of $0.28 \pm 0.03 \text{ M}_\text{J}$ and a radius of $1.27 \pm 0.04 \text{ R}_\text{J}$. The study also estimated an equilibrium temperature of $\sim 1100 \text{ K}$. The parent star, WASP-39 A, was studied by Faedi

et al. (2011); Mancini et al. (2018); Bonomo et al. (2017); Maciejewski et al. (2016), among others: it is a G8 type star with a mass of $0.93 \pm 0.03 \text{ M}_\odot$, a radius of $0.895 \pm 0.023 \text{ R}_\odot$, an effective temperature of $5400 \pm 150 \text{ K}$ and [Fe/H] of -0.12 ± 0.1 . The stellar age was estimated to be 8.5–9 Gyrs (Mancini et al. 2018; Bonomo et al. 2017).

Prior to JWST, observations of WASP-39 b using the Wide Field Camera 3 (WFC3) onboard the Hubble Space Telescope indicated the presence of water vapour in its atmosphere (Wakeford et al. 2018; Tsiaras et al. 2018; Pinhas et al. 2018, 2019; Fisher & Heng 2018). Additionally, sodium and potassium were suggested by observations using the Hubble Space Telescope Imaging Spectrograph (STIS, Sing et al. 2016; Fischer et al. 2016), the ground-based VLT (0.411–0.810 μm , Nikolov

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et al. 2016) and LRG-BEASTS survey (0.4–0.9 μm , Kirk et al. 2019). Wakeford et al. (2018) and Kirk et al. (2019) reported highly supersolar metallicities to interpret these datasets. Thorngren & Fortney (2019) estimated the maximum atmospheric metallicity of WASP-39 b to be $54.5 \times$ solar.

Saba et al. (2024) analysed archive data obtained with Hubble STIS and WFC3 instruments of WASP-39 at various epochs. The metrics used as stellar activity indicators leaned towards WASP-39 being an inactive star. These results are in agreement with previous studies (Sing et al. 2016; Mancini et al. 2018), with the exception of Pinhas et al. (2018), who suggested stellar heterogeneities.

1.2. JWST observations of WASP-39 b

Transit spectra of WASP-39 b using different JWST’s instrument modes were published by Ahrer et al. (2023, NIRCam, 2.4–4.0 μm), Feinstein et al. (2023, NIRISS, 0.6–2.8 μm), Alderson et al. (2023, NIRSpec G395H, 2.7–5.2 μm), Rustamkulov et al. (2023, NIRSpec PRISM, 0.5–5.5 μm), and Sarkar et al. (2024, NIRSpec G395H & PRISM). A single transit of WASP-39 b was observed by NIRISS in SOSS mode on 26 July 2022; by NIRCAM in both long-wavelength (LW) and short-wavelength (SW) channels on 22–23 July 2022; by NIRSpec with its G395H grating using the Bright Object Time Series mode (BOTS) on 30–31 July 2022 and in the PRISM mode on 10 July 2022. Additionally, it was observed with MIRI LRS, from 5 to 12 μm , on 14 February 2023. By combining all available JWST’s observations of WASP-39 b, we obtain a spectral coverage from 0.6 to 12 μm .

The transit data obtained with each of these instruments have undergone extensive scrutiny by the exoplanet community (JWST Transiting Exoplanet Community Early Release Science Team et al. 2023; Grant et al. 2023; Tsai et al. 2023b; Esparza-Borges et al. 2023; Louca et al. 2023; Tsai et al. 2023a; Khorshid et al. 2024; Arfaux & Lavvas 2024; Roy-Perez et al. 2025). A variety of data analysis pipelines, saturation handling techniques (Sarkar et al. 2024), noise mitigation methods (Holmberg & Madhusudhan 2023) and spectral extraction algorithms (Darveau-Bernier et al. 2022) have been developed. Beyond providing open access to the data, one of the goals of the ERS program was to invite the community to perform independent data analysis and compare results. NIRISS data were reduced with six different pipelines: `nirHiss` (Feinstein et al. 2023; Bell et al. 2022), `supreme-SPOON` (Radica et al. 2023), `Transitspectroscopy` (Espinoza 2022), `Iraclis` (Tsiaras et al. 2016), `NAMELESS`, `FIREFLy` (Rus-

tamkulov et al. 2022). NIRCAM data was processed using `Eureka!` (Bell et al. 2022), `tshirt`, `HANSOLO` (Lendl et al. 2016, 2017) and chromatic-fitting. NIRSpec G395H data was reduced by six separate teams using `ExoTiC-JEDI` (Alderson et al. 2022), `Aesop`, `ExoTEP` (Benneke et al. 2019), `Tiberius` (Kirk et al. 2019) and `Transitspectroscopy`. For NIRSpec PRISM data, `Eureka!`, `Tiberius`, `FIREFLy`, and `tshirt` were utilised. MIRI LRS data was processed with `Eureka!`, `Tiberius`, and `SPARTA` (Kempton et al. 2023).

The data obtained with different JWST instrument modes have not always suggested a consistent story, possibly due to uncertainties in instrumental performance and/or reduction processes (e.g., Holmberg & Madhusudhan 2023; Davey et al. 2024; Lueber et al. 2024). For instance, depending on the instrument mode used, WASP-39 b’s C/O ratio has been reported to be sub-stellar (Ahrer et al. 2023), sub-solar (Feinstein et al. 2023), sub-solar to solar (Alderson et al. 2023) or supersolar (Rustamkulov et al. 2023). It is known that different data pipelines can potentially produce inconsistent results (Mugnai et al. 2024): this inconsistency can pose challenges when combining datasets processed by different pipelines. Offsets in the spectral data may arise due to different data analysis approaches, variations in intrinsic instrumental calibrations, and different choices of system parameters (see e.g. Yip et al. (2021)). Currently, no single pipeline has been used to uniformly reduce WASP-39 b’s data from all JWST instruments and their corresponding observing modes. We use here the spectral data published in Carter et al. (2024) and Powell et al. (2024) for the reasons described below.

Although the datasets for WASP-39 b were processed using different data reduction pipelines, Carter et al. (2024) selected the nominal reductions for each available dataset. They used `Eureka!` to extract a white light curve from each JWST dataset, resulting in a total of seven light curves: NIRISS order 1 and order 2, NIRSpec G395H NRS 1 and NRS 2, NIRSpec PRISM, NIRCam SW photometric channel, and LW spectroscopic channel. A joint white light curve fitting with `juliet` (Espinoza et al. 2019) was performed, incorporating one TESS light curve, six NGTS light curves, and radial velocity measurements from CORALIE and SOPHIE. This combined fitting yielded highly precise constraints on the system parameters, achieving a minimum precision of 0.5%. `Eureka!` was also used to extract chromatic light curves at native resolution for each JWST dataset. The spectral light curve fitting was performed by fixing the orbital parameters to those derived from the joint fitting. This procedure ensured a reduction in the observable offsets among the initial data release

presented in Lueber et al. (2024). Carter et al. (2024) applied an additional manual offset of -177 ppm to the NIRSpec PRISM data. Moreover, their final combined spectrum excluded the saturated region of the NIRSpec PRISM data between $0.62\text{--}2.1\,\mu\text{m}$.

MIRI observations were scheduled approximately seven months after the observations were recorded with NIRISS, NIRSpec, and NIRCam. MIRI transit data were observed in the low-resolution spectroscopy (LRS) slitless prism mode at an average resolution of approximately 100. Powell et al. (2024) reports that the white light-curve fitting of MIRI data performed with *Eureka!* adopted the same orbital parameters as those used by Carter et al. (2024). Although the MIRI data were reduced with three different pipelines, we include here only the reduction obtained with *Eureka!* to minimise offsets. This choice ensures further consistency across all instruments. Meanwhile, Flagg et al. (2024) have suggested that MIRI data beyond $10\,\mu\text{m}$ might be contaminated by circumstellar debris disk features that need to be considered in data analysis.

1.3. *Scientific interpretation of WASP-39 b transit spectra recorded with JWST*

Various molecules were reported in the literature to be present in the atmosphere of WASP-39 b, including H_2O , CO, CO_2 , K, H_2S and CH_4 (Lueber et al. 2024; Constantinou & Madhusudhan 2024; Ahrer et al. 2023; Alderson et al. 2023; Rustamkulov et al. 2023; Feinstein et al. 2023; Esparza-Borges et al. 2023). There are also tentative detections of SO_2 from Tsai et al. (2023b); Alderson et al. (2023); Rustamkulov et al. (2023); Constantinou & Madhusudhan (2024) and Powell et al. (2024). Lueber et al. (2024) re-examined the spectral feature around $4.1\,\mu\text{m}$ attributed to SO_2 absorption and suggested that its interpretation appears to be model-dependent: models with clouds favour the detection of SO_2 in the NIRSpec PRISM spectrum. They also discussed the use of grey clouds and non-grey ones, as implemented in Helios-r2 (Kitzmann et al. 2020), in the simulations.

Lueber et al. (2024) considered CH_4 , H_2O , CO, CO_2 and SO_2 as C- and O-bearing molecules in their retrieval simulations of NIRCAM and NIRSpec PRISM ERS spectra. Their retrieved values of C/O using random forest are consistent with the stellar value of 0.46 ± 0.09 from Polanski et al. (2022). Their NIRSpec PRISM free retrieval results are closer to the solar value of 0.55 from Asplund et al. (2009) (see Fig. 13 in Lueber et al. 2024). Their nested-sampling retrievals suggest C/H and O/H values to be consistent with solar.

The spread in the reported metallicities in the literature suggests that factors beyond instrumental modes may play a role in these discrepancies. For instance, when using different data analysis techniques, Alderson et al. (2023), Feinstein et al. (2023) and Rustamkulov et al. (2023) reported super-solar metallicities, Ahrer et al. (2023) constrained it to be solar to super-solar, while Lueber et al. (2024) found sub- to solar metallicity in most of the free retrievals and super-solar metallicity in the random-forest retrieval. Another identified source of discrepancy is the spectroscopic line lists used to interpret the data. For example, Niraula et al. (2023) tested different opacity sources and found different abundances of the same molecules.

1.4. *Retrieval techniques*

Spectral retrieval methods have often been used in recent years to interpret exoplanetary atmospheric spectra. These algorithms use statistical techniques and high-performance computers to sample a broad parameter space and to search for optimised solutions through a considerable number of iterations. Robust convergence, especially in high-dimensional retrievals, requires a large number of iterations and steps, making the computing power requirements more onerous. A notable example of such sampling algorithms is Multinest (Feroz et al. 2019), a Bayesian inference tool that calculates the evidence with an associated error estimate while generating posterior samples from distributions that may exhibit multiple modes and complex degeneracies in high dimensions.

Our paper focuses on improving the atmospheric retrieval strategy, using WASP-39 b as an example. Our approach has led to a different interpretation of the available JWST data, opening up a new perspective in our understanding of the chemical composition of WASP-39 b, and other similar planets.

2. METHODOLOGY

2.1. *Possible offsets among spectra recorded with different instruments*

We used the observational data described in Section 1.2 and detailed in Table 1. For our retrieval experiments, we used a resolution (~ 100) for each instrument to maintain a uniform resolution across instruments and modes. However, we have tested our results at higher spectral resolution in the spectral ranges where higher resolution data are available. We followed Carter et al. (2024) and applied a manual offset of -177 ppm to the NIRSpec PRISM data, while adding 68 ppm offset to the NIRISS (we assumed orders 1 and 2 have the same offsets) data and 132 ppm to NIRCam according to the

NIRSpec data. To align with the shorter wavelengths, we add a 420 ppm offset to MIRI data. The final data we use in further atmospheric analysis is shown in Fig. 1

2.2. Transit and atmospheric models

2.2.1. TauREx

TauREx 3 (Al-Refaie et al. 2021; Al-Refaie et al. 2022) is a state-of-the-art modelling framework to simulate exoplanetary atmospheres and to interpret exoplanet atmospheric data collected with different techniques through inverse models based on Bayesian statistics. Several plugins can be activated to simulate, e.g., atmospheric chemistry (Al-Refaie et al. 2022), cloud microphysics (Ma et al. 2023), stellar activity (Thompson et al. 2024) and phase-curves interpretation (Changeat et al. 2024). Parameters that are included and tested in retrievals with TauREx 3 include but are not limited to instrumental, atmospheric thermal, chemical, and cloud profiles, as well as planetary and stellar parameters. The radiative transfer calculations performed by TauREx 3 include molecular/atomic/ionic opacities, Rayleigh and Mie scattering, and collision-induced absorptions (CIAs).

2.2.2. GGChem

GGChem (Woitke et al. 2018) is an equilibrium chemistry model that estimates the chemical abundances by minimising the system’s Gibbs’ Free Energy, including scenarios with equilibrium condensation and charged particles. The elemental abundances adopted as initial conditions can be customised. A comparison and cross-validation of all the chemical equilibrium models implemented in TauREx 3 can be found in Al-Refaie et al. (2022). These include GGChem, FastChem (Stock et al. 2018) and ACE (Agúndez et al. 2020, 2012).

2.2.3. YunMa

YunMa (Ma et al. 2023) includes cloud microphysics models to estimate the vertical size distributions of cloud particles expected in an atmosphere according to its thermodynamical and chemical conditions, following, e.g. the approach described in Ackerman & Marley (2001). YunMa can also adopt simplified assumptions, such as homogeneous particle size (HPS) distributions, when there is limited knowledge of the atmospheric conditions and/or efficiency needed for retrieval studies. The current YunMa estimates cloud opacities using the BH-Mie approach (Bohren & Huffman 2008) of the cloud particles’ Mie scattering and absorption, from

refractive indices available in the literature. When integrated into TauREx 3, YunMa enables the generation of, or retrieval from, transmission and emission spectra of cloudy atmospheres.

2.3. Hybrid approach adopted here

To interpret the JWST’s observations of WASP-39 b, we adopt here a novel approach that combines free retrievals and ab initio models to explore more efficiently the parameter space of possible, physically viable solutions compatible with the data, as depicted in Fig. 2). We first use equilibrium chemistry models, assuming certain metallicity values, elemental ratios and thermodynamical conditions, to estimate the most plausible gaseous and condensed species – *Eq.* – expected to be present in the atmosphere (Step 1). Then, we perform a spectral retrieval analysis (with TauREx 3 and YunMa) with a sub-sample of the chemical species identified in Step 1 as priors, selecting those that have a detectable spectral signature in the wavelength range probed by the observations. We then compare the results from retrievals – *Ref.* – to the ones from *Eq.*: if they do not match, we change the assumptions of elemental ratios and/or thermodynamical conditions and repeat the process until convergence is reached (Step 2). To identify optimal solutions – *Opt.* – to explain the observed spectra, we first consider the *T-p* profile, which can be refined through retrieval simulations focused on selected spectral bands that contain information about the atmospheric thermal structure (Step 3). Finally, we use the optimal atmospheric thermal profile from Step 3 to better constrain the chemical environment identified in Step 2, including condensates from equilibrium chemical models (Step 4).

We note that the approach adopted in Steps 3 and 4 cannot guarantee the uniqueness of the optimal solutions found. We explain the key steps of our approach in the following sections.

2.3.1. Pre-selection of chemical and cloud species as priors to retrievals (Step 1)

To identify the most abundant molecular species within the expected temperature and metallicity ranges, we start by assuming the atmosphere to be in chemical equilibrium. We used the GGChem model integrated into TauREx 3 to identify the chemical species and their expected abundances. Elements used in the simulations include H, He, Li, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zr and W (Woitke et al. 2018) with the elemental ratios of the outer solar convection zone as provided by Lodders (2021). For the pre-selection of the chemical species, we have run

Table 1. A list of the datasets used in this study, the reduction algorithms they were processed with, the native spectral resolution and the offsets applied.

Instrument Mode	Reduction Algorithms	Native Res.	Offset [ppm]
NIRISS SOSS	supreme-SPOON	350 - 1,390	68
NIRSpec G395H	ExoTiC-JEDI	1,340 - 2,630	0
NIRSpec PRISM	FIREFLy	20 - 290	-177
NIRCam LW	Eureka!	850 - 1,360	132
MIRI LRS	Eureka!	100	420

the simulations with metallicities ranging from 0.01 to $100 \times$ solar.

In Step 1, instead of simulating condensations with GGChem in the broad parameter space considered, we compared the condensation curves of relevant cloud species at different metallicities occurring in the temperature-pressure regime of WASP-39 b (see Fig. 10 in Woitke et al. 2018) to exclude cloud species that are unlikely to form in the atmosphere of WASP-39 b. MgSiO₃ and SiO₂ are condensable species in the atmosphere of WASP-39 b, according to our estimations.

2.3.2. Free retrieval simulations (Step 2)

As input to the free retrieval simulations, we adopted the values of planetary and stellar parameters reported by Faedi et al. (2011); we started with assuming an isothermal T - p profile. The chemical priors identified in Step 1 were organised into two sets, as detailed in Table 2: we define the active/inactive gases as the molecules in the gas phase being radiatively active/inactive in the relevant wavelength range.

We narrowed the list of chemical species from Step 1 to a sub-sample selected according to their contributions to the atmospheric opacity, either because of their predicted abundance at the equilibrium or because of the strengths of their molecular/atomic transitions in the wavelength range observed by JWST. Opacity data for 80 species were sourced from the ExoMol database¹ (Chubb et al. 2021; Tennyson et al. 2024). The versions of cross-sections used in this work and the references align with Chubb et al. (2024). Among the key opacities used in our simulations and plots, we should mention: SiO (Yurchenko et al. 2022), CO₂ (Yurchenko et al. 2020), H₂O (Polyansky et al. 2018), Na (Allard et al. 2019) and K (Allard et al. 2016), NaH (Rivlin et al. 2015), CO (Polanski et al. 2022), CH₄ (Yurchenko et al. 2024), PN (Semenov et al. 2025), PO (Prajapat et al. 2017), TiO (McKemmish et al. 2019), VO (McKemmish

et al. 2016), SiS (Upadhyay et al. 2018), PS (Prajapat et al. 2017), NaOH (Owens et al. 2021), H₂S (Azzam et al. 2016), NH₃ (Coles et al. 2019), PH₃ (Sousa-Silva et al. 2014), SO₂ (Underwood et al. 2016) and HS (Gorman et al. 2019).

The ExoMol database offers cross-sections at a resolving power of 1.5×10^4 and k -tables for the wavelength range of 0.3–50 μm , which can be directly used by TauREx 3 and many other retrieval models. In addition, we also included collisional-induced absorption (CIA) and Rayleigh scattering. For CIA, we took opacity data for H₂-H₂ and H₂-He pairs from the HITRAN database (Karman et al. 2019)². The Rayleigh scattering estimates for H₂, He, H₂O, and CO₂ were taken from Cox (2015).

To simulate the impact of clouds/hazes in the retrievals, we adopted a distribution of homogeneous cloud particle size and number density to provide a first-order representation of the upper cloud layers, which empirically have smaller optical densities than the deeper layers. We added the contribution of grey clouds to mimic the optically thick cloud layers, as caused by large cloud particle size and/or number density in more complex models. With the addition of grey clouds, the retrieval analysis can focus on exploring the contribution of the smaller particles. Refractive indices of different types of MgSiO₃ clouds and temperature conditions at which these can form are available in the literature (e.g. Jäger et al. (2003), Jaeger et al. (1994), Dorschner et al. (1995), Jaeger et al. (1998), Scott & Duley (1996), Fabian et al. (2000) and Zeidler et al. (2015)). For our analysis, we chose refractive indices of amorphous silicates from Jäger et al. (2003) to estimate their scattering contributions. We chose not to include the absorption estimation for MgSiO₃ clouds due to the uncertainties of the Lorentz-oscillator fit method for amorphous particles. The refractive indices of crystalline SiO₂ are from Zeidler et al. (2013) collected by the HITRAN database.

¹ <https://www.exomol.com/>

² <https://hitran.org/>

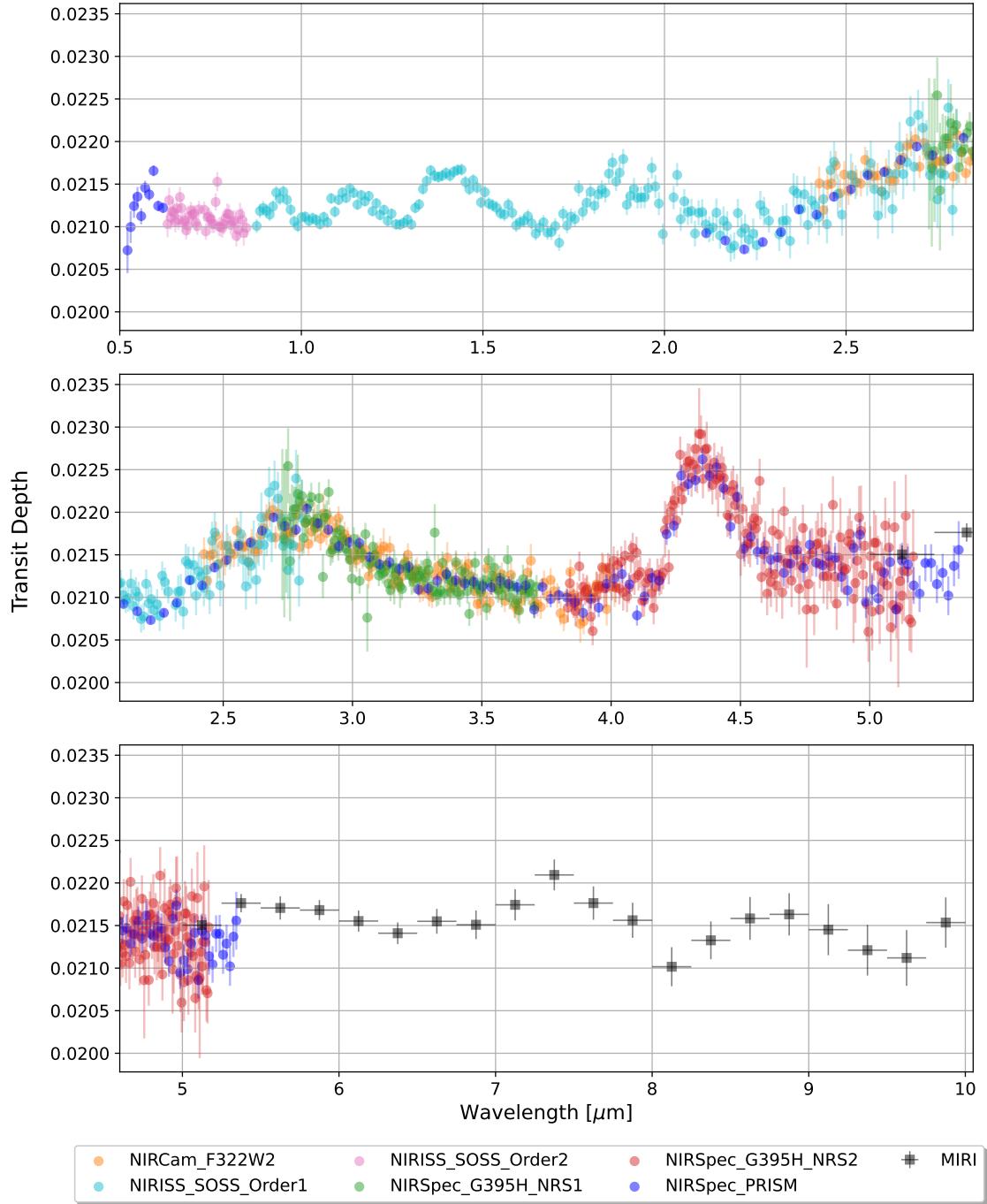


Figure 1. JWST NIRISS, NIRCam, NIRSpec and MIRI observations of WASP-39 b with offsets. The original NIRISS, NIRCam and NIRSpec data are from Carter et al. (2024) and the MIRI data are from Powell et al. (2024). We tuned the offsets according to data in resolutions available; from resolving power of 100 to native resolutions, and here we plotted the native resolution of NIRSpec PRISM data and 1/5 native resolution for the rest of the instruments and modes. We added offsets to data from each instrument using the NIRSpec data as a baseline, as detailed in the main text.

A summary of databases with these refractive indices is provided in Chubb et al. (2024).

In addition, we tested the impact of including CO among our priors. We also added the inactive gases N₂ and Li as proxies of undetectable species potentially

contributing to the atmospheric mean molecular weights (μ) and Rayleigh scattering slopes.

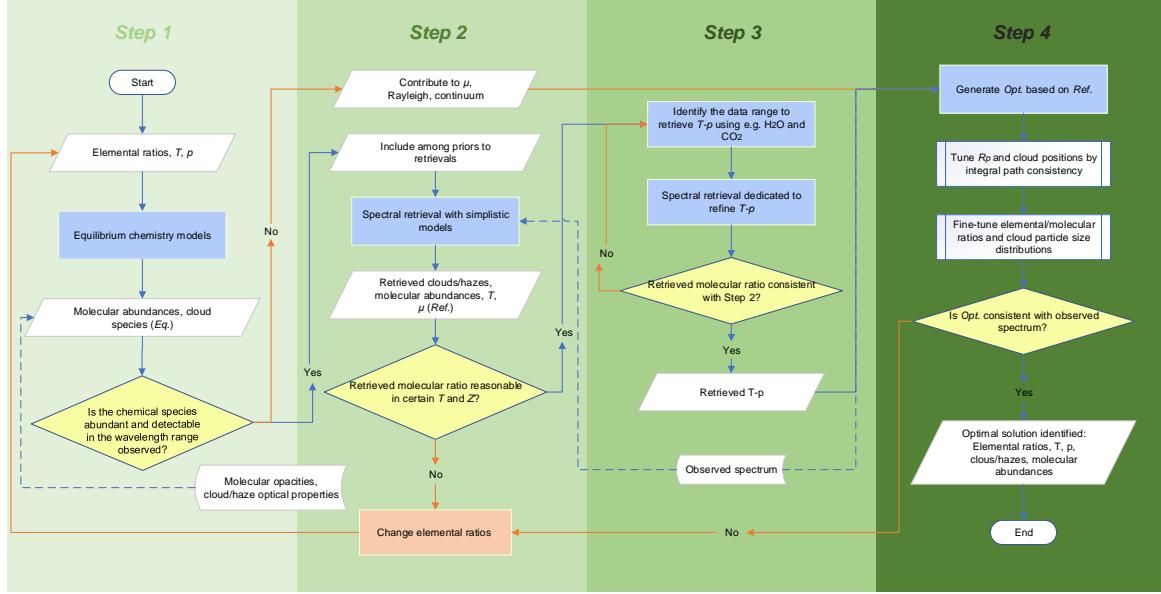


Figure 2. Sketch of the approach to analyse exoplanet transit data adopted in this paper.

Table 2. Priors of spectral retrieval experiments and parameter definitions.

Parameter	Definition	Unit	Mode	Priors
R_p	Distance from planet center to atmosphere base	$\mathcal{R}_{\text{Je}}^N$	factor	0.80 – 1.80
T	Atmospheric temperature	K	linear	500 – 2000
$X_{\text{H}_2\text{O}}$	VMR of H_2O	...	log	$10^{-12} - 10^{-1}$
X_{CO_2}	VMR of CO_2	...	log	$10^{-12} - 10^{-1}$
X_{SiO}	VMR of SiO	...	log	$10^{-12} - 10^{-1}$
X_{Na}	VMR of Na	...	log	$10^{-12} - 10^{-1}$
X_{K}	VMR of K	...	log	$10^{-12} - 10^{-1}$
X_{CO}^*	VMR of CO	...	log	$10^{-12} - 10^{-1}$
$X_{\text{N}_2}^*$	VMR of N_2 , representing heavy-inactive gases	...	log	$10^{-12} - 10^{-1}$
X_{Li}^*	VMR of Li , representing light-inactive gases	...	log	$10^{-12} - 10^{-1}$
r_{HPS}	HPS cloud particle size	m	log	$10^{-7} - 10^{-4}$
N_{HPS}	HPS cloud particle number density	m^{-3}	log	$10^0 - 10^8$
$p_{\text{HPS,deck}}$	HPS cloud deck pressure	Pa	log	$10^{-1} - 10^4$
$p_{\text{HPS,base}}$	HPS cloud base pressure	Pa	log	$10^{-1} - 10^4$
p_{grey}	Grey cloud deck pressure	Pa	log	$10^{-1} - 10^4$

NOTE—VMR represents volume mixing ratio. HPS represents homogeneous particle-size clouds.

*Retrieved parameters in non-reference model experiments.

2.3.3. Optimisation of the atmospheric thermal profile using retrieval techniques (Step 3)

From the posteriors obtained in Step 2, we learned that H_2O and CO_2 are key species absorbing in the atmosphere of WASP-39 b. These molecules have cross sections that are very sensitive to the temperature, as showcased in Fig. 3, so we can use them to constrain the atmospheric T - p profile.

2.3.4. Optimisation of retrieved chemical abundances including clouds (Step 4)

In Step 4, we ran the full equilibrium chemistry model using the T - p profiles obtained in Step 3 as input. Condensation processes and charges were included in the simulations. Approximately 600 chemical species were estimated by GGChem to be present in the atmosphere. However, only a small fraction contributes significantly to the transit spectrum. Through retrieval simulations, we converged to the set of molecular abundances and T - p profiles that better fit the observations and compared them to the predictions of GGChem to verify their consistency and estimate the relative abundances of the muted species a posteriori. This last step is important

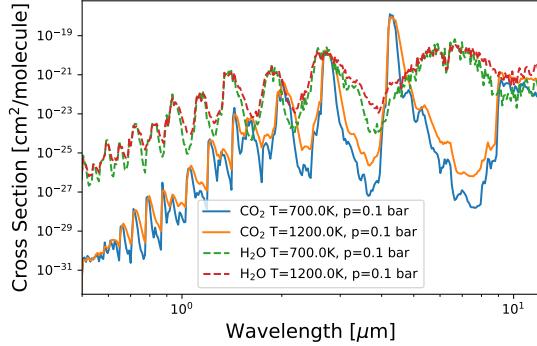


Figure 3. Cross sections of H_2O and CO_2 at two different temperatures at 0.1 bar.

to constrain the metallicity and elemental ratios of the atmosphere.

Given the time gap between the MIRI observations and those obtained with NIRSpec, NIRCam, and NIRISS, we have also conducted a separate cloud particle size distribution optimisation that considers only the MIRI observations alongside the homogeneous analysis across the entire spectrum available. For the potential contamination longwards $10 \mu\text{m}$ mentioned in Section 1, we have prioritised the observations shortwards $10 \mu\text{m}$ in model optimisation. Our iterative approach, moving from equilibrium chemistry modelling to retrievals and back to equilibrium chemistry modelling, aims to constrain molecular species – in gaseous form or condensed – with prominent spectral features, and then use their molecular abundances as baseline assumptions for deeper analysis with more complex atmospheric models.

3. RESULTS

3.1. Selection of chemical species for free retrievals

The selection process described in 2.3.1 (Steps 1 and 2) identifies species that are expected to be abundant according to models assuming chemical equilibrium but also to have large cross sections in the wavelength range probed by JWST, making them the most likely contributors to the transit spectra of WASP-39 b. The active gaseous species playing a major role in our retrieval experiments are: H_2O , CO_2 , SiO , Na and K . A more comprehensive selection of active chemical species is reported in Appendix A. We also report there how molecular abundances change with metallicity and temperature at the relevant pressures probed in the exoplanet atmosphere.

Some gaseous species were excluded from the selection of priors during preliminary retrieval tests because their spectral features are completely masked by other species within a reasonable abundance range, despite being highlighted in the initial selections and showing

features similar to those in observations. For example, SiS is predicted to be abundant in the atmosphere of WASP-39 b under chemical equilibrium conditions. However, its spectral features are less prominent than those of other selected species. Only if SiS 's abundance exceeded those of H_2O and CO_2 by an order of magnitude, an unlikely scenario, would its features become discernible in the transit depth rather than being obscured by other molecular signatures. However, in such a case, SiS would significantly increase the mean molecular weight, reducing the atmospheric scale height and compressing the overall molecular features in a way that is not compatible with the observations.

3.2. Free retrieval results

In Steps 2 and 3, we performed free retrievals to constrain the gas abundances and thermal profiles. Fig. 4 shows the posterior distributions obtained in Step 2, where T - p profiles are kept constant. Here, two islands of solutions (Solution 1 and 2) are found, stemming from the degeneracy of the MgSiO_3 HPS clouds. Both retrieved solutions fit the observed spectrum with no statistical preference as suggested by their Bayesian evidence. Despite the apparent degeneracy, the gas-phase species' abundances in the two cloud solutions are consistent. While the cloud particle radius in Solution 2 is larger than in Solution 1, the particle number density is three orders of magnitude lower. As a result, the opacity density of the HPS cloud in Solution 2 is lower, but it is still detectable in transit due to its high altitude. We show the spectral fit and optical depth details of the optimised retrieval in Appendix B. Test cases where CO or muted species (N_2 or Li) are displayed in Appendix C.

From the free retrieval tests in Step 2, we identified the spectral windows 2.5 – 3.5 and 4.2 – $4.8 \mu\text{m}$ – where H_2O and CO_2 absorb – as being the most informative to further constrain the T - p profile. We show in Fig. 5 the optimal T - p profile as retrieved in Step 3 and an example of GGChem simulations with condensates using the optimal T - p profile as input.

3.3. Optimal solutions to Webb data

Fig. 6 shows the abundances of the gaseous species as a function of pressure for the optimal solution: these were obtained by fine-tuning the results obtained with GGChem to better reproduce Webb's data. Only the VMRs of the most abundant active gases are shown in Fig. 6. The optimal solution in the gas phase corresponds to the following elemental ratios: $2.27 \times \text{O/H}$, $1.39 \times \text{C/H}$, $1.67 \times \text{Si/H}$, $3.35 \times \text{S/H}$, $2.06 \times \text{Na/H}$, $0.55 \times \text{K/H}$ with respect to the solar photospheric abundance ratios from Lodders (2021).

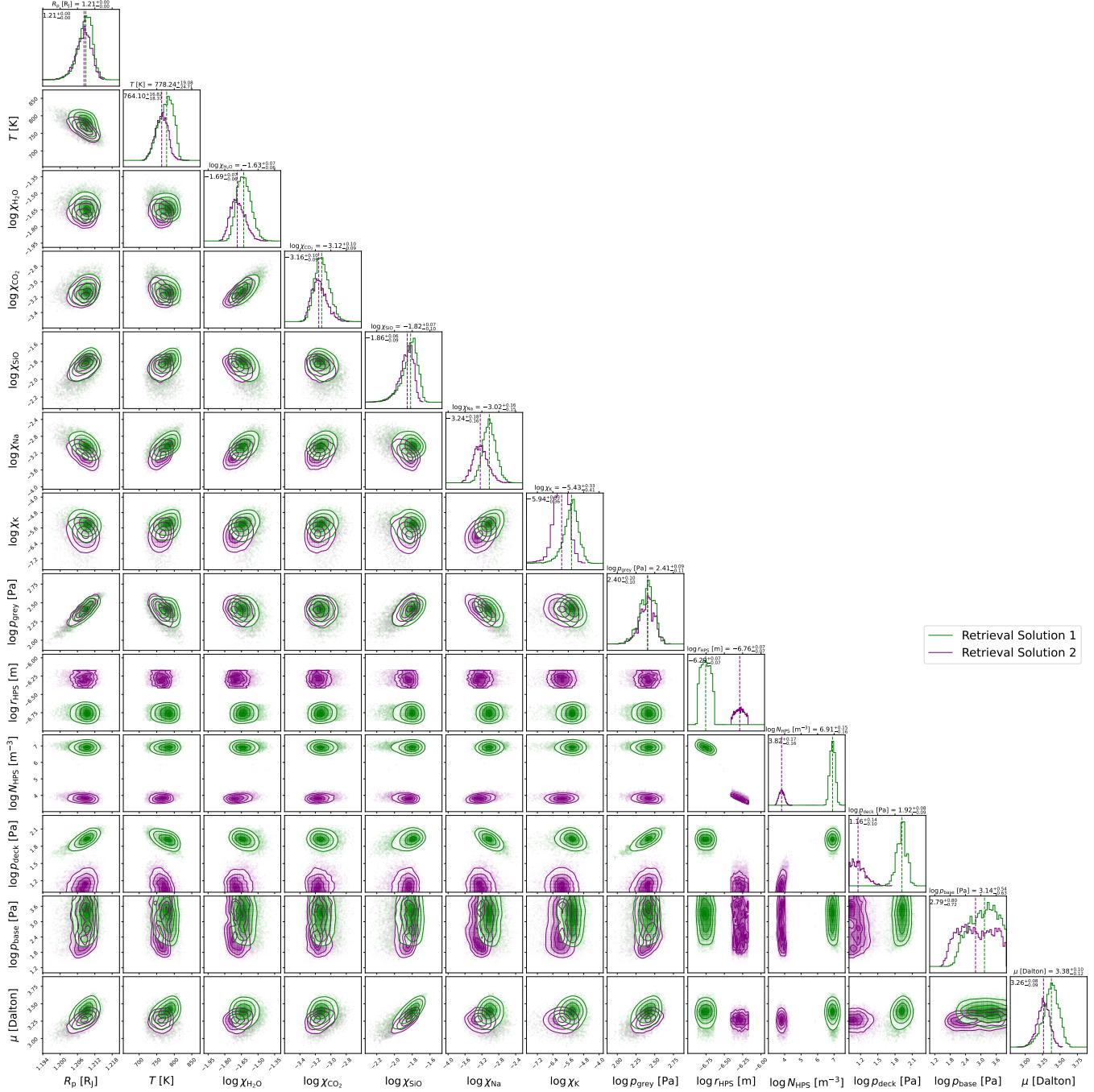


Figure 4. Posterior distributions obtained with free retrievals of NIRISS, NIRSpec and NIRCam spectra. We find two islands of solutions (green and purple) originating from the degeneracy of HPS clouds. The numbers above each block represent the median value of the posteriors. The results suggest a significant amount of H_2O , SiO and CO_2 in the observable atmosphere. We plot the highest weighted 2×10^4 traces for visual ease.

In addition to the gaseous species, we have found that HPS clouds of multiple particle sizes are needed for an optimal fit. In our simulations, we have included three particle sizes for SiO_2 , i.e. 0.01, 0.4 and $0.8 \mu\text{m}$, and one for MgSiO_3 clouds, i.e. $10 \mu\text{m}$. The fit to the MIRI data can be improved if we use $1 \mu\text{m}$ particle-size for SiO_2 while keeping the MgSiO_3 particle size.

In Fig. 7, 8, 9, 10 & 11 the final simulated spectra are plotted against the data.

4. DISCUSSION

4.1. Silicon versus sulphur chemistry to explain JWST spectra of WASP-39 b

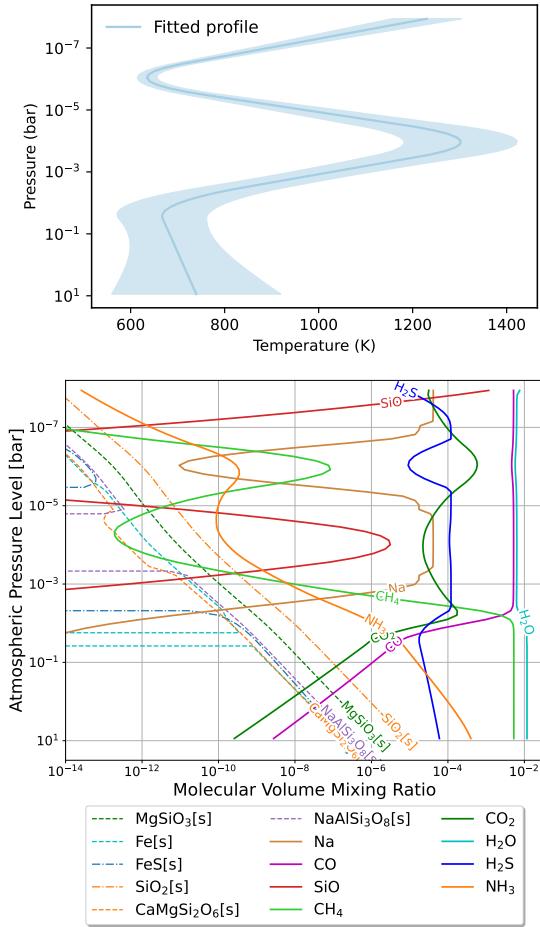


Figure 5. Retrieved T - p profile (Opt. T - p) and an example of the most abundant active gas (max. VMR $> 10^{-5}$) and condensate species (max. VMR $> 10^{-7}$) obtained with GGChem simulations using the median retrieved T - p values as input.

The previous literature suggested SO₂ as an explanation of the features at 4.1, 7.7 and 8.5 μm (see Section 1.3 and Fig. 12). Strong photochemical processes in the upper atmosphere are needed to explain the abundance of SO₂. While we are not excluding the presence of SO₂, we propose here that the spectral feature observed at 4.1 μm is mainly caused by SiO (Fig. 9) and the features at 7.7 and 8.5 μm can be explained by silicate clouds (Fig. 11). Results from our retrieval analyses suggest H₂O, CO₂, SiO, silicate clouds, Na, and K can fit well NIRISS, NIRSpec, NIRCam and MIRI observations. Further optimisation with both shorter wavelengths and MIRI observations helped to constrain the particle sizes, composition and location of silicate clouds. The presence and abundances of both gas and condensate species are compatible with a scenario of chemical equilibrium at the temperatures expected for this planet.

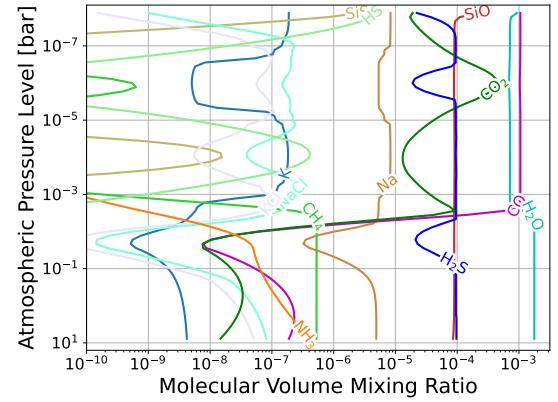


Figure 6. Optimised VMRs of the active gases as a function of pressure: these were obtained by fine-tuning the results obtained with GGChem to better reproduce JWST's data. Only the most abundant gases are plotted here for visual ease.

4.2. Self-consistency with equilibrium chemistry and condensation

Chemical equilibrium simulations that do not account for condensation represent an extreme case, where the gas-phase molecules remain abundant in the atmosphere; in other words, gas-phase molecules supersaturate instead of condensing out. By contrast, chemical equilibrium simulations including condensation represent another extreme case, as they predict maximum depletion from condensation processes. In the simulations performed as part of this study with GGChem assuming condensation, multiple species of silicate form, with MgSiO₃ and SiO₂ having the highest abundance in the observable atmosphere. We expect the real situation to be more complex, due, e.g., to atmospheric circulation and mixing, and with silicate clouds and gases being transported from different temperature-pressure regions to where we observe them. For these reasons, in Step 4 we have examined both the simulations with and without condensation, to find a reasonable middle ground of the distribution of clouds and gas species compatible with the observations.

Additional complexity arises from uncertainties in cloud particle materials, forms, shapes and size distributions. A more detailed understanding of the annealing and crystallisation processes might be needed to fully grasp the cloud microphysics and properties. However, we defer these aspects to future studies, pending more advanced laboratory and observational data from both within and beyond the solar system.

4.2.1. Cloud properties in retrievals

Our retrieval simulations have indicated that gas-phase species alone may not account for the observed

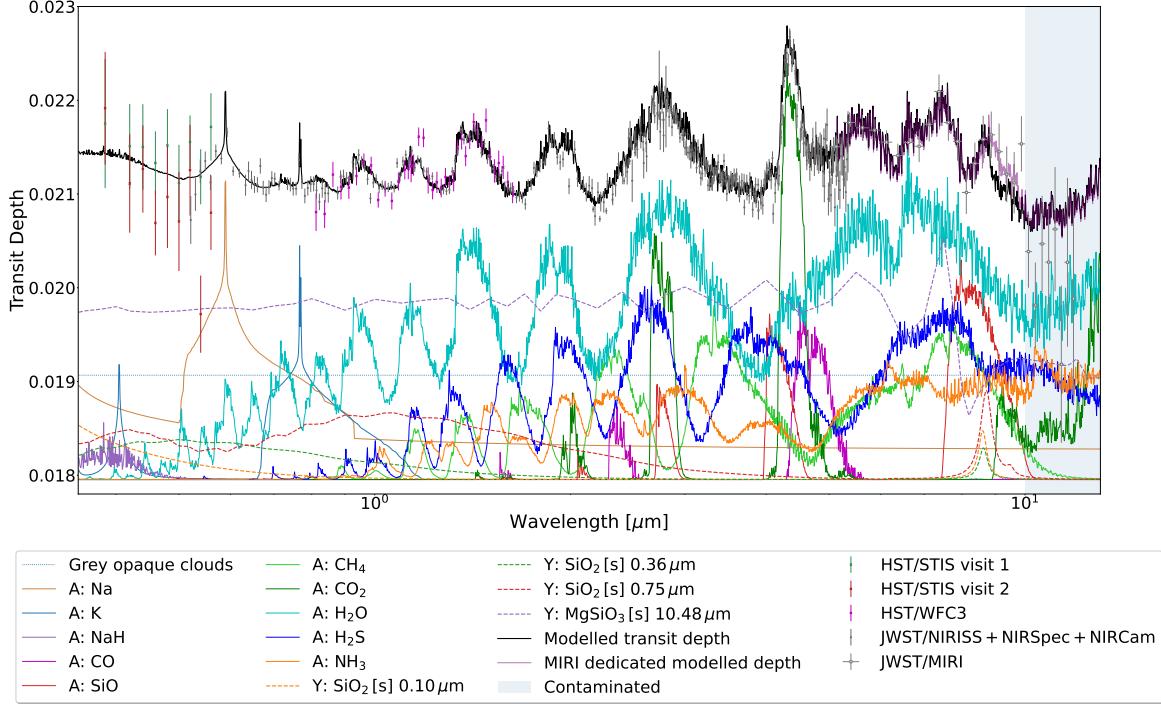


Figure 7. Best fit to the JWST spectral data (black and purple spectra). A : individual gas-phase absorption, Y : cloud absorption and scattering assuming specific cloud particle radii in the simulations. We only plotted the most significant opacity contributors for visual ease. Rayleigh scattering and collision-induced absorption (CIA) are not shown for the same reason. NIRISS, NIRSpec and NIRCam spectral data are taken from Carter et al. (2024), MIRI data from Powell et al. (2024) and Hubble STIS and WFC3 data from Saba et al. (2024). Details of the data used and offsets adopted here are described in section 2.1. Beyond $10\mu\text{m}$, the MIRI spectrum is potentially contaminated according to Flagg et al. (2024).

opacity in the optical and infrared wavelength range. While clouds can explain the missing opacity, they also represent a complex challenge for atmospheric characterisation, requiring significantly higher statistical and computing capabilities. Studies that include clouds need to balance the trade-offs between parametric/characteristic models and more complex micro-physics models. There have been efforts to model cloud formation on WASP-39 b, as discussed by Arfaux & Lavvas (2024), who compared cloud models of varying complexity, highlighting their respective strengths and limitations. However, due to the uncertainties in the underlying atmospheric chemistry and dynamics, key aspects of the cloud properties on WASP-39 b, such as cloud composition and size distribution, remain ambiguous. Detailed parameters like particle shapes, contact angles and surface tension are beyond the reach of current observational capabilities. Therefore, an optimal strategy for interpreting the available data is to begin with simplified cloud models in retrievals, allowing optimised flexibility in particle size distributions. More advanced cloud retrieval methods, such as those proposed by Ma et al. (2023), are theoretically feasible but are better suited for follow-up studies once a more precise understanding of the basic atmospheric chemistry

and dynamics is established. By constraining the dimensionality of the models and refining the priors to fit the parameters, our approach allows for more efficient and tailored retrievals. Therefore, as an optimisation for the current JWST retrieval studies, we chose to use a characteristic HPS model plus a grey cloud model, as detailed in Section 2.3.2.

4.2.2. Optimisation using self-consistent models

As explained in Section 3.3, the direct indication from retrieval results is the ratios between major tracers. The relative abundances between species determine the shape of the transit depth versus wavelengths. Indirectly, the retrieved results constrain the metallicity and temperature.

Parameters such as the absolute abundances of major tracers may shift due to the exclusion of most of the species (see Section 2.3.1 and 3.1) during retrieval. These unselected species have two major impacts on the spectrum: their mass tunes the atmospheric scale height, and their cumulative opacities contribute directly to the spectrum's continuum. While the inclusion of a grey cloud model mitigates the latter impact to a certain extent, as a result, the retrieval algorithm adjusts other atmospheric properties, such as density

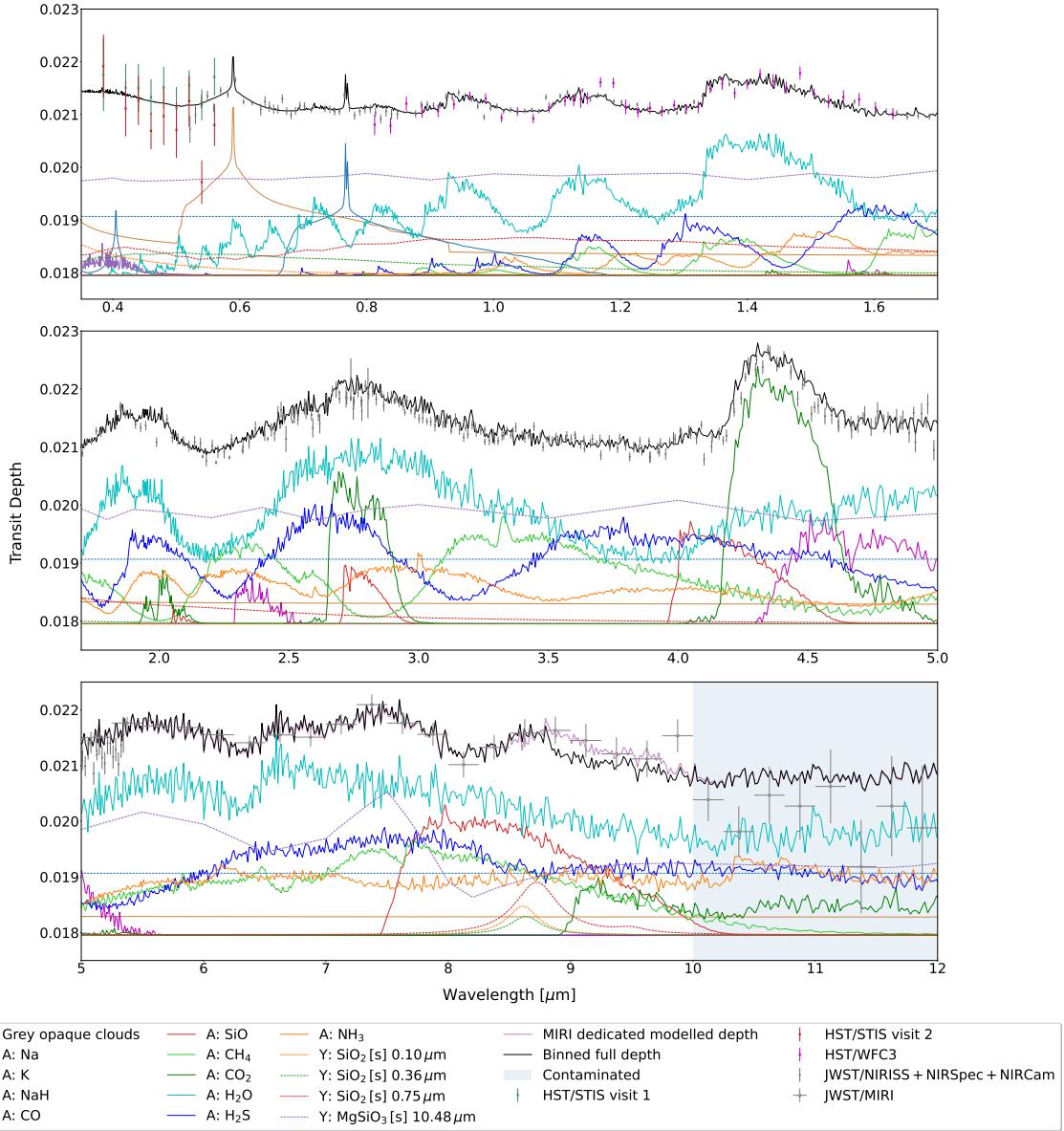


Figure 8. Zoom in of Fig. 7 in different spectral windows.

and temperature, to optimise the integration path and maintain the strength of key spectral features.

4.3. Uncertainties and suggestions

Attention is needed to select the initial elemental ratios and condensation processes. Although certainty cannot be guaranteed, our study relies on accepted knowledge, with sufficient margins to account for uncertainties in thermal profiles, elemental ratios, and condensation processes. Additionally, more accurate opacity data of varied temperature and pressure could help resolve the degeneracy between temperature, metallicity, and other parameters. However, conducting laboratory experiments under conditions that replicate those

found in extraterrestrial environments remains challenging.

As the reported values for the atmospheric properties are sensitive to and heavily dependent on atmospheric model assumptions – including the species considered in the chemistry and opacity – we highlight the importance of clarifying in models the molecular species assumed:

- in calculating the basic atmospheric properties, e.g., mean molecular weight;
- as opacity sources contributing to the transit depth;

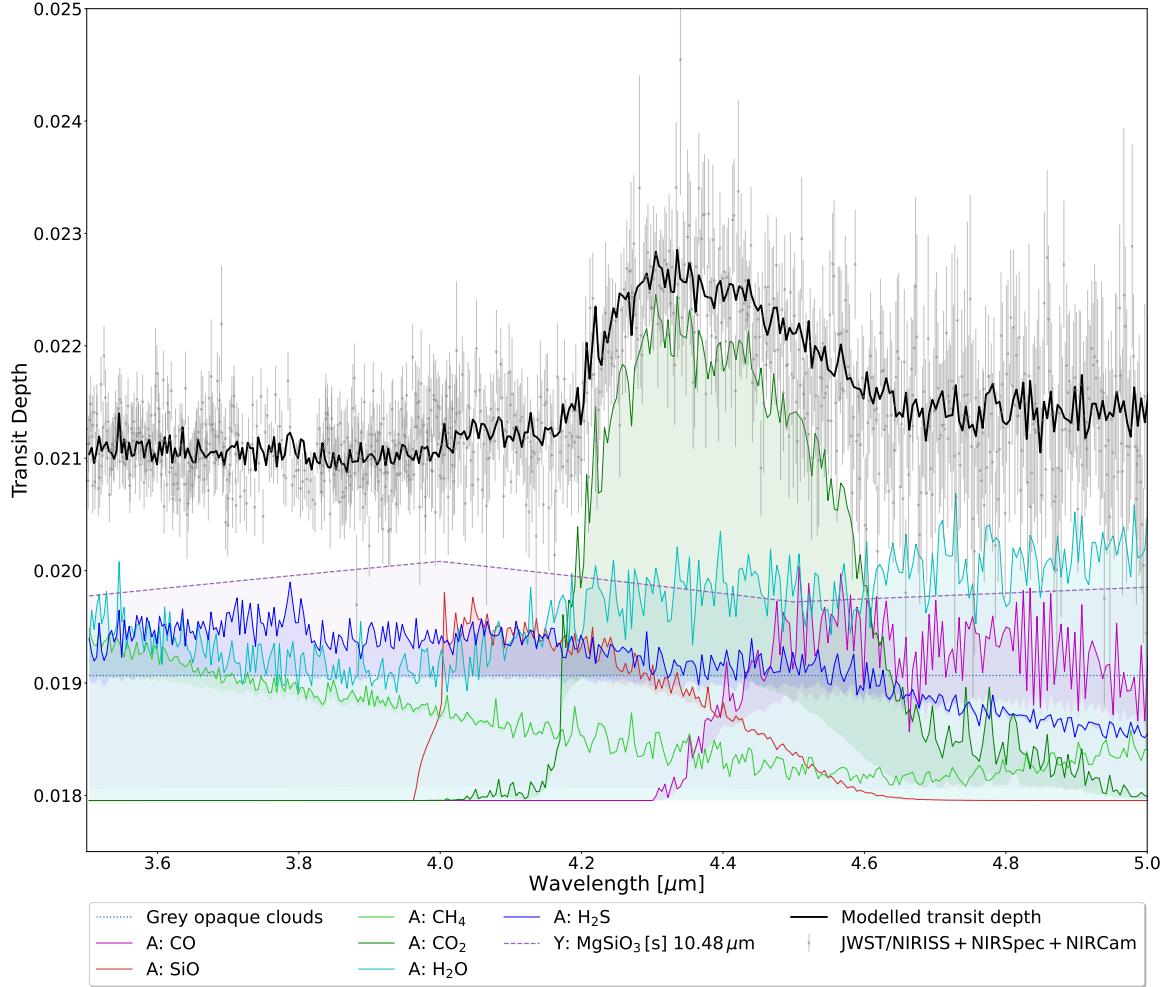


Figure 9. Zoom in around $4.1\ \mu\text{m}$ of Fig. 7. The model is compared with the native-resolution observations (grey data points with error bars). To reveal their altitude dependence, we plot as shaded areas the gas-phase molecular absorptions integrated from $10^{-1}\ \text{bar}$ to the top of the atmosphere.

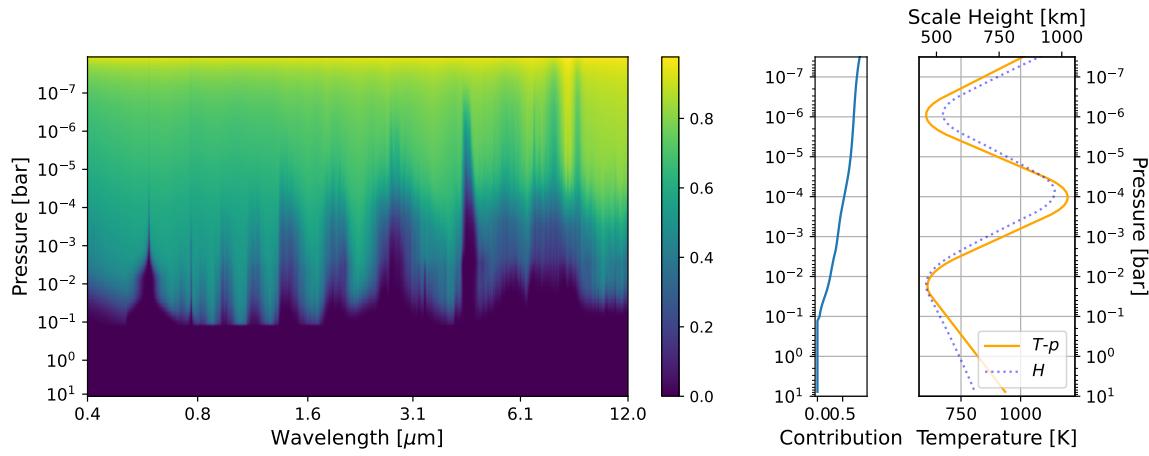


Figure 10. Estimated optical depths through optical paths centred at each pressure level (left panel), wavelength-normalised opacity contributions (central panel), adopted temperature profile and estimated scale heights (right panel).

- in deriving the elemental ratios to facilitate easier understanding and comparison of results in future work.

In addition, some misunderstanding of literature values may stem from different definitions of metallicity.

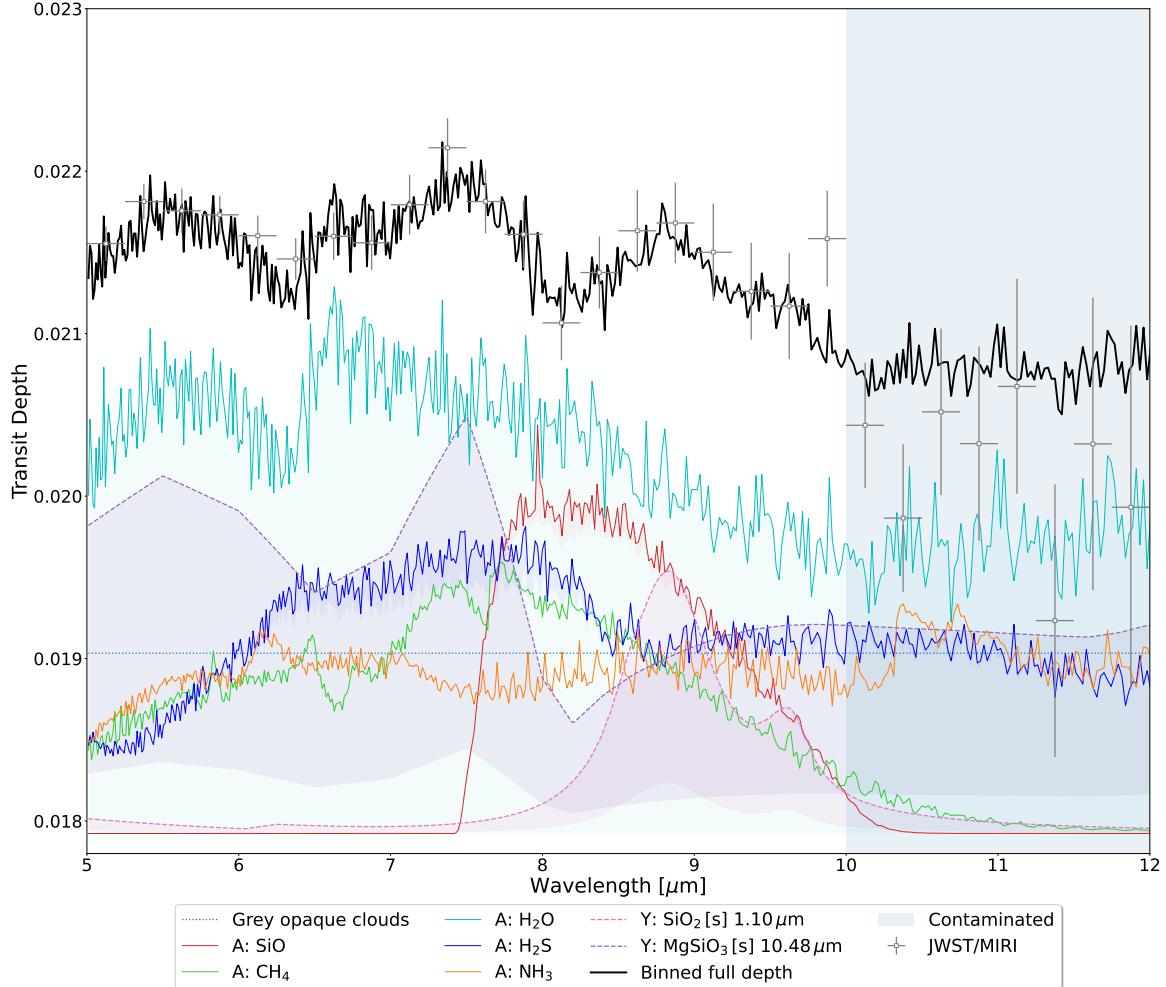


Figure 11. Similar to Fig. 9, zoom in of the MIRI window of the MIRI-focused fit in Fig. 7. We plot as shaded areas the gas-phase molecular absorptions integrated from 10^{-3} bar to the top of the atmosphere.

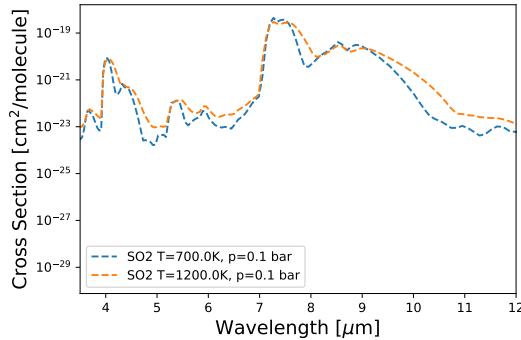


Figure 12. Cross sections of SO₂ from Underwood et al. (2016) collected by the ExoMol database.

In this paper, we followed the definitions summarised by Hinkel et al. (2022) (see also the review by Swain et al. (2024)). We report the values of the total volume fraction for all elements other than H₂ and He relative to solar and report the elemental ratios to H directly in

the final results. For the benefit of future work in the field, we advocate for clarity in specifying the reference and which elemental abundance (e.g., solar photosphere or protostellar disk) is being used, whether in mass ratios or volume ratios, linear or log scales, solar units or absolute values when referring to the term "metallicity".

5. CONCLUSIONS

We have studied the chemical composition and cloud/haze formation in the atmosphere of WASP-39 b, using recent JWST spectroscopic, transit observations of this planet to inform our hypotheses and models. For this work, we have used a novel, hybrid approach that combines multistep, free retrieval simulations using the results of equilibrium chemistry models and cloud microphysics to constrain the priors.

Our analysis suggests that, in addition to H₂O, CO₂, Na and K, already identified in previous works in the literature, Silicon-based chemistry plays a major role in shaping the chemistry and condensates of the atmos-

sphere of WASP-39 b. Our Bayesian retrievals strongly support the presence of the gas-phase SiO together with MgSiO₃ and SiO₂ clouds to explain the observed spectral features around 4.1, 7.5 and 8.8 μm . This scenario is compatible with results from equilibrium chemistry models. H₂O and CO₂ absorptions in the 2.5–3.5 and 4.2–4.8 μm spectral windows were used to constrain the thermal profile as a function of pressure.

Previous literature suggested SO₂ as an explanation of the features at 4.1, 7.7 and 8.5 μm . While we are not in a position to exclude this possibility, strong photochemical processes in the upper atmosphere are needed to explain the high abundance of SO₂ required to fit the data and it is therefore important to explore alternative scenarios.

Our optimal solution in the gas phase corresponds to the following elemental ratios: $2.27 \times \text{O/H}$, $1.39 \times \text{C/H}$, $1.67 \times \text{Si/H}$, $3.35 \times \text{S/H}$, $2.06 \times \text{Na/H}$, $0.55 \times \text{K/H}$ with respect to the solar photospheric abundance ratios from [Lodders \(2021\)](#). In addition to the gaseous species, our optimal solution includes three particle sizes for SiO₂, i.e. 0.01, 0.4 and 0.8 μm , and one for MgSiO₃ clouds, i.e. 10 μm . The fit to the MIRI data is improved if we use 1 μm particle-size for SiO₂ while keeping the MgSiO₃ particle size.

While the solution proposed here is able to faithfully match all JWST and HST data, we are not in a position to claim its uniqueness, as the method adopted does not comprehensively scan the parameter space of possible chemical species – in gas or solid/liquid phase – and thermodynamical conditions. However, our hybrid approach that combines optimised free retrievals and complex forward models, offers higher flexibility and robustness to interpret spectroscopic data compared to previous efforts. For instance, it leverages Bayesian statistics for the sampling algorithm to search for solutions based on observational data, while minimising biases from prior scientific knowledge. In addition, self-consistent atmospheric models allow to limit the number of implausible scenarios considered by free retrievals, by constraining the priors with physically informed models.

To further investigate and confirm the chemical and elemental composition of the atmosphere of WASP-39 b, additional spectroscopic data, such as very high-spectral resolution data from the ground aimed at detecting SO₂ and SiO, would be needed.

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Facility: JWST (NIRISS, NIRCAM, NIRSpec), HST (STIS, WFC3)

Software: python 3.10.0, numpy 1.26.0 ([Harris et al. 2020](#)), scipy 1.14.0 ([Virtanen et al. 2020](#)), pymultinest 2.12 ([Buchner et al. 2014](#)), astropy 5.3.4 ([Astropy Collaboration et al. 2022, 2018, 2013](#)), numba 0.59.0 ([Lam et al. 2015](#))

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APPENDIX

A. CHEMICAL SPECIES SELECTION IN WIDE PARAMETER SPACE

We conducted the chemical species selection following the methodology described in Section 2.3.1 covering the parameter space expected for WASP-39 b, i.e. assuming as temperatures 700, 900, 1100, 1300 and 1500 K, and as volume metallicities 0.4, 4, 29 and $67 \times$ solar volume metallicity. The metallicity values are estimated

from the constant species' abundance cases with molecular volume mixing ratios (VMRs) of 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} . To maintain consistency between the equilibrium and homogeneous abundance simulations, we aim to keep the atmospheric metallicity and mean molecular weight within 20% difference between the two sets of simulations. We list the highlighted species in Table 3. Examples of key molecular abundances as a function of metallicity and temperature are given in Fig. 13.

Table 3. Highlighted chemical species by the methodology in Section 2.3.1.

V/MR*	Met. Δ	T_{eq} [K]	Highlighted Species
<i>Eq.</i> Profiles	0.4	700	CH_4 , Na, H_2O , CrH, PH_3 , NH_3 , SiH_4 , H_2S , SiO
Constant Profiles 10^{-6}	0.4	700	SiH_4 , PH ₃ , CO ₂ , CrH, Na, CH ₄ , NH ₃ , CO, H ₂ O
<i>Eq.</i> Profiles	0.4	900	H ₂ O, Na, CH ₄ , CrH, PH_3 , CO, H ₂ S, SiO, NH ₃ , SiH ₄
Constant Profiles 10^{-6}	0.4	900	SiH_4 , PH ₃ , CrH, CH ₄ , Na, NH ₃ , H ₂ O, CO, H ₂ S, SiO
<i>Eq.</i> Profiles	0.4	1100	H ₂ O, Na, CrH, CO, CH ₄ , H ₂ S, SiO, NH ₃
Constant Profiles 10^{-6}	0.4	1100	CrH, CH ₄ , Na, NH ₃ , H ₂ O, CO, H ₂ S, SiO
<i>Eq.</i> Profiles	0.4	1300	H ₂ O, Na, CO, CrH, H ₂ S, CH ₄ , SiO, NH ₃
Constant Profiles 10^{-6}	0.4	1300	Cr, CH, N, NH, H ₂ , C, H ₂ , Si, SH
<i>Eq.</i> Profiles	0.4	1500	H ₂ O, Na, CO, H ₂ S, SiO, CH ₄ , NH ₃
Constant Profiles 10^{-6}	0.4	1500	CH ₄ , Na, NH ₃ , H ₂ O, CO, H ₂ S, SiO, SH
<i>Eq.</i> Profiles	4	700	CO_2 , CH ₄ , Na, PH_3 , H ₂ O, C H , K, NaOH, H ₂ S, NH ₃ , SiO, SiH ₄ , CO
Constant Profiles 10^{-5}	4	700	SiH_4 , PH ₃ , CO ₂ , NaOH, CH ₄ , CrH, K, Na, NH ₃ , H ₂ O, CO, H ₂ S, SiO
<i>Eq.</i> Profiles	4	900	CaOH, CO ₂ , H ₂ O, Na, CH ₄ , PH ₃ , CO, CH ₄ , K, H ₂ S, SiO, NaOH, NH ₃ , SiH ₄
Constant Profiles 10^{-5}	4	900	CaOH, SiH ₄ , PH ₃ , CO ₂ , NaOH, CH ₄ , CrH, Na, K, NH ₃ , H ₂ O, CO, H ₂ S, SiO
<i>Eq.</i> Profiles	4	1100	CaOH, CO ₂ , H ₂ O, Na, CH ₄ , CO, PH ₃ , K, H ₂ S, MgH, CH ₄ , SiO, NH ₃ , SiS
Constant Profiles 10^{-5}	4	1100	CaOH, CO ₂ , PH ₃ , CH ₄ , MgH, CrH, Na, K, NH ₃ , H ₂ O, H ₂ S, CO, PS, SiO, SH
<i>Eq.</i> Profiles	4	1300	CaOH, TiO, H ₂ O, CO ₂ , Na, CO, CrH, H ₂ S, MgH, K, PH ₃ , SiO, CH ₄ , NH ₃ , SiS
Constant Profiles 10^{-5}	4	1300	CaOH, TiO, CO ₂ , PH ₃ , MgH, CH ₄ , CrH, NH ₃ , Na, K, H ₂ O, PS, H ₂ S, CO, PO, SiO, SH
<i>Eq.</i> Profiles	4	1500	TiO, H ₂ O, CO ₂ , Na, CO, MgH, CrH, H ₂ S, K, PH ₃ , SiO, CH ₄ , NH ₃ , SiS, SH
Constant Profiles 10^{-5}	4	1500	TiO, CO ₂ , PH ₃ , MgH, CH ₄ , CrH, NH ₃ , Na, K, H ₂ O, PS, H ₂ S, CO, SO, PO, SiO, SH, SiS, AF
<i>Eq.</i> Profiles	29	700	CO_2 , CH ₄ , Na, H ₂ O, PH ₃ , C H , CO, NaOH, K, H ₂ S, SiO, NH ₃
Constant Profiles 10^{-4}	29	700	SiH_4 , PH ₃ , NaOH, CO ₂ , CH ₄ , CrH, K, Na, NH ₃
<i>Eq.</i> Profiles	29	900	CaOH, CO ₂ , H ₂ O, Na, CrH, CO, PH ₃ , K, H ₂ S, CH ₄ , NaOH, SiO, NH ₃
Constant Profiles 10^{-4}	29	900	CaOH, SiH ₄ , PH ₃ , CO ₂ , NaOH, CH ₄ , CrH, NH ₃ , Na, K, H ₂ O, H ₂ S,
<i>Eq.</i> Profiles	29	1100	CaOH, CO ₂ , H ₂ O, Na, CrH, CO, H ₂ S, K, PH ₃ , MgH, NaOH, SiO, CH ₄ , NH ₃ , SiS
Constant Profiles 10^{-4}	29	1100	CaOH, CO ₂ , PH ₃ , NaOH, CH ₄ , MgH, CrH, NH ₃ , Na, K, H ₂ O, H ₂ S, PS, CO, PO, SiO
<i>Eq.</i> Profiles	29	1300	CaOH, CO ₂ , TiO, H ₂ O, Na, H ₂ S, CO, CrH, MgH, K, PH ₃ , SiO, NaOH, CH ₄ , NaH, NH ₃ , SiS
Constant Profiles 10^{-4}	29	1300	CaOH, TiO, CO ₂ , PH ₃ , NaOH, CH ₄ , MgH, CH ₄ , NH ₃ , NaH, Na, K, H ₂ O, PS, H ₂ S, SO, CO, PO, SiO
<i>Eq.</i> Profiles	29	1500	CO_2 , TiO, H ₂ O, Na, CO, H ₂ S, MgH, CrH, K, SiO, PH ₃ , AlO, NaOH, NaH, PS, NH ₃ , CH ₄ , SiS, PO, SH
Constant Profiles 10^{-4}	29	1500	TiO, CO ₂ , PH ₃ , AlO, NaOH, CH ₄ , MgH, CrH, NH ₃ , NaH, SO ₂ , Na, K, H ₂ O, PS, H ₂ S, SO, CO, PO, SiO, SH, HF
<i>Eq.</i> Profiles	67	700	CO_2 , CH ₄ , Na, H ₂ O, CrH, PH ₃ , NaOH, CO, K, H ₂ S
<i>Eq.</i> Profiles	67	900	CaOH, CO ₂ , H ₂ O, Na, CrH, CO, PH ₃ , H ₂ S, K, NaOH, CH ₄ , SiO
<i>Eq.</i> Profiles	67	1100	CaOH, CO ₂ , H ₂ O, Na, CrH, H ₂ S, CO, K, PH ₃ , MgH, NaOH, SiO, CH ₄ , NH ₃ , NaH
<i>Eq.</i> Profiles	67	1300	CaOH, CO ₂ , H ₂ O, TiO, Na, H ₂ S, CO, CrH, MgH, K, PH ₃ , NaOH, SiO, NaH, CH ₄ , NH ₃ , SiS
<i>Eq.</i> Profiles	67	1500	CO_2 , TiO, H ₂ O, Na, CO, H ₂ S, MgH, CrH, K, SiO, PH ₃ , NaOH, AlO, PS, NaH, PO, NH ₃ , CH ₄ , SiS, SiO ₂ , SH

Note.—*Volume mixing ratio of the species used in the transit depth simulation. Δ Volume metallicity in solar abundances.

B. OPTIMIZED RETRIEVAL CONVERGENCE AND TRACE DETAILS

In both solutions reported in Section 3.2, H₂O and CO₂ fit the main spectral features, while SiO supports the feature around 4.1 μm . Na and K align with features around 0.6 and 0.8 μm in the optical. Grey clouds provided the continuum from optical to near-infrared. In both cases, the homogeneous particle-size (HPS) clouds contributed to the optical continuum. We show the details of the altitude-dependent optical depths and cloud contribution for the two solutions in Fig. 14.

The Maximum A Posteriori (MAP) results, representing the statistical local optimisation, are consistent with the medium values shown in Fig. 4 above each his-

togram. The MAP values are the sets of parameter values that reach the maximum likelihood. In well-constrained retrieval with chi-square posterior distributions, the set of median values is expected to fit the spectrum despite not being from the same retrieval sampling trace, which shows the good convergence of the algorithm. When the parameters obtain a non-normal probability distribution, the median values will not necessarily fit the spectrum; however, this should not be the case in our study, given the nature of the parameters we are investigating. We list the median values of posteriors and the first ten MAP traces in Table 4 of the two retrieval solutions of our reference model in Section 3.2.

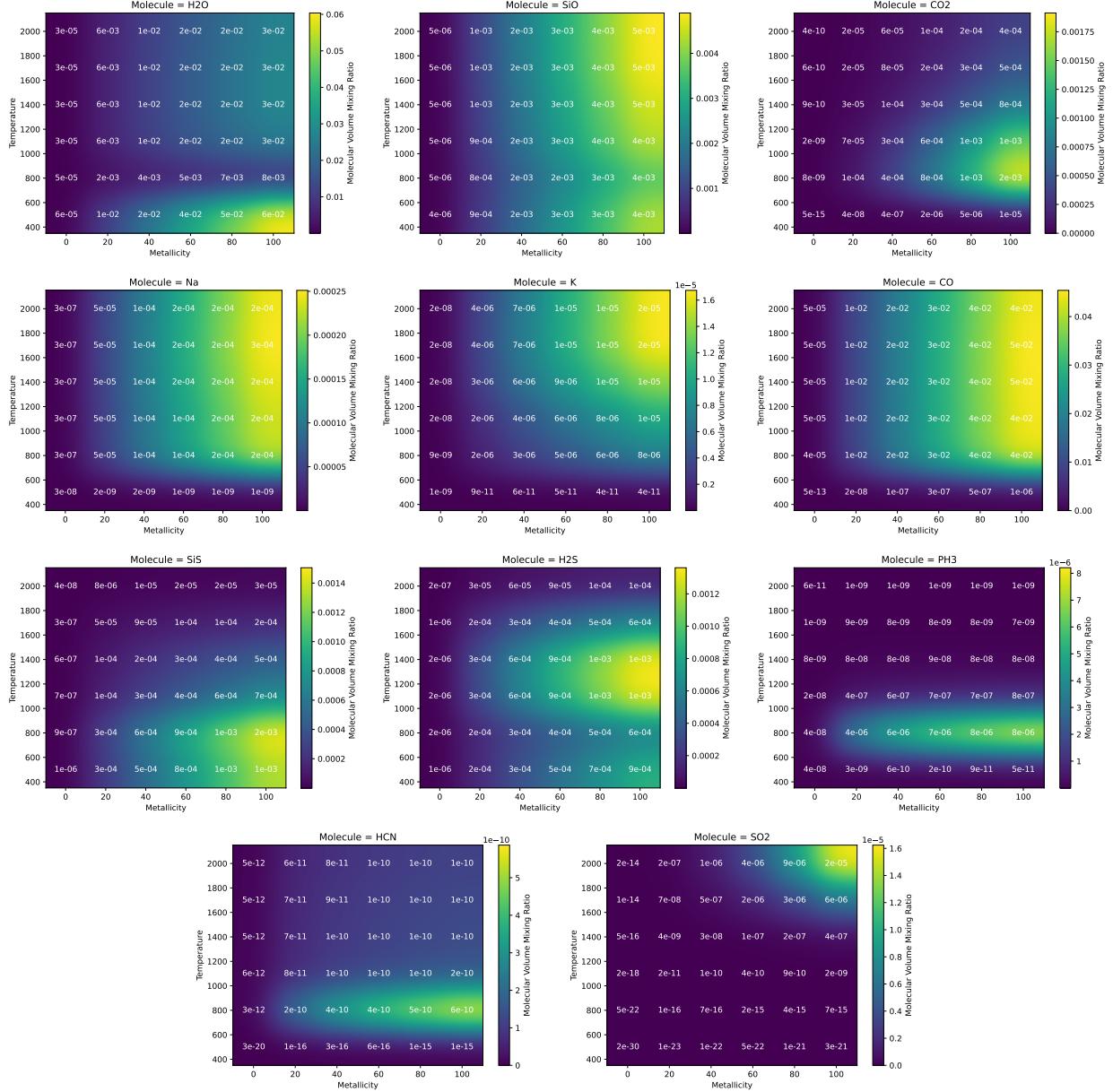


Figure 13. Examples of molecular abundances from equilibrium chemistry in the temperatures and metallicities regime of WASP-39 b's atmosphere. These plots showcase results at a pressure of $\sim 10^{-3}$ bar. Note the colour scales vary for each plot.

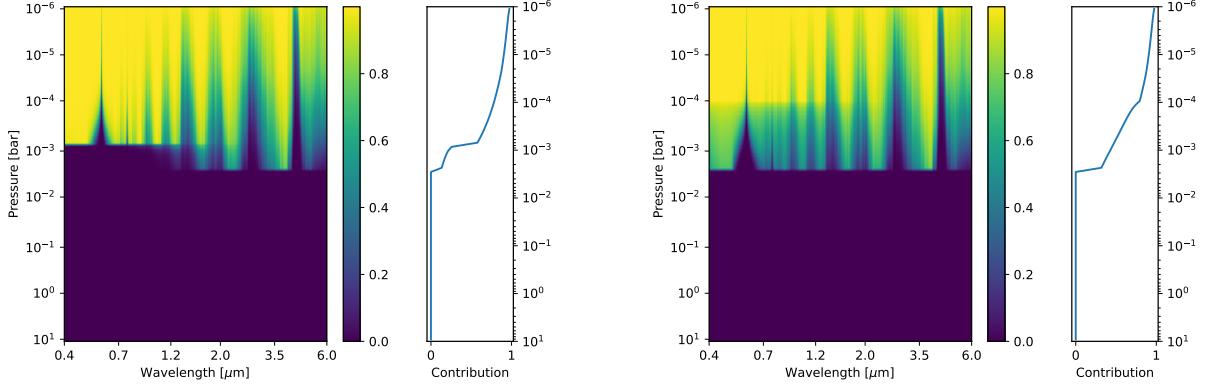


Figure 14. Optical depths for the two solutions identified by free retrievals in Fig. 4.

Table 4. Reference model retrieved median and MAP values of two solutions.

Value	R_p	T	$\log \chi_{\text{H}_2\text{O}}$	$\log \chi_{\text{CO}_2}$	$\log \chi_{\text{SiO}}$	$\log \chi_{\text{Na}}$	$\log \chi_{\text{K}}$	$\log p_{\text{grey}}$	$\log r_{\text{HPS}}$	$\log N_{\text{HPS}}$	$\log p_{\text{HPS,deck}}$	$\log p_{\text{HPS,base}}$	μ	Weight
	[R _J]	[K]						[Pa]	[m]	[m ⁻³]	[Pa]	[Pa]	[Dalton]	
NIRISS + NIRSpec + NIRCam Solution 1														
Median	1.209	7.782e+02	-1.629	-3.118	-1.818	-3.024	-5.434	2.406	-6.755	6.906	1.921	3.142	3.377	...
MAP 1	1.209	8.014e+02	-1.704	-3.221	-1.721	-3.035	-5.247	2.424	-6.655	6.738	1.930	2.967	3.461	7.277e-04
MAP 2	1.209	7.898e+02	-1.657	-3.195	-1.762	-3.055	-5.332	2.399	-6.697	6.851	1.956	2.181	3.426	7.201e-04
MAP 3	1.209	7.960e+02	-1.695	-3.169	-1.714	-3.013	-5.232	2.456	-6.839	7.119	1.914	2.168	3.486	6.555e-04
MAP 4	1.209	7.877e+02	-1.668	-3.180	-1.757	-3.045	-5.364	2.442	-6.695	6.908	1.931	2.190	3.428	5.709e-04
MAP 5	1.208	8.032e+02	-1.714	-3.259	-1.728	-3.070	-5.499	2.456	-6.835	7.103	1.955	3.099	3.439	5.512e-04
MAP 6	1.211	7.930e+02	-1.696	-3.205	-1.698	-3.110	-5.121	2.523	-6.760	7.000	2.015	2.290	3.509	4.822e-04
MAP 7	1.211	7.664e+02	-1.711	-3.205	-1.776	-3.217	-5.562	2.460	-6.749	6.953	2.017	2.294	3.357	4.751e-04
MAP 8	1.210	7.952e+02	-1.662	-3.105	-1.716	-3.039	-5.674	2.439	-6.682	6.825	1.919	2.182	3.510	4.524e-04
MAP 9	1.211	7.635e+02	-1.728	-3.194	-1.771	-3.204	-5.478	2.541	-6.782	6.947	2.043	3.858	3.355	4.513e-04
MAP 10	1.208	7.939e+02	-1.735	-3.244	-1.745	-3.108	-5.507	2.444	-6.716	6.853	1.972	3.140	3.394	4.472e-04
NIRISS + NIRSpec + NIRCam Solution 2														
Median	1.208	7.640e+02	-1.687	-3.157	-1.857	-3.239	-5.942	2.403	-6.290	3.817	1.156	2.792	3.264	...
MAP 1	1.209	7.875e+02	-1.736	-3.163	-1.739	-3.257	-5.788	2.395	-6.263	3.686	1.099	3.987	3.403	1.136e-03
MAP 2	1.208	7.769e+02	-1.749	-3.201	-1.783	-3.322	-5.740	2.443	-6.192	3.499	1.006	3.514	3.318	1.134e-03
MAP 3	1.210	7.687e+02	-1.720	-3.163	-1.754	-3.347	-6.174	2.540	-6.257	3.676	1.030	3.619	3.386	9.423e-04
MAP 4	1.208	7.806e+02	-1.780	-3.249	-1.784	-3.354	-5.972	2.400	-6.320	3.781	1.077	3.560	3.293	9.354e-04
MAP 5	1.208	7.759e+02	-1.740	-3.235	-1.789	-3.352	-5.993	2.449	-6.372	3.888	1.037	3.369	3.311	9.112e-04
MAP 6	1.209	7.846e+02	-1.740	-3.204	-1.740	-3.215	-5.996	2.420	-6.362	3.849	1.039	3.581	3.398	8.759e-04
MAP 7	1.211	7.801e+02	-1.728	-3.195	-1.717	-3.346	-5.764	2.517	-6.221	3.577	1.082	3.235	3.443	8.450e-04
MAP 8	1.207	7.845e+02	-1.671	-3.167	-1.819	-3.242	-5.786	2.361	-6.382	3.990	1.010	1.770	3.321	7.704e-04
MAP 9	1.209	7.867e+02	-1.748	-3.202	-1.734	-3.232	-5.528	2.370	-6.401	3.943	1.038	3.813	3.403	7.471e-04
MAP 10	1.210	7.750e+02	-1.700	-3.152	-1.754	-3.306	-5.856	2.529	-6.249	3.636	1.101	3.388	3.401	6.851e-04

C. RETRIEVAL OPTIMIZATION: SCALE HEIGHTS

After optimising the retrieval simulations in Step 2 using a minimal set of free parameters (reference model), we introduced higher retrieval freedom by allowing the algorithm to adjust scale heights through the mean molecular weight. By incorporating N₂ and Li as representative gases for heavy and light spectrally inactive species, this approach avoids introducing unwanted spectral signatures from the added species. Additionally, we include CO, which was excluded from the reference model to decrease the retrieval dimensionality due to its features being masked by H₂O and CO₂, although it has been suggested in molecular selection alongside other molecules.

We present the posterior distributions in Fig. 15 (Solution 1) and 16 (Solution 2). The results from the other three models show no significant deviation from the reference model in either solution. None of the models constrain the abundances of CO, N₂, or Li.

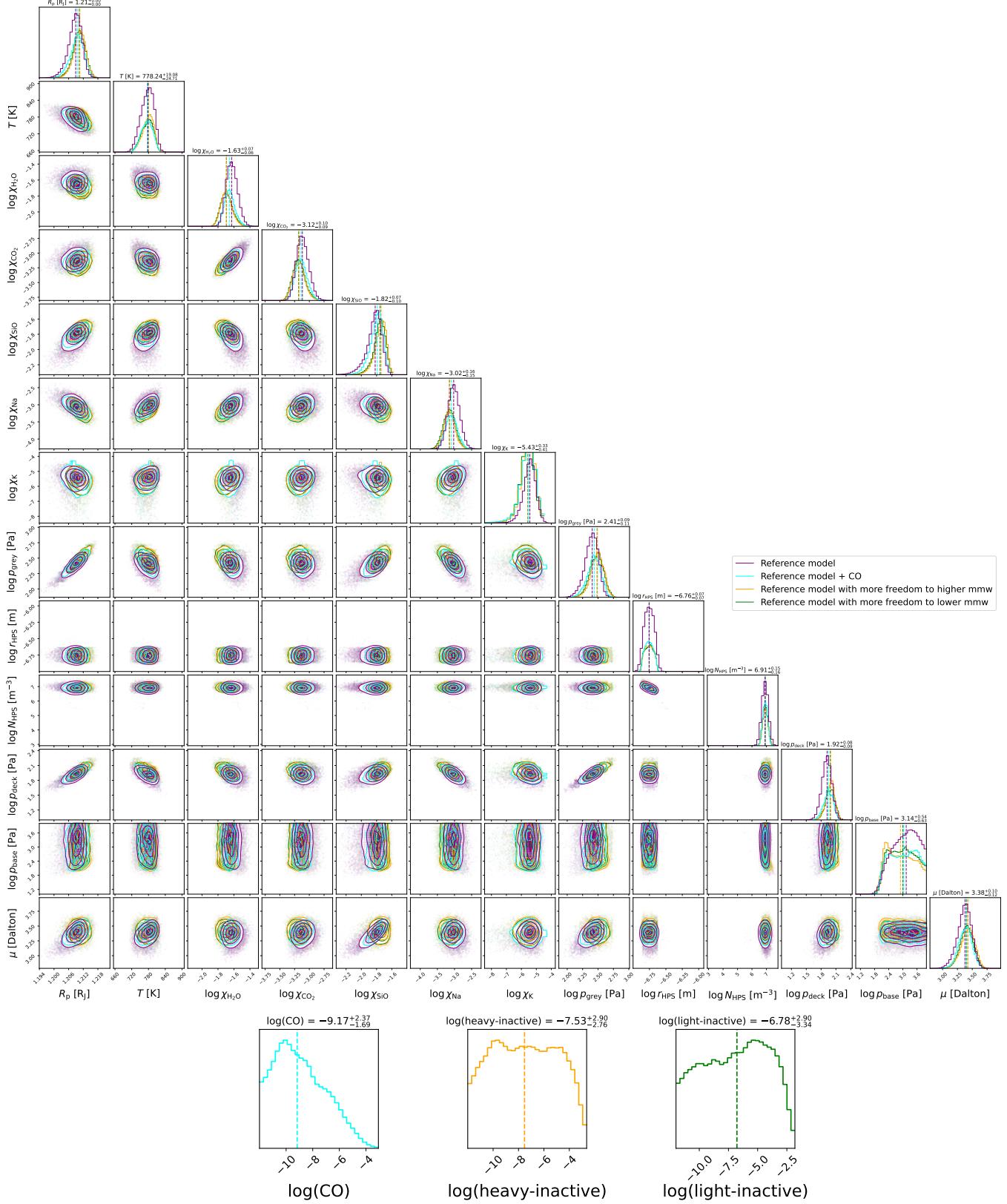


Figure 15. Posterior comparison (Solution 1) of retrievals of the reference model in Step 2 (purple), with CO (cyan), with N_2 to have more freedom to higher mean molecular weight (yellow) and with Li to have more freedom to lower mean molecular weight (green).

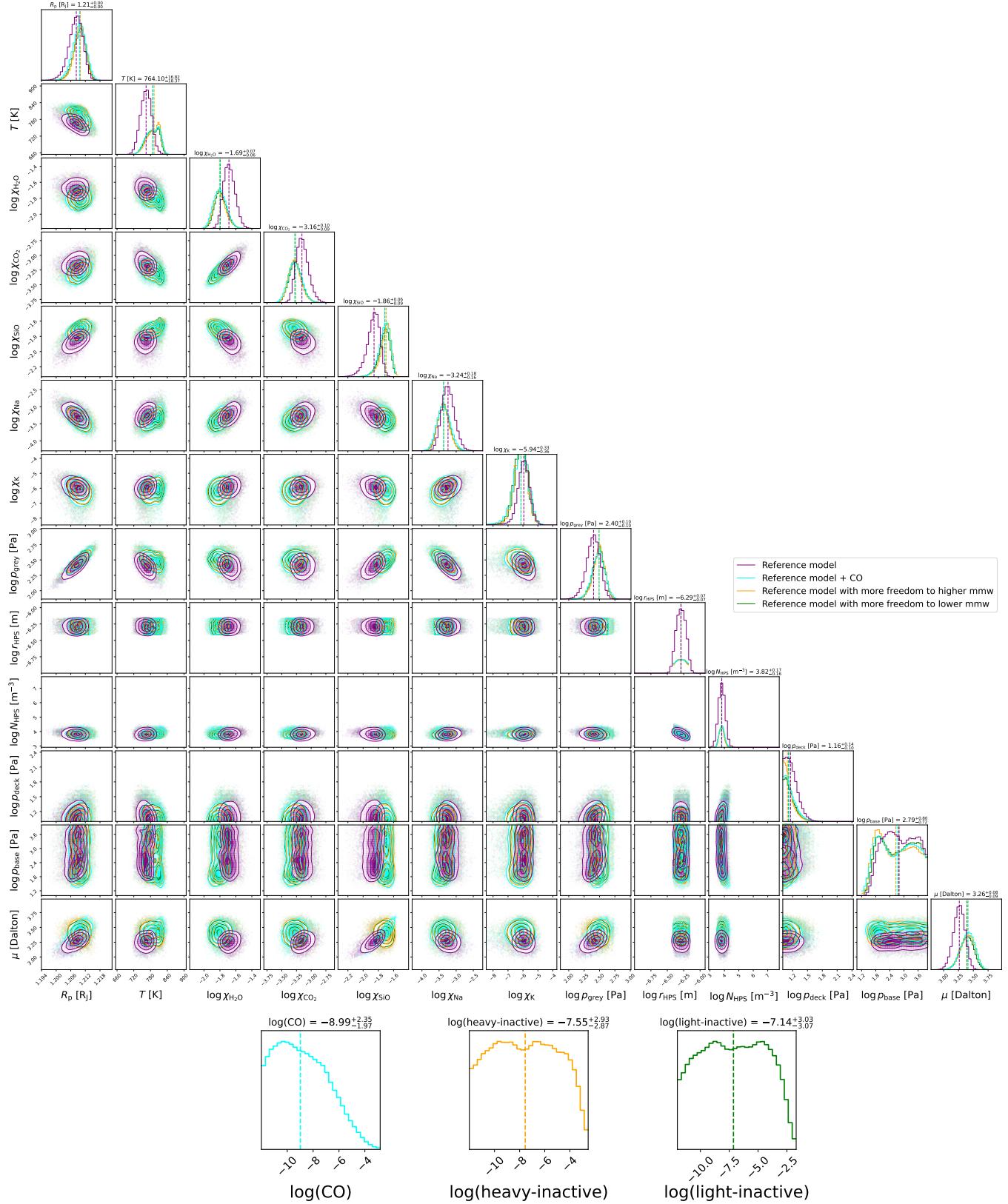


Figure 16. Posterior comparison (Solution 2) of the four models in Fig. 15.