## Rate constants for the non-enzymatic hydrolysis of Na<sub>2</sub>ATP at 80 °C to 120 °C: A constraint for metabolic pathways for extremophiles

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In recent decades increasing evidence was found for life under extreme conditions, ranging from deep oceanic sediments and crust to hydrothermal vents at mid-ocean ridges. The present communities show a fascinating tolerance against the prevailing conditions of pressure, temperature, and chemical composition. However, only little is known about the physicochemical boundary conditions to maintain active metabolic pathways, such as the stability of the essential molecule ATP in water at elevated temperatures.

Previous studies determined hydrolysis rate constants of ATP up to 80 °C using quenched high-temperature experiments followed by subsequent analysis. A recently developed method allows obtaining the hydrolysis rate constants in-situ at temperatures of up to 120 °C by application of micro-Raman spectroscopy and a hydrothermal diamond anvil cell. The hydrolysis of Na<sub>2</sub>ATP in aqueous solutions with starting pH values of 3 and 7 was successfully analysed as a function of time. Rate constants were determined using the rate law of a first order reaction. Initial observations show a linear temperature dependence in an Arrhenian plot with activation energies of  $14.661 \text{ kJ mol}^{-1} \pm 0.580 \text{ kJ mol}^{-1}$  at pH 3 and  $14.713 \text{ kJ mol}^{-1} \pm 0.497 \text{ kJ mol}^{-1}$  at pH 7.

These early results suggest half-lives for Na<sub>2</sub>ATP in water in the range of roughly 2.30 min to 4 min at 120 °C. Such high reaction rates indicate that a simple mechanism must exist to counteract the hydrolysis at elevated temperatures in order to enable metabolism of extremophiles. Moreover, it sets a time constraint for theories on the development of metabolic pathways in extreme environments in the overall context of the origin of life.