Laser-Induced Time-Resolved Cryogenic U(VI) Fluorescence Spectroscopic Characterization of Hanford 300 Area Sediments

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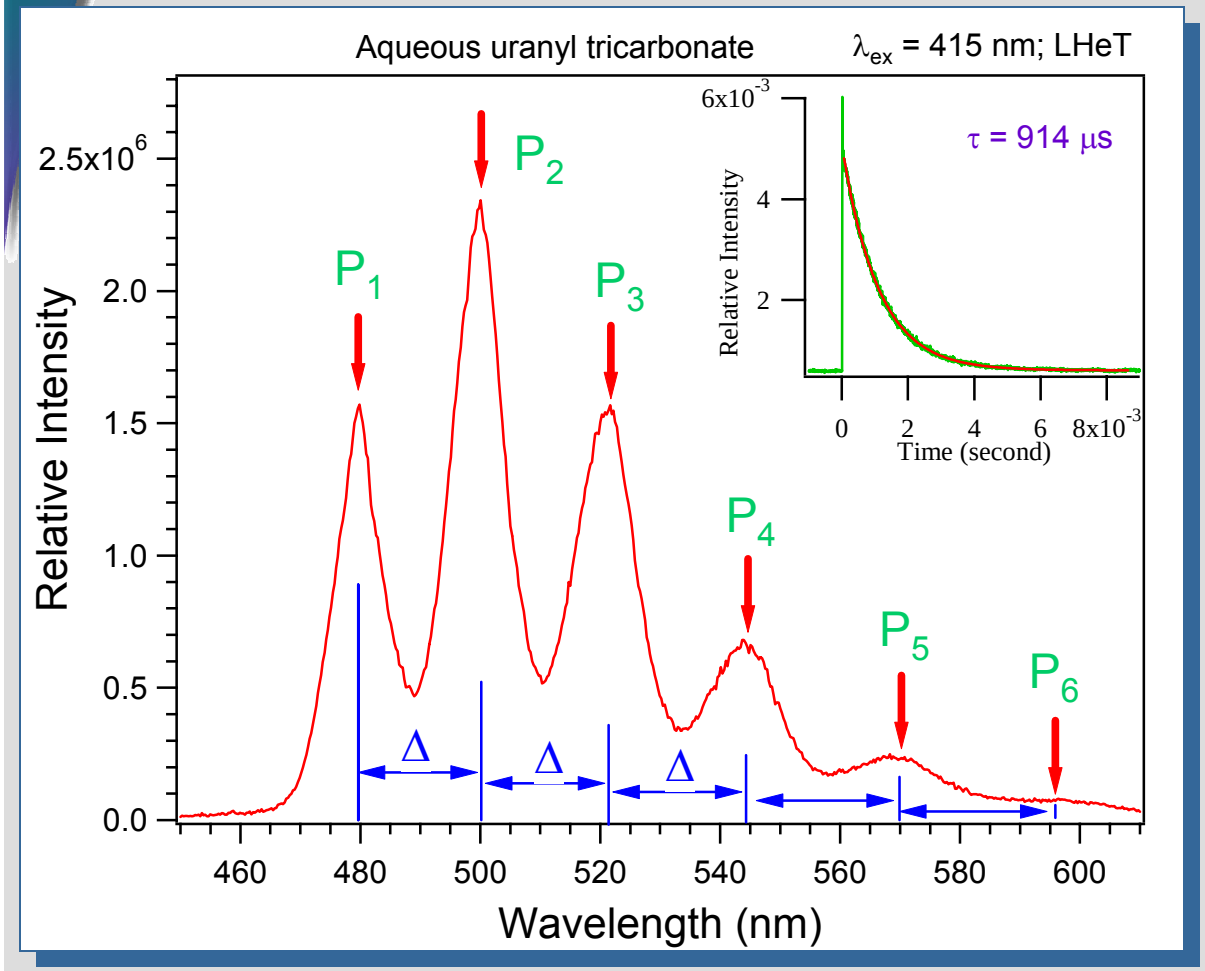
Scientific Objectives

Utilizing cryogenic U(VI) fluorescence spectroscopy

- To delineate the speciation of uranyl in the 300 area sediments and groundwaters
- To define relationships between uranyl speciation and the location, depth, chemical/mineralogical composition and grain size of the sediments
- To examine the changes of uranyl speciation that follow adsorption and dissolution/desorption

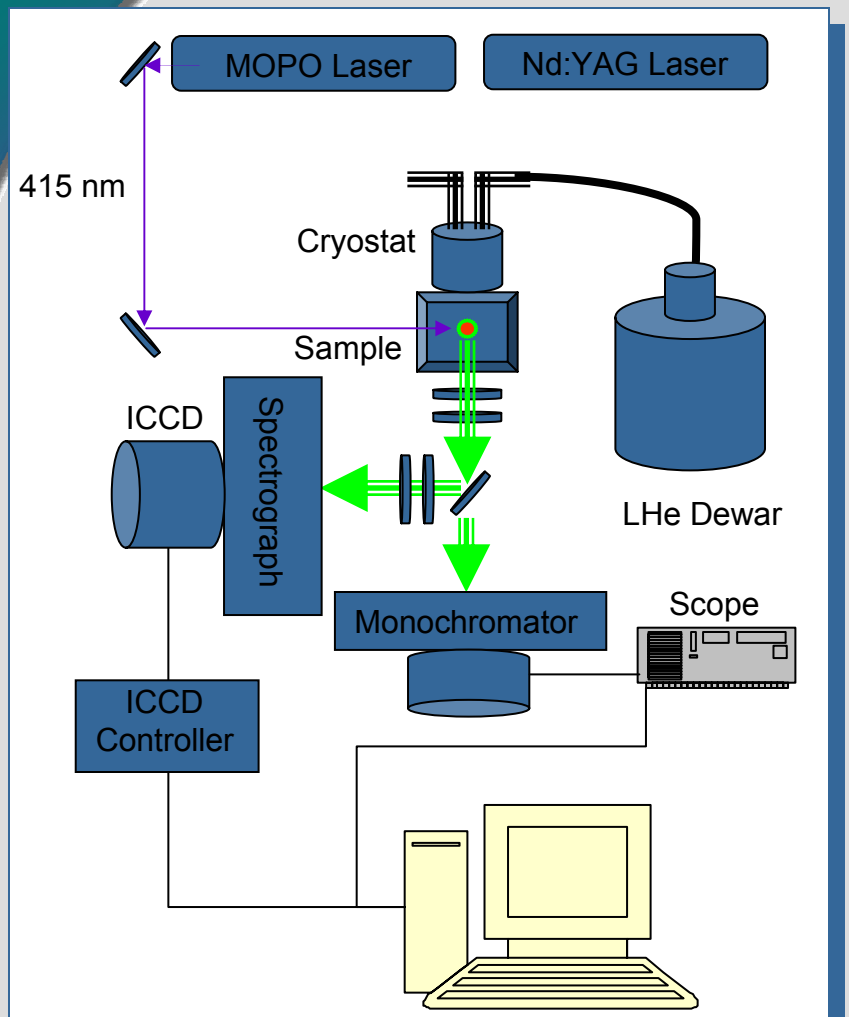
U(VI) Fluorescence Spectroscopy



- Uranyl compounds absorb at 415 nm and fluoresce above 470 nm with characteristic vibronic progressions

- The position (↓), spacing (Δ), relative intensities (Pi/Pi+1) of the vibronic bands and the fluorescence lifetime (t) are sensitive to the composition, structure and local chemical environments

Instrumentation

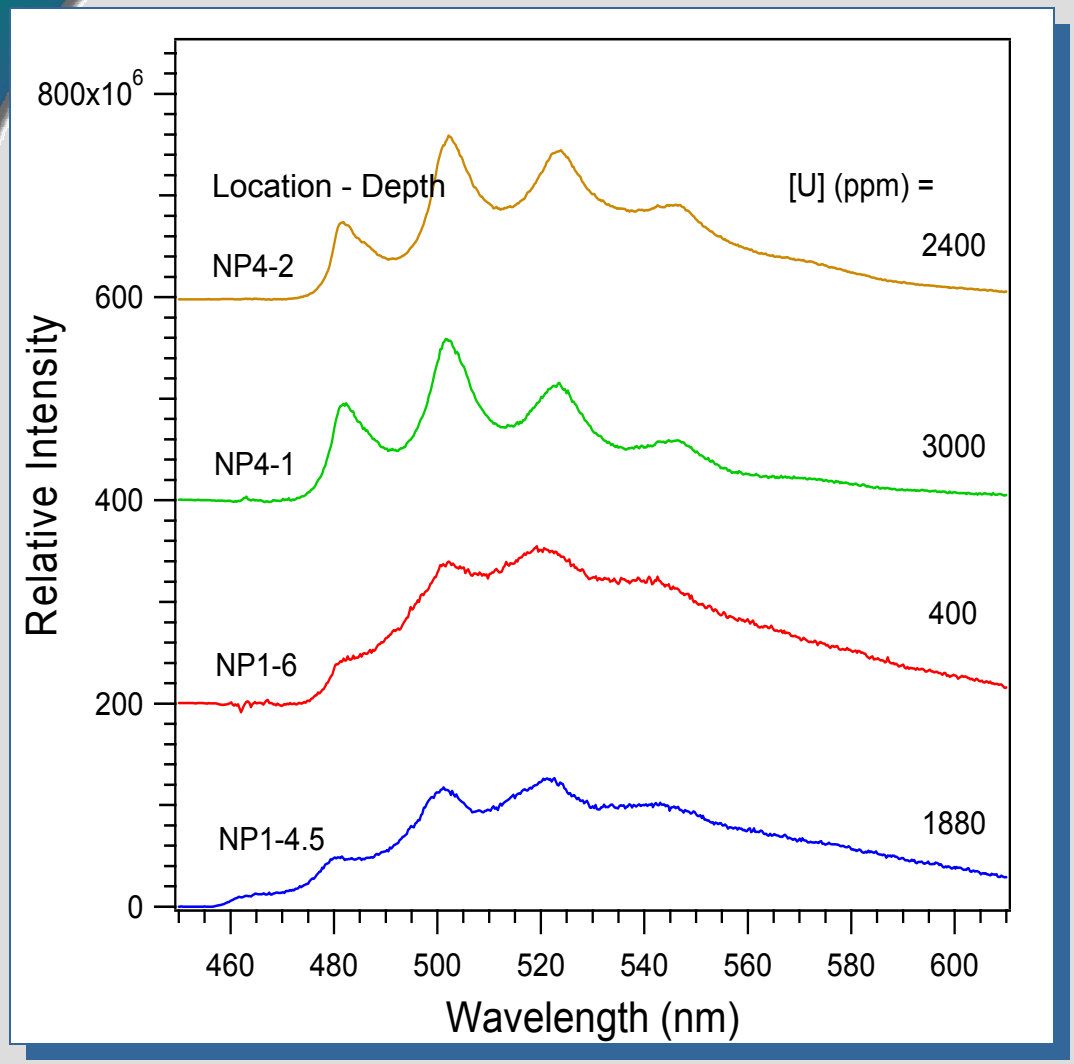


A Schematic Diagram of the Cryogenic LIF System

Specifications:

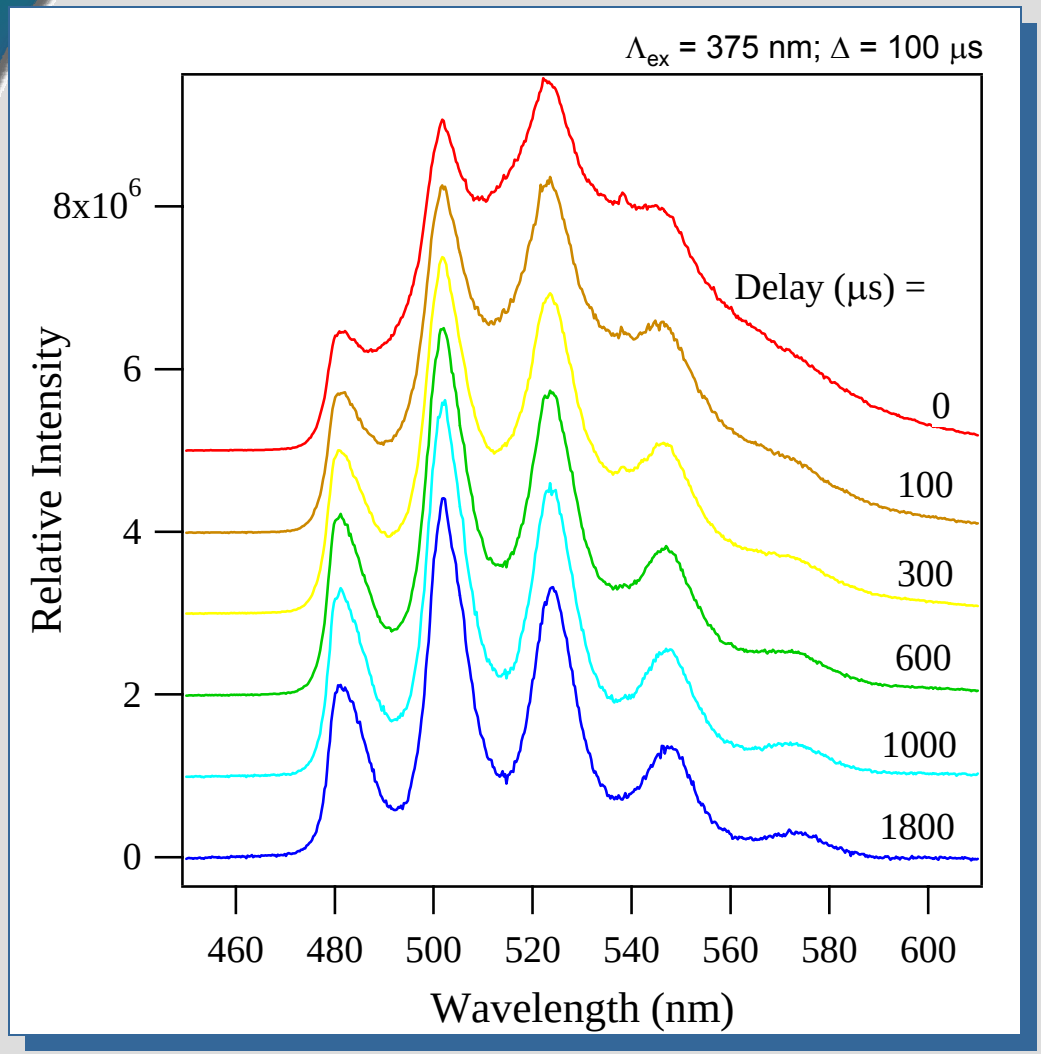
- Laser wavelength: 220 nm – 1800 nm
- Detector response: 440 nm – 900 nm
- Time resolution: 5 ns
- Temperature range: 4.2 K – 298 K
- Detection of U(VI) (aquo): up to 10^{-7} M

Time-Resolved U(VI) Fluorescence Spectra of NPP Process Pond Sediments



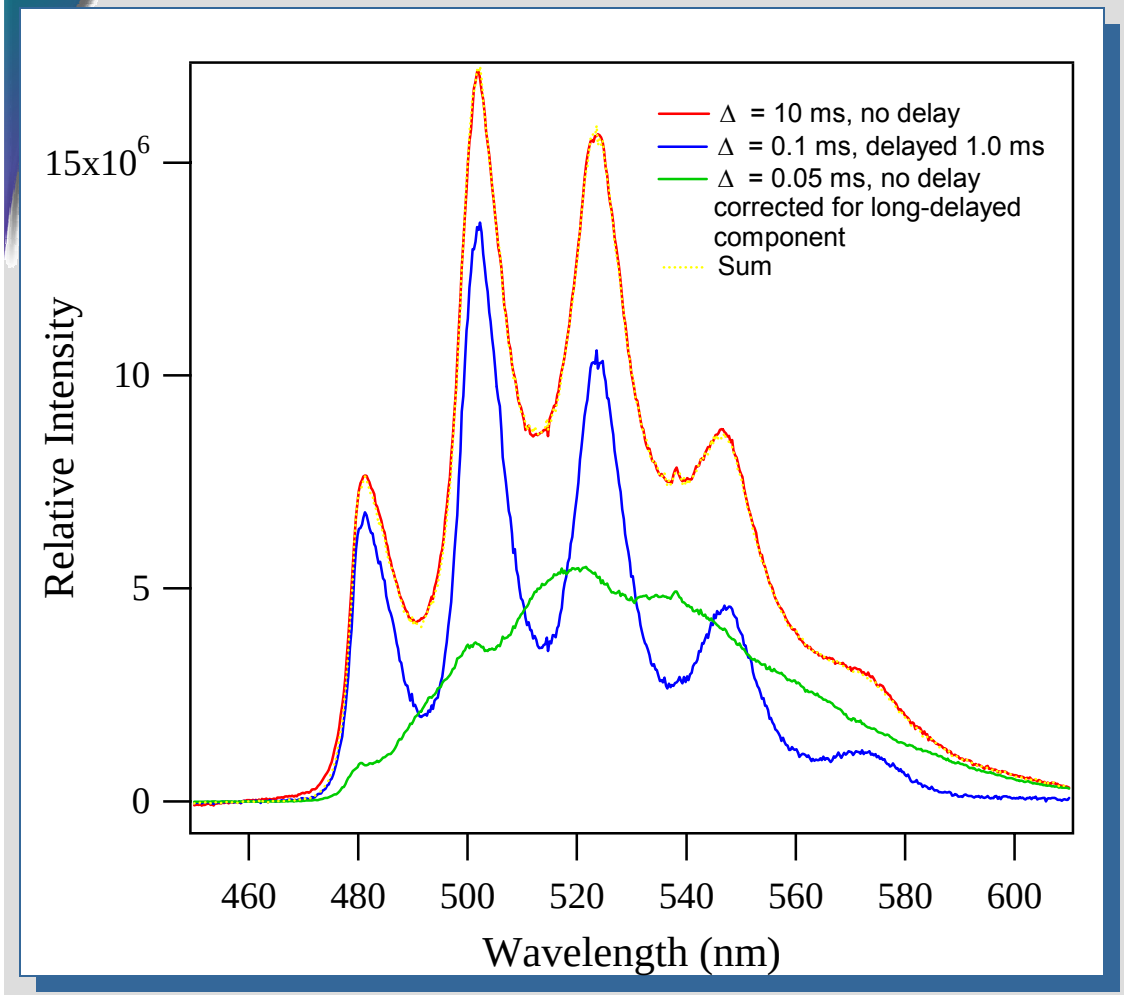
- The spectral features for all sediments were similar, suggesting similar U(VI) speciation
- The fluorescence decays indicated the presence of two or more U(VI) species

Time-Resolved Fluorescence Spectra of Process Pond Sediment (NP4-2)



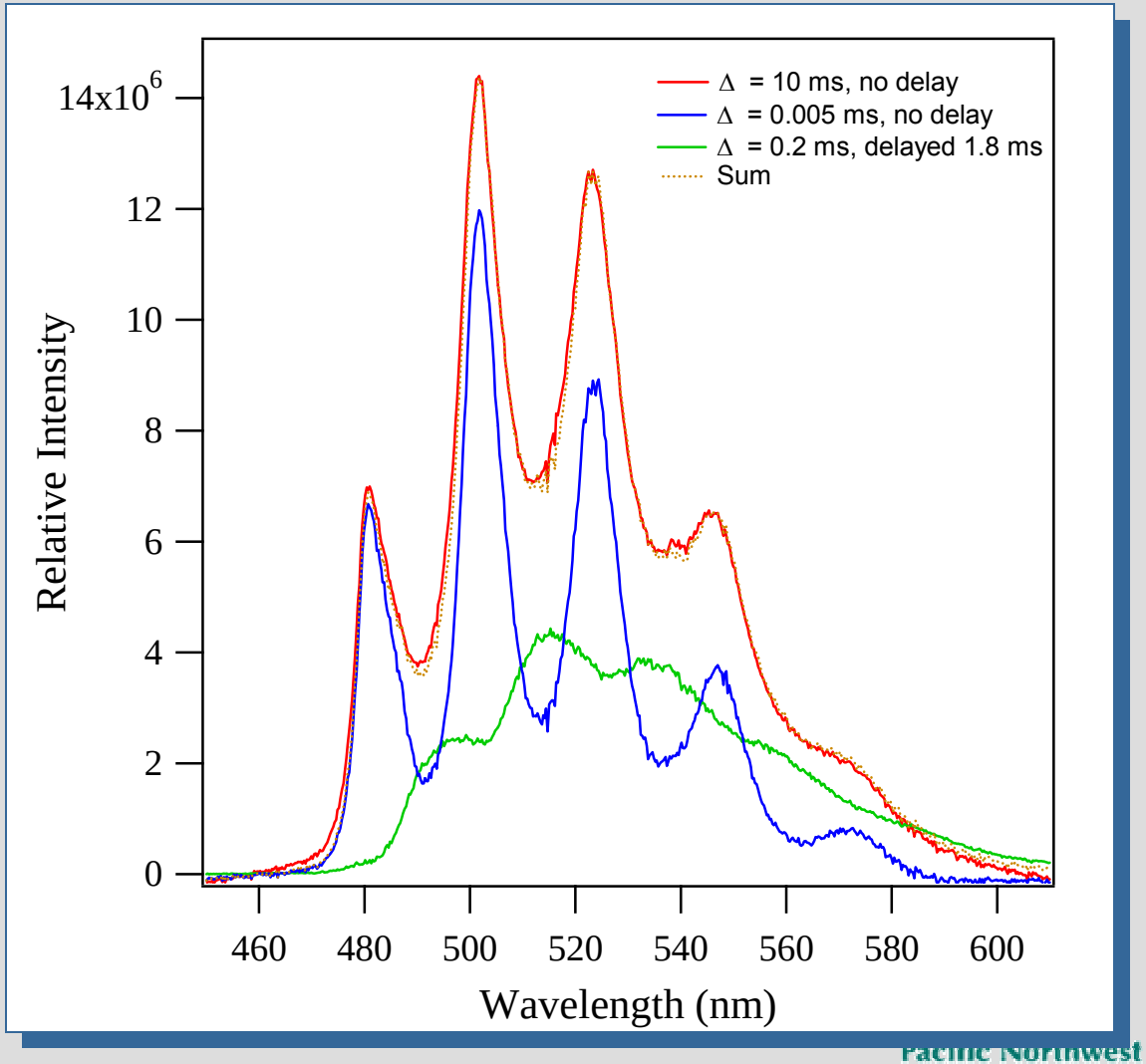
- Spectral changes with delay time indicate the presence of more than one U(VI) species
- The U(VI) species with long lifetime is the U(VI) precipitate or well-structured surface complex
- Fluorescence decays were fit with a double exponential with τ's of 584 ms and 103 ms

Deconvolution of the Time-Resolved Fluorescence Spectra of Process Pond Sediment (NP4-2)

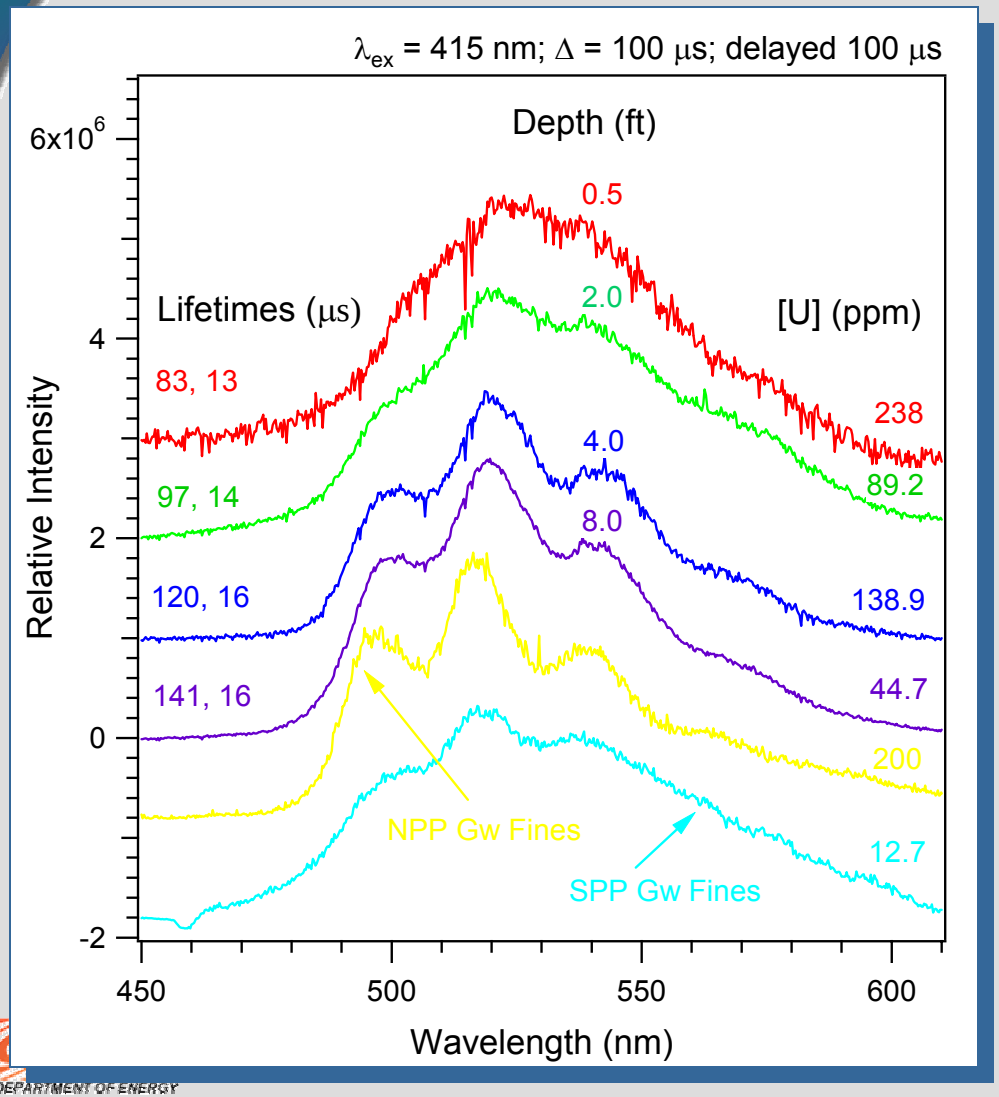


- The fluorescence spectra were deconvoluted into two spectral components, an indication of two major U(VI) species
- Geochemical conditions favor co-precipitation in calcium carbonates, such as calcite and aragonite

Deconvolution of the Time-Resolved Fluorescence Spectra of Process Pond Sediment (NP4-2) after Contact with Sodium Bicarbonate Solution (pH 9.5)



Time-Resolved U(VI) Fluorescence Spectra of Contaminated Vadose Zone Sediments (NPP2) at different Depths (ft)

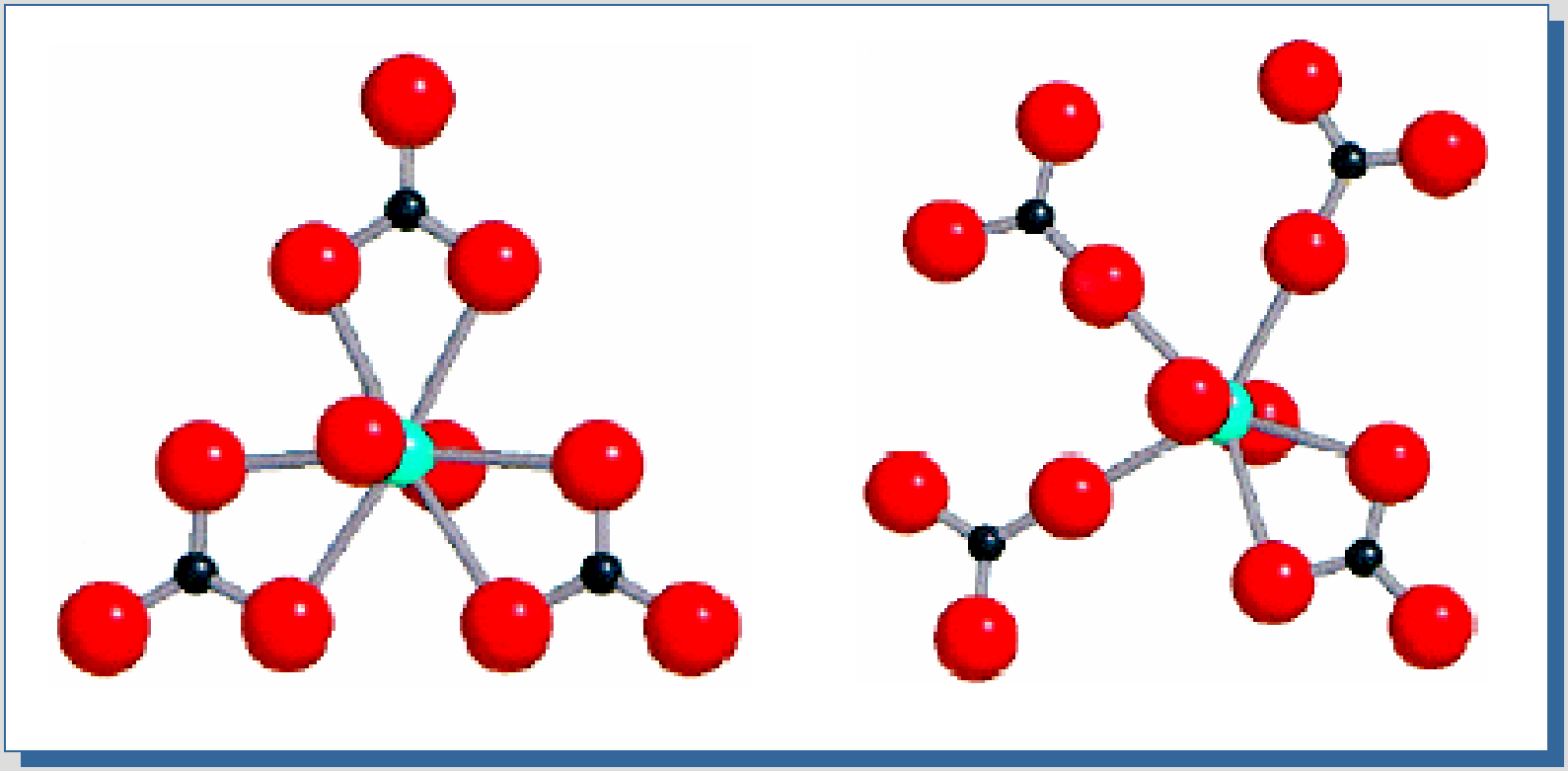


The spectral intensity and resolution increase at deeper depth even though the overall uranium concentration declines, suggesting:

- A reduction in the concentration of associated fluorescence quenchers, such as Fe, Mn, and natural organics
- Conversion of heterogeneous U species to well-defined U phases

The main spectral feature was similar to the less-resolved component in process pond sediments

The Potential Structures of Uranyl Incorporated Into Aragonite and Calcite*

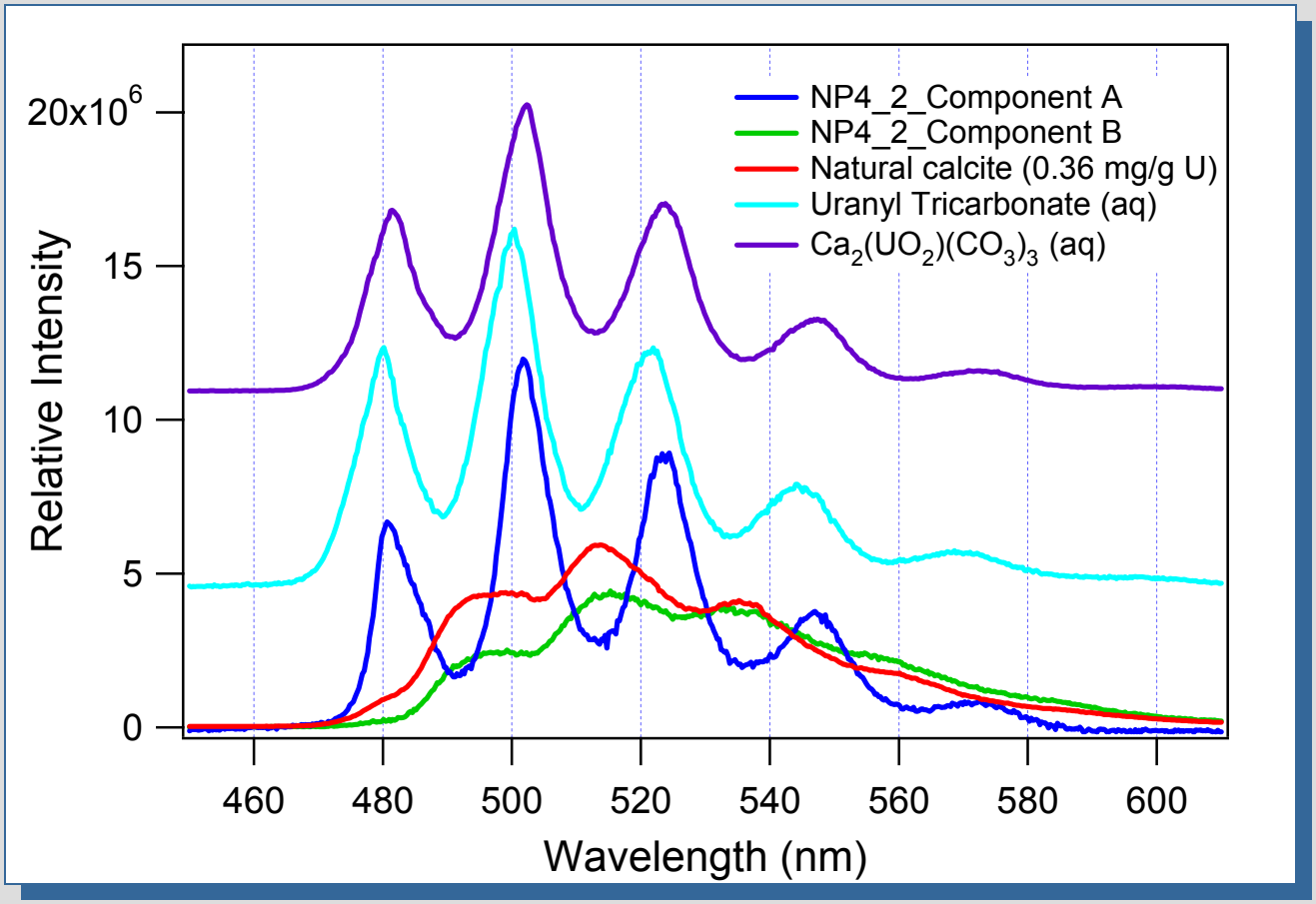


UO_2^{2+} in aragonite

UO_2^{2+} in calcite

* Reeder, R.J., Nugent, M., Lamble, G.M., Tait, C, D., and M Morris, D.E. , *Environmental Science & Technology*, **34**, 638-644.

Comparison of the Deconvoluted U(VI) Fluorescence Spectra in Process Pond Sediment with various UO_2^{2+} Reference Phases



* Kelly, S.D., Newville, M.G., Cheng, L., Kemner, K.M., Sutton, S.R., Fenter, P., Sturchio, N.C., Spotl, C., *Environmental Science & Technology*, **37**, 1284-7.

Findings

- The fluorescence spectra of the process pond and vadose zone sediments showed differences
- Deconvolution of the process pond sediment spectra indicated the presence of two species
  - U(VI) in calcite
  - U(VI) in aragonite or dicalcium-uranyl-tricarbonate (the latter is not consistent with solubility)
- Fluorescence spectra of the vadose zone sediments showed evolution with depth
  - One major spectral feature in common with process pond sediments
  - Increased spectral resolution with depth implies homogeneity and structure