Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19616

Phosphorus speciation in low-temperature ferruginous conditions and the supply of phosphorus for the origin and early evolution of life

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Phosphorus is critical to the origin and early evolution of life as it is a key component of many biomolecules. Unlike other essential nutrient elements such as H, N, S, O and C, which may form volatile phases, P is sourced mainly from orthophosphate minerals that have lower solubility in natural fluids. The release of P from minerals and its incorporation into organic compounds (e.g., phosphorylation) in a prebiotic world are not straightforward, but these processes may have been facilitated by two possible mechanisms: formation of reduced P (e.g., phosphite) and abiotic condensation of phosphate. The former has much higher solubility compared to orthophosphate whereas the latter can be thought of as an abiotic precursor of ATP. Previous studies showed phosphate reduction at the expense of Fe oxidation during dry heating. Also, phosphate condensation into pyrophosphate, triphosphate, and/or trimetaphosphate has been demonstrated experimentally. However, many relevant early Earth scenarios have remained to be explored, including temperature settings relevant to hydrothermal springs, the role of bivalent cations (e.g., Ca), and the influence of minerals such as vivianite. Here we experimentally simulate anoxic, ferruginous, evaporative conditions to explore the possibility of phosphate reduction and condensation in environments such as volcanic hot springs. Experiments focusing on the evaporation of Fe- and Fe-Ca-bearing phosphate solutions at 85 ^{o}C suggest the formation of minor pyrophosphate but no other reduced or condensed P-species. In contrast, experiments under anhydrous hot conditions (200 ^{o}C) result in the formation of pyrophosphate (as high as 55%) triphosphate (up to 4%), and possibly some metallic phosphide compounds (e.g., Fe-phosphide). Such metallic phosphides, if present, may upon dissolution produce aqueous (hypo-)phosphite. We further observed that if the initial phosphate is locked in apatite or vivianite, instead of being in the dissolved state, the formation of both reduced and condensed phosphorus species is inhibited, even at elevated temperature. In summary, we suggest that water-poor, ferruginous environments, such as around evaporitic hot springs on the early Earth or Mars, might have provided both reduced and highly condensed P-species for the origin and early evolution of life.