Microscopic pH gradients and the potential for carbon fixation at alkaline hydrothermal vents.

V. Sojo[1,2,3,*], F. M. Möller[1], S. McGlynn[2], R. Nakamura[2,3], and D. Braun[1]. [1]Systems Biophysics, Ludwig-Maximilian University of Munich (LMU), Amalienstrasse 54, Munich, Germany. [2]Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan. [3]Biofunctional Catalysis Research Team, Riken, Wako, Japan.
(*v.sojo@lmu.de)

Introduction: Multiple types of hydrothermal systems exist on Earth today, including geothermal pool fields such as those in Kamchatka, on-ridge deep-sea volcanic vents of the black-smoker type, and off-ridge serpentinizing alkaline vents such as Lost City. On the prebiotic Earth, the lack of oxygen would have made each of these systems drastically different from their modern counterparts, giving rise to rich chemistries that have spawned multiple corresponding theories for the origin of life[1-3]. Many open questions remain for each of these theories. In the case of alkaline vents, one major suggested advantage is the spontaneous geologically sustained pH gradient between the alkaline vent effluent (pH 9~12) and the comparatively acidic ocean (pH 5~7). This disequilibrium matches the polarity of modern cells and would have potentially driven the origin of both bioenergetics and carbon fixation[3-6]. However, it remains to be shown whether these large macroscopic gradients remain at the microscale. Here we will present experimental results that demonstrate the maintenance of up to 6-unit pH gradients at the microscale[7]. We will also discuss the implications of these pH gradients for a potential origin of carbon fixation in alkaline vents, from oceanic CO_2 and geothermal H_2.

Methods: We have used microfluidics and pH sensitive fluorescent dyes to assess the dynamic behavior of pH gradients at a minimalistic simulation of an alkaline vent system. As a minimal ocean simulant, we have used a 10 mM FeS solution at pH 5.8, whereas the minimal alkaline vent simulant was a 10 mM Na_2S solution at pH 11.8. The pH distribution within the microfluidic reactor was imaged at micrometer resolution using the ratiometric, pH-dependent fluorescent dye SNARF1. To elucidate the role of precipitation, control experiments were performed in which the $FeCl_2$-solution was substituted by a non-precipitate-forming NH_4Cl solution (10 mM, pH 6.8).

Results and discussion: We find that pH gradients of up to 6 units are maintained over micrometer scales (see Figure). Precipitation of metal-sulfides at the interface strengthens the gradients, but even in the absence of precipitates, laminar flow sustains the disequilibria. Our results confirm that alkaline vents can provide an exploitable pH gradient, supporting their potential role at the emergence of chemiosmosis and the origin of life, while shifting the focus to other open questions and challenges, including the origin of carbon fixation, and the stability of lipids under these conditions.

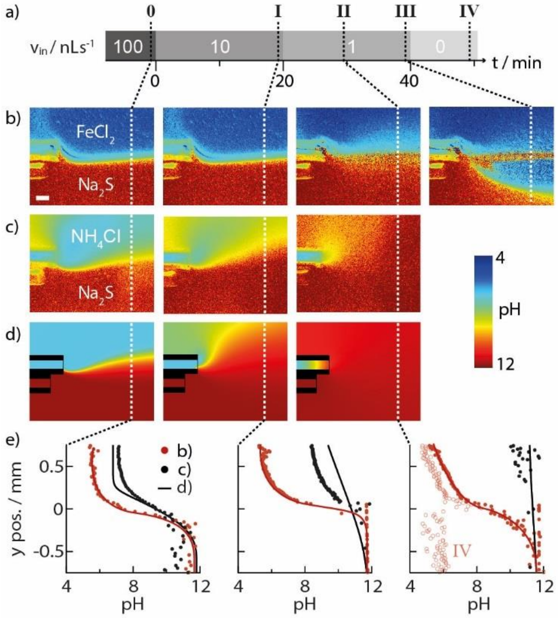

Figure - Stability of the pH gradient. (a) The inflow rate is reduced stepwise to test the stability of the pH gradient. **(b)**With precipitation, a steep and stable pH gradient builds up. The relaxation of the gradient only sets in 600 s after the decresase of inflow rate to 1 nLs^{-1}. The scale bar measures 200 µm. Without precipitation, a less stable pH gradient is observed both experimentally **(c)** and in simulation **(d)**. **(e)** pH profiles along the dashed, white cut lines in panels **(b-d)**.

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