

Nitrate and its N and O isotopes in a tropical marine boundary layer

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Isotopic investigations are instrumental in deciphering sources and processes affecting atmospheric nitrate. Combining the analysis of the ¹⁷O-excess ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \delta^{18}\text{O}$) with the nitrogen stable isotope ratio (¹⁵N/¹⁴N) on the same sample is a powerful tool to reveal unexpected processes happening in the air [1].

Despite recent successes in using the isotope composition of nitrate for deciphering atmospheric chemical processes in polar and mid latitude regions [2, 3], the strong oxidative atmosphere of the sub tropical and tropical regions has been largely forgotten [4]. In order to partially fill this gap, we present a full seasonal cycle of the nitrate isotope systematic at the Cap Verde (Lat 16° 85'N, Long. 24° 87' W, Alt. 20m), characteristic of a tropical marine boundary layer (MBL).

While the concentration of nitrate at this MBL do not show any season variations, the oxygen isotopic characteristics display a pronounced seasonal cycle that is compatible with nitrate formation chemistry, which includes the BrNO₃ sink at a level of ca. 20 ± 10% of nitrate formation pathways. The results also suggest that the N₂O₅ pathway is a negligible NO_x sink in this environment. Observations further indicate a possible link between the NO₂/NO_x ratio and the nitrogen isotopic content of nitrate in this low NO_x environment, possibly reflecting the seasonal change in the photochemical equilibrium among NO_x species.

[1] Thiemens, M. H. (2006) *Annual Review of Earth and Planetary Sciences*, **34**, 217-262. [2] Morin, S. *et al. Science*, **322**, 730-732, doi: 10.1126/science.1161910. Michalski, G. *et al. (2003) Geophys Res Lett*, **30**, 1870, doi: 10.1029/2003gl017015. [4] Alexander, *et al. (2009), Atmos Chem Phys*, **9**, 5043-5056, doi: 10.5194/acp-9-5043-2009.

Experimental modeling of silicates phosphatization in the hypergenesis zone

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Now there was a concept that immobilization of dissolved phosphates on silicate minerals in the hypergenesis zone occurs on the mechanism of superficial adsorption. At the same time it is possible to assume that alongside with it process of silicates phosphatization similar to widespread process of silicates carbonatization proceeds. This hypothesis was verified during the longtime experiments.

The phosphatization of two basic clay minerals (kaolin and montmorillonite) was studied after two-year long interaction with 0.25–5.0 mM orthophosphate solutions under acidity conditions ranged pH 1.8–8.8. The results have shown (figure) that variation of dissolved phosphorus and silicon concentrations at pH 3.7–8.8 is close to equivalent: $\Delta[\text{Si}] \approx -\Delta[\text{P}]$ whereas $\Delta[\text{Si}]$ value at pH 1.8 is in 1.5–2 times exceeds decrease in phosphates concentration. Quantity of phosphorus immobilized by clay minerals is in direct proportion of its equilibrium concentration in the solution: $-\Delta[\text{P}] = k[\text{P}]_{\text{eq}}$. The proportionality factor k is identical to all studied samples and decreases from 0.58 till 0.44 at the pH increase with 1.8 up to 8.8. Quantity of silicon passing in the dissolved forms reaches 6–20% of total amount of silica in the solid phase. It specifies phosphatization of clay minerals which products are dissolved silica and poorly soluble basic aluminium phosphates.

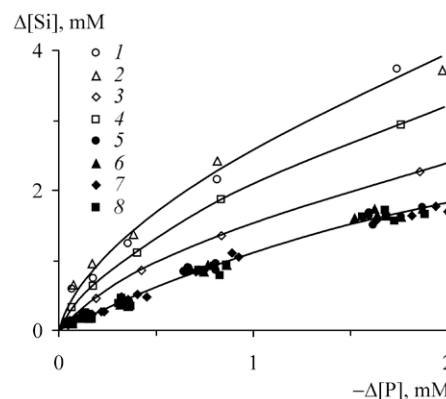


Figure: Relationship between variation of dissolved phosphorus and silicon concentrations at the clay minerals phosphatization. pH 1.8/3.7–8.8: 1/5 – kaolin, Glukhoveck; 2/6 – ditto, Podolsk; 3/7 – montmorillonite, Askanija, sample 1; 4/8 – ditto, sample 2.