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

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Phosphorus, P, is a key biological element with major roles in replication, information transfer, and metabolism. Interplanetary dust particles (IDPs) contain ~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  $\leq +3$ ) are however far more bio-available. Previous studies have focused on the direct delivery of P to the surface in meteorites. In contrast, the atmospheric chemistry of P has so far been ignored.

The vaporized P atoms entering the upper atmospheres of the terrestrial planets will undergo chemical processing to form a variety of compounds in which P may exist in different oxidation states due to the presence of both oxidizing and reducing agents. Initial oxidation of P will proceed to produce PO<sub>2</sub>. From PO<sub>2</sub>, an exothermic route to phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) exists via the formation of HOPO<sub>2</sub>; however, the bio-available compound phosphonic acid (H<sub>3</sub>PO<sub>3</sub>) should also form via HPO<sub>2</sub>.

Using a combination of both experiment and theory, rate coefficients for the reactions of meteor ablated P have been determined. Using a pulsed laser photolysis-laser induced fluorescence (LIF) technique, the reactions of P, PO, and PO<sub>2</sub> with atmospherically relevant species have been studied as a function of temperature for the first time. Rate coefficients for the subsequent reactions of PO<sub>2</sub> leading onto to phosphoric and phosphonic acid were calculated from high-level electronic structure calculations.

In addition to understanding the reaction kinetics, the delivery of P to the upper atmospheres of Earth, Mars, and Venus via the ablation of IDPs has also been investigated. Using a meteor ablation simulator, micron-size particles were flash heated, and the ablation of PO and Ca recorded simultaneously by LIF. These ablation profiles were used to validate the output of a Chemical Ablation Model (CABMOD), a thermodynamic model that predicts the ablation rates of different elements from IDPs. By combining CABMOD with an astronomical model of dust sources, the global injection rates of P into the atmospheres of Earth, Mars, and Venus has been estimated to be 0.017,  $1.15 \times 10^{-3}$ , and 0.024 t d<sup>-1</sup> (tonnes per Earth day) respectively.

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). Using WACCM, the relative amounts of phosphoric and phosphonic acid produced from meteor ablated P in the Earth's atmosphere can be assessed. Preliminary results indicated that both  $\text{H}_3\text{PO}_4$ , and the bio-available  $\text{H}_3\text{PO}_3$  are formed, with around a third of the ablated P ending up as  $\text{H}_3\text{PO}_3$ . Further work is also underway to determine where on the Earth's surface  $\text{H}_3\text{PO}_3$  will be deposited, to understand how accretion rates would have differed on the early Earth, and to input the P chemical scheme into a Mars atmospheric model.