

# Characterisation of uranium redox state in organic-rich marine sediments of the Cretaceous Toolebuc Formation, Australia

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Throughout geological history, marine organic-rich shales show variable but appreciable enrichment in uranium (U), < 5 to > 500 ppm. Here we report the results of high-energy resolution fluorescence detection (HERFD) x-ray absorption spectroscopy at U L<sub>3</sub> and M<sub>4</sub> edges to characterize U speciation in marine sediments.

We characterised U oxidation state in samples from the Cretaceous Toolebuc Formation, Australia. The latter is one of Australia's most organic-rich marine sediments enriched in trace metals. Nine samples were carbonaceous shales with high total organic carbon (TOC) content of 5.9 to 13.4 wt % and with low maturity organic matter. Two samples of coquinite were selected for comparison (TOC 0.3 and 2.4 wt %).

Our results suggest that a significant proportion of U in marine black shales (~20 to 30%) exists as U(VI), despite the extremely reducing (anoxic to euxinic) conditions during sediment precipitation and diagenesis. Within individual samples, spot analyses indicate variation in the estimated oxidation state within a range of ~20% of U(VI). Uranium is unevenly distributed at millimetre to nanometre scale. Nanoscale secondary ion mass spectrometry (NanoSIMS) reveals different associations that often coexist in single samples; nano-particulate U is associated with organic matter matrix or sulphide minerals, whereas phosphate minerals display diffuse U enrichment. The coquinite has a higher proportion of U(VI), consistent with the dysoxic depositional environment (Boreham and Powell, 1987, doi:10.1016/0146-6380(87)90001-5).

The unexpectedly enhanced proportion of U(VI) relative to U(IV) within marine organic-rich shales implies that U might not be immediately fixed by reduction processes during

sedimentation, but adsorbed by accumulating organic matter, at least in part as U(VI). This is consistent with the behaviour of U reported within the water column of the anoxic Black Sea (Anderson, 1989, doi:10.1016/0016-7037(89)90345-1), experiments on U(VI) sorption by organic matter (e.g., Bhat et al., 2008, doi:10.1016/J.JHAZMAT.2008.02.042), and previously documented redox state of U from continental organic-rich Eocene (56-34 Ma) sediments of paleochannel and lacustrine origin (Cumberland et al., 2018, doi:10.1016/j.chemosphere.2017.12.012).

The results are significant for improving hydrocarbon exploration in known fields, economic geology (U, base-metal, and critical-metal deposits), and environmental management (evaluating potential mobilization of U by groundwaters).

