

H₂S and SO₂ Photochemistry in Anoxic Atmospheres of Terrestrial Exoplanets. R. Hu^{1,2,3} and S. Seager⁴, ¹Jet Propulsion Laboratory, Pasadena, CA 91109, Email: Renyu.Hu@jpl.nasa.gov, ²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, ³Hubble Fellow, ⁴Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139.

Introduction: Terrestrial exoplanets are exciting subjects to study because they are potential habitats for extraterrestrial life if they receive the right amount of radiative heating from their host star. Both the search and the characterization of terrestrial exoplanets are growing rapidly. NASA's *Kepler* spacecraft, monitoring 160,000 stars in the sky, has discovered an exquisite ensemble of terrestrial exoplanets that shows their ubiquity in the Milky Way [1].

The study of habitability and biosignatures (the atmospheric components that indicate biogenic surface emissions) on a terrestrial planet requires a deep understanding of the interactions between its atmosphere and surface. In this regard, atmospheric photochemistry is pivotal, because it is the interface between the geological – and potential biological – sources and the observables (i.e., atmospheric composition and its spectral signatures).

This work focuses on H₂S and SO₂ photochemistry in the atmospheres of terrestrial exoplanets. The chemistry of these sulfur compounds is important because terrestrial planets could have a wide range of sulfur emissions. In our solar system, sulfur gases emitted from the surface and their photochemical products significantly shape the spectra of rocky planets and moons, including Venus [2], Io [3], and probably early Earth with an anoxic atmosphere [4]. On Earth, there are currently numerous ways that life can produce H₂S, including the reduction of sulfate [5] and the disproportionation of sulfur compounds of intermediate oxidation states [6].

For a terrestrial exoplanet, it is still largely unknown whether or not spectral features of H₂S and SO₂ in the atmosphere can be observed and whether or not the emission rates of sulfur compounds from the surface can be inferred. Here we systematically investigate the abundances of sulfur compounds resulting from H₂S and SO₂ surface emission in atmospheres having very different oxidation states ranging from reducing to oxidizing. We focus on terrestrial exoplanet atmospheres that have habitable surface temperatures, because those planets hold the most interest on the path to characterizing planets that might harbor life.

Methods: We have used a recently developed one-dimensional photochemistry and radiative transfer model [7,8] to study the sulfur chemistry in atmospheres ranging from reducing to oxidizing on terrestri-

al exoplanets. We choose H₂-dominate atmospheres as the archetype of reducing atmospheres, and N₂- and CO₂-dominated atmospheres as the archetype of oxidized atmospheres that could be both reducing and oxidizing. With the photochemistry model, we simulated the chemical compositions of 1-bar H₂-, N₂-, and CO₂-dominated atmospheres, with sulfur compounds emitted from the surface at various rates. The surface temperature is assumed to be 288 K and the distance between the modeled planet and its parent star is determined by the balance between stellar irradiation and planetary thermal emission.

The photochemistry model self-consistently treats formation and sedimentation of H₂SO₄ and S₈ aerosols, with the average aerosol particle diameter assigned as a free parameter. We explore a particle diameter from 0.1 to 10 μm, a sensible range for terrestrial planets [9]. The contribution of aerosol particles to radiative transfer in the atmosphere is computed for a lognormal size distribution having a typical particle size dispersion parameter of 1.5-2.0 [9].

Results: The primary sulfur emission from the surface (e.g., H₂S and SO₂) is chemically short-lived on terrestrial exoplanets having atmospheres ranging from reducing to oxidizing. The sulfur emission leads to photochemical formation of elemental sulfur (S₈) and sulfuric acid (H₂SO₄) in the atmosphere, which would condense to form aerosols if saturated. S₈ aerosols are photochemically formed based on H₂S and SO₂ emission in reducing atmospheres (e.g., H₂ atmospheres), and both S₈ and H₂SO₄ aerosols are formed in oxidized atmospheres (e.g., N₂ and CO₂ atmospheres). In the latter case, the aerosol composition is controlled by the H₂S/SO₂ ratio in the surface emission.

Due to photochemical production of S₈ and H₂SO₄, terrestrial exoplanets with a habitable surface temperature (e.g., 270–320 K) and substantial sulfur emission from the surface are likely to have hazy atmospheres. Even for a sulfur emission rate comparable to that of volcanoes on Earth, 1 bar H₂-dominated atmospheres on habitable rocky exoplanets are hazy with S₈ aerosols. If the sulfur emission rate is greater than Earth's current volcanic sulfur emission rate by 30–300 folds, N₂ and CO₂ atmospheres become hazy with S₈ and H₂SO₄ aerosols. Generally, the aerosol opacity in the atmosphere is determined by the surface sulfur emission rate, the dry deposition velocity of sulfur compounds, and the aerosol particle size. The parameter

regime for sulfur-loaded hazy atmospheres is illustrated in Figure 1.

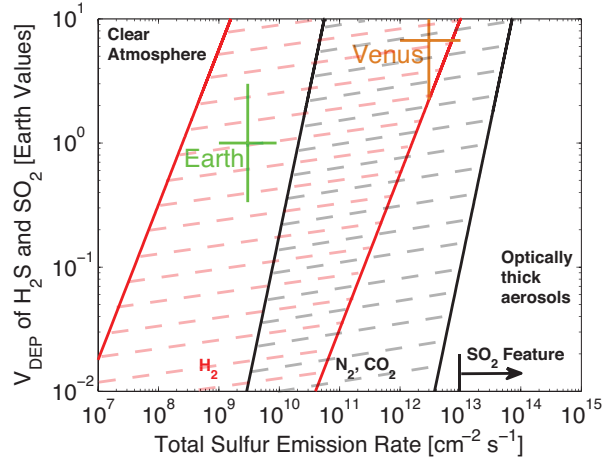


Figure 1: Formation of optically thick aerosols in atmospheres on rocky exoplanets in the habitable zone of their host star as a result of surface sulfur emission and deposition. The shaded areas are the parameter regime boundaries between a clear atmosphere and an optically thick atmosphere (defined as aerosol optical depth at 500 nm wavelength greater than 1), for reducing (H_2) and oxidized (N_2 and CO_2) atmospheres. The upper left corner of the parameter regime (small sulfur emission rates, large deposition velocities) leads to clear atmospheres; whereas the lower right corner of the parameter regime (large sulfur emission rates, small deposition velocities) leads to optically thick aerosols in the atmosphere composed of sulfur (S_8) and sulfate (H_2SO_4). The SO_2 features at $7.5\mu\text{m}$ and $20\mu\text{m}$ requires a mixing ratio on the order of ppm to be spectrally significant, which corresponds to a sulfur emission flux of more than $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ due to rapid photochemical removal of SO_2 in the atmosphere. Figure reprinted from [8].

Discussions: The photochemistry models show that both H_2S and SO_2 are chemically short-lived in virtually any types of atmospheres. This implies that great fluxes of surface emission are required to maintain a detectable level of either H_2S or SO_2 in the atmosphere. As a result, direct detection of H_2S or SO_2 via their spectral features will be difficult – contrary to the finding of a previous study [10]. Quantitatively, for SO_2 to be detectable, its emission rate must be 1000 times greater than current Earth's volcanic emission rate (see Figure 1). Direct detection of H_2S will be more complicated than SO_2 due to contamination of its spectral feature by strong H_2O absorption.

Looking ahead, the emission of sulfur compounds might be indirectly inferred by detecting sulfur and sulfate aerosols. This work reveals a monotonic relationship between the abundance of aerosols in the at-

mosphere and the emission rates of H_2S and SO_2 . An intriguing fact is that the composition of aerosols is correlated with the $\text{H}_2\text{S}/\text{SO}_2$ ratio in the surface emission. The existence of aerosols in the atmosphere can generally be indicated by featureless low atmospheric transmission and high planetary albedo. For specific features, elemental sulfur aerosols (S_8) will lead to an absorption edge at 400 nm, and sulfate aerosols (H_2SO_4) will lead to absorption features at 5-10 μm . We however stress that none of these features are unique for certain types of aerosols, and identification of aerosol composition will likely suffer model degeneracy. In the solar system exploration, the most important piece of information for aerosol identification on Venus comes from polarization of reflected stellar light [11,12]. Aerosol identification on terrestrial exoplanets and inference of surface sulfur emission might also require observation of polarized reflected light as a function of the planetary illumination phase.

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