The fate of phosphorus in boiling hydrothermal systems: A way of prebiotic ATP synthesis

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Thermodynamic modeling of phosphorus behavior in hydrothermal systems was calculated using HCh software. In general, geochemistry of phosphorus in dense solutions is controlled by phosphate ion. Accumulation of phosphate in aqueous solution is limited by the solubility of apatite and phosphorus can not reach high concentration, except in the ultra-acid waters. Phosphorus compounds with other valence are of minor importance in dense for the wild range of redox conditions. The limits of the accumulation of phosphorus in the solution are depending on the acidity and the water/rock ratio. Phosphate concentration in neutral hydrothermal fluid is 10-60 mmol/kg, which is insufficient for prebiotic ATP synthesis.

The results of thermodynamic calculations of boiling hydrothermal systems have shown that at 150-300ºC in vapor phase for phosphorus the molecule PO_2(gas) prevails with formal valence of +4. Other gas species (PH_3, P_4O_{10}, P_4O_6, etc.) do not have any importance at the redox conditions, controlled by basalt (NNO, QFM). Condensation of the hydrothermal vapor leads to a reaction:

$2P^{IV}O_2$ (gas) + $3H_2O$ = $H_3P^{V}O_4$ + $H_3P^{III}O_3$.

Accumulation of P(III) allows to ATP synthesize, even at relatively low phosphorus concentration. Calculations show that condensates may contain phosphite up to 6 mol/kg. In modern hydrothermal systems significant concentrations of phosphite were found up to 30 mmol/kg. The results of thermodynamic calculations allow explaining the origin of the low valence phosphorus under hydrothermal conditions and providing additional justification for the selection of their environment as the origin of life.

Experimental study of gas-liquid phosphorus partition at 200-250ºC shows, that the addition of a reducing agent increases concentration in vapor. These results are approximate to gas-liquid phosphorus partition of volcanic hydrothermal springs from Kamchatka.

Results of the study suggest that the continental hydrothermal systems are the most likely environment for the origin of first cell organisms on the Earth. In the oxygen-free atmosphere thermal springs can provide high concentrations of phosphorus(III) for the prebiotic synthesis of ATP.

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