School of Chemistry
FACULTY OF MATHEMATICS AND PHYSICAL SCIENCES

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Meteor Ablated Phosphorus as a Source of Bioavailable Phosphorus to the Terrestrial Planets

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Overview & Introduction

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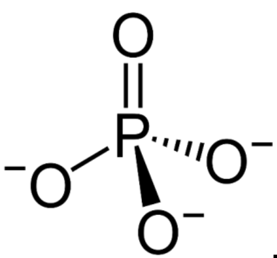
1. Introduction & Aims
2. Gas Phase Kinetics – Experiment and Results
3. Meteoric Ablation – Experiment and Modelling
4. Atmospheric Implications

1. Introduction – Phosphorus

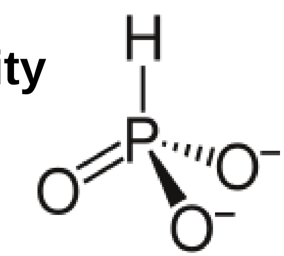
- Phosphorus, P, is a key biological element with major roles in replication, information transfer, and metabolism. Interplanetary dust contains 0.8 % P by elemental abundance, and meteoric ablation in a planetary atmosphere is a significant source of atomic P.

- Orthophosphate (oxidation state +5) is the dominant form of inorganic P at the Earth's surface, however, due to their low water solubility and reactivity, such P(V) salts have a poor bio-availability. Less oxidised forms of P (oxidation state ≤ +3) are however far more bio-available.



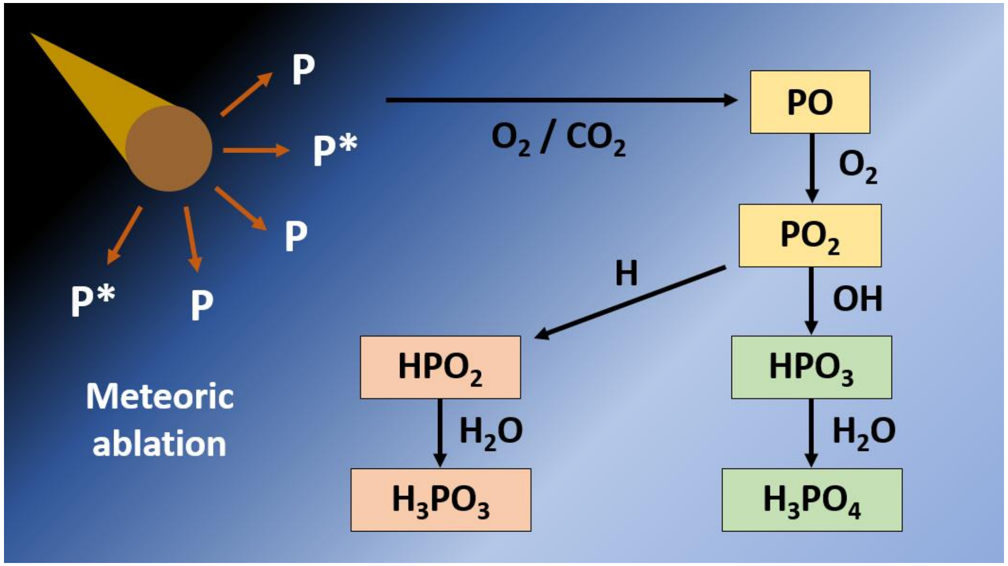
P(V)
Less bio-available

P(III)
Greater bio-availability



1. Introduction & Aims

- Previous studies have focused on the direct delivery of P to the surface in meteorites, to undergo processing through aqueous phase chemistry.
- In contrast, the atmospheric chemistry of P has so far been ignored.
- We have constructed a schematic diagram of the likely chemistry of meteor ablated P atoms in an oxidising upper atmosphere (below).

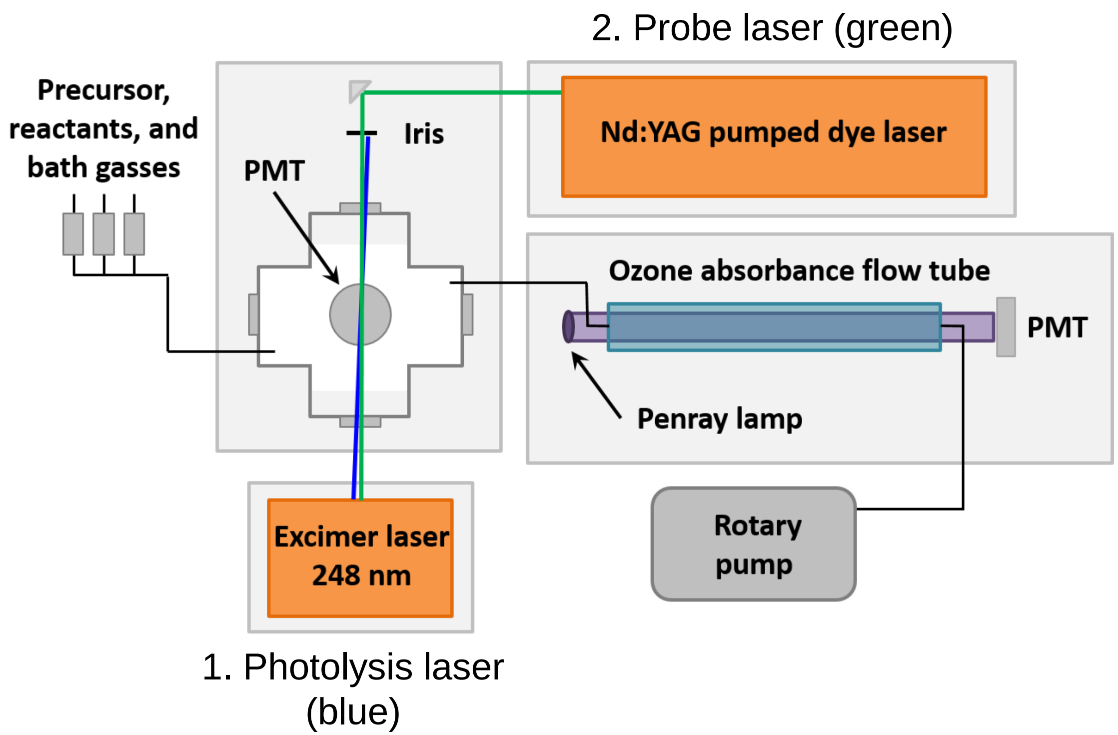


Aims of this study:

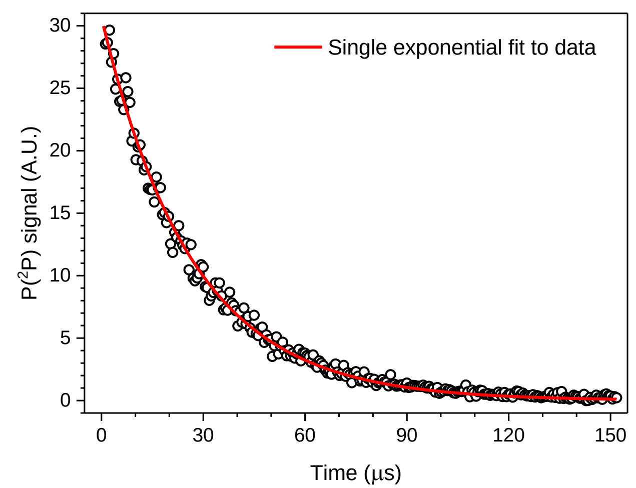
1. To determine rate coefficients for the reactions in the scheme above.
2. To study the ablation process and determine how much P enters the Earth's atmosphere.
3. To incorporate these results into a model and determine if the bioavailable H_3PO_3 is formed.

2. Kinetics - Experimental

- The kinetics of the reactions of P, PO, and PO_2 with atmospherically relevant species have been studied using the pulsed laser photolysis (PLP)-laser induced fluorescence (LIF) technique.



3. Fluorescence signal shows how fast P or PO reacts with co-reagent



1. Firing the photolysis laser dissociates the PCl_3 or $POCl_3$ precursor to P or PO respectively.
2. The prove laser fires, and the amount of P or PO is detected by Laser Induced Fluorescence.
3. Varying the time between the photolysis and probe laser, we get a decay of the P or PO species.

2. Kinetics – $P(^4S) + O_2$ Results

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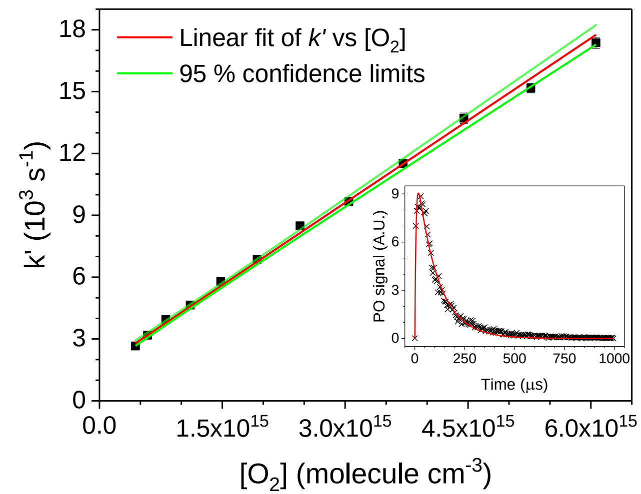
- P atoms produced in the presence of O_2 by the PLP of PCl_3 react according to the following scheme:

  R1: $P + O_2 \rightarrow PO + O$ (growth of PO)

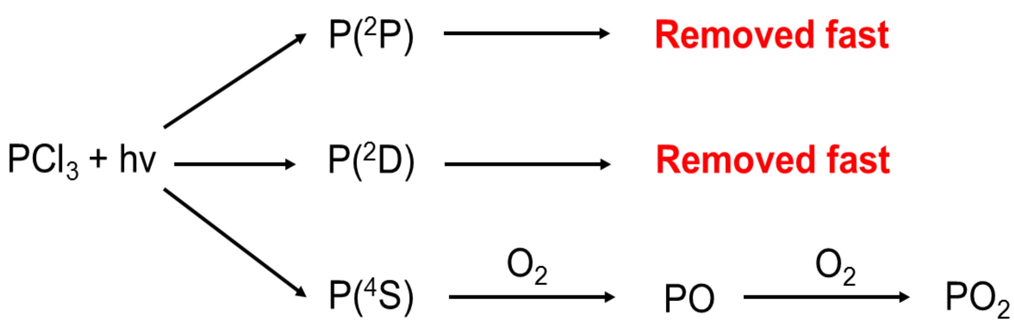
  R2: $PO + O_2 \rightarrow PO_2 + O$ (loss of PO)

- The growth and loss of PO is monitored by LIF, and a bi-exponential fitted to the trace (right inset) to obtain the psuedo-first order rate constants, *k′*:

$$[\mathrm{PO}]_t = \left(\frac{k'_{\mathrm{growth}}}{k'_{\mathrm{loss}} - k'_{\mathrm{growth}}}\right)[\mathrm{P}]_0\left(e^{-k'_{\mathrm{growth}}.t} - e^{-k'_{loss}.t}\right)$$



- The concentration of the O_2 co-reactant is varied to acquire bi-molecular plots (above), the gradients of which give bimolecular rate constants for the reaction of P and PO with O_2.
- For $P + O_2$, we observed an inverse pressure dependence. We attribute this pressure dependence to the interference of two reactive low-lying metastable states of P (the ^2D and ^2P states), which are quenched at higher bath gas pressures.
- To measure the removal of ground state $P(^4S)$ with O_2, experiments at higher bath gas pressures and $[O_2]$ were conducted.



Rate obtained: **$k\ (P(^4S) + O_2) =$**

$3.08 \times 10^{-13} \times (T / 298)^{2.24}$

Can monitor the **slow growth** of PO from ground state $P(^4S)$

Douglas *et. al.*, *J. Phys. Chem. A* 2019, 123, 9469-9478

2. Kinetics – Excited state P reactions

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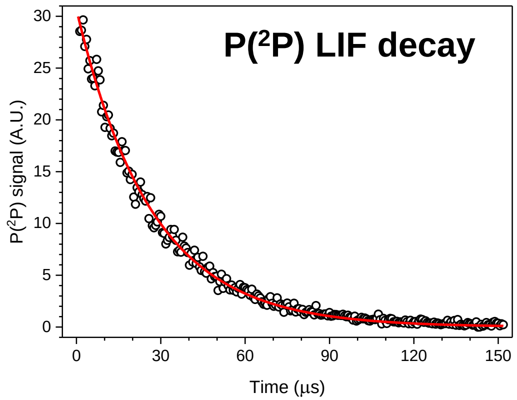
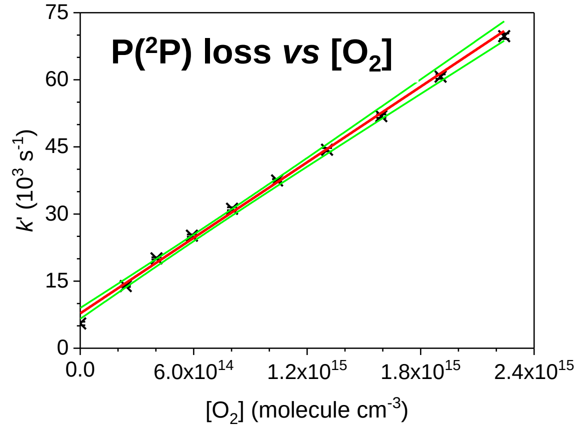
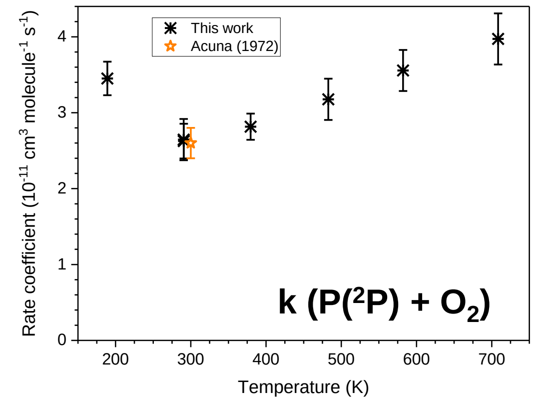
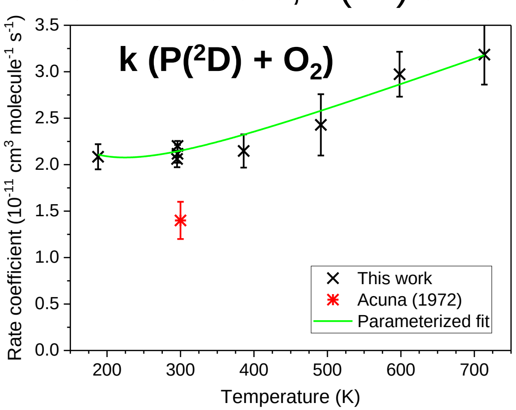
- Meteor ablation of interplanetary dust will likely produce both ground (^{4}S) and excited (^{2}D and ^{2}P) states of P. We can directly monitor the first two excited states of P by LIF.
- When monitoring P(^{2}P) in the presence of O_2 we observe a single exponential loss (below left), with no evidence of any growth of the P(^{2}P) signal at short times, suggesting no higher states of P are produced following PLP of PCl_3. Rates were determined over a range of temperatures (below right).

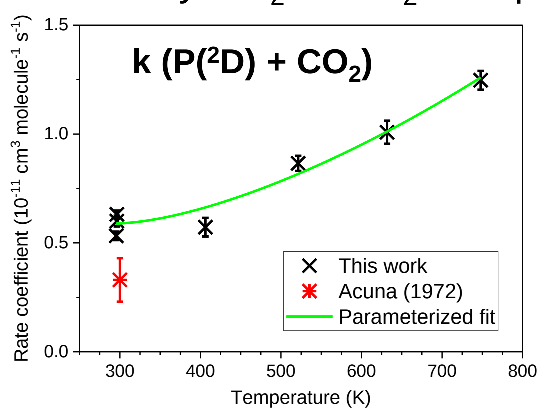


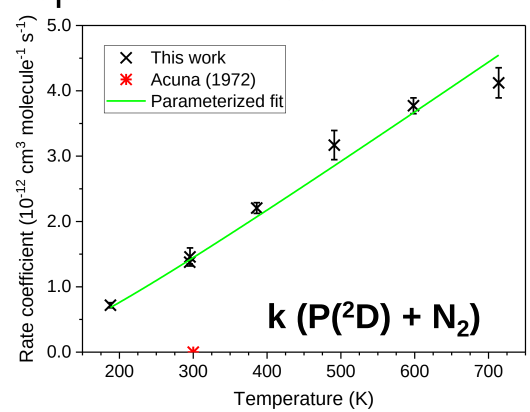




- Profiles for P(^{2}D) in the presence of O_2, also show a single exponential loss. Unlike the second excited state, P(^{2}D) also is also removed by CO_2 and N_2. Temperature dependent rates below.







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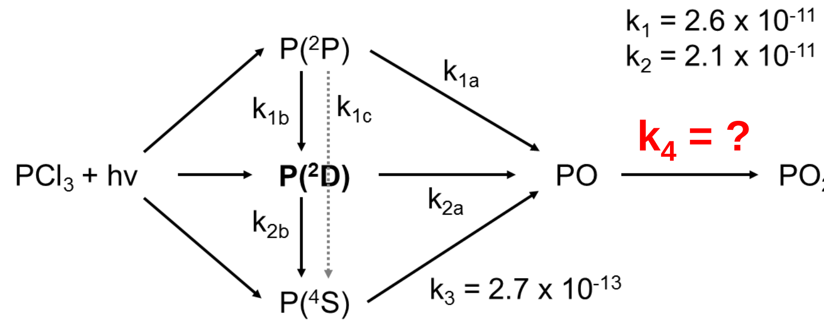
2. Kinetics – PO and PO_2 reactions

- **$PO + O_2$:** Many PO traces were obtained when measuring the rate of $P(^4S) + O_2$. However the complicated reaction scheme (right) makes extracting a rate for $PO + O_2$ from such profiles difficult.

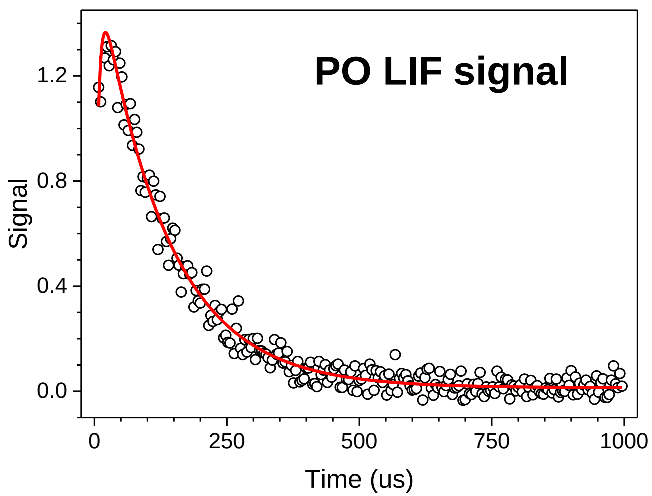
- To determine the rate of $PO + O_2$, experiments were carried out in which PO was produced directly from the photolysis of $POCl_3$:

$$POCl_3 + n.hv \rightarrow PO + 3\ Cl$$



Relative populations of states following photolysis of PCl_3 unknown

- We observed a small pressure dependence for $PO + O_2$ indicating both a 2 and 3 body channel:

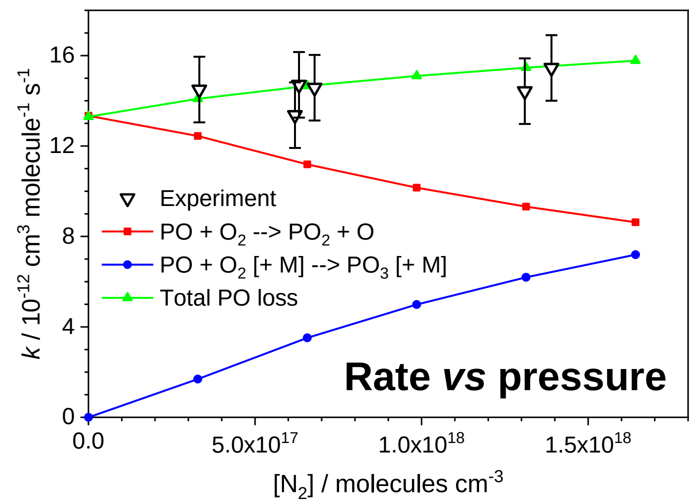


2 body channel

$$PO + O_2 \rightarrow PO_2 + O$$

3 body channel

$$PO + O_2 \xrightarrow{[M]} PO_3$$



- **$PO_2 + O_3$:** O_3 concentrations in the reaction cell can be determined using an absorption cell.

- Removal rates of PO_2 in the presence of O_3 give a room temperature rate coefficient of 8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. This is ~ 20000 times faster than the reaction of the isovalent NO_2 with O_3.

3. Meteoric Ablation - Experiment

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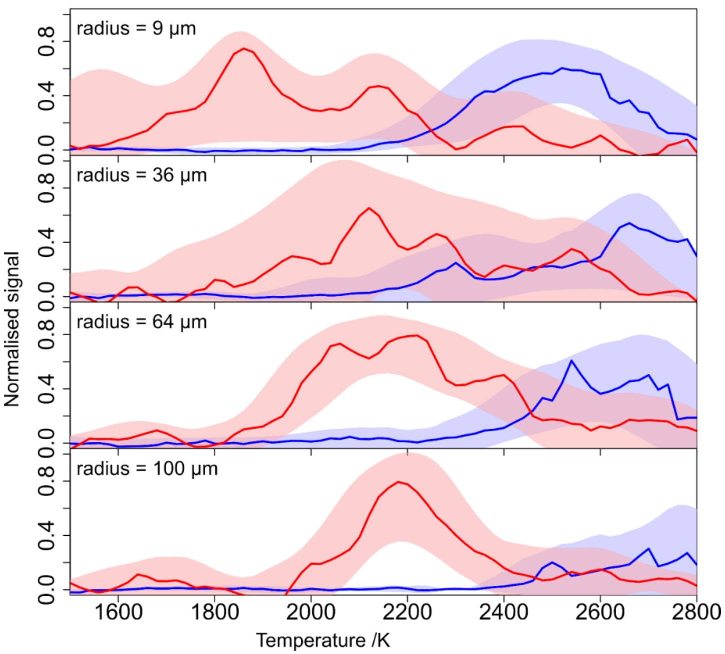
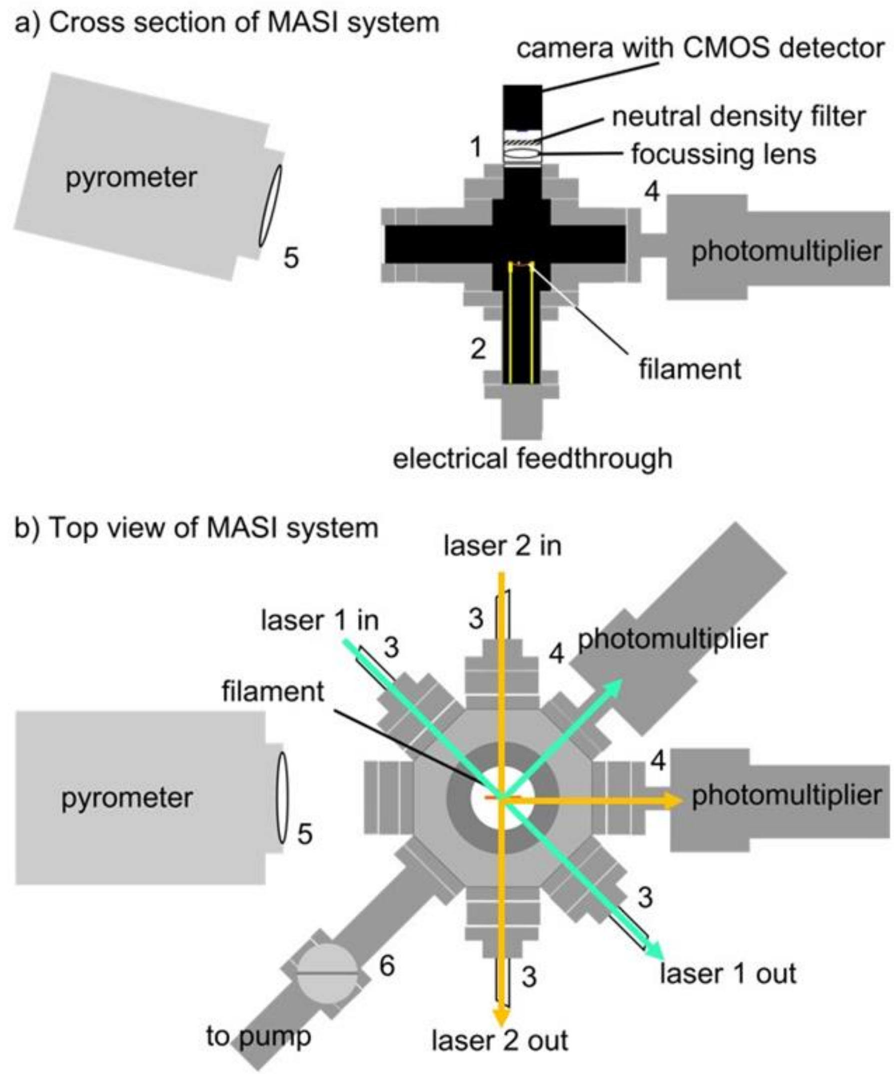
Meteoric Ablation Simulator (MASI) – Measures the rate at which different elements ablate from meteorites and meteorite analogues as a function of temperature.

1. Meteorite sample are crushed and separated into different sized bins using a sieve.
2. The different sized samples of meteorite fragments are heated rapidly on a filament.
3. The production of two different species is monitored by Laser Induced Fluorescence.



Above: Relative amounts of PO and Ca ablating *vs T*



Carrillo-Sánchez, J.D., *et. al.*, *Planetary and Space Science* (2020), doi: https://doi.org/10.1016/j.pss.2020.104926.

3. Meteoric Ablation – Chemical Ablation Model

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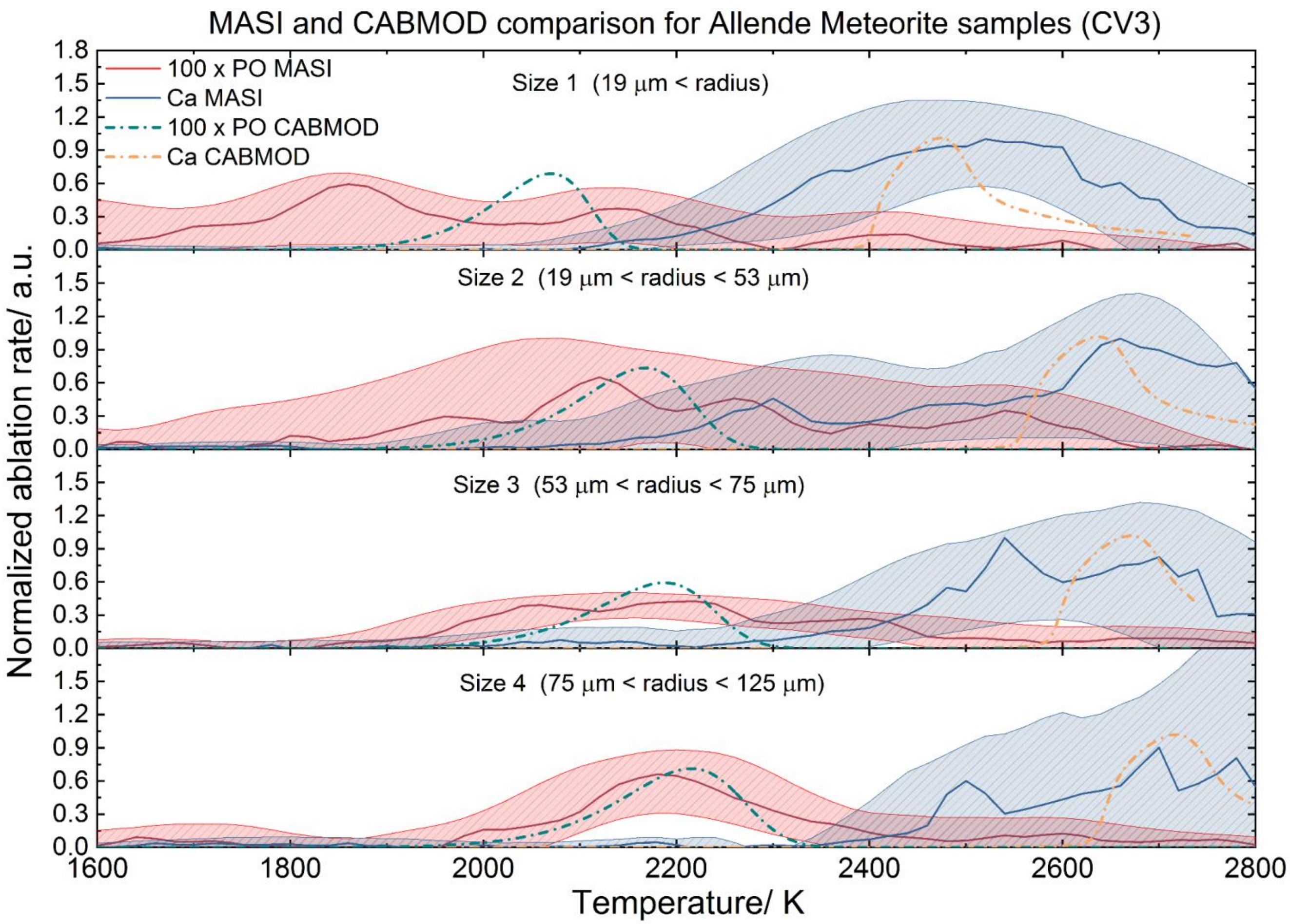
- **Chemical Ablation Model (CABMOD) –** a thermodynamic model that predicts the ablation rate of different elements.
- The model has been updated to allow us to predict P ablation rates. The model output is validated by comparison to the experimental MASI profiles:



- By combining CABMOD with an astronomical model of dust sources, the injection rates of phosphorus into the atmospheres of Venus, Earth, and Mars have been determined:

Venus	24
Earth	17
Mars	1.2

Global mass input of ablated P (as P, PO, or PO_2), kg day^{-1}

Carrillo-Sánchez, J.D., *et. al.*, *Planetary and Space Science* (2020), doi: https://doi.org/10.1016/j.pss.2020.104926.

4. Atmospheric Implications - WACCM

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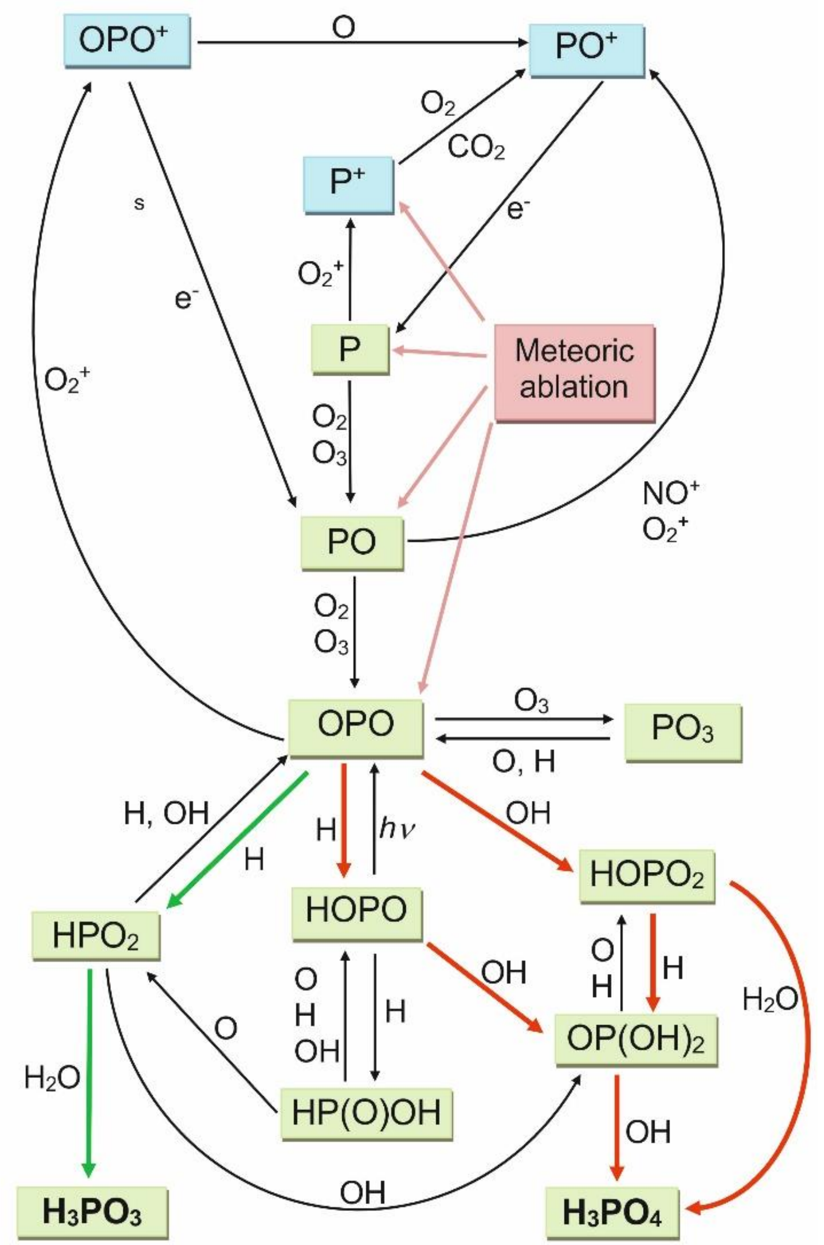
- The results from the kinetics experiments, together with the P injection rates from CABMOD, have been input into a global chemistry-climate model of the Earth's atmosphere (WACCM).

- The full chemical scheme (right) contains both neutral and ion chemistry. Rate coefficients not measured experimentally have been calculated from high level electronic structure calculations.

- Using WACCM, the relative amounts of phosphoric and phosphonic acid produced from meteor ablated phosphorus in the Earth's atmosphere can be assessed.



4. Atmospheric Implications – WACCM Outputs

- Preliminary results (right) indicate that both H_3PO_4, and the bio-available H_3PO_3 are formed between 50 and 90 km, with **around a third of the ablated P ending up as H_3PO_3.**

- The WACCM outputs can also be used to determine where on the Earth's surface H_3PO_3 will be deposited.

- Further work is under way to determine how accretion rates of H_3PO_3 would differ on the early Earth during the heavy bombardment period, and to input the chemical scheme into a Mars atmospheric model.