

The coupling of particle acidity and gas phase ammonia in the biosphere-atmosphere system

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Ammonia is the most important gas phase base in the atmosphere and is known to influence the formation and growth of atmospheric particles. While the magnitude and trends of ammonia emissions are highly uncertain, it is likely that a legacy of synthetic fertilizer application has led to an increased potential for ammonia emissions from many ecosystems. We have obtained observational evidence for the bi-directional exchange of ammonia between the surface and the atmosphere, and the coupling of this process to gas-particle partitioning. From intensive field campaigns in urban and rural environments, simultaneous measurements of particle composition and gas phase ammonia permit the calculation of particle acidity, which affects gas-particle partitioning of ionizable species and may influence toxicity and secondary organic aerosol formation. In a complementary analysis, we use long-term measurements (1990-2010) of particle composition from Canada's Chemistry and Precipitation Monitoring Network (CAPMoN) to calculate trends in strong acidity and infer trends in gas phase ammonia.

Fractionation of ²³⁸U/²³⁵U by reduction during low T uranium mineralisation processes

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Investigations of 'stable' uranium isotope fractionation during low temperature, redox transformations may provide new insights into the usefulness of the ²³⁸U/²³⁵U isotope system as a tracer of palaeoredox processes. Sandstone-hosted uranium deposits accumulate at an oxidation/reduction interface within an aquifer from the low temperature reduction of soluble U(VI) complexes in groundwaters, forming insoluble U(IV) minerals. This setting provides an ideal environment in which to investigate the effects of redox transformations on ²³⁸U/²³⁵U fractionation. Here we present coupled measurements of ²³⁸U/²³⁵U isotopic compositions and U concentrations for groundwaters and mineralised sediment samples collected in the vicinity of the high-grade Pepegooona sandstone-hosted uranium deposit, Australia.

The mineralised sediment samples display extremely variable ²³⁸U/²³⁵U ratios, spanning a 5 ‰ range. The groundwaters show a greater than 2 ‰ variation in their ²³⁸U/²³⁵U ratios, and exhibit a clear systematic relationship between ²³⁸U/²³⁵U isotopic composition and U concentration; samples with the lowest U concentrations have the lowest ²³⁸U/²³⁵U ratios. The preferential incorporation of ²³⁸U during the precipitation of uranium minerals leaves the groundwaters enriched in ²³⁵U, resulting in a progressive shift in ²³⁸U/²³⁵U towards lighter values in the aqueous phase as U is removed. Previous studies on the same groundwaters have shown significant disequilibrium between ²³⁴U and ²³⁸U. ²³⁸U/²³⁵U ratios however, show a poor correlation with (²³⁴U/²³⁸U) activity ratios, which suggests that mineral leaching during weathering is unlikely to control the observed uranium ²³⁸U/²³⁵U isotopic variability within this low temperature, redox-controlled mineralised system. Rather, the results imply that ²³⁸U/²³⁵U fractionation may be controlled by the nuclear field shift effect during the reduction of U(VI) to U(IV) during mineralisation processes. The findings of this study support the use of the ²³⁸U/²³⁵U isotopic system as a palaeoredox tracer to constrain the nature and timing of palaeoredox conditions.