EGU21-1311
https://doi.org/10.5194/egusphere-egu21-1311
EGU General Assembly 2021

Using Triple Oxygen Isotopes of Pedogenic Carbonate to Identify Ancient Evaporation: First Steps from Modern Soils

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The stable isotope composition of soil carbonates is commonly used to reconstruct continental paleoclimates, but its utility is limited by an incomplete understanding of how soil carbonates form. In particular, it is often unclear if the parent soil water has been enriched in ^{18}O due to evaporation, muddying our ability to infer meteoric water $\delta^{18}O$ from paleosol carbonates. Here we demonstrate the potential use of triple oxygen isotopes (termed $\Delta'^{17}O$) to account for evaporation and identify formation process through a study of modern soil carbonate isotope values. Evaporation results in a decreased slope in the relationship between $\delta^{17}O$ and $\delta^{18}O$ and deviations from the global meteoric water line, such that $\Delta'^{17}O$ values in soil water and resulting carbonate decrease with increased evaporation. We report $\Delta'^{17}O$ values of CO_2 derived from soil carbonates and measured as O_2 on a mass spectrometer, with 1-4 replicates per soil carbonate. We find a step-like relationship between $\Delta'^{17}O$ in globally distributed Holocene soil carbonate samples and aridity, where aridity is defined using the aridity index (AI, mean annual precipitation/potential evapotranspiration). Low $\Delta'^{17}O$ values occur in hyper-arid climates (AI < 0.05), with mean $\Delta'^{17}O$ = -0.164 ‰, SD = 0.004 ‰. A transition, or step, occurs in arid climates (AI from 0.05 to 0.2), with $\Delta'^{17}O$ values that range from -0.129 ‰ to -0.165 ‰, and mean $\Delta'^{17}O$ of -0.148 ‰, SD = 0.010‰. High $\Delta'^{17}O$ values occur in semi-arid through humid climates (AI >0.5) with mean $\Delta'^{17}O$ of -0.135 ‰, SD = 0.008 ‰. The lowest observed $\Delta'^{17}O$ values are consistent with extensive evaporation – for context, the $\Delta'^{17}O$ values are similar to those measured in lacustrine carbonates from closed lake basins. The highest $\Delta'^{17}O$ values are consistent with little soil water evaporation. We interpret the step-like pattern in $\Delta'^{17}O$ values as an indication of the threshold in the importance of evaporation vs. transpiration in soil dewatering. This data highlights the potential to use $\Delta'^{17}O$ to identify the extent of evaporation in paleosol carbonates. Eventually, we hope that this novel technique will lead to quantitative accounting of evaporation in soil water and improved reconstructions of meteoric water $\delta^{18}O$ from soil carbonates. The ability to constrain the evaporative conditions of soil carbonate formation will also aid interpretations of $\delta^{13}C$ (including pCO_2 reconstructions) and clumped isotope-based temperatures. These efforts will ultimately aid in our ability to integrate paleoclimate data from soil carbonates with data from other terrestrial records.

How to cite: Kelson, J., Huth, T., Passey, B., and Levin, N.: Using Triple Oxygen Isotopes of Pedogenic Carbonate to Identify Ancient Evaporation: First Steps from Modern Soils, EGU General Assembly 2021, online, 19–30 Apr 2021, EGU21-1311, https://doi.org/10.5194/egusphere-egu21-1311, 2021.