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AN INVESTIGATION OF MARTIAN ATMOSPHERIC TRACE SPECIES USING LABORATORY AND COMPUTER-BASED SIMULATION.

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Introduction:

The study of trace gas species in the Martian atmosphere has the potential to shed new light on wide-ranging topics such as the search for life and the history of liquid water on the planet. Investigating the way that molecules such as ozone, water and HCl are cycled in the atmosphere will give insights into the interactions taking place between the atmosphere, lithosphere and any potential biosphere. Numerous missions are currently being planned; for example the NASA/ESA Trace Gas Orbiter which will probe the trace constituents of the Martian atmosphere and to try to explain recent observations such as the Tharsis methane plumes [1] and the presence of perchlorate in the North polar plains [2].

Currently there are two Mars General Circulation Models (MGCMs) that have fully coupled photochemistry modules: the 3D Mars Global Multiscale Model (GM3) [3] and the Laboratoire de Météorologie Dynamique (LMD) MGCM [4], [5]. Both modules focus on odd-hydrogen (HOx) and odd-oxygen (Ox) chemistry and are not yet capable of simulating more complex chemical interactions. However, the benefit of fully-coupled MGCMs is that both the chemistry and the global transport of trace species can be investigated.

In the current project we plan to study the more exotic chemical reactions occurring in the Martian atmosphere and to constrain their mechanisms and rates using both laboratory analogues and computer-based simulation.

Observations:

Species such as ozone and water have long been known to be present in the Martian atmosphere. As remote sensing techniques have improved, further species such as methane and formaldehyde have been observed. Indeed the detection of methane in 2009 [1] sparked much interest due to the possible implication it had for the chance of extant microbial life being present. The temporal and spatial variability seen in the observations indicate an active process, one that cannot yet be explained by conventional chemistry [6].

Another mystery lies in the presence of perchlorate salts in the Northern polar plains, as seen by the Phoenix lander [2]. On Earth, these salts accumulate in arid regions such as Antarctica and the Atacama Desert. Indeed, perchlorate salts are very soluble and so are indicative of prolonged periods of drought. Whilst the exact mechanism of their deposition is still unknown an atmospheric origin is suspected [7],

[8]. The formation requires a chlorine species to be present in the atmosphere; a potential source on Mars being the outgassing of HCl by geological processes. An understanding of the mechanism of perchlorate production could therefore be invaluable in ascertaining the recent history of volcanism and surface water on Mars.

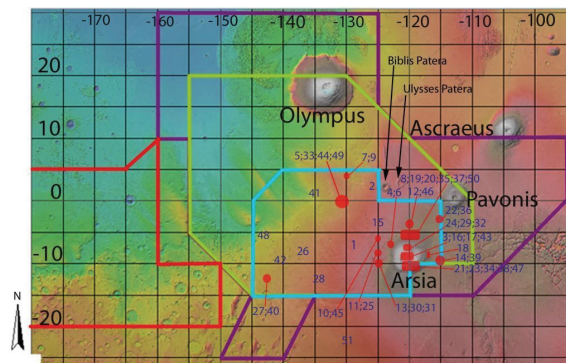


Figure 1. A close up of one of the chemically striking regions found by Karunatillake et al, 2009 [10]. The blue box shows enhanced Cl and depletion of Fe and Si. It is superimposed onto a topographical map from MOLA, the blue toned areas being a lower elevation than the red toned ones.

Recently the Heterodyne Instrument for the Far Infrared (HIFI) on the Herschel Space Observatory searched for HCl in the Martian atmosphere. Though no HCl was detected an upper limit estimation of 200 p.p.t was possible [9]. Trace species have been seen in the soil, in 2009 Karunatillake et al [10] published a paper detailing chemically striking regions on the Martian surface as observed by the Mars Odyssey Gamma Ray Spectrometer. Specifically the high abundances of Ca, Cl, Fe, H, K, Si and Th were noted at particular locations on the surface. An interesting chlorine-rich area near to Olympus Mons may be seen in Figure 1. Whilst the high relative abundance of species like chlorine in volcanic regions may not be surprising their presence cannot yet be explained by current coupled MGCMs. To obtain an overall understanding of the way that the Martian atmosphere and lithosphere interact, both in the past and present, we must be able to simulate observations such as these.

Laboratory:

Preliminary experiments to assess relevant reaction mechanisms and rate constants have been undertaken using coronal discharge experiments. Mars-

like gas mixtures were flowed through a reaction chamber and subjected to coronal discharges in order to simulate the action of UV photons in the atmosphere. This work is now being expanded using a Mars environmental simulation chamber. The chamber can be seen in Figure 2.

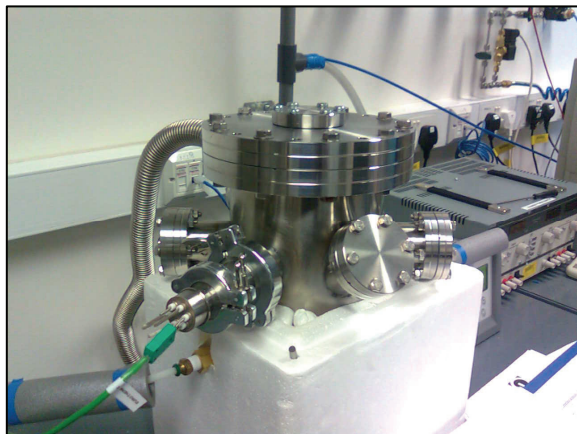


Figure 2. The Mars environmental simulation chamber. The chamber is made from stainless steel and is 130mm in diameter.

The chamber is capable of creating an environment similar to Mars in temperature and pressure, with an added diurnal cycle if required. The chamber will be fitted with a UV solar simulator and a Mars analogue basalt regolith. A prescribed mixture of Mars gases will be flowed into the chamber with trace amounts of water, methane and HCl added. The species' effects on the chemistry will then be analysed using infrared spectroscopy and gas chromatography. The regolith will also be analysed before and after each run using techniques such as laser induced mass spectroscopy to assess changes to the soil composition.

Modelling:

The MGCM used is a collaboration between The Open University, Oxford University and the LMD in Paris. The model is composed of a dynamical core that is coupled with physical, radiative transfer, regolith and chemical routines [4], [5]. It is given an initial state, and then runs for a set number of Martian sols to give spatially and temporally resolved data on the global system. The chemistry module within the MGCM has been used extensively to investigate the global distribution of ozone [5] with the addition of such elements as heterogeneous reactions [11]. Ozone abundance is anti-correlated with water vapour abundance. This behaviour was simulated by the LMD-MGCM chemistry module in 2004 [5] and can be seen in Figure 3.

Numerical experiments will be conducted in order to identify sources of trace species on the surface, by conducting trial releases and observing the species' distribution after a set period of time. The

interaction of the current chemical module with new reactions as determined by the laboratory simulations will also be investigated.

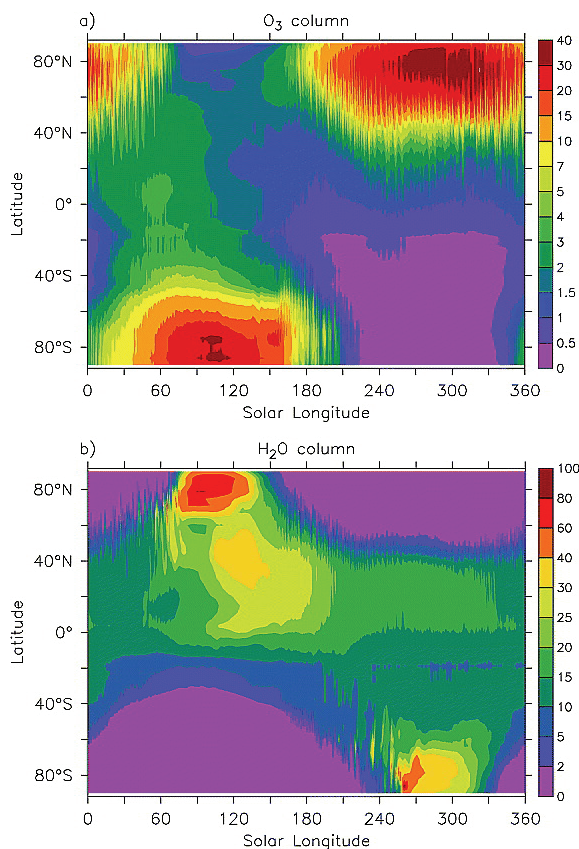


Figure 3. a) The zonally averaged ozone column ($\mu\text{-atm}$)
b) the zonally averaged water vapour column (precipitable μm) both as a function of solar longitude.

This has been taken from Lefèvre et al, 2004 [5].

Summary:

Initial results will be presented from a combined numerical and laboratory study of trace species chemistry on Mars. The laboratory studies will inform the chemical processes in the model by giving better estimates of rate constants and the relative importance of different reactions that may need to be introduced into the model schemes. The numerical modelling will tie these results to observations of the Martian atmosphere both for model validation and to guide the interpretation of observations, ultimately by chemical data assimilation for Mars [12] as is already performed on Earth [13]. Improved knowledge of source and sink regions will be of vital importance for guiding selection of future spacecraft mission landing sites. An understanding of trace species, particularly ones identified as possible biomarkers is important not just for the study of Mars and other solar system bodies but will also have implications for the study of exoplanet atmospheres.

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