



**Experiment title:**  
**The nature of uranium in shales**

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**Shifts: 18** **Local contact(s):** Elena F.BAZARKINA

*Received at ESRF:*

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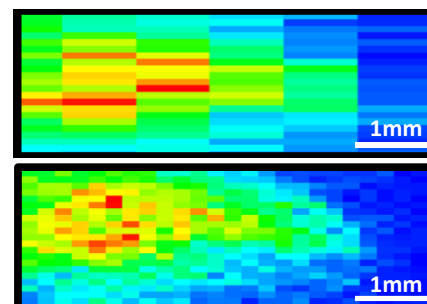
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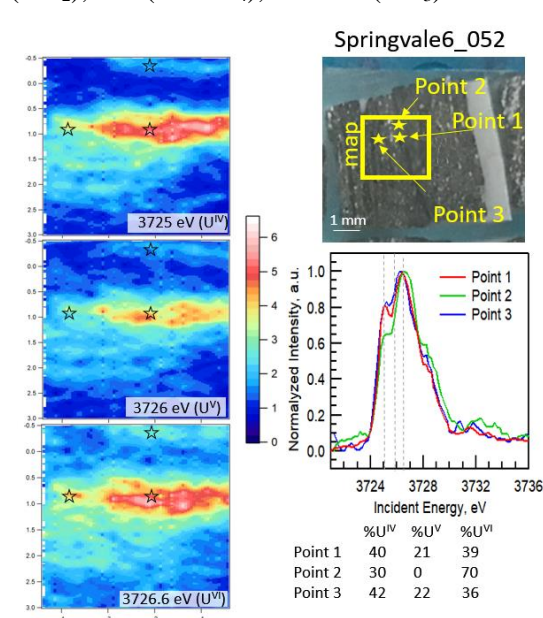
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## Report:

Four key samples of Australian black shales (Westmoreland, Mayneside, Dobbyn, Springvale) were selected and analyzed. Two techniques were used: HERFD-XANES measurements at U M<sub>4</sub> edge and XRF mapping at U M<sub>4</sub> edge. The shape of HERFD-XANES at U M<sub>4</sub> is sensitive to the oxidation state of uranium. The mixed oxidation state was analyzed by PCA (principle component analyses) and modeled by LCF (linear combination fit) using the spectra of reference compounds of U<sup>4+</sup> (UO<sub>2</sub>), U<sup>5+</sup> (MoUO<sub>4</sub>), and U<sup>6+</sup> (UO<sub>3</sub>). In each sample, 3 to 6 points were probed by



**Fig. 1.** XRF map recorded Westmore sample at 3725 eV without (top) and with (bottom) oversampling, i.e. map steps 1mm (horizontal)×0.05mm (vertical) and 0.25mm×0.05mm, correspondingly. The size of beam was 2.5mm×0.05mm.



**Fig. 2.** The photo of the sample Springvale with indicated area chosen for the XRF maps, individual HERFD-XANES spectra recorded in 3 points from this area and the distribution of U<sup>IV</sup>, U<sup>V</sup>, U<sup>VI</sup> in individual spectra as quantified by LCF analyze.

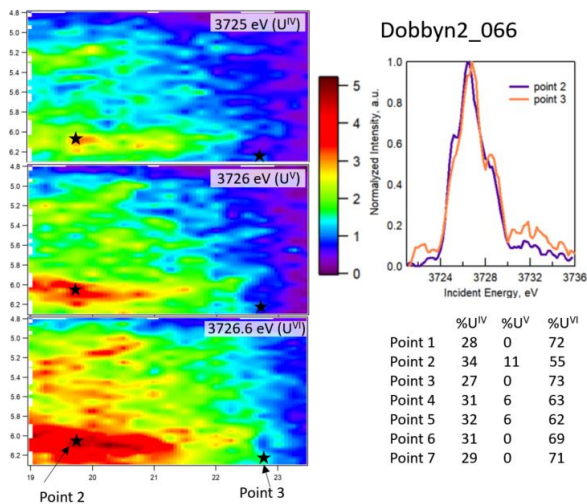
HERFD-XANES. For mapping, the incoming energy was fixed at 3725eV (maximum of HERFD-XANES of UO<sub>2</sub>, pure U<sup>4+</sup> compound), 3726.0eV (maximum of HERFD-XANES of MoUO<sub>4</sub>, pure U<sup>5+</sup>), and 3726.6 eV (maximum of HERFD-XANES of UO<sub>3</sub>, pure U<sup>6+</sup> compound). Thus, the same region was scanned at 3

different incident energies. The 0 background of HERFD technique makes XRF maps not (or only very poorly) affected by the presence of other elements. To improve the quality of XRF maps, the oversampling technique was applied (the step size was smaller than the beam size). The effect of oversampling is demonstrated in Fig. 1 for the Westmoreland sample. Below the summary for each sample is given, followed by the comparison of the samples and the main conclusions.

### Springvale sample

The average concentration of U estimated by ICP-MS is about 50 ppm. The maps are presented in Fig. 2. The size of the map is 3.5mm (vertical) x 4.0 mm (horizontal). The zonation of U does not coincide with rock texture (layers present in the rock, see the photo in Fig.2). The distribution of uranium is not homogeneous. The spectrum from the zone with the low U fluorescence signal (i.e. lower U concentration or higher absorption from matrix) shows a more oxidized U state (70% of U<sup>VI</sup>, point 2). The 2 points from the high U-signal zone show very similar proportions of O oxidation states (36-39% U<sup>VI</sup>, 21-22% U<sup>V</sup>, 40-42% U<sup>IV</sup>).

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**Fig. 3.** XRF maps and examples of individual HERFD-XANES spectra recorded in 3 points in the sample, and the distribution of U<sup>IV</sup>, U<sup>V</sup>, U<sup>VI</sup> in individual spectra as quantified by LCF analyze.

### Dobbyn sample

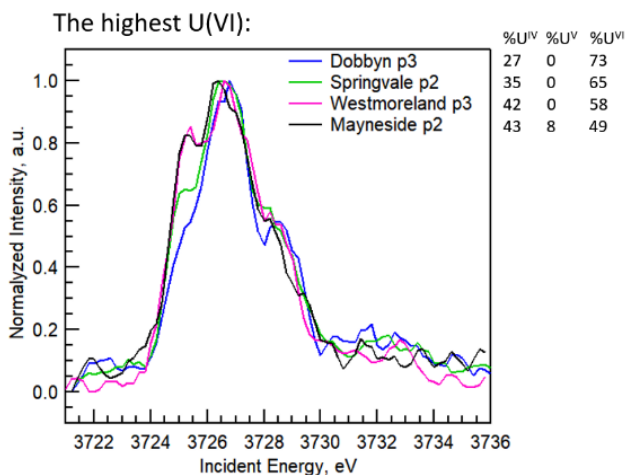
The average concentration of U in the Dobbyn sample is 30 ppm. The maps are presented in Fig. 3. Seven points were analyzed, two of them are on the maps. Compared to other samples, Dobbyn shows the highest concentration of U(VI), i.e. up to 73%. Consequently, the concentration of U(IV) counts 27-41%, and the concentration of U(V) is generally below 11%. The HERFD-XANES indicating the highest fluorescence concentration of U(VI) (73%) was obtained in this sample (point 3).

### Westmoreland sample

This sample has the highest average U concentrations (300 ppm). The HERFD-XANES probed at 6 different spots show mixed oxidation state of uranium, the main state is U(VI), i.e. 43-58%. The concentration of U(IV) counts 34-44%, and the concentration of U(V) varies from 0 to 15%. The XRF maps obtained in this sample are close to those obtained in other samples.

### Mayneside sample

The average concentration of U is estimated to be 30 ppm. 5 points were analyzed. The concentrations of U(VI) and U(IV) are 34-48% and 37-44%, correspondingly. The concentration of U(V) varies from 5 to 19%. The shape of XANES-HERFD is rather close to those recorded in the Westmoreland sample.



**Fig. 4.** HERFD XANES spectra of samples with the highest concentrations of U(VI), and the distribution of U<sup>IV</sup>, U<sup>V</sup>, U<sup>VI</sup> in individual spectra as quantified by LCF analyze.

### Comparison of U state in different samples

The most important findings from our new measurements at the U-M<sub>4</sub> edge are 1) local heterogeneity in U distribution; 2) common mixed oxidation state and 3) the common presence and significant amounts of U(V). Despite the slight difference in the mixed oxidation state revealed by HERFD-XANES, a comparison of XRF maps indicates a similar distribution of U(IV), U(V) and U(VI). These observations are in line with the hypothesis that the initial distribution of U in the samples was controlled by the same processes (sorption by organic matter). In contrast, the degree of later reduction can be slightly different (probably controlled by the host rock and newly formed minerals). The highest fraction of U(VI) is found in the Dobbyn sample (Fig. 4, the spots with the highest U(VI) are compared for all samples). The order of U(VI) preservation can be figured as Dobbyn > Springvale > Westmoreland ≥ Mayneside. The fraction of U(V) does not exceed 20%. Interestingly, there is a general positive correlation between U(IV) and U(V), i.e. the highest U(V) fractions were found when

U(IV) dominates or close to U(VI) (several spots in the samples Springvale and Mayneside). This allows us to propose that the reduction of U(VI) goes through the formation of U(V).

### Conclusions and perspectives

Our new measurements at the U-M<sub>4</sub> edge, show local heterogeneity in U chemical state and the presence of U(V). HERFD M<sub>4</sub>-edge U XANES/EXAFS data confirms the hypothesis that sorption rather than simple reduction controls the primary correlation between organic carbon content and U in shales, and reveals that U in different samples shows various degrees of oxidation and that U oxidation state is dominated by U(VI) [1]. The M<sub>4</sub>-edge measurements are in line with the results obtained with L<sub>3</sub>-edge XANES measurements in the same samples [2]. The presence of U(V) in black shales is demonstrated for the first time. We believe that the distribution of U(IV), U(V), and U(VI) are controlled by the primary sorption of U from the seawater and further remobilization and reduction. Thus, our recent nano-SIMS measurements [2] coupled with L<sub>3</sub>-edge and M<sub>4</sub>-edge XANES data present in this report makes it possible to reconstruct the geological history of black shale diagenesis and metamorphism and to better constrain the main geochemical factors controlling U content and oxidation state in these rocks.

### References

[1] Cumberland et al. (2018) Characterization of uranium redox state in organic-rich Eocene sediments. *Chemosphere* 194, 602-613. | [2] Bastrakov et al. (2022) ESRF experimental report ES-1032.