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Variety in atmospheric compositions of terrestrial exoplanets: effects of surface H_2O mass

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Theoretical models predict that a significant part of Earth-sized to super-Earth-sized terrestrial exoplanets possess a deep surface H_2O ocean (e.g., $>$ 100 km depth), given accretion of H_2O-rich planetesimals (e.g., carbonaceous chondrites and comets). The atmospheric compositions of these exoplanets also may have a wide variety depending on the surface H_2O mass, because the redox state of degassing volatiles from the mantle is significantly influenced by the depth of ocean. According to studies of Earth's volcanoes (Holland, 2002), the chemical compositions of gas species degassed from subaerial volcanoes are generally oxidizing, while those from submarine volcanoes are more reducing. The difference between the compositions of volcanic gas species reflects the difference of the thermodynamic conditions of the magmas (Kump & Barley, 2007). Here, we investigate the variety of atmospheric compositions of terrestrial exoplanets by focusing on surface H_2O mass. We discuss the possibility of presence of reducing atmospheres on exoplanets with deep surface oceans.

To investigate CH_4/CO_2 ratios in degassing volatiles from mantle as a function of ocean depth, we adopted thermodynamic equilibrium between CH_4 and CO_2 in a hydrothermal fluid. We assumed that the equilibrium is determined by the hydrogen fugacity, controlled by mineral redox buffers. Terrestrial subaerial volcanic gases are considered to equilibrate with fayalite-magnetite-quartz (FMQ) buffer (Holland, 2002). Measured oxidation states of deep-sea hydrothermal systems are close to the pyrrhotite-pyrite-magnetite (PPM) buffer (McCollom & Seewald, 2007). By assuming that the rock components of terrestrial exoplanets are similar to those of Earth, we used the FMQ and PPM buffers to calculate the hydrogen fugacity and consequent CH_4/CO_2 ratios of gas species from hydrothermal systems on these planets.

We investigated the atmospheric compositions for a given flux and composition of gas species degassed from mantle, developing a one dimensional photochemical model based on an early-Earth model (Pavlov et al., 2001). Our model contains 337 reactions and 69 species involved in H, C, N, O, and S chemistry. Calculations were carried at 1 bar and 275 K of surface condition. The model also includes UV shielding effect by organic haze using an experimental relation between C/O ratio and produced aerosol mass (Trainer et al., 2006). The partial pressure of CO_2, pCO_2, is considered to be controlled by chemical weathering rate in the carbon cycle. We varied pCO_2 from 0.1 to 1000 times the present atmospheric level, because of the large uncertainty in chemical weathering rate on exoplanets.

The thermodynamic calculations show that the redox state of outgassing fluids become significantly reducing under high-pressure conditions ($>$ 7000 bar). Even if the rock components of exoplanets are similar to that of Earth, CH_4 would be predominant in carbon-bearing species degassing from mantle when the surface oceans are deeper than 70 km.

Our photochemical calculations indicate that exoplanets with deep surface oceans would have reducing atmospheres (CH_4/CO_2 ratio $>$ 1), when the degasing fluxes reach a level several times that of Earth. Considering the variations in Earth's CO_2 degassing flux in the past (Tajika & Matsui, 1993), exoplanets with deep surface ocean are capable of possessing a Titan-like, hazy atmosphere, which could be detectable by future observations. The photochemical model also shows that the CH_4 mixing ratios reach high levels (i.e., 10 - 1000 ppm) at the degassing fluxes comparable to that of current Earth. These results suggest that radiative forcing of CH_4 should be taken into account when considering surface temperature and habitability of exoplanets with deep surface oceans.

Keywords: exoplanets, hydrothermal system, photochemistry, atmospheric composition