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**PHOTOCHEMISTRY OF THE RECENT MARTIAN ATMOSPHERE AT DIFFERENT OBLIQUITIES.**

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**Introduction:** Photochemistry of the Martian atmosphere shapes the atmospheric composition of Mars [1]. It also affects the evolution of the Martian atmosphere by contributing to atmospheric escape. Moreover, photochemistry produces reactive species, such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), that could interact with potential surface organic materials that could be produced by Martian life in the past [2].

Photochemistry of the Martian atmosphere is initiated by CO<sub>2</sub> photolysis and water vapor photolysis, the latter producing highly reactive HO<sub>x</sub> radicals (HO<sub>x</sub> = H + OH + HO<sub>2</sub>) that catalyze many important reactions, such as the recombination of CO<sub>2</sub> and the destruction of ozone, thus altering the atmospheric composition. The water vapor photolysis rate depends on atmospheric water content, which then depends on the supply of water vapor from the sublimation of the polar water ice caps.

The present-day obliquity of Mars is 25.19°. Over its history, Mars has undergone drastic obliquity change [3]. In the recent 5 million years, the obliquity of Mars has varied between 15° and 35°. At higher obliquities, the polar regions receive more solar insolation in spring and summer, which drives higher sublimation rates of water vapor into the atmosphere. The greenhouse effect of the increased water ice cloud further warms up the polar regions, enhancing the water vapor supply. The resulting higher atmospheric water content and hence faster water vapor photolysis could reshape the present-day photochemistry. At lower obliquities, the Martian atmosphere could be depleted of water vapor and the highly reactive catalysts produced from water vapor photolysis, so the atmospheric composition could also be very different. The objective of this study is to understand the effect of obliquity variations on the photochemistry of the Martian atmosphere and to reconstruct plausible atmospheric compositions in the past. A special focus of this study is on the concentration of the photochemically produced H<sub>2</sub>O<sub>2</sub> that could oxidize organics materials on the surface and in the shallow subsurface.

**Model:** Only 3D models can resolve the atmospheric transport of water vapor that sublimates from the localized water ice reservoirs in the polar

regions and reconstruct the 3D distribution of water vapor, which affects the photolysis of water vapor and the subsequent photochemistry. We therefore use the Mars Planetary Climate Model (PCM), a 3D general circulation model coupled with photochemistry [4], to simulate the atmospheric composition at different obliquities. We use a 5.6° (in longitude) × 3.75° (in latitude) horizontal resolution and 36 vertical layers to discretize the Martian atmosphere below ~150 km altitude. Given the lack of knowledge about dust loadings in the past, we set a uniform dust opacity value in the visible band in all simulations. We explore obliquities between 20° and 35° by 5°.

**Simulation Results:** As the obliquity of Mars changes from 20° to 35°, the annual mean surface temperature of the polar regions increases by 30 K. As a result, the water content of the atmosphere increases by about two orders of magnitude, with the annually and globally averaged precipitable water increasing from 5 microns to 400 microns. Resulting from the increase in the photolysis rate of water vapor, the concentration of OH radicals in the atmosphere increases by 2–3 orders of magnitude. This means that the oxidizing capacity of the Martian atmosphere is significantly elevated at high obliquities. A concomitant, significant decrease in the CO concentration from 20° to 35° obliquity is produced by the simulations. However, by contrast, the concentrations of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> are much more stable than those of OH and CO as obliquity varies—the concentration of HO<sub>2</sub> only changes by a factor of 1.4 and the concentration of H<sub>2</sub>O<sub>2</sub> only changes by a factor of 3.5 as the obliquity varies between 20° and 35°. Furthermore, a non-monotonic behavior in the concentrations of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> is produced by the model—they both peak around the present-day ~25° obliquity. This suggests favorable conditions for preserving organic materials on the surface and in the shallow subsurface. The stability of the concentrations of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> against obliquity variations and their non-monotonic behaviors are explained by elucidating a number of negative feedbacks in the photochemical and climate system.

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**References:** [1] Lefèvre F. and Krasnopolsky V. (2017) *Atmos. Clim. Mars*, 18, 405–432. [2] Quinn R. C. and Zent A. P. (1999) *Orig. Life Evol. Biosph.*, 29, 59–72. [3] Laskar J. et al. (2002) *Nature*, 419, 375–377. [4] Lefèvre F. et al. (2021) *JGR Planets*, 126, e2021JE006838.