Pluri-millennial evolution of uranium speciation in lacustrine sediments

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Pierre Lefebvre[1], Alkiviadis Gourgiotis[2], Arnaud Mangeret[2], Pierre Le Pape[1], Olivier Diez[2], Pierre Sabatier[3], Pascale Louvat[4], Pauline Merrot[1], Camille Baya[1], Mathilde Zebracki[2], Emmanuel Malet[3], Didier Jézéquel[4], Jean-Louis Reyss[3], John Bargar[5], Jérôme Gaillardet[4], Charlotte Cazala [2], Guillaume Morin[1]

[1] IMPMC, Sorbonne Université-CNRS-MNHN-IRD, Paris (France)
[2] IRSN, Fontenay-aux-Roses (France)
[3] EDYTEM, Université Savoie Mont-Blanc-Université Grenoble Alpes-CNRS, Le Bourget-Du-Lac (France)
[4] Université de Paris-Institut de Physique du Globe de Paris-CNRS, Paris (France)
[5] SSRL, SLAC, Menlo Park, CA (USA)

IRSN INSTITUT DE RADIOPROTECTION ET DE SÛRETÉ NUCLÉAIRE

Context: U mobility and scavenging

- U is a toxic radionuclide that is redox-sensitive
  - **U(IV)** ➔ solid phase ➔ **immobile**
  - **U(VI)** ➔ aqueous ➔ **mobile**

- U release from mine tailings, waste storage, ores… may spread out in the environment and be **immobilized in anoxic sediments**

- **U remobilization** driven by its **speciation = distribution of U-bearing phases**

- U(IV) solid phases
  - **Crystalline (uraninite, U-PO_4)** ➔ **more stable**
  - **Non-crystalline/mononuclear** ➔ **less stable**

- **Few and contradictory information on ageing and potential recrystallization of non-crystalline U(IV)**

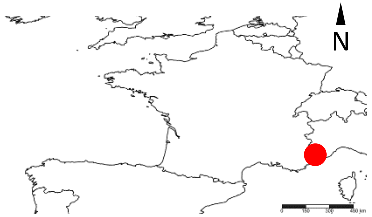
Objectives

- Assessing the **long-term evolution of U geochemical behavior**, and **ageing of U-bearing phases** during burial and diagenesis under anoxic conditions

  - ✓ Do U-bearing phases evolve over time? How fast?
  - ✓ What is the subsequent impact on U mobility? Is U sustainably immobilized by natural recrystallization processes ?

Study site : Lake Nègre

- Alt 2354 m, Mercantour National Park, SE France
- Granitic environment, stratified and oxygenated lake
- Sediments naturally enriched in U (no radioactive hazard)
- 2 m sediment cores preserved under anoxic conditions
- Sediments = long-term continuous record of U speciation



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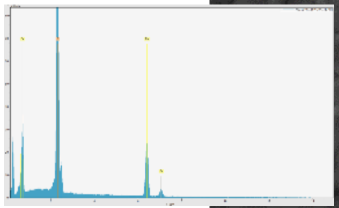
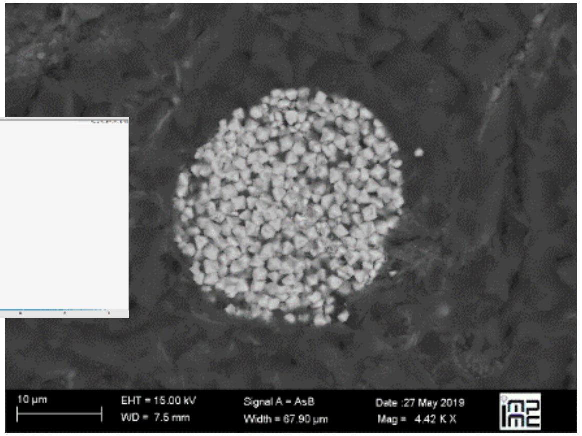
Characterization of the sediment column

- OM- and Si-rich silty sediments: diatoms, granitic minerals, organic matter
- Early diagenesis at the top of the sediments
- Progressive enrichment in solid-phase U from 350 to 760 µg/g
- U is readily reduced in the first cm and fully reduced at depth
- Deeper sediments dated back to 3300 years BP

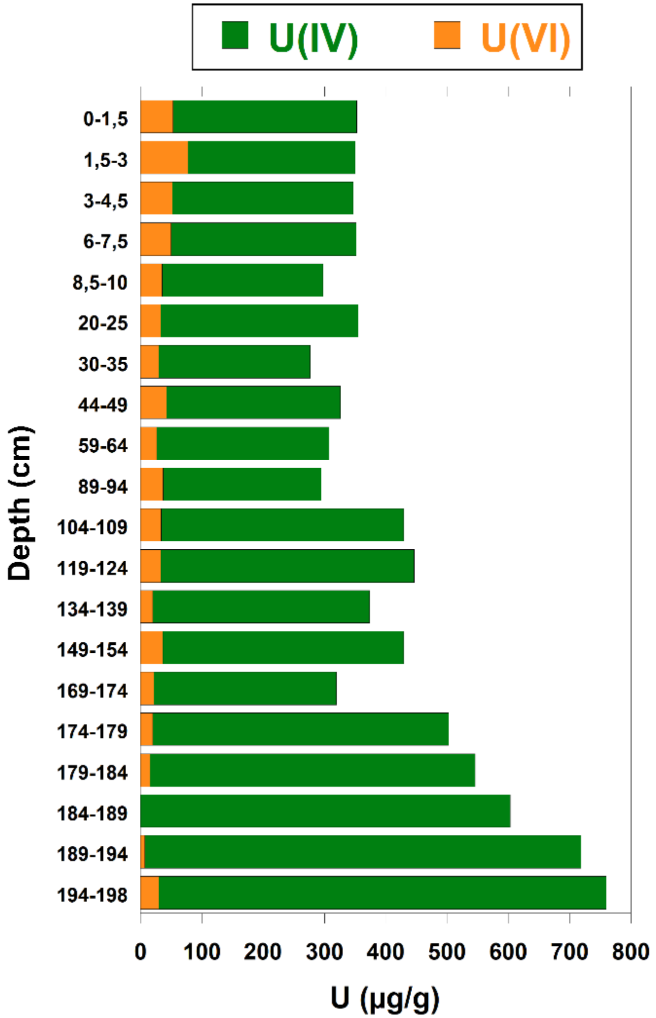
Diatoms observed by SEM at 190 cm depth





Framboidal pyrite (190 cm depth)

U redox state determined by U-L_3 XANES spectroscopy



U transport and deposition

In order to assess the sole effect of diagenesis on U solid speciation, it is necessary to determine if U sources and deposition into Lake Nègre sediments evolved over time.

➢ Isotopic ratios as proxies of sources and processes determined by MC-ICP-MS:

- ($^{234}U/^{238}U$) activity ratios → U sources
- $^{238}U/^{235}U$ ratios (noted as $\delta^{238}U$) → U deposition mode (reduction, adsorption,…)
- $^{238}U/^{232}Th$ (along with ($^{234}U/^{238}U$) ratios) → proportion of lithogenic (detrital) U versus non-lithogenic/authigenic U

Evolution of U speciation over time

- The evolution of U solid speciation over 3300 years in Lake Nègre sediments can be assessed using synchrotron-based Extended X-Ray Absorption Fine Structure (EXAFS) at the U-L_3 edge

  ➢ Enables the determination of coordination numbers and distances of U neighboring atoms, allowing us to observe potential changes in U speciation along the sediment core

- Extraction of non-crystalline U by HCO_3^- 1 M as a complementary tool to determine a potential impact on U mobilization

More to come…
Thank you for reading!