Oscillations in Martian Atmospheric Composition and Oxidizing Capacity Driven by Obliquity Variations

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Introduction: Understanding how Mars' atmospheric composition responds to changes in planetary obliquity is critical for reconstructing past climate conditions and assessing their implications for habitability. Over the past five million years, Mars' obliquity has varied significantly, ranging between approximately 15° and 40°. At high obliquity, the polar regions of Mars receive more solar insolation, which results in stronger water ice sublimation and a more humid atmosphere. At low obliquity, the Martian atmosphere is dryer.

The photolysis of atmospheric water vapor produces highly reactive radicals, which catalyze many important photochemical reactions, shaping the atmospheric composition of Mars. Therefore, variations in Mars' obliquity are expected to induce significant changes in its photochemistry and atmospheric composition. Understanding these changes over Mars' history is a key area of interest.

Additionally, water vapor photolysis produces oxidants, such as H_2O_2, which can potentially react with surface materials and destroy any organics that might have been produced by life. Investigating whether Mars has experienced periods with exceptionally high concentrations of these oxidants could provide insights into biosignature preservation on Mars and the chances of future Mars missions finding life-produced organics on the surface.

In this study, we use the Mars Planetary Climate Model (Mars PCM) to investigate the atmospheric composition of Mars in response to variations in obliquity in the recent past.

Methods: We use the Mars Planetary Climate Model (Mars PCM), a three-dimensional general circulation model equipped with a photochemical module for Mars' atmosphere. The spatial distribution of water vapor and its photolysis rate are determined by the processes of water ice sublimation and water vapor transport, and these processes can only be simulated self-consistently using a 3D model.

The spatial resolution of the PCM is 5.6° in longitude, 3.75° in latitude, and 36 vertical layers up to ~130 km altitude.

We use the model to investigate the atmospheric composition at 20°, 25°, 30°, and 35° obliquity. In all simulations, the orbital eccentricity is set to zero, and dust opacity in the visible band is set to 0.2. As we are investigating the recent Mars, we keep surface water reservoirs at their present-day locations.

Results: Our simulations show that from 20° to 35° obliquity, the water vapor abundance in the atmosphere increases by two orders of magnitude. The annual mean global mean column density of water vapor changes from ~4 precipitable microns to more than 400 precipitable microns, as shown by the figure below:

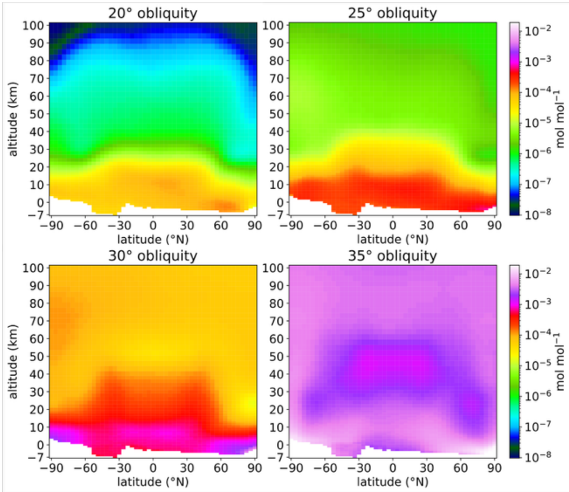

Figure 1. Zonal mean volume mixing ratio of water vapor at 20°, 25°, 30°, and 35° obliquity.

As expected, the oxidizing capacity of the atmosphere, which is determined by the concentration of hydroxyl radicals (OH), a photolytic product, changes in response to changes in the atmospheric water content. From 20° to 35° obliquity, OH concentration increases by 2–6 orders of magnitude, depending on the altitude, as shown by the figure below:

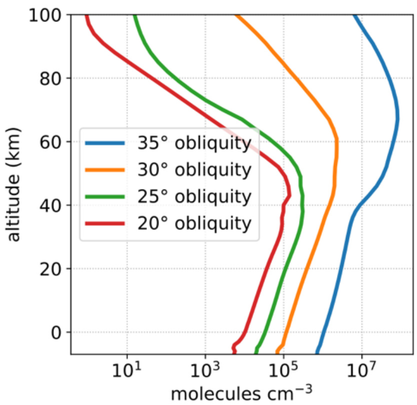

Figure 2. Global mean number density of hydroxyl radicals (OH) at different altitudes at 20°, 25°, 30°, and 35° obliquity.

As the major destruction mechanism for carbon monoxide (CO) is the reaction with OH, CO concentration decreases by two orders of magnitude. The annual mean global mean column density of CO decreases from 3×10^{20} molecules/cm^2 to 1.7×10^{18} molecules/cm^2 as the obliquity increases from 20° to 35°, as shown by the figure below:

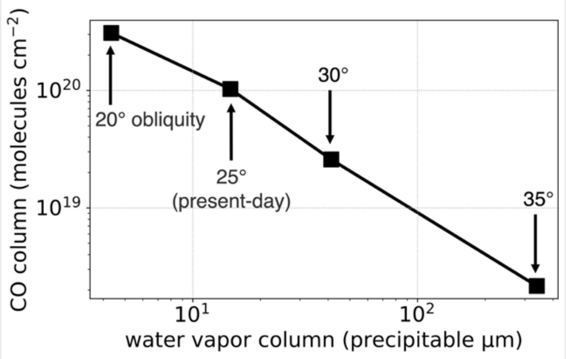

Figure 3. Response of the column density of CO to the atmospheric water content as obliquity of Mars varies.

Hydrogen peroxide (H_2O_2), a strong oxidant for surface and subsurface organic matter, is formed from the reaction of HO_2 and HO_2, while HO_2 is derived from water vapor photolysis. Therefore, it is of interest to investigate whether the concentration of H_2O_2 will be much higher than its present-day value at high obliquity, as the water vapor photolysis rate is much higher at high obliquity due to the exceptionally high water vapor concentration in the atmosphere. An exceptionally high concentration of H_2O_2 could remove organic matter biosignatures produced by possible ancient Martian life.

However, our simulations denied such possibility. We find that although the concentration of H_2O_2 at high altitudes increases significantly with increasing obliquity, the low-altitude concentration of H_2O_2 remains stable across obliquity variations. The low-altitude concentration peaks around 25° obliquity (the present-day value), which is favorable for surface organic matter preservation. The figures below show the distribution of H_2O_2 concentration at different obliquity and the response of near-surface H_2O_2 concentration to obliquity variations.

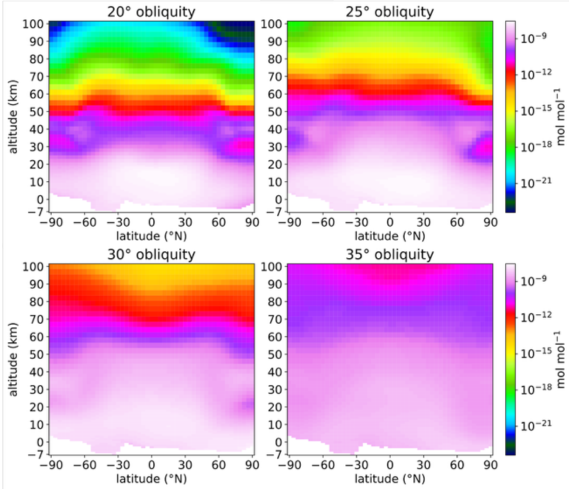

Figure 4. Zonal mean volume mixing ratio of hydrogen peroxide (H_2O_2) at different altitudes at 20°, 25°, 30°, and 35° obliquity.

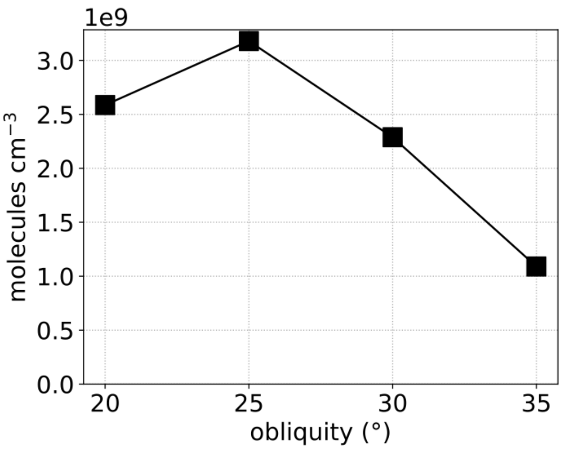

Figure 5. Near-surface number density of hydrogen peroxide (H_2O_2) at 20°, 25°, 30°, and 35° obliquity.

Summary and future work: At high obliquity, the atmosphere of Mars is significantly more humid and more oxidizing than the present-day atmosphere. At low obliquity, the opposite occurs.

In the recent past, Mars has not experienced exceptionally high concentrations of surface oxidants (in particular, H_2O_2) and the resulting high destruction rates of surface organic matter, which is favorable for biosignature preservation.

Future work will investigate potentially CO-rich atmospheres at even lower obliquities.