Microbially-mediated and abiotic synthesis of siderite from 10 to 70°C: a new $\Delta_{47}$ and $\delta^{18}O$ calibration

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The clumped and oxygen isotope composition of pedogenic siderite (FeCO$_3$) can be exploited to reconstruct climate in humid continental environments. The only published siderite $\Delta_{47}$-$T$ calibration [Fernandez et al. 2014] is based on few data points and does not cover the entire temperature range that can be expected in palaeosols. Furthermore, interlaboratory discrepancies regarding $\Delta_{47}$-$T$ calibrations are yet to be resolved. For oxygen isotopes, two calibrations exist. One is derived from abiotic [Carothers et al. 1988] and the other from microbially-mediated precipitation experiments [Zhang et al. 2001]. These calibration are consistent between 45 and 75°C, but but diverge below 33°C and disequilibrium between DIC and water cannot be ruled out [Zhang et al. 2001]. In this contribution, we present a new siderite $\Delta_{47}$ and $\delta^{18}O$ calibration that was produced by inorganic precipitation through active degassing and with microbial cultures using the iron reducing bacteria Sheewanella Putrefaciens. Our aim is to cover a temperature range from 10 to 70°C. To promote DIC equilibrium, the enzyme carbonic anhydrase is used in both active degassing [Fernandez et al. 2014] and bacterial culture experiments. Experiments between 25 and 35°C will be performed both inorganically and with bacterial cultures. Siderites were digested offline at 100°C and analyzed with a MAT 253+ isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany). $\Delta_{47}$ values were pressure baseline corrected, transferred to the absolute reference frame and projected on an acid digestion temperature of 25°C [Meckler et al. 2014]. Preliminary results based on 4 precipitation temperatures indicate that the derived $\Delta_{47}$-$T$ calibration has the same temperature sensitivity as the previously published calibration of Fernandez et al. [2014]. Furthermore, both $\Delta_{47}$ and $\delta^{18}O$ to temperature regressions are highly linear. $\Delta_{47}$ and $\delta^{18}O$ fractionation at 30°C is the same for both abiotic and microbially mediated siderites.


