The diversity of planetary atmospheric chemistry: Lessons and challenges from our solar system and extrasolar planets

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Abstract
Atmospheres in our solar system range from oxidizing to reducing, transient to dense, veiled by clouds to transparent. Observations already suggest that exoplanets occupy an even more diverse range of stellar environments. Potentially this means an even more diverse range of atmospheric chemistry and composition. Nevertheless, there are commonalities across the atmospheres of our solar system that provide valuable guidance and lessons for observing and interpreting exoplanetary atmospheres. Lessons gleaned from decades of study of planetary atmospheric chemistry are synthesized and explored to understand their implications for extrasolar planetary atmospheres.

1. Introduction
Atmospheric chemistry is complex due, in part, to its sensitivity to trace species whose relative abundance may be a few parts per billion or parts per trillion. Atmospheric composition co-evolves as the planet's parent star, interior, and surface interact and change with time. Consequently, our initial views of extrasolar planetary atmospheres will be snapshots in time of systems undergoing changes on a broad range of temporal and spatial scales.

Further complexity in interpreting observations arises from the indirect relationship between an atmosphere's observable and bulk compositions. Clouds and refraction are obvious barriers to determining an atmosphere's composition from remote observations, but the dominant chemistry in a planetary atmosphere can change significantly with altitude. One example is the transition from ion photochemistry to neutral photochemistry to thermal equilibrium chemistry as the stellar photons available to drive atmospheric chemistry have lower energies.

2. Modelling tools
Most atmospheric chemistry studies use one-dimensional models intended to represent global-average conditions. Well-constrained, carefully-interpreted one-dimensional simulations can provide tremendous insight into complex processes and global-average simulations can yield significant insight into large-scale chemical processes. However, global-average one-dimensional simulations are strongly biased towards day side chemistry and do not usually represent the average one would get from averaging conditions as a function of altitude around a planet.

Three-dimensional general circulation models that incorporate interactive chemistry or effective chemical relaxation times have begun to be applied to extraterrestrial planets as computational power has increased. By necessity, the chemistry that can be incorporated into these models has to be greatly simplified so it is important to assess the uncertainties in these simulations that arise from the simplified chemical schemes using a lower-dimension chemistry model with more complete chemistry. In addition, interpretation of atmospheric chemistry simulations using a GCM is further complicated by the need to consider the impacts of imperfect dynamics on the calculated distributions of chemical species.

There is an intermediate class of models that historically was very important in understanding terrestrial atmospheric chemistry but has seen limited application in extraterrestrial studies. Specifically,
two-dimensional and three-dimensional chemical transport models, typically with transport derived from GCM simulations.

3. Factors affecting observability

The detectable portion of a planetary atmosphere depends on the observing technique, but many factors can cause the composition of the detectable portion of the atmosphere to differ from that in the lower portions of the atmosphere. Clouds form an obvious barrier to photons, but they also indicate a significant transition in composition as the gas-phase concentration of the condensable species decreases by orders of magnitude within and above the cloud. Similarly, condensation on hazes can strongly impact the gas-phase abundances of species. When condensation occurs at depth, it removes species and potentially prevents some chemical elements from appearing in the observable region of the planet's atmosphere.

4. Synthesis of lessons learned

The presented work will synthesize and explore key factors controlling the observable composition of a planetary atmosphere, focusing on the factors that are most significant for differentiating the observable and bulk compositions. Key chemical cycles and processes that have been identified from theoretical and observational studies will be summarized. Finally, challenges and future directions for studies of exoplanetary atmospheric chemistry will be outlined.

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