

## Nitrogen isotope ratios trace high pH in a terrestrial Mars analog site

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High-pH lakes are among the most productive ecosystems on Earth and prime targets in the search for extinct life on Mars; however, a robust paleoproxy for such settings does not yet exist. While mineral associations mirror a broad combination of salinities, temperatures, redox, and pH, a specific approximation of ancient pH conditions is not possible on this basis. Nitrogen isotopes have the potential to fill this gap because ammonia (NH<sub>3</sub>) gas is produced in large proportions above a pH of 9.2. Residual aqueous ammonium (NH<sub>4</sub><sup>+</sup>) is left isotopically heavy when volatile NH<sub>3</sub> is lost from a system [1]. To explore this potential, we analyzed nitrogen isotopes in a drill core from the 15-Ma-old Nördlinger Ries impact crater in southern Germany, a Mars analog of the highest order because—like craters on Mars—it possesses a well-preserved, dual-layer ejecta (DLE) blanket composed of materials that resettled after impact. An ancient lake was housed in the crater, and previous studies have inferred that DLE blanket erosion led to pH values of up to 9.8 based on mineralogy, biomarkers, and aqueous modelling [2]. The pH may have dropped to ~8.5 later in the lake's history, but the water column likely remained redox stratified and saline based on paleontological and biomarker evidence. Our nitrogen isotope data track this inferred pH trend with a maximum δ<sup>15</sup>N of +17‰ in the highest pH interval, followed by a gradual decline to ~+5‰, concurrent with a proposed pH decline. This pattern indicates that redox stratification and associated denitrification were probably not responsible for the isotopic enrichments of > +10‰. Instead, our data highlight the diagnostic isotopic effects of NH<sub>3</sub> volatilization [3]. This new perspective may provide a much-needed fingerprint for identifying environments with a high potential for habitability. Co-occurrence of high total alkalinity based on mineralogical evidence and circumneutral pH, where NH<sub>3</sub> volatilization is suppressed, would point to the multi-bar pCO<sub>2</sub> atmosphere that ancient Mars likely needed to sustain liquid surface water. [1]Li et al. (2012), *GCA* 84, 280-296. [2]Arp et al. (2013), *GSA Bull.* 125, 1125–1145. [3]Stüeken and Tino, et al. (2020), *Science Advances*, In Press.