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Testing the late Silurian seawater 'carbonate hypersaturation' with stable Ca, Sr and Cr isotopes

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The origin and primary cause(s) of the globally-recognized large positive C isotope excursions (CIE), recorded in the Paleozoic marine carbonates, and their links to the global C cycle and/or coeval changes in paleo-environmental and climatic conditions are controversial and highly disputed [1]. The largest positive $\delta^{13}C$ excursion of the entire Phanerozoic, i.e., the mid-Ludfordian CIE (~9‰), is documented in late Silurian marine carbonates worldwide [2]. Recently, it has been proposed that the origin of this CIE is related to a purported 'carbonate hypersaturation' of the late Silurian surface oceans [3], leading to a rapid and massive carbonate precipitation (i.e., whitings) with associated kinetically-controlled evasion of isotopically light CO_2 (and possibly also CH_4) gases from the surface oceans [3]. This in turn would cause a complementary enrichment of the remaining seawater DIC pool in heavy C, the latter reflected in positive $\delta^{13}C$ of coeval marine carbonates [3]. Our recent study of stable Ca isotopes from this late Silurian CIE also confirmed the importance of *kinetic* and/or *rate-controlled* fractionation effects on $\delta^{44/40}Ca$ in precipitated carbonates [4].

Here, we test the above 'carbonate hypersaturation' hypothesis with the application of coupled stable Ca and Sr isotope proxies ($\delta^{44/40}Ca$ and $\delta^{88/86}Sr$), as these has been shown to be highly correlated in calcite from laboratory-precipitation experiments [5], due to rate-controlled effects linked to changes in $CaCO_3$ saturation of a solution. Importantly, our preliminary data confirmed tight correlations between $\delta^{44/40}Ca$ and $\delta^{88/86}Sr$ (also Sr/Ca) proxies across the late Silurian CIE, with slopes similar to those expected from the kinetically-controlled $CaCO_3$ precipitation. We will also present our preliminary paleo-redox proxy records (Ce/Ce*, $\delta^{53/52}Cr$) to identify possible sources of *alkalinity* to late Silurian seawater (i.e., from *continental weathering* versus *oceanic anoxia,* e.g., linked to bacterial sulfate reduction).

[1] Saltzman & Edwards (2017) *EPSL,* **464,** 46–54. [2] Fryda & Manda (2013), *Bull. Geosci.* **88**, 463–482. [3] Kozlowski (2015) *Bull. Geosci.* **90**, 807–840. [4] Farkas et al. (2016) *EPSL,* **451,** 31–40. [5]. Böhm et al. (2012) *GCA,* **93**, 300–314