

Understanding Valanginian continental climate using $\delta^{18}\text{O}$ from sphaerosiderites as a proxy for precipitation

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Terrestrial carbon isotope records indicate a significant carbon cycle perturbation during the Valanginian stage (Valanginian Carbon Isotope Event, CIE). However, the hydrological response is poorly understood as evidence is present for both cool and warm conditions [1, 2]. Sphaerosiderites, or iron carbonate concretions (FeCO_3) which formed mainly in wetland environments, are ideal recorders of terrestrial precipitation patterns because their $\delta^{18}\text{O}$ is locally invariant and decoupled from $\delta^{13}\text{C}$ [3, 5]. Their compositional and isotopic heterogeneity is thought to reflect their mode of formation [4], although this is yet to be fully tested in the laboratory. Our experiments examine chemical controls in fresh to brackish porewater by synthesising siderite from solution matrices with varying Fe^{2+} , Mg^{2+} , Mn^{2+} and Ca^{2+} concentrations, pH and salinity. As only freshwater sphaerosiderites would preserve the $\delta^{18}\text{O}$ of precipitation, it is important to develop a fingerprint for this depositional mode in the geological record. Preliminary results show preferential Mn^{2+} uptake into siderite compared to Ca^{2+} . Natural samples from the Lower Cretaceous, non-marine Wealden beds (southern England) show high Mn concentrations compared to Ca and Mg. Chemical analysis shows anti-correlation between Fe-Ca, Mn-Ca and a positive correlation between Mg-Ca. Through experimental synthesis, we hope to better understand this record, and then use $\delta^{18}\text{O}$ of Wealden sphaerosiderites as a reliable proxy record for terrestrial precipitation during the Valanginian CIE.

[1] Gröcke, D R et al., (2005) *Earth Planet. Sci. Lett.* **240** 495–509; [2] Littler, K., et al (2011) *Nature Geosciences* **4.3**, 169-172; [3] Ludvigson, G A et al., (1998) *Geology* **26** 1039–42; [4] Mozley, P.S (1989) *Geology* **17**, 704–706.; [5] Robinson, S A et al., (2010) *J. Geol. Soc. London.* **167** 303–11