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A Unified Framework for Modeling the Chemistry of Secondary and Hybrid Atmospheres of Super Earths and Sub-Neptunes

DR. MENG TIAN[1,2] AND KEVIN HENG[1,2]

[1]Ludwig-Maximilians-Universität München

[2]University of Bern

Presenting Author: mengtian@usm.lmu.de

Geochemical outgassing joins forces with primordial gases left over from planet formation to control the atmospheres of small exoplanets. Atmospheres of Earth, Mars and Venus are secondary because they are sourced from interior outgassing. Hybrid atmospheres form by persistent outgassing into long-lived, primordial, hydrogen-helium envelopes, for which there are no Solar-system examples. We construct a unified theoretical framework for calculating the outgassing chemistry of both secondary and hybrid atmospheres. Input parameters are surface pressure, oxidation and sulfidation states of the mantle, as well as the primordial atmospheric hydrogen, helium and nitrogen content, whereas output results are volume mixing ratios of gas species. Fugacity and activity coefficients are introduced to account for the respective pressure and mixing effects of the gaseous phase. The modeled secondary and hybrid atmospheres both exhibit a rich diversity of chemistries, including hydrogen-dominated atmospheres. Among all the gas species considered, the abundance ratio of carbon dioxide to carbon monoxide serves as a powerful diagnostic for the oxygen fugacity of the rocky mantle, which may conceivably be constrained by James Webb Space Telescope spectra in the near future. Of particular interest is the conditions for methane-dominated atmospheres, and our Monte Carlo results suggest the following: atmospheric surface pressures exceeding ~10 bar, a reduced (poorly oxidised) mantle, and diminished magma temperatures (compared to modern Earth). Future work should consider the role of photochemistry and atmospheric escape in modifying the atmosphere chemistry predicted by our model.