

Uranyl-citrate complexes: solution speciation and surface interactions

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Introduction: Contamination of soils by uranium and other actinide species is a topic of concern in many parts of the United States. Citric acid was used as a decontamination agent at nuclear fuel reprocessing facilities, and is a component of mixed radioactive wastes, as well as being representative of chelating agents commonly found in soils and groundwater. Citric acid forms strong complexes with uranium and is currently being investigated for use as a solubilizing agent for enhancement of phytoremediation and soil-washing processes.

We have used Raman and ATR-FTIR spectroscopies, as well as Electrospray Ionization Mass Spectrometry to examine the nature of the complexes formed between the uranyl ion and citric acid in aqueous solution. We have also examined the adsorption of these complexes to model aluminum oxide surfaces.

Results: Spectrochemical titrations were performed to monitor pH-dependent changes in the UO_2 vibrational envelope. Three major UO_2 -citrate complexes with progressively increasing U=O bond lengths are present from pH 2.0 to pH 9.5. The first species is dominant from approximately pH 3.0 to pH 5.0. Results from ESI-MS and Raman spectroscopy indicate that this complex contains two UO_2 groups in spectroscopically equivalent coordination environments, and that it corresponds to the 2:2 UO_2 -citrate complex previously proposed to exist in this pH range [1,2,3]. At higher pH values complexes with UO_2 :citrate ratios of 3:2 and 3:3, respectively, exist in equilibrium. pH- and temperature-related interconversions between these two complexes are evident. Differences in U=O bond lengths among the three complexes may indicate differences in the type of coordination by citrate carboxylate groups. ATR-FTIR has been used to determine the nature of UO_2 -citrate coordination in each complex. Structures for these complexes will be proposed.

Adsorption of the uranyl-citrate complexes to Al_2O_3 has been examined using ATR-FTIR spectroscopy. The complexes are strongly bound to the surface. Significant perturbation of the uranyl coordination environment is evident upon adsorption, indicating possible complex dissociation. The strong surface interactions may hinder cleanup of contaminated soils. Molecular pictures describing these interactions will be proposed.

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Tropical sea surface temperature and salinity change in the Cariaco Basin at the Last Glacial Maximum

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Accurate reconstructions of past tropical temperatures are essential for assessing the influence of tropical climate variability on global climate change, as well as for understanding the sensitivity of the climate system to increased greenhouse gas levels and perturbations in radiative balance. Yet, discrepancy still exists concerning the amplitude of regional glacial cooling in the tropics derived by various proxy parameters. Within the Cariaco Basin, there is a direct disparity among SST proxies derived from ODP Site 1002. The alkenone unsaturation index indicates very little glacial-interglacial SST change (Herbert and Schuffert, 2000), while planktonic foraminiferal $\delta^{18}\text{O}$ records display a more than 2‰ increase (Peterson et al., 2000), most certainly representing some SST variability. Hence, new methods of reconstructing paleotemperature are necessary so that a consensus of tropical LGM cooling can be derived.

As an alternative method for determining the magnitude of glacial tropical temperature variability, interstitial waters recovered from ODP, Site 1002 in the Cariaco Basin are used in a numerical model to constrain the $\delta^{18}\text{O}$ of seawater since the Last Glacial Maximum. During the glaciation, the basin became almost completely isolated due to sea-level fall, leaving only a shallow sill across which surface-water exchange with the Caribbean occurred. Amplified trade-wind strength and isolation of the basin initiated intensified vertical mixing, causing surface waters enriched in ^{18}O to be transferred to the basin's deep waters. Model runs indicate that glacial-interglacial change in the $\delta^{18}\text{O}$ value of Cariaco Basin bottom waters was about $2.4 \pm 0.2\text{‰}$. Since the modern surface-water $\delta^{18}\text{O}$ value in the Cariaco is heavier than the bottom water at 900 m, we infer that the glacial-interglacial surface water $\delta^{18}\text{O}$ change is on the order of 1.4‰, of which 0.4-0.6‰ can be attributed to increased salinity. Subsequent comparison with the oxygen isotopic record of planktonic foraminifer *Globigerinoides ruber* (white) indicates approximately 3-4°C of cooling in surface waters of the Cariaco Basin at the Last Glacial Maximum.

References

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