



	Experiment title: Characterization of uranium oxidation state in calcite and aragonite speleothems from the Aranzadi gallery	Experiment number: 20-01-67
Beamline: BM 20	Date of experiment: from: 02/03/02 to: 05/03/02	Date of report: October 10, 2002
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Report:

Project objectives

The aim of this experiment was to determine the oxidation state of uranium in subterranean concretions, or speleothems, formed of an unusual mixture of calcite and aragonite, using x-ray absorption near edge structure (XANES) spectroscopy.

The understanding of uranium chemistry in speleothems is of great interest because the U/Th method is generally used for the radiometric age dating of this objects. In addition, these samples constitute excellent models to study the geochemistry of uranium on environmental systems, such as natural calcium carbonates. The oxidation state determination of uranium is important to determine the stability of U storage in such natural systems over geological timescales.

The studied speleothems have been sampled in the cave of Pierre Saint-Martin located in the department of "Pyrénées-Atlantiques" (France). Aragonite and calcite speleothems contain significant amounts in uranium (up to 350 µg/g) and strontium (up to 18000 µg/g) measured spatially and chemically by nuclear microprobe analysis. These uranium and strontium contents are the most important measured in supergene speleothems, connected with infiltration of meteoric waters.

Main achievements

X-ray absorption measurements were successfully performed at ROBL, BM-20, ESRF Grenoble, enabling the determination of uranium oxidation state in aragonite and calcite of speleothems from the Aranzadi gallery. Measurements were made in fluorescence mode at the U L2 edge (20498 eV) as interference from Sr K-edge fluorescence precluded the use of U L3 edge (17166 eV).

Xanes experiments revealed that uranium is present in its hexavalent form both in aragonite and in calcite (Fig. 1). This result confirms that aragonite structure can concentrate relatively large amounts of hexavalent U, hundreds of $\mu\text{g/g}$, in natural systems. Moreover, it suggests that the relatively high U content found into calcite from the Aranzadi gallery speleothems is not due to the sequestration of U in its tetravalent state.

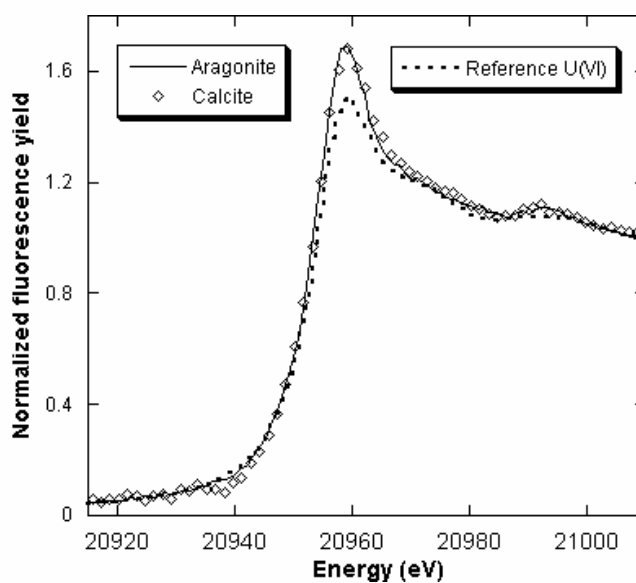


Figure 1. U-L2 edge XANES spectra of U(VI) standard, and from calcite and aragonite speleothems collected in the Aranzadi Gallery. The absorption edge energy of uranium in both samples, calcite and aragonite, is consistent with U(VI) oxidation state.