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Laboratory simulation of Martian trace gas chemistry

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Introduction

Recently there has been a great deal of interest in modelling the concentration and distribution of gases within the Martian atmosphere due to the observation of trace species such as methane [1,2] that could hold clues to currently unobserved processes such as volcanism or perhaps even life.

Mars Global Circulation Models (MGCMs) can predict both the seasonal and spatial variability of trace gases on Mars. Current models are very effective at predicting the variability due to transport (dynamical) processes [3] though there are only two MGCMs in the world that can model the effects of the chemical reactions that act on the gases [4,5].

To improve the accuracy of these models more must be learnt about the mechanisms and rates of these reactions under Martian environmental conditions.

The Laboratory

Set-up

Figure i. Shows a photo of the current laboratory set-up. Figure ii. is a schematic diagram of the apparatus.

A: Environmental simulation chamber

A stainless steel vacuum chamber is evacuated and then filled with a Mars mix gas (95% CO₂ + 5% N₂) at a pressure of ~1 bar to approximate a “standard” Mars atmosphere.

B: FTIR spectrometer

The FTIR measures the IR spectrum of the gases within the chamber. The spectra are analysed to calculate the concentrations of the gases being produced and destroyed. Spectra are taken at 1 minute intervals to examine the evolution of the gases with time and to ascertain if an equilibrium has been reached.

C: Heating/cooling plate

The chamber is cooled to a standard Mars temperature of -50°C by flowing liquid nitrogen through a compartment at the base of the chamber. A heating element can heat the chamber to simulate diurnal heating effects.

D: Gas inlet

A gas inlet pipe is used to add trace gases such as HCl, H₂O, SO₂ into the chamber in small concentrations. A sample container can be attached to sample the gases in the chamber to perform mass spectrometry on.

E: Deuterium UV lamp

The UV light emits a spectrum similar to the UV output of the Sun. The UV photons are what drive the photochemical reactions within the chamber.

F: Regolith

A basalt powder can be added at the base of the chamber to simulate possible effects of basalt regolith on the reactions occurring in the atmosphere.

The UK-LMD MGCM

The UK-LMD MGCM is a state of the art MGCM developed by researchers from the Laboratoire de Météorologie Dynamique (LMD), France; the Instituto de Astrofísica de Andalucía, Spain and Oxford University and The Open University in the UK. The UK-LMD version utilises a spectral dynamical core [6] and a semi-Lagrangian advection scheme [7,8] developed in the UK along with physical sub-models developed by researchers at LMD [9]. These sub-models include radiative transfer, cloud microphysics and a water cycle [3].

The chemical sub-model contains 16 species (CO₂, CO, O/P, O/D, O₅, H, H₂O, HO₂, HO₃, CH₄, N₂, H₂O ice and H₂O vapour) undergoing 42 chemical reactions per period centered cap. The concentration of each gas species is calculated every 30 minutes taking into account advection, vertical diffusion, convection and chemistry plus any effects of the CO₂ and water cycles.

The Problem

The reaction rates and mechanisms used are assumed to be the same as those for reactions occurring in the Earth’s atmosphere but this might not be the case.

Important differences between Earth and Mars:

• The average temperature of Mars is much lower and so reaction rates must be extrapolated to these lower temperatures.

• The bulk constituent on Mars is CO₂ experiments using CO₂ rather than N₂ or O₂ have been shown to increase the efficiency of certain three-body reactions by ~2.5 times [10].

• Basalt dust is an important constituent in the Martian atmosphere but not on Earth so it is possible that some reaction mechanisms haven’t yet been observed.

To characterise these effects on rates and mechanisms we must measure reactions under Martian conditions.

An example: The effect of heterogeneous reactions on ozone

Heterogeneous chemistry involves reactions between species in different phases. In the Earth’s atmosphere reactions that occur on the surface of liquid aerosols and solid particles in the air can be very important, particularly to reactive species such as ozone.

The figures to the right show zonally-averaged seasonal plots of ozone column density (µm-atm) on Mars. Figure A is a run using purely gas-phase chemistry in the chemical sub-model while in Figure B a suite of heterogeneous reactions have been added. These simulations were run using the UK-LMD version of the MGCM and agree with the published results for similar conditions from the LMD MGCM [4,11].

The model predicts the qualitative distribution of ozone well. In both Figures the maximum value of ozone column density occurs during polar winter (Winter solstice is at LS≈90° in the South and LS≈270° in the North). The maxima occur when the concentration of water vapour in the atmosphere is lowest. This is because species that form from the photolysis of water (HO₂=H₂O₂, HO₃) catalyse the destruction of ozone.

However, the LMD team found that the predicted ozone distribution did not agree quantitatively when compared with observations from the IR spectrometer aboard SPICAM [11]. The model underpredicted the maximum concentration at aphelion (LS=71°) and in late summer where the ozone did not increase quickly enough to match the observations. This was remedied by the addition of heterogeneous reactions involving HO₃ occurring on the surface of water ice cloud particles as seen in Figure B.

These are unlikely to be the only heterogeneous reactions of interest. Indeed, reactions that occur on the surface of dust particles will likely be important on Mars though laboratory simulations are required to characterise them as they are not currently well understood.

Summary

The study of trace gas chemistry on Mars is interesting as it offers clues into underlying active processes such as volcanism.

To understand observations of trace gases they must be modelled by MGCMs that are capable of predicting their seasonal and spatial distribution because of both transport and chemical processes.

Laboratory simulations of chemistry under Martian environmental conditions are needed both to improve the accuracy of current MGCM reaction schemes but also to identify possible new reactions of interest such as ones occurring on the surface of basalt dust particles.

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