Chapter 12
Photochemistry of Terrestrial Exoplanet Atmospheres

Renyu Hu

Abstract Terrestrial exoplanets are exciting objects to study because they could be potential habitats for extraterrestrial life. Both the search and the characterization of terrestrial exoplanets are flourishing. Particularly, NASA's *Kepler* spacecraft has discovered Earth-sized planets receiving similar amount of radiative heat as Earth. Central in the studies of terrestrial exoplanets is to characterize their atmospheres and to search for potential biosignature gases (the atmospheric components that indicate biogenic surface emissions). To achieve this goal, a deep understanding of the key physical and chemical processes that control the atmospheric composition and the atmosphere-surface interaction is pivotal.

Keywords Terrestrial exoplanets • Astrobiology • Photochemistry • Radiative transfer

12.1 Terrestrial Exoplanets in Our Interstellar Neighborhood

One of the most exciting progresses in planetary exploration in the past decade is the discovery of terrestrial exoplanets. These celestial objects are planetary bodies outside the Solar System with masses within ten times Earth's mass or with radii within two times Earth's radius. Terrestrial exoplanets were first discovered by the "radial velocity" method (Rivera et al. 2005), i.e., by measuring the wobbling of a star via the Doppler shift of the stellar spectrum induced by an orbiting planet's gravitational force. The precision required for detecting an Earth-mass planet at the 1-AU orbit to a Sun-like star (referred to as a "true Earth analogue") is on the order of 0.1 m s^{-1}. The precision of the radial velocity measurements of bright stars is getting close to this requirement, and as a result, the radial velocity search has been finding terrestrial exoplanets that have sizes closer and closer to Earth (Udry et al.

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S. Jin et al. (eds.), *Planetary Exploration and Science: Recent Results and Advances*,
Springer Geophysics, DOI 10.1007/978-3-662-45052-9_12

2007; Mayor et al. 2009; Vogt et al. 2010; Rivera et al. 2010; Dawson and Fabrycky 2010; Howard et al. 2011; Bonfils et al. 2011). Recently, an Earth-mass terrestrial exoplanet was reported around Alpha Centauri B, one of the closest stellar systems from Earth (Dumusque et al. 2012).

Another method to search for terrestrial exoplanets is to observe the dimming of a star when a planet passes in front of the star as viewed from Earth (i.e., the transit method). The signal of the transit is proportional to the ratio between the size of the planet and the size of its parent star. Earth transiting the Sun as viewed from another planetary system would have a transit signal of $\sim$80 parts per million (ppm). Modern photometry technique has been able to provide this level of precision and therefore enabled the detection of terrestrial exoplanets via transits (Leger et al. 2009; Charbonneau et al. 2009; Winn et al. 2011; Demory et al. 2011; Dragomir et al. 2012; Van Grootel et al. 2014). In recent years, the exoplanet community has witnessed an explosive increase of the number of terrestrial exoplanets discovered by transits as a result of the *Kepler* mission that monitored 160,000 stars in the sky (Batalha et al. 2011; Lissauer et al. 2011; Cochran et al. 2011; Fressin et al. 2012; Gautier et al. 2012; Borucki et al. 2012; Muirhead et al. 2012; Borucki et al. 2013; Gilliland et al. 2013; Swift et al. 2013; Rowe et al. 2014). The smallest transiting planet that has been confirmed is only slightly larger than the Moon (Barclay et al. 2013a, b).

Based on the discoveries made by *Kepler*, statistically, we now know that a large number of stars in our interstellar neighborhood have terrestrial exoplanets. The occurrence rate of terrestrial exoplanets can be estimated based on the *Kepler* observations, with correction of the geometric effect (due to the fact that the transit technique is only sensitive to those planets that pass in front of their host stars periodically), the incompleteness of detection, and the false positive of signals (Howard et al. 2012; Fressin et al. 2013). It has been estimated that $\sim$30 % of stars in our interstellar neighborhood have terrestrial exoplanets that have radii within two times Earth's radius and orbital periods within 85 days (Fressin et al. 2013). It also turns out that the planets below twice the size of Earth are more populous than the planets above (Fressin et al. 2013; Petigura et al. 2013a, b). The occurrence rate of exoplanets found by the Kepler transit survey is also consistent with the finding of radial velocity surveys that are sensitive to very different observational biases, supporting the fidelity of this result (Figueira et al. 2012). When calculating the occurrence rate, terrestrial exoplanets are usually defined by their radii, because the transit technique can only measure the radii but not the masses. Measuring the masses of these small planets and confirming their rocky nature are ongoing and have been successful for a number of close-in objects (Pepe et al. 2013; Howard et al. 2013; Marcy et al. 2014).

A handful of the discovered terrestrial exoplanets are potentially habitable. A habitable planet is defined as a planet on the surface of which liquid water is stable. As the stellar radiation is the major heat source for a terrestrial exoplanet, the conventional habitable zone, the range of semimajor axes in which planets could be habitable, has been studied for main-sequence stars (Kasting et al. 1993). The conventional definition of the habitable zone relies upon the assumption that the planet has an N_2-dominated atmosphere with variable levels of CO_2 to provide appropriate levels of greenhouse effects. Such defined habitable zone around a Sun-like star is evaluated most recently at 0.99–1.70 AU (Kopparapu et al. 2013). Moreover, the range of the habitable zone can be considerably widened, if the atmosphere is H_2 dominated (with H_2-H_2 collision-induced absorption as the source of the greenhouse effect; Pierrehumbert and Gaidos 2011) or if the water content in the atmosphere is much lower than Earth (Zsom et al. 2013).

The search of habitable terrestrial exoplanets is difficult because both the radial velocity method and the transit method are more sensitive to planets that are closer to their parent stars. The amplitude of the radial velocity signal falls with the semimajor axis a as $a^{-1/2}$; the amplitude of transit signal does not depend on the semimajor axis, but the probability of transit due to the alignment between the star, the planet, and the observers is R_*/a, where R_* is the radius of the star. Several Jupiter- and Neptune-sized planets that are in the conventionally defined habitable zones of their host stars have been discovered by the radial velocity method (Udry et al. 2007; Vogt et al. 2010; Pepe et al. 2011; Bonfils et al. 2011; Tuomi et al. 2013). *Kepler* has found several sub-Neptune-sized planets in the habitable zones by the transit method (Borucki et al. 2012, 2013; Barclay et al. 2013a, b; Quintana et al. 2014). The frequency of terrestrial exoplanets in habitable zones of their host stars is estimated using *Kepler* observations to be $\sim$15 % for cool stars (Dressing and Charbonneau 2013) and $\sim$20 % for FGK stars (Traub 2012; Petigura et al. 2013b). Therefore, it is reasonable to expect at least one potentially habitable terrestrial planet in our interstellar neighborhood of a few tens of parsecs.

One sweet spot to look for habitable terrestrial exoplanets is around M dwarf stars. M dwarf stars have sizes of a fraction of that of the Sun, and M dwarf stars are the most common type of stars in the neighborhood of the Sun (Salpeter 1955). Recent surveys by *Kepler* have suggested that planets having radii within two times Earth's radius are more frequent around small M dwarfs than around FGK stars (Howard et al. 2012; Dressing and Charbonneau 2013). Moreover, because M dwarfs are considerably sub-luminous compared with the Sun, the habitable zone around an M dwarf is much closer to the star than the habitable zone around a Sun-like star (Kasting et al. 1993). As a result, habitable planets around M dwarfs would have higher transit probabilities and larger transit signals compared with their counterparts around FGK stars. In fact, the first Earth-sized exoplanet in a star's habitable zone was detected around an M dwarf (Quintana et al. 2014). However, this planet is too far away from Earth to allow atmospheric characterization. In parallel with *Kepler*, ground-based searches for terrestrial exoplanets around nearby M dwarfs have been ongoing (e.g., Nutzman and Charbonneau 2008), which have resulted in the discovery of a 2.7 Earth-radius planet orbiting an M4.5 star only 13 parsecs away (GJ 1214 b; Charbonneau et al. 2009).

The discovery of terrestrial exoplanets, especially those potentially habitable, has impacted profoundly our inquiry of the Universe. It is the first time when the human being can say for sure there are locations outside the Solar System that may have rocky environment, widely accepted as a prerequisite for life to emerge. As a milestone in the search for planets that might harbor life, terrestrial exoplanets are important objects to study for at least three reasons: (1) the detection of terrestrial exoplanets provides a large ensemble of planets and planetary systems that enable comparative planetology of Earth-like planets beyond the Solar System; (2) terrestrial exoplanets may themselves be habitable if they receive appropriate radiative heat from their parent stars; (3) characterization of atmospheres and surfaces of terrestrial exoplanets, starting from planets that are larger than Earths (referred to as “super-Earths”), and the expertise of instrumentation, observation, and data interpretation techniques gained will serve as indispensable stepping stones for eventually characterizing Earth-sized planets that are potentially habitable.

12.2 Observations of Exoplanet Atmospheres

The atmosphere on an exoplanet can be analyzed by spectroscopy. If an exoplanet could be directly imaged, the light from the planet’s atmosphere, either planetary thermal emission or reflection of the stellar light, could be analyzed via spectroscopy to determine the composition of its atmosphere. Such observations are extremely challenging due to the existence of a much stronger radiation source at close angular proximity (i.e., the host star). Therefore, direct spectroscopy studies of exoplanets have only been performed for Jupiter-sized or even larger giant planets. The first high-resolution spectrum of a directly imaged exoplanet (a nascent gas giant 40 AU from its host star) has recently been reported (Konopacky et al. 2013).

A newly developed method to mitigate the weak signal of an exoplanet without spatially resolving the planet or nulling the stellar light is to make use the information of the planet’s orbital motion. A correlation between the star’s radial velocity and the radial velocity of a certain group of molecular lines (e.g., CO) was used to establish the existence of the molecule in several giant planets’ atmosphere (Brogi et al. 2012; Rodler et al. 2012, 2013; de Kok et al. 2013; Birkby et al. 2013; Lockwood et al. 2014).

At current stage and in the near future, however, characterization of the atmospheres of terrestrial exoplanets focuses on the planets that transit. The predictable on-and-off features of a planet’s radiation when the planet passes behind its host star (referred to as “occultation”) can be observed by monitoring the total light from the star-planet system in and out of transits (e.g., Seager and Sasselov 1998; Seager et al. 2000). In addition, when the planet passes in front of its host star (referred to as “transit”), parts of the stellar radiation may transmit through the planet’s atmosphere and carry the information of the atmospheric composition (Seager and Sasselov 2000). Soon after the first detection of an exoplanet atmosphere via transit (Charbonneau et al. 2002) and the first detection of thermal emission from an exoplanet atmosphere via occultation (Charbonneau et al. 2005; Deming et al. 2005), both methods have been successful in characterizing extrasolar giant planets (e.g., Seager and Deming 2010 and references therein). Recently, attempts to observe super-Earth atmospheres are growing (e.g., Demory et al. 2012; Knutson et al. 2014), and the super-Earth/mini Neptune GJ 1214 b is being observed in as much detail as possible (e.g., Bean et al. 2010; Croll et al. 2011; Desert et al. 2011; Berta et al. 2012; de Mooij et al. 2012; Kreidberg et al. 2014).

Besides spectral characterization, exoplanet atmospheres have also been studied via the phase curves (e.g., Seager et al. 2000; Knutson et al. 2007), and *Kepler* has made the first observation of a phase curve from a terrestrial exoplanet (Batalha et al. 2011; Fogtmann-Schulz et al. 2014).

12.3 Physical and Chemical Processes in Terrestrial Exoplanet Atmospheres

Central in the studies of terrestrial exoplanets is to characterize their atmospheres and to search for potential biosignature gases, i.e., the atmospheric components that indicate biogenic surface emissions. For this goal, a deep understanding of the key physical and chemical processes that control the atmospheric composition is crucial.

One important process for terrestrial exoplanet atmospheres is chemical and photochemical reactions. The network of chemical reactions in the atmosphere may serve as sources for certain gases and sinks for the others. Chemical reactions occur when two molecules collide, and the reaction rates are therefore proportional to the number density of both molecules. Certain reactions would require a third body in the collision to remove excess energy or angular momentum. The rates of such termolecular reactions are therefore also dependent on the total number density of the atmosphere. Near the top of the atmosphere, photon-driven reactions contribute dominantly to the source and sink, as ultraviolet (UV) photons from the parent star that could dissociate molecules usually penetrate to the pressure levels of $\sim$0.1 bar (e.g., Yung and Demore 1999; Hu et al. 2012). The UV photodissociation produces reactive radicals that facilitate some reactions that are otherwise kinetically prohibited. A generic reaction network should include bimolecular reactions, termolecular reactions, photodissociation reactions, and thermodissociation reactions for the study of terrestrial exoplanet atmospheres (Hu 2013).

The other process that controls the compositions is transport. Both large-scale mean flows and small-scale turbulence and instability can transport molecules in the atmosphere and affect the composition (e.g., Brasseur and Solomon 2005; Seinfeld and Pandis 2006). One could focus on the transport in the vertical direction and explore the compositions of terrestrial exoplanet atmospheres as a function of altitude. Altitude is the most important dimension because the temperature and the pressure are strong functions of altitude. For example, the composition of Earth's atmosphere is primarily a function of altitude instead of longitude or latitude (Seinfeld and Pandis 2006). Also, the vertically resolved compositions are critical for prediction and interpretation of spectra of a terrestrial exoplanet, because the spectra probe different altitudes of the atmosphere depending on the wavelength (Seager 2010).

The major mechanisms for vertical transport in an irradiated atmosphere on a terrestrial exoplanet include convection (the same mechanism required to transport heat), small-scale instability driven by shear of horizontal flows, and molecular diffusion. The first two processes can be approximated by the so-called eddy diffusion coefficients (e.g., Seinfeld and Pandis 2006), and the last process can be approximated by the molecular diffusion coefficients. Therefore, the atmospheres on terrestrial exoplanets can be treated as gravitationally stratified, plan-parallel irradiated atmospheres, in which vertical mixing can be parameterized (Hu 2013).

Models for terrestrial exoplanet atmospheres can be developed to compute the chemical reaction kinetics and transport processes. Such models are often called "photochemistry-thermochemistry kinetic-transport model" or simply "photochemistry-thermochemistry model." The purpose of such models is to provide a tool to predict the amounts of component gases in the atmospheres of terrestrial exoplanets and in the meantime quantify the links between the observables (e.g., abundances of trace gases and their spectral signatures) and the fundamental unknowns (e.g., geological and biological processes on the planetary surface, mixing and escape of atmosphere gases, heat sources from planetary interior and exterior).

Photochemistry models have been successful in simulating the compositions of the atmospheres of Earth (Seinfeld and Pandis 2006) and the atmospheres of planets in our Solar System (Yung and Demore 1999). The photochemistry models are also critical for the study of molecular compositions of any exoplanet atmosphere, including the atmospheres of terrestrial exoplanets, because the composition of the observable part of an exoplanet atmosphere (0.1 mbar to 1 bar, depending on the wavelength) is controlled by the competition between chemical reaction kinetics and transport. Figure 12.1 schematically shows the architecture of such a model developed by Hu et al. (2012) and Hu and Seager (2014). A handful of other photochemistry models are available (e.g., Kasting et al. 1985; Yung and Demore 1999; Liang et al. 2003; Atreya et al. 2006; Zahnle et al. 2009; Line et al. 2010; Moses et al. 2011, 2013), and these models solve the same continuity equation in Fig. 12.1 and likely have similar architectures.

Eventually, the steady-state composition of a terrestrial exoplanet atmosphere is controlled by the boundary conditions. The upper boundary conditions are the fluxes of atmospheric escape or the material exchange fluxes between the neutral atmospheres and the ionospheres (not modeled) above. The lower boundary conditions depend on whether or not thermochemical equilibrium holds near the lower boundary. One could therefore consider the following two categories of atmospheres on terrestrial exoplanets: thin atmospheres and thick atmospheres. The thick atmospheres are defined as the atmospheres that are thick enough to maintain thermochemical equilibrium at high pressures, and the thin atmospheres are defined as the atmospheres at the surface of which achieving thermochemical equilibrium is kinetically prohibited. In the following we will focus on thin atmospheres because the thin atmospheres are more akin to creating a potentially habitable environment.

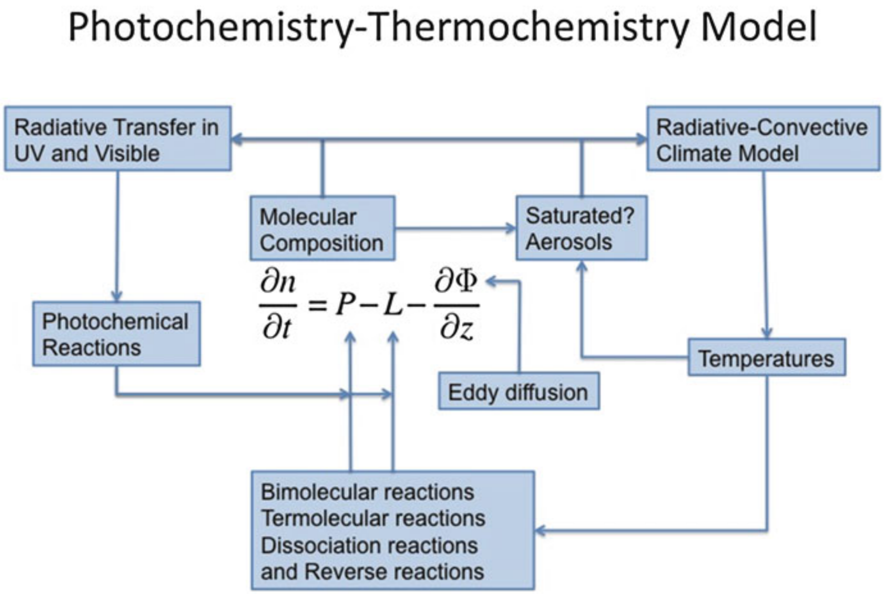

Fig. 12.1 Architecture of the photochemistry-thermochemistry model for terrestrial exoplanet atmospheres developed by Hu et al. (2012) and Hu and Seager (2014). The central equation to solve is a continuity equation that has terms for the chemical and photochemical production and loss, and terms for transport

The main components of a thin atmosphere of a terrestrial exoplanet result from its long-term geological evolution. For example, the N_2–O_2 atmosphere on Earth, the CO_2 atmosphere on Mars, and the N_2 atmosphere on Titan are results of long-term evolution (e.g., Kasting and Catling 2003; Coustenis 2005). For terrestrial exoplanets, the main components of their thin atmospheres can only be determined by observations, and the oxidation states of the thin atmospheres can range from reducing (e.g., H_2 atmospheres), to oxidized (e.g., N_2 and CO_2 atmospheres), to even oxic (O_2 atmospheres).

The photon-driven chemical reactions are especially important for thin atmospheres. UV and some visible-wavelength photons can dissociate gases, produce reactive radicals, and facilitate the conversion from emitted gases to photochemical products. These processes are key for thin atmospheres because (1) ultraviolet photons that cause photodissociation penetrate to the pressure levels of $\sim$0.1 bar, relevant to the bulk part of a thin atmospheres (Yung and Demore 1999; Hu 2013), and (2) in many cases, the photochemical processes in a thin atmosphere are irreversible. For example, the photochemical production of unsaturated hydrocarbons and haze from CH_4 occurs in the upper atmosphere of Titan, and the photochemical formation of C_2H_6 is irreversible and is therefore the dominant sink for CH_4 on Titan (Yung et al. 1984). This is in contrast to Jupiter's atmosphere, in which the photochemically formed C_2H_6 is converted back to CH_4 in deep atmosphere via pyrolysis (Strobel 1969, 1973; Gladstone et al. 1996).

The fundamental parameters that define a thin atmosphere are the surface source (i.e., emission rates), the surface sink (i.e., deposition velocities of emitted gases and their photochemical products in the atmosphere) of trace gases (Yung and Demore 1999; Seinfeld and Pandis 2006), and, in some cases, atmospheric loss to space. A photochemistry model, when applied to thin atmospheres, is to seek steady-state mixing ratios for trace gases of interest that are either emitted from the surface or produced by the chemical network in the atmosphere. The amounts of these trace gases are eventually controlled by the mass exchange between the surface and the atmosphere. It is important to study the amounts of trace gases by photochemistry models because an atmospheric spectrum may have strong features from spectroscopically active trace gases whose lifetime is controlled by the full chemical network in the atmosphere, and some of these trace gases may be hallmarks for specific atmospheric scenarios (e.g., Hu 2013).

The fact that the surface emission and deposition control the steady-state mixing ratios of trace gases in thin atmospheres on terrestrial exoplanets is pivotal to the ultimate goal of characterizing terrestrial exoplanets that might harbor life. Potential metabolic activities on a rocky planet emit a gas to the atmosphere that is otherwise not emitted or consume a gas that is otherwise not consumed. Both processes occur on Earth and regulate the composition of Earth's atmosphere. For example, Earth-based photosynthesis leads to the emission of O_2 that sustains a high O_2 mixing ratio in Earth's atmosphere, and Earth-based hydrogen-oxidizing bacteria provide an appreciable deposition velocity for H_2 from the atmosphere to the surface (e.g., Kasting and Catling 2003; Seinfeld and Pandis 2006). The photochemistry model provides the interface between the observables (atmospheric compositions) and the fundamental unknowns (surface source and sinks that may or may not be attributed to life), and the photochemistry model is therefore critical for determining the habitability of a terrestrial exoplanet and investigating whether a habitable planet is inhabited.

12.4 Exoplanet Benchmark Scenarios

Several benchmark scenarios can be set up for the atmospheres of terrestrial exoplanets (Hu et al. 2012). The goal of these benchmark scenarios is to provide baseline models to assess the stability of molecules in different kinds of atmospheres in order to calculate the lifetime of spectrally significant gases and, in particular, the lifetime of potential biosignature gases.

The most important parameter that determines the molecule lifetimes is the oxidation power of the atmosphere – the ability to reduce or oxidize a gas in the atmosphere. The main reactive species in the atmosphere provide the oxidizing or reducing power. In an oxidizing atmosphere, OH and O are created by photochemistry and are the main reactive radicals. In a reducing atmosphere, H, also created by photochemistry, is the main reactive species. One could expect that the atmospheric composition of exoplanets will be highly varied, based on the nearly continuous range of masses and orbits of exoplanets. In this large parameter space, the primary dimension of chemical characterization for terrestrial exoplanet atmospheres is their oxidation states.

The main components of the atmosphere in large part, and the surface emission ad deposition of trace gases to a lesser extent, determine its oxidation power. In the extreme cases of the atmospheric redox state, i.e., the H_2-dominated atmospheres and the O_2-rich atmospheres, the atmospheric redox power is surely reducing or oxidizing for a wide range of surface emission or deposition fluxes. However, for an intermediate redox state, the atmosphere would be composed of redox-neutral species like N_2 and CO_2, and the redox power of the atmosphere can be mainly controlled by the emission and the deposition fluxes of trace gases (i.e., H_2, CH_4, and H_2S) from the surface. For example, the higher the emission of reducing gases is, the more reducing the atmosphere becomes.

Here we describe the benchmark scenarios proposed by Hu et al. (2012) for reducing, weakly oxidizing, and strongly oxidizing atmospheres on an Earth-size and Earth-mass habitable terrestrial exoplanet around a Sun-like star. The three scenarios are a reducing (90 % H_2–10 % N_2) atmosphere, a weakly oxidizing N2 atmosphere (>99 % N_2), and a highly oxidizing (90 % CO_2–10 % N_2) atmosphere. Hu et al. (2012) consider Earth-like volcanic gas emission rate and composition that consists of CO_2, H_2, SO_2, CH_4, and H_2S and assume that the planet surface has a substantial fraction of its surface covered by a liquid water ocean so that water is transported from the surface and buffered by the balance of evaporation/condensation. Key nonequilibrium processes in these scenarios are schematically shown in Fig. 12.2, and the molecular composition of the three benchmark scenarios is shown in Fig. 12.3.

Summarizing the benchmark scenarios, several general chemistry properties of thin atmospheres on habitable terrestrial exoplanets stand out. These properties are results of physical structures of molecules, and how they interact, and therefore are independent of detailed planetary scenarios (Hu et al. 2012; Hu 2013).

First, atomic hydrogen (H) is a more abundant reactive radical than hydroxyl radical (OH) in anoxic atmospheres. Atomic hydrogen is mainly produced by water vapor photodissociation (Hu et al. 2012; Seager et al. 2013). The production of atomic hydrogen is catalyzed by water vapor:

$$H_2O + hv \rightarrow H + OH,$$

$$OH + H_2 \rightarrow H_2O + H,$$

$$\text{Net}: \; H_2 + hv \rightarrow 2H.$$

It is difficult to remove hydrogen once produced in anoxic atmospheres, which is in contrast to oxygen-rich atmospheres (e.g., current Earth's atmosphere) in which H can be quickly consumed by O_2. As a result, removal of a gas by H is likely to be an important removal path for trace gases in an anoxic atmosphere. Atomic oxygen

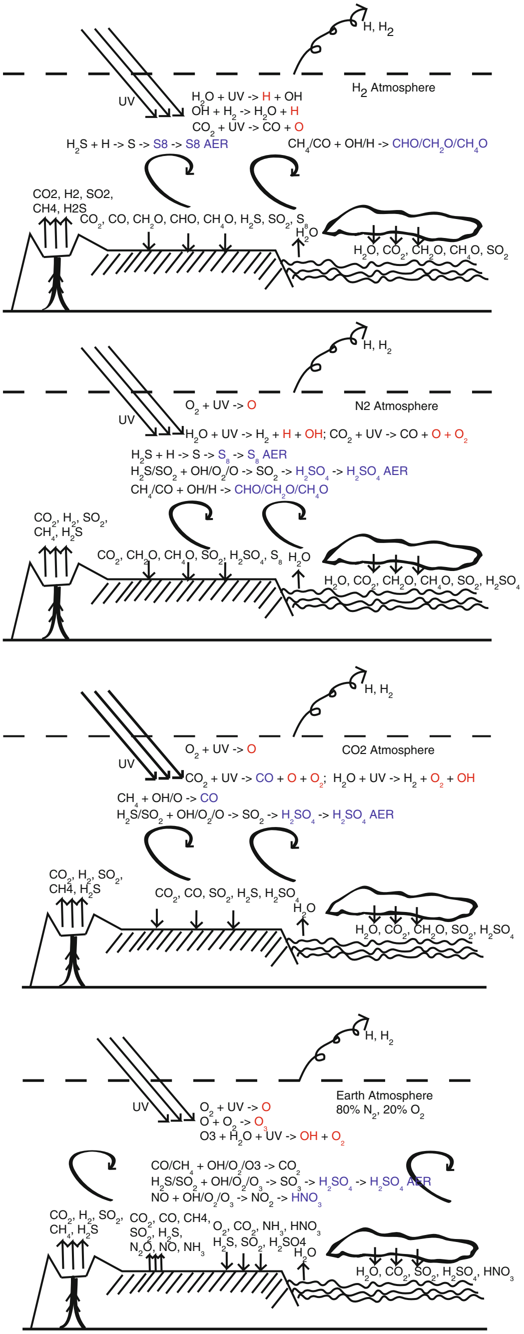

Fig. 12.2 Schematic illustrations of key nonequilibrium processes in the three scenarios of rocky exoplanet atmospheres in comparison with the current Earth. From *top* to *bottom*, the four panels correspond to the H_2, N_2, CO_2 atmospheres and the atmosphere of Earth. The *red color* highlights the reactive radicals in each atmospheric scenario, and the *blue color* highlights the major photochemical products in the atmosphere (Reproduced from Hu et al. 2012 with the permission of the AAS)

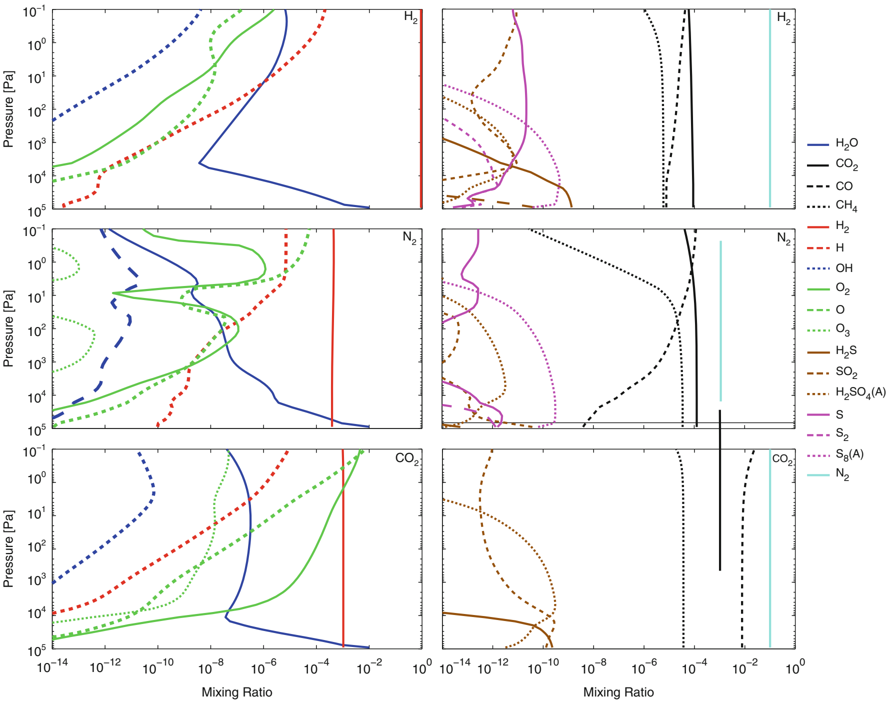

Fig. 12.3 Compositions of the benchmark scenarios of rocky exoplanet atmospheres. The *left column* shows mixing ratios of H and O species, and the *right column* shows mixing ratios of N, C, and S species. From *top* to *bottom*, the three panels correspond to the reducing (H_2-dominated), oxidized (N_2-dominated), and highly oxidized (CO_2-dominated) atmospheres. The vertical scales are expressed in pressure, which allows comparison between different scenarios that have very different mean molecular masses. *Thick lines* highlight the profiles of three reactive species, H, OH, and O (Reproduced from Hu et al. 2012 with the permission of the AAS)

is likely to be the most abundant reactive radical in CO_2-dominated atmospheres. Due to the photochemical origin of the reactive species, their abundances in the atmosphere around a quiet M dwarf star are 2 orders of magnitude lower than their abundances around a Sun-like star, because a quiet M dwarf emits much less UV radiation than a Sun-like star.

Second, dry deposition velocities of long-lived compounds, notably major volcanic carbon compounds including methane, carbon monoxide, and carbon dioxide, have significant effects on the atmospheric oxidation states. The specific choice of dry deposition velocities for emitted gases and their major photochemical by-products in the atmosphere is critical to determine the atmospheric composition and the redox power on terrestrial exoplanets (Hu et al. 2012). For example, if the dry deposition velocity of CO were greater for a CO_2-dominated atmosphere, the steady-state mixing ratio of CO in the atmosphere would be lower, and consequently, the atmosphere would have less H_2 and more O_2.

Third, volcanic carbon compounds (i.e., CH_4 and CO_2) are chemically long-lived and tend to be well mixed in terrestrial exoplanet atmospheres, whereas volcanic sulfur compounds (i.e., H_2S and SO_2) are short-lived (Fig. 12.3). CH_4 and CO_2 have chemical lifetime longer than 10,000 years in all three benchmark atmospheres ranging from reducing to oxidizing, implying that a relatively small volcanic input can result in a high steady-state mixing ratio. The chemical lifetime CO, another possible volcanic carbon compound, ranges from 0.1 to 700 years depending on the OH abundance in the atmosphere. Unlike carbon compounds, both H_2S and SO_2 are chemically short-lived in virtually all types of atmospheres on terrestrial exoplanets (Hu et al. 2013). This implies that the carbon compounds are more likely to be spectroscopically detected than the sulfur compounds. In particular, direct detection of surface sulfur emission is unlikely, as their surface emission rates need to be extremely high ($>$1,000 times Earth's volcanic sulfur emission) for these gases to build up to a detectable level. Sulfur compounds emitted from the surface will lead to photochemical formation of elemental sulfur and sulfuric acid in the atmosphere, which would condense to form aerosols if saturated.

12.5 Is O_2 a Biosignature Gas?

Oxygen and ozone are the most studied biosignature gases for terrestrial exoplanet characterization, due to their biogenic origin on Earth and their strong spectral features at visible and infrared wavelengths (e.g., Angel et al. 1986; Leger et al. 1993, 1996; Beichman et al. 1999; Snellen et al. 2013). When we consider using O_2/O_3 as biosignature gases, a natural question is whether O_2 may be produced without involving life. Indeed, photodissociation of H_2O and CO_2 produce free oxygen in the atmosphere (Fig. 12.3).

The abiotic production of oxygen in terrestrial atmospheres has been studied either for understanding prebiotic Earth's atmosphere (e.g., Walker 1977; Kasting et al. 1979; Kasting and Catling 2003) or for assessing whether abiotic oxygen can be a false positive for detecting photosynthesis on habitable exoplanets (Selsis et al. 2002; Segura et al. 2007; Hu et al. 2012; Tian et al. 2014; Wordsworth and Pierrehumbert 2014). Selsis et al. (2002) found that photochemically produced oxygen may build up in CO_2-dominated atmospheres, if there is no surface emission or deposition. The results of Selsis et al. (2002) was later challenged by Segura et al. (2007), who had additionally considered the surface emission of reducing gases including H_2 and CH_4, and found that abiotic oxygen would not build up in the atmosphere on a planet having active hydrological cycle.

Hu et al. (2012) first pointed out that the steady-state number density of O_2 and O_3 in the CO_2-dominated atmosphere is mainly controlled by the surface emission of reducing gases such as H_2 and CH_4, and without surface emission of reducing gas, photochemically produced O_2 can build up in a 1-bar CO_2-dominated atmosphere. Figure 12.4 shows the simulated CO_2-dominated atmospheres with relatively low and zero emission rates of H_2 and CH_4. The O_2 mixing ratio near the surface increases dramatically in 1-bar CO_2 atmospheres when the emission of

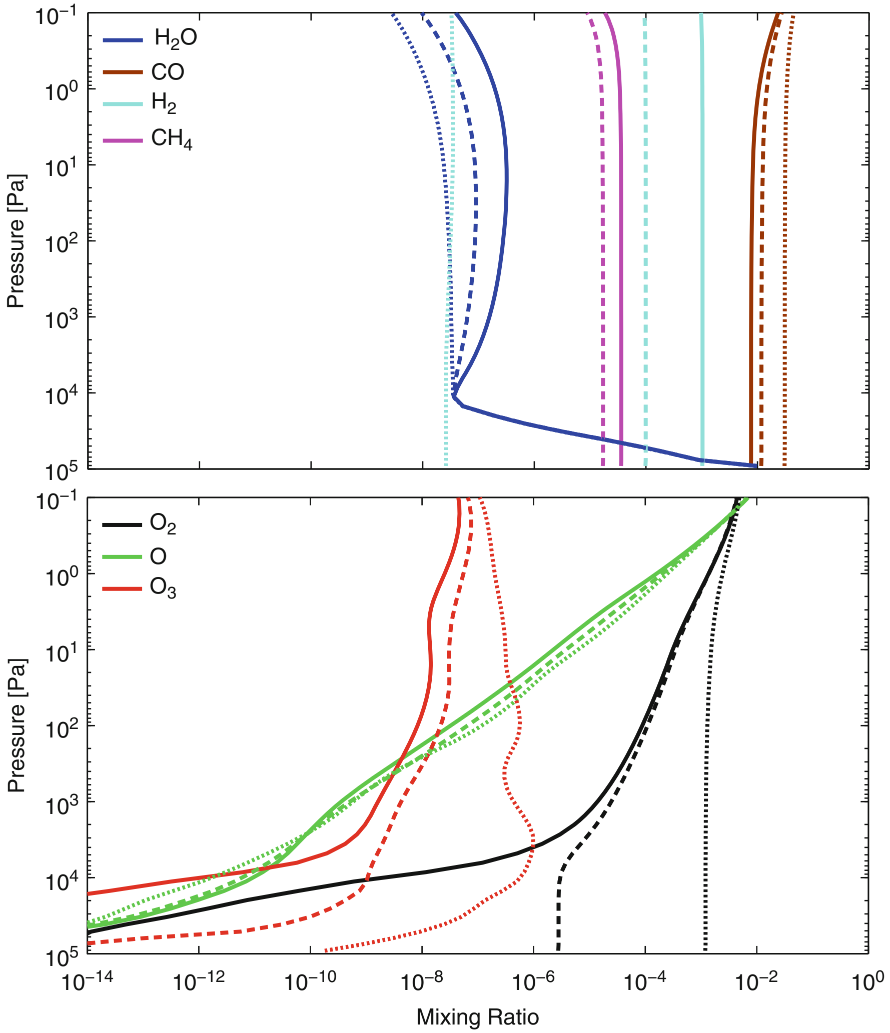

Fig. 12.4 Effects of the surface emission reducing gases on CO_2-dominated atmospheres of rocky exoplanets. The *upper panel* shows mixing ratios of H_2O, CO, H_2, and CH_4, and the *lower panel* shows mixing ratios of O_2, O, and O_3. The *solid lines* show the chemical composition of the benchmark scenario. In particular the emission rate of H_2 is 3×10^{-10} cm^{-2} s^{-1}. The *dashed lines* show the chemical composition of the same scenario, but with an H2 emission rate of 3×10^{-9} cm^{-2} s^{-1}, and the *dotted lines* show the chemical composition for zero emission of H_2 and CH_4. A dramatic increase of O_2 and O_3 mixing ratios is caused by a decrease of the surface emission of reduced gases (Reproduced from Hu et al. 2012 with the permission of the AAS)

reducing gases decreases. O_2 is virtually nonexistent at the surface for the Earth-like emission rates of H_2 and CH_4, but O_2 mixing ratio can be as high as 10^{-3} if no H_2 or CH_4 is emitted (Fig. 12.4). In particular, if no H_2 or CH_4 is emitted, the O_3 column integrated number density can reach one third of the present-day Earth's atmospheric levels, which constitutes a potential false positive.

Figure 12.4 shows that O_3 can potentially build up in the 1-bar CO_2-dominated atmosphere to a false positive level even on a planet with active hydrological cycle. Segura et al. (2007) have based their conclusion on simulations of 20 % CO_2 1-bar atmospheres with and without emission of H_2 and CH_4 and simulations of 2-bar CO_2 atmospheres with emission of H_2 and CH_4. Where Hu et al. (2012) models differ from Segura et al. (2007) is that Hu et al. (2012) model successfully simulated 90 % CO_2 1-bar atmospheres with minimal volcanic reducing gas emission. This is a parameter space that Segura et al. (2007) did not cover, but this is the parameter space for high abiotic O_2. Recently, it has further been found that around M dwarf stars that have low near-UV radiation and strong far-UV radiation, O_2 produced from CO_2 photodissociation is even easier to build up in the atmosphere (Tian et al. 2014).

Therefore one should exercise caution to use spectral features of O_2 as a probe of oxygenic photosynthesis on a terrestrial exoplanet. The risk of such false positives would affect the inference of photosynthesis via O_2 features detected in the visible wavelengths, potentially by either the Terrestrial Planet Finder – Coronagraph (e.g., Beichman et al. 2006) or the cross-correlation method applied to high-resolution spectroscopy on the 40-m class telescopes (Snellen et al. 2013). The risk of false positive is however not relevant to the detection of O_3 (a photochemical derivative of O_2) features in the mid-infrared, because the O_3 feature would be masked by strong CO_2 features and therefore not detectable for CO_2-dominated atmospheres (Selsis et al. 2002). Eventually, detecting both O_2 features and CH_4 features may mitigate the risk of false positive. A methane mixing ratio of $\sim$10 ppm would imply a surface source of reducing gases that could prevent the abiotic buildup of O_2 (Fig. 12.4).

12.6 Prospect of Terrestrial Exoplanet Characterization

Determination of the atmospheric compositions on terrestrial exoplanets is one of the most significant challenges facing astronomers. To achieve this goal, both advanced observational techniques and suitable targets are required (e.g., Deming et al. 2009). The ratio between the radiation from a terrestrial exoplanet and that from its parent star is in the orders of 10^{-10} in the visible wavelengths and 10^{-7} in the mid-infrared wavelengths. This means in the transit scenario, many observations of transits need to be stacked to lower the noise level in order to reveal the planet's signal (e.g., Seager and Deming 2010; Kreidberg et al. 2014), and in the direct imaging scenario, the stellar radiation has to be almost perfectly annihilated in order to reveal the planet (e.g., Kuchner and Traub 2002; Lawson and Dooley 2005; Trauger and Traub 2007). Even with advanced observational techniques, atmospheric characterization of terrestrial exoplanets will be confined to nearby systems (e.g., within tens of parsecs; Guyon et al. 2006; Oppenheimer and Hinkley 2009; Belu et al. 2011).

Full-sky surveys intended to discover terrestrial exoplanets around nearby main-sequence stars are being planned. The survey of terrestrial exoplanets around nearby systems is far from complete in several important areas: (1) Earth-mass planets around FGK stars have just become in the reach of the radial velocity method (Dumusque et al. 2012); (2) precise spectroscopic and photometric measurements of M dwarfs, despite their dominant numbers in our interstellar neighborhood, have been long impeded by the faintness of these stars and the concentration of their radiation in the near-infrared wavelengths that are strongly contaminated by Earth's atmosphere (Nutzman and Charbonneau 2008); (3) *Kepler*, although sensitive to Earth-sized planets, targets a small patch of sky and focuses on faint stars to maximize its scientific return (Batalha et al. 2010). One could expect rapid developments in all these areas. In particular, an all-sky space-based TESS mission (Transiting Exoplanet Survey Satellite) has recently been selected by NASA for launch in 2017 (Ricker et al. 2010). And the CHaracterising ExOPlanet Satellite (CHEOPS) and the PLAnetary Transits and Oscillations of stars (PLATO), also designed to search for terrestrial exoplanets around nearby bright stars, have been selected by European Space Agency (ESA) for launch in the next decade (Broeg et al. 2013; Rauer et al. 2013). One could expect a rapid growth in the number of terrestrial exoplanets that are suitable for follow-up observations of their atmospheres in the coming years.

The next-generation observation facility will allow thick atmospheres to be observed in great detail and even allow characterization of thin atmospheres on terrestrial exoplanets around late-type stars. Today's studies on hot Jupiter's atmospheres are flourishing with the Hubble Space Telescope and the Spitzer Space Telescope (see Seager and Deming 2010 and references therein), but much detection of atmospheric molecules remains controversial (Deming et al. 2013). In 5–10 years, larger and more sophisticated facilities will allow measurements of molecular abundances and characterization of atmospheric chemistry in thick atmospheres of gas giants, and super-Earths around M dwarf stars, to great detail (Traub et al. 2008; Kaltenegger and Traub 2009; Belu et al. 2011). These anticipated facilities include the James Webb Space Telescope (JWST) slated for launch in 2018 (Gardner et al. 2006), and the giant 20- to 40-m class ground-based telescopes that include the Extremely Large Telescope (Gilmozzi and Spyromilio 2008), the Giant Magellan Telescope (Johns et al. 2012), and the Thirty Meter Telescope (Crampton and Simard 2006).

In the more distant future, the community still holds hope that a direct-imaging space-based mission under the Terrestrial Planet Finder concept (e.g., Traub et al. 2006; Beichman et al. 2006; Levine et al. 2009) will enable Earth-like terrestrial exoplanets to be characterized. The technique of exoplanet direct imaging has been advancing rapidly and proceeding into spectroscopic observations of giant planets (Konopacky et al. 2013). A number of coronagraph instruments are mounted on state-of-the-art 10-m class telescopes, which will enable spectroscopic studies of extrasolar gas giants (e.g., Gemini Planet Imager, Chilcote et al. 2012). Notably, both coronagraph and external occultor instruments are being studied for space flights in the next decade, for directly imaging and spectrally characterizing Neptune- and Jupiter-sized exoplanets (Spergel et al. 2013; Stapelfeldt et al. 2014; Seager et al. 2014). These ground-based and space-based efforts of direct imaging and spectroscopic measurements of exoplanets will pave the way to a future space-based direct-imaging mission that will allow characterization of true Earth analogues.

References

Angel JRP, Cheng AYS, Woolf NJ (1986) Nature 322:341–343
Atreya SK, Adams EY, Niemann HB et al (2006) Planet Space Sci 54:1177
Barclay T, Rowe JF, Lissauer JJ et al (2013a) Nature 494:452–454
Barclay T, Burke C, Howell SB et al (2013b) Astrophys J 768:101
Batalha NM, Borucki WJ, Koch DG et al (2010) Astrophys J Lett 713:L109–L114
Batalha NM, Borucki WJ, Bryson ST et al (2011) Astrophys J 729:27
Bean JL, Miller-Ricci Kempton E, Homeier D (2010) Nature 468:669–672
Beichman CA, Woolf NJ, Lindensmith CA (1999) The Terrestrial Planet Finder (TPF): a NASA Origins Program to search for habitable planets
Beichman C, Lawson P, Lay O et al (2006). Status of the terrestrial planet under interferometer (TPF-I). In: Society of Photo-Optical Instrumentation Engineers (SPIE) conference series, vol 6268
Belu AR, Selsis F, Morales J-C et al (2011) Astron Astrophys 525:A83
Berta ZK, Charbonneau D, Desert J-M et al (2012) Astrophys J 747:35
Birkby JL, de Kok RJ, Brogi M et al (2013) Mon Not R Astron Soc 436:L35
Bonfils X, Gillon M, Forveille T et al (2011) Astron Astrophys 528:A111
Borucki WJ, Koch DG, Batalha N et al (2012) Astrophys J 745:120
Borucki WJ, Agol E, Fressin F et al (2013) Science 340(6132):587–590
Brasseur GP, Solomon S (2005) Aeronomy of the middle atmosphere. Springer, Dordrecht
Broeg C, Fortier A, Ehrenreich D et al (2013). CHEOPS: a transit photometry mission for ESA's small mission programme. In: European Physical Journal web of conferences, vol 47, p 3005
Brogi M, Snellen IAG, de Kok RJ et al (2012) Nature 486:502–504
Charbonneau D, Brown TM, Noyes RW, Gilliland RL (2002) Astrophys J 568:377–384
Charbonneau D, Allen LE, Megeath ST et al (2005) Astrophys J 626:523–529
Charbonneau D, Berta ZK, Irwin J et al (2009) Nature 462:891–894
Chilcote, J. K., Larkin, J. E., Maire, J et al Performance of the integral field spectrograph for the Gemini Planet Imager. In volume 8446 of Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series.
Cochran WD, Fabrycky DC, Torres G et al (2011) Astrophys J Suppl Ser 197:7
Coustenis A (2005) Space Sci Rev 116:171–184
Crampton, D. and Simard, L. (2006). Instrument concepts and scientific opportunities for TMT. In volume 6269 of Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series.
Croll B, Albert L, Jayawardhana R et al (2011) Astrophys J 736:78
Dawson RI, Fabrycky DC (2010) Astrophys J 722:937–953
de Kok RJ, Brogi M, Snellen IAG et al (2013) Astron Astrophys 554:A82
de Mooij EJW, Brogi M, de Kok RJ et al (2012) Astron Astrophys 538:A46
Deming D, Seager S, Richardson LJ, Harrington J (2005) Nature 434:740–743
Deming D, Seager S, Winn J et al (2009) Publ Astron Soc Pac 121:952–967
Deming D, Wilkins A, McCullough P et al (2013) Astrophys J 774:95
Demory B-O, Gillon M, Deming D et al (2011) Astron Astrophys 533:A114
Demory B-O, Gillon M, Seager S et al (2012) Astrophys J Lett 751:L28

Desert J-M, Bean J, Miller-Ricci Kempton E et al (2011) Astrophys J Lett 731:L40

Dragomir D, Mathews JM, Howard AW et al (2012) Astrophys J 759:L41

Dressing CD, Charbonneau D (2013) Astrophys J 767:95

Dumusque X, Pepe F, Lovis C et al (2012) Nature 491:207–211

Figueira P, Marmier M, Boue G et al (2012) Astron Astrophys 541:A139

Fogtmann-Schulz A, Hinrup B, Van Eylen V et al (2014) Astrophys J 781:67

Fressin F, Torres G, Rowe JF et al (2012) Nature 482:195–198

Fressin F, Torres G, Charbonneau D et al (2013) Astrophys J 766:81

Gardner JP, Mather JC, Clampin M et al (2006) Space Sci Rev 123:485–606

Gautier TN III, Charbonneau D, Rowe JF et al (2012) Astrophys J 749:15

Gilliland RL, Marcy GW, Rowe JF et al (2013) Astrophys J 766:40

Gilmozzi R, Spyromilio J (2008) The 42 m European ELT: status. In: Society of Photo-Optical Instrumentation Engineers (SPIE) conference series, vol 7012

Gladstone GR, Allen M, Yung YL (1996) Icarus 119:1–52

Guyon O, Pluzhnik EA, Kuchner MJ et al (2006) Astrophys J Suppl Ser 167:81–99

Howard AW, Johnson JA, Marcy GW et al (2011) Astrophys J 730:10

Howard AW, Marcy GW, Bryson ST et al (2012) Astrophys J Suppl Ser 201:15

Howard AW, Sanchis-Ojeda R, Marcy GW et al (2013) Nature 503:381–384

Hu R (2013) Atmospheric photochemistry, surface features, and potential biosignature gases of terrestrial exoplanets, Ph.D. thesis, MIT

Hu R, Seager S (2014) Astrophys J 784:63

Hu R, Seager S, Bains W (2012) Astrophys J 761:166

Hu R, Seager S, Bains W (2013) Astrophys J 769:6

Johns M, McCarthy P, Raybould K et al (2012) Giant Magellan Telescope: overview. In: Society of Photo-Optical Instrumentation Engineers (SPIE) conference series, vol 8444

Kaltenegger L, Traub WA (2009) Astrophys J 698:519–527

Kasting JF, Catling D (2003) Annu Rev Astron Astrophys 41:429–463

Kasting JF, Liu SC, Donahue TM (1979) J Geophys Res 84:3097–3107

Kasting JF, Holland HD, Pinto JP (1985) J Geophys Res 90:10497

Kasting JF, Whitmire DP, Reynolds RT (1993) Icarus 101:108–128

Knutson HA, Charbonneau D, Allen LE et al (2007) Nature 447:183–186

Knutson HA, Dragomir D, Kreidberg L et al (2014) ApJ 794:795

Konopacky QM, Barman TS, Macintosh BA, Marois C (2013) Science 339:1398–1401

Kopparapu RK, Ramirez R, Kasting JF et al (2013) Astrophys J 765:131

Kreidberg L, Bean JL, Desert JM et al (2014) Nature 505:69–72

Kuchner MJ, Traub WA (2002) Astrophys J 570:900–908

Lawson PR, Dooley JA (2005) Technology plan for the terrestrial planet finder interferometer. NASA STI/Recon Tech Rep News 6:15630

Leger A, Pirre M, Marceau FJ (1993) Astron Astrophys 277:309

Leger A, Mariotti JM, Mennesson B et al (1996) Icarus 123:249–255

Leger A, Rouan D, Schneider J et al (2009) Astron Astrophys 506:287–302

Levine M, Lisman D, Shaklan S et al (2009) Terrestrial Planet Finder Coronagraph (TPF-C) flight baseline concept. ArXiv e-prints

Liang M-C, Parkinson CD, Lee AY-T, Yung YL, Seager S (2003) ApJ 596:247

Line MR, Liang MC, Yung YL (2010) ApJ 717:496

Lissauer JJ, Fabrycky DC, Ford EB et al (2011) Nature 470:53–58

Lockwood AC, Johnson JA, Bender CF et al (2014) Astrophys J 783:L29

Marcy GW, Issacson H, Howard AW et al (2014) Astrophys J Suppl Ser 210:20

Mayor M, Udry S, Lovis C et al (2009) Astron Astrophys 493:639–644

Moses JI, Visscher C, Fortney JJ et al (2011) ApJ 737:15

Moses JI, Line MR, Visscher C et al (2013) ApJ 777:34

Muirhead PS, Hamren K, Schlawin E, et al (2012), ApJ 750:L37

Nutzman P, Charbonneau D (2008) Publ Astron Soc Pac 120:317–327

Oppenheimer BR, Hinkley S (2009) Annu Rev Astron Astrophys 47:253–289

Pepe F, Lovis C, Segransan D et al (2011) Astron Astrophys 534:A58

Pepe F, Cameron AC, Latham DW et al (2013) Nature 503:377–380
Petigura EA, Marcy GW, Howard AW (2013a) Astrophys J 770:69
Petigura EA, Howard AW, Marcy GW (2013b) PNAS 110:19273–19278
Pierrehumbert R, Gaidos E (2011) Astrophys J Lett 734:L13
Quintana EV, Barclay T, Raymond SN et al (2014) Science 344:277–280
Rauer H, Catala C, Aerts C et al (2013) Exp Astron (submitted)
Ricker GR, Latham DW, Vanderspek RK et al (2010) Transiting Exoplanet Survey Satellite (TESS). In: Bulletin of the American Astronomical Society, vol 42, p 450.06
Rivera EJ, Lissauer JJ, Butler RP et al (2005) Astrophys J 634:625–640
Rivera EJ, Butler RP, Vogt SS et al (2010) Astrophys J 708:1492–1499
Rodler F, Lopez-Morales M, Ribas I (2012) Astrophys J Lett 753:L25
Rodler F, Kurster M, Barnes JR (2013) Mon Not R Astron Soc 432:1980–1988
Rowe JF, Bryson ST, Marcy GW (2014) Astrophys J 784:45
Salpeter EE (1955) Astrophys J 121:161
Seager S (2010) Exoplanet atmospheres: physical processes. Princeton University Press, Princeton
Seager S, Deming D (2010) Annu Rev Astron Astrophys 48:631–672
Seager S, Sasselov DD (1998) Astrophys J Lett 502:L157
Seager S, Sasselov DD (2000) Astrophys J 537:916–921
Seager S, Whitney BA, Sasselov DD (2000) Astrophys J 540:504–520
Seager S, Bains W, Hu R (2013) Astrophys J 777:95
Seager S, Turnbull M, Sparks W et al (2014) Exo-S: Starshade probe-class exoplanet direct imaging mission concept – interim report
Segura A, Meadows VS, Kasting JF et al (2007) Astron Astrophys 472:665–679
Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. Wiley, Hoboken
Selsis F, Despois D, Parisot J-P (2002) Astron Astrophys 388:985–1003
Snellen IAG, de Kok RJ, le Poole R et al (2013) Astrophys J 764:182
Spergel D, Gehrels N, Breckinridge J et al (2013) Wide-field infrared survey telescope-astrophysics focused telescope assets. WFIRST-AFTA final report. ArXiv e-prints
Stapelfeldt K, Belikov R, Bryden G et al (2014) Exoplanet direct imaging: coronagraph probe mission study “Exo-C” – Interim report
Strobel DF (1969) J Atmos Sci 26:906–911
Strobel DF (1973) J Atmos Sci 30:489–498
Swift JJ, Johnson JA, Morton TD et al (2013) Astrophys J 764:105
Tian F, France K, Linsky J et al (2014) Earth Planet Sci Lett 385:22–27
Traub WA (2012) Astrophys J 745:20
Traub WA, Levine M, Shaklan S et al (2006) TPF-C: status and recent progress. In: Society of Photo-Optical Instrumentation Engineers (SPIE) conference series, vol 6268
Traub WA, Kaltenegger L, Jucks KW (2008) Spectral characterization of Earth-like transiting exoplanets. In: Society of Photo-Optical Instrumentation Engineers (SPIE) conference series, vol 7010
Trauger JT, Traub WA (2007) Nature 446:771–773
Tuomi M, Anglada-Escude G, Gerlach E et al (2013) Astron Astrophys 549:A48
Udry S, Bonfils X, Delfosse X et al (2007) Astron Astrophys 469:L43–L47
Van Grootel V, Gillon M, Valencia D et al (2014) Astrophys J 786:2
Vogt SS, Wittenmyer RA, Butler RP et al (2010) Astrophys J 708:1366–1375
Walker JCG (1977) Evolution of the atmosphere. Wiley, New York
Winn JN, Matthews JM, Dawson RI et al (2011) Astrophys J Lett 737:L18
Wordsworth R, Pierrehumbert R (2014) Astrophys J Lett 785:L20
Yung YL, Demore WB (1999) Photochemistry of planetary atmospheres. Oxford University Press, New York
Yung YL, Allen M, Pinto JP (1984) Astrophys J Suppl Ser 55:465–506
Zahnle K, Marley MS, Freedman RS, Lodders K, Fortney J (2009) ApJ 701:L20
Zsom A, Seager S, de Wit J, Stamenkovic V (2013) Astrophys J 778:109