

A Late Miocene stable isotope paleosoil record of Andean foreland precipitation

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The topography of the Andes induces two major climatic effects: a) S-ward deflection of Atlantic-derived moisture that results in monsoonal climate along the East and hyperaridity on the West side of the central Andes and b) north-to-south asymmetry in SST and position of the ITCZ in the equatorial Pacific. We present multi-isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$) data from pedogenic carbonate in the Eastern Andean foreland (Bolivia) that record the onset of such seasonality and distribution of precipitation. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from pedogenic carbonate suggest a rapid change in precipitation patterns consistent with a deflection of the low-level Andean jet to more southerly latitudes at ca. 8.5 Ma. A contemporaneous increase in $^{87}\text{Sr}/^{86}\text{Sr}$ of pedogenic carbonate indicates a transition to higher silicate weathering rates and/or accelerating headward erosion and higher river discharge. Such a rapid (<100 ka) transition to more cyclic climate either due to enhanced seasonality or as a response to the onset of ENSO, strongly affects isotopes in precipitation and provides previously unavailable boundary conditions for Andean climate and topography reconstructions.

Spectroscopic comparison of aqueous Np(VI) and U(VI) species

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The distribution of aqueous species of actinide(VI) ions primarily defines their geochemical reactions and, thus, influences their migration behaviour in the environment. In aqueous solution, uranium and neptunium exist as actinyl ions AnO_2^{2+} (An = U, Np). They form different complexed species depending on their concentration level, pH range and the presence of potential ligands, such as carbonate. In recent years, the aqueous U(VI) system has been investigated intensively, in contrast to Np(VI). However, the thermodynamic data often arise from non-spectroscopic experiments mostly performed in the millimolar concentration range. [1] Up to now, a verification of the data of the different actinyl species by spectroscopic techniques providing direct molecular structural information is still incomplete. In particular, actinide solutions at lower concentrations and at neutral pH values, reasonably in an environmental context, were addressed seldom. [2]

In this study, the Np(VI) speciation at a submillimolar concentration range was investigated applying ATR FT-IR and NIR absorption spectroscopy, and computed modeling of updated NEA thermodynamic data. The findings are comparatively discussed with results obtained from U(VI) under identical conditions.

At ambient atmosphere, the formation of similar actinyl(VI) species can be derived from IR spectroscopic results at $\text{pH} \leq 4$, namely the fully hydrated AnO_2^{2+} (An = U, Np) and monomeric hydrolysis products. At higher pH, the spectra evidence structurally different species contributing to the speciation of both actinides. At pH 5, the formation of $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$ probably occurs which is supported by modeling NEA data and results from NIR spectroscopy. For uranium, the presence of additional hydroxo complexes is assumed in this pH range.

[1] Guillaumont, R. *et al.* *Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc*. Elsevier: Amsterdam, (2003); p 970. [2] Müller, K. *et al.* *Inorganic Chemistry* (2008), **47**, (21), 10127-10134.