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

***Sengupta, R.**[1,*], **Robinson, S.A.**[1], **Tosca, N.J.**[1]*

*1) Department of Earth Sciences, University of Oxford, Oxford, UK, *E-mail: ritwika.sengupta@seh.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), that may have been associated with decreased pCO_2 and climatic change (GRÖCKE et al., 2005), however evidence shows low latitude sea surface temperatures remained warm (LITTLER et al., 2011). Therefore, climate change during the Valanginian CIE, and the hydrological response is not fully understood yet. Sphaerosiderites, or iron carbonate concretions ($FeCO_3$) which formed mainly in wetland environments, are ideal recorders of terrestrial precipitation patterns because their $\delta^{18}O$ is locally invariant and decoupled from $\delta^{13}C$ (LUDVIGSON, 1998; ROBINSON et al., 2010). Despite their utility in preserving the isotopic composition of meteoric groundwater, sphaerosiderites are compositionally and isotopically heterogeneous. Chemical variation in sphaerosiderites is thought to reflect their mode of formation, although this is yet to be fully tested in the laboratory. Marine influence is thought to be represented by elevated Mg concentrations, while freshwater environments have, typically, higher Mn and lower Mg and Ca (MOZLEY, 1989). To better understand the sphaerosiderite proxy, we utilise microanalytical and experimental approaches to understand the significance of chemical and isotopic variations in sphaerosiderites. 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 $\delta^{18}O$ of precipitation, it is important to develop a fingerprint for this depositional mode in the geological record. Preliminary results show Mn^{2+} uptake into siderite structure is preferential to Ca^{2+} and proportional to the concentration in solution. Mg^{2+} is not taken into the siderite structure under these low concentrations. Natural samples from the Lower Cretaceous, non-marine Wealden beds (southern England) show high Mn concentrations compared to Ca and Mg. Two types of internal growth patterns were noted; concentric zoning and core-rim separate growth. Chemical analysis shows anti-correlation between Fe-Ca, Mn-Ca and positive correlation between Mg-Ca. Through experimental synthesis, we hope to better understand this record, and then use $\delta^{18}O$ of Wealden sphaerosiderites as a reliable proxy record for precipitation during the Valanginian CIE.

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