

Heat flows liberate phosphate from apatite leachates

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Rocks and their constituent phases likely played an essential role as molecular feedstock during the emergence of life on earth. We aim to combine this geological scenario with physical non-equilibria such as thermal gradients, offering unique opportunities for molecular selection.

Prebiotic reactions often require a defined set of ion concentrations. One example is the activity of some important RNA enzymes that vanish without divalent magnesium salt, whereas an excess of monovalent sodium salt reduces enzyme function. However, it is known from leaching experiments that prebiotically relevant geomaterials such as basalts release mainly sodium and only little magnesium. A ubiquitous non-equilibrium solution to this problem is heat flowing through thin rock fractures that drives thermogravitational convection and solute thermophoresis. The superposition of both effects actively enriches magnesium ions against sodium and establishes a habitat for ribozyme function from basaltic leachates [1]. The process plausibly occurs within connected rock cracks, which increases the strength and stability of the selective accumulation. Interestingly, thermal gradients also lead to the formation of pH gradients in mixtures of only formic acid and sodium hydroxide, which can be understood and predicted by a separation of timescales [2].

While phosphate is essential to all life, its prebiotic accessibility poses major problems. For instance, one of the most abundant phosphate minerals on the early Earth, Apatite, is insoluble at neutral and alkaline pH. Here, we show that heat flows can spatially separate the constituents of Apatite, phosphate and calcium, under acidic conditions into distinct volumes. The neutralization of the phosphate-enriched and calcium depleted volume yields considerable amounts of free phosphate. We find that the resulting concentrations are sufficient to form more reactive phosphate species such as trimetaphosphate. Using a variety of minerals, glasses, and clays, we show which surfaces can promote such reactions.

[1] Matreux, T., Le Vay, K., et al. (2021), *Nature Chemistry* 13(11), 1038-1045.

[2] Matreux, T., Altaner, B., Raith, J., et al. (2023), *Communications Physics* 6(1), 14.