

Technique dependent oxygen isotope fractionation during siderite digestion by phosphoric acid

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The clumped and oxygen isotope composition of soil siderites (FeCO_3) can be exploited to reconstruct the temperature and precipitation conditions (i.e., $\delta^{18}\text{O}$ value of meteoric water) that occurred during the warm greenhouse climates of the Phanerozoic. Paleoprecipitation reconstructions, however, can be biased by the use of incorrect acid digestion fractionations factors ($\alpha_{\text{siderite-CO}_2}$). Moreover, siderites are relatively more resistant to phosphoric acid attack than calcite requiring longer reaction times and/or higher reaction temperatures. Here, we discuss our experiences measuring the clumped isotope composition of natural siderite samples, and we present $\delta^{18}\text{O}$ estimates of four siderite samples obtained using three different acid digestion techniques (offline, Kiel Device, and GasBench). We find a constant 1.5‰ difference between the GasBench and the Kiel/offline digestion data. Preliminary results from the complete high-temperature pyrolysis (TC/EA) of the same siderites suggest that the published $\alpha_{\text{siderite-CO}_2}$ value [1] is only appropriate for one of these digestion techniques. This observation will be confirmed using conventional CO_2 fluorination. Our results are similar to the technique dependent fractionations reported for calcite [2], and may explain some of the disagreements in the temperature dependence of the siderite-water oxygen isotope fractionations reported by different workers.

[1] Rosenbaum, J., & Sheppard, S. M. . (1986). *GCA*, 50(6), 1147–1150. [2] Swart, P., Burns, S., & Leder, J. (1991). *Chem. Geo.* 86. 89-96