

## Insights into continental hydrology during the Valanginian (Early Cretaceous) using sphaerosiderites from the Wealden beds of Southern England

Ritwika Sengupta, Stuart Robinson, and Nicholas Tosca

Department of Earth Sciences, University of Oxford, Oxford, United Kingdom (ritwika.sengupta@earth.ox.ac.uk)

Terrestrial carbon isotope records indicate that during the Valanginian stage, the carbon cycle experienced a significant perturbation (the Valanginian positive Carbon Isotope Event, CIE)<sup>1</sup>. This event has been associated with decreased pCO<sub>2</sub> and cooling<sup>2</sup>, but evidence shows low latitude sea surface temperatures remained warm<sup>3</sup>. If temperatures did change during the Valanginian, then it might be expected that the hydrological cycle also varied. The non-marine Wealden strata of Southern England (Berriasian – Hauterivian) span the Valanginian CIE and provide an ideal record for reconstructing low latitude continental palaeoclimate during this event. These strata contain abundant sphaerosiderites and organic matter. Sphaerosiderites are spherical iron carbonate concretions (FeCO<sub>3</sub>), forming mainly in wetland environments and are thought to record the local precipitation signal because their  $\delta^{18}\text{O}$  is locally invariant and decoupled from  $\delta^{13}\text{C}$ .

Despite their utility, sphaerosiderites are compositionally and isotopically heterogeneous and thus mineralogical and geochemical characterisation is necessary to identify samples suitable for stable isotope analyses. Sphaerosiderites from four cores spanning the entire Wealden stratigraphy were studied using XRD, SEM, FTIR and Electron Microprobe. Elemental characterisation showed a variety of trace element uptake behaviour (Mn, Ca, Mg) with concentrations varying from 0.5 – 8 Wt%, and some evidence of anti-correlation between Mn and Fe.  $\delta^{18}\text{O}$  from sphaerosiderites are, on average, more positive in Late Berriasian-age samples (-0.8 to 0.2 ‰), and lighter in Early Valanginian-age samples (-2 ‰). From early to mid Valanginian  $\delta^{18}\text{O}$  trends to heavier values with the highest value of 0.3 ‰ occurring just before the start of a positive excursion in the  $\delta^{13}\text{C}$  of bulk organics, which is interpreted to be the start of the Valanginian CIE. The variations in  $\delta^{18}\text{O}$  start before the CIE and are, therefore likely reflective of independent local changes in hydrology, and are not associated with the global carbon cycle perturbation.

To better our understanding of this non-marine record, in addition to geochemically pure samples, samples hosting multiple chemically distinct phases were also studied to fully assess palaeoenvironmental and diagenetic implications. Data reveal multiple intervals of sulphide and carbonate precipitation within individual spheres at some stratigraphic levels. Palaeoenvironmental interpretations of this data is informed by modern<sup>4</sup> analogues and our own experimental constraints. This provides improved context for understanding the palaeoclimatic changes through the Wealden and further constrains siderite as a proxy for palaeohydrology.

1. Gröcke, D. R. *et al.* The Upper Valanginian (Early Cretaceous) positive carbon-isotope event recorded in terrestrial plants. *Earth Planet. Sci. Lett.* **240**, 495–509 (2005).
2. Price, G. D. & Nunn, E. V. Valanginian isotope variation in glendonites and belemnites from Arctic Svalbard: Transient glacial temperatures during the Cretaceous greenhouse. *Geology* **38**, 251–254 (2010).
3. Littler, K., Robinson, S. A., Bown, P. R., Nederbragt, A. J. & Pancost, R. D. High sea-surface temperatures during the Early Cretaceous Epoch. *Nat. Geosci.* **4**, 169–172 (2011).
4. Pye, K., Dickson, J. A. D., Schiavon, N., Coleman, M. L. & Cox, M. Formation of siderite-Mg-calcite-iron sulphide concretions in intertidal marsh and sandflat sediments, north Norfolk, England. *Sedimentology* **37**, 325–343 (1990).