

Controls of acid dissolution of P in mineral dust during atmospheric processing

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Phosphorus is a critical nutrient element controlling primary productivity in large areas of the surface ocean [1] [2]. In the offshore parts of the ocean atmospheric inputs are the most important source of externally supplied nutrients (P, N and Fe) and the major forms of P (and Fe) are minerals. However, these are generally poorly soluble in seawater and hence not directly bioavailable. The dominant form of P in dusts is soil-derived dust apatite, and to a lesser extent, P bound to iron minerals [3] [4]. Nenes et al. [5] found a clear increase in soluble P in samples which had been in contact with acid in the atmosphere.

To experimentally validate this link, we carried out acid-dust leaching experiments, under laboratory conditions designed to mimic the conditions in clouds and wet aerosols in the atmosphere. Our results show that apatite dissolves rapidly (~ minutes) under conditions relevant to atmospheric processes. At increased H^+ ion concentration a competitive dissolution between $CaCO_3$ and apatite in dusts dominates the reactions, with the total amount of H^+ consumed being controlled by the $CaCO_3$ that is dissolved. We found a linear log-log relationship between the amount of H^+ ions initially present and the amount of P liberated, which was controlled by the relative kinetics of calcite and apatite dissolution. At higher ionic strength (IS = 2M NaCl) there was ~10% more P desorbed into solution, while at higher IS of ammonium sulphate (2M) the increased dissolution was controlled by the number of H^+ ions present. The amount of P liberated from internally mixed calcite and apatite grains is lower than that released when apatite and calcite are externally mixed i.e., present on individual particles. Our results will be incorporated into a global aerosol model to predict the amount of P liberated by atmospheric acid processes globally.

[1] Howarth R.W. 1988. *Ann. Rev. Ecol.* **19**, 89-110 [2] Elser J.J., et al. 2007. *Ecol. Lett.* **10**, 1135-1142 [3] Singer A., et al. 2004. *Atmos. Environ.* **38**, 1745-1753 [4] Eijssink L.M., et al. 2000. *Am. J. Sci.* **300**, 483-504 [5] Nenes A., et al. 2011. *Atmos. Chem. Phys.* **11**, 6265-6272