Outline

Intro

Isotope values of pedogenic carbonates are important terrestrial climate proxies, reflecting environmental conditions during soil formation. Carbon isotope values of pedogenic carbonate has been have been used as a proxy for *p*CO2, oxygen isotope values are mostly used for paleoelevation reconstruction, and clumped isotopes have been used for paleotemperature proxies. However, pedogenic carbonate carbon and oxygen isotope values can be difficult to interpret because their isotope values are derived from a suite of both seasonal and annual climate variables. For example, the ratio of atmospheric CO2 to respired CO2 in soil CO2 and the temperature of formation vary seasonally. The timing and season of pedogenic carbonate precipitation has also been debated in recent years, with significant consequences to paleoclimatic inference (Breecker, Passey, Quade, Peters). Clumped isotope temperatures of modern pedogenic carbonates have found a variety of formation temperatures, relative to MAT, in different environments (Mintz, Peters, Quade, Gallagher). These temperatures are usually at or above MAT, indicating a warm-season bias in most environments, but can vary significantly with the calibration curve used to calculate the temperatures. The main drivers of pedogenic carbonate formation are increasing temperatures, decreasing *p*CO2, root-water uptake, and evaporation; however, the relative importance of these drivers is debated (Quade, Gallagher, Meyer). Some studies invoke soil drying, lowering soil *p*CO2, while other studies suggest transpiration could play a larger role in concentration Ca2+ ions the growing season (Gallagher, Meyer). Modelling suggests that pedogenic carbonate precipitates and dissolves in both short and long time periods, but the last precipitation event of the year is usually best preserved (Meyer). Overall, the main season and timing of pedogenic carbonate formation remains unresolved and likely varies with C3 vs. C4 vegetation and different precipitation patterns. Here, we create a model that predicts oxygen and carbonate isotope values of pedogenic carbonate in C3 ecosystems with arid to sub humid climates. We then compare predicted model results with modern studies of pedogenic carbonate that include clumped isotope temperatures to gain insight into the season and mechanisms of carbonate precipitation.

Methods

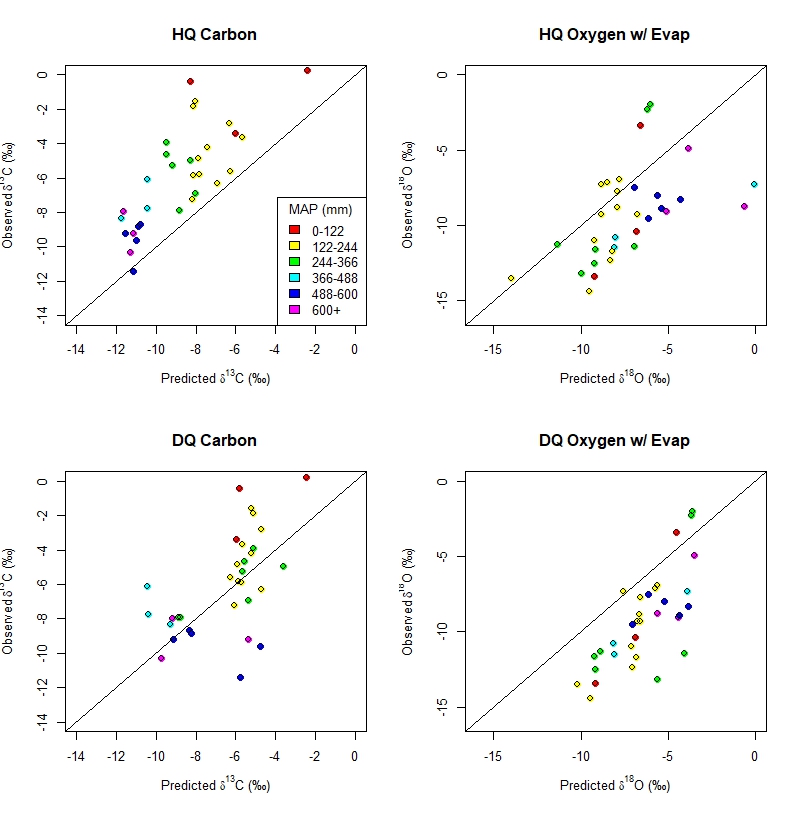
We assume pedogenic carbonate formation takes place over a 3-month season (DJF, MAM, JJA, SON), hereby referred to as the pedogenic carbonate quarter (PCQ). Here we explore a complimentary, model-based approach to evaluating the conditions of soil carbonate formation, creating a mechanistic model connecting carbon and oxygen isotope values of pedogenic carbonate to both seasonal and annual climatic drivers. The model is as follows:

\* Model equations \*

We explore the effectiveness of the model with different model assumptions and its implications for the timing and mechanisms of pedogenic carbonate formation. Gridded climate data are obtained for each site from. The result is a set of hypotheses, which are discussed in depth in section.

Results/Discussion

B: Carbonate saturation is reached when pCO2 decreases, temperature increases and/or there is rapid evaporation. Therefore, hot and/or dry conditions have been suggested to facilitate pedogenic carbonate precipitation, with the relative importance of these conditions debated. Examining model results when it is run in hot quarter and dry quarter conditions reveals that carbon isotope values more closely match the one to one line in the dry quarter, while oxygen isotope values more closely match the one to one line in the hot quarter. No clear support for one season over the other. Even in the hot quarter, the model is overestimating the oxygen isotope values of pedogenic carbonate, indicating that we may have to include seasonal biasing in precipitation (toward winter) or evaporation may not be very influential in these carbonates. More revisions need to be developed in the model to fully match either hot or dry season.



\*Side Note\*

Given that the model does not fully resolve season of formation, clumped temperatures might be useful to help inform the season of carbonate formation. Comparing gridded climate temperatures of hot and dry seasons to clumped temperatures reveals that, while there is significant variation and calibration curves affect the clumped temperatures, overall hot season temperatures are preferred in clumped temperature calculations. However, this is far from definitive because of the aforementioned issues with clumped temperature calculations.

clumped: 17.71 +/- 12.34 C (Kelson 2017 calibration)

dry: -0.22 +/- 5.72 C

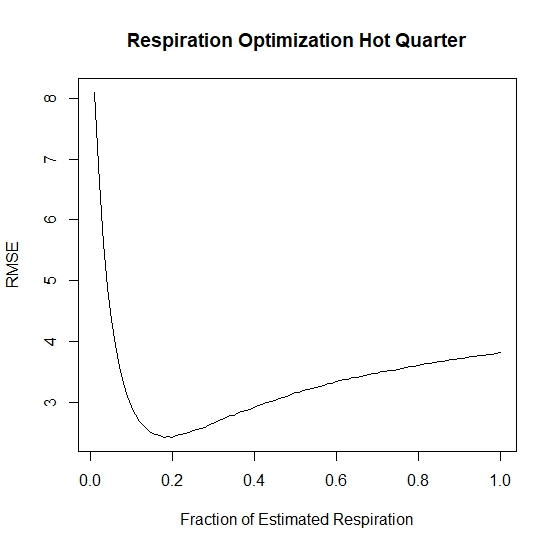
hot: 7.02 +/- 1.61 C

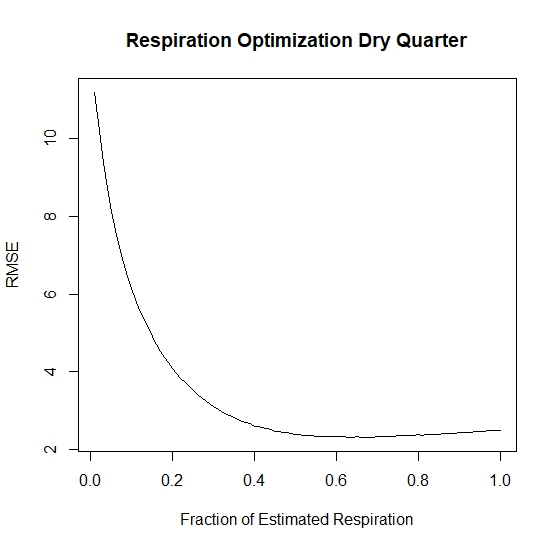
B: Decrease in respiration rate has been suggested as a mechanism of carbonate precipitation

Q: If hot season is assumed to be the season of formation, can we explain the underestimation of d13C values with lower respiration rates?

A: Run the model at successively decreasing fractions of the estimated respiration (respiration ratio).

R: RMSE of measured vs. predicted d13C values is lowest at ~20% of the estimated respiration rate based on mean climate.





I: Respiration rates could decrease at times within the hot season, leading to selective precipitation of pedogenic carbonate at those times, which would not match mean respiration rate over that season. The decrease of soil pCO2 could be the main driver of carbonate precipitation during the hot season.

\* Side Note \*

B: Lower MAP could affect the relationship between soil respiration and climate (temperature and precipitation).

Q: Does filtering respiration sites for lower MAP affect the relationship between respiration rate and climate?

A: Run the JAGS model for the filtered sites (annual respiration, MAP < 760 mm)

R: This filtering affects it only slightly, with a small increase in the effect of precipitation and temperature and small decrease in basal respiration rate. K from 4.25 to 4.87 and Q from 0.054 to 0.055. R0 from 1.25 to 1.24.

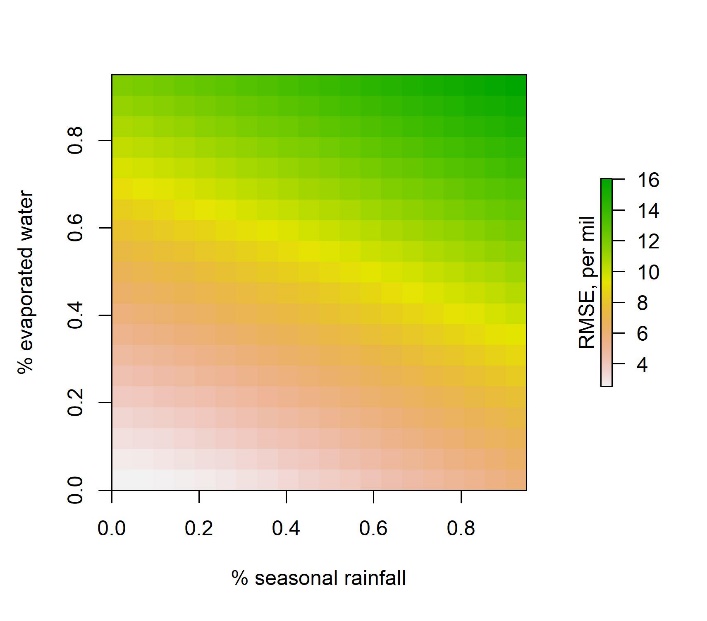
I: The very small change in these parameters does not appreciably affect any results so the relationship holds at low precipitation regimes.

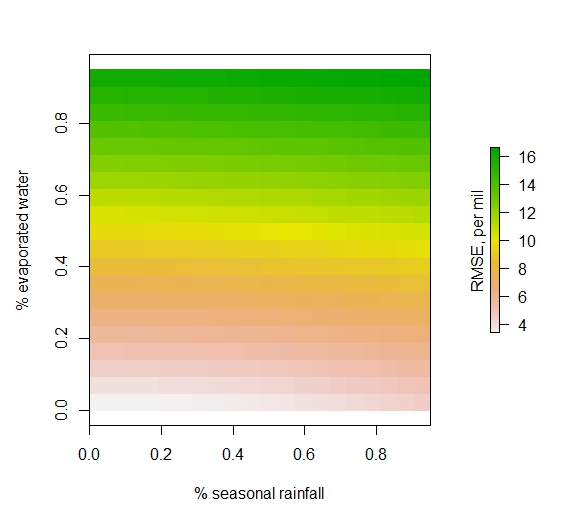
B: The effects of evaporation and seasonal rainfall on d18O values of pedogenic carbonate have been proposed to complicate the relationship between d18O of mean annual precipitation and d18O of pedogenic carbonate.

Q: Do evaporation and/or seasonal rainfall significantly affect d18O values of pedogenic carbonate?

A: Run the model with successively increasing amounts of seasonal rainfall bias and evaporative effects.

R: RMSE of predicted vs. measured d18O is lowest with no seasonal rainfall bias and no evaporative effects.





I: Therefore, d18O seems to be most influenced by MAT and temperature of formation, with minimal influence of evaporation or seasonal rainfall.

Comparison w/ no evap

Transpiration leading to upward water movement may be more important than evaporation? (e.g. Meyer).

One interesting thing that I have been thinking, which may be out of the scope of this particular paper:

Most of these modern sites are still very low MAP (even when culling for >100mm)

Seasonal precipitation patterns likely drive carbonate formation in most envrs

For paleo-applications, at least in our PETM sites, MAP is predicted to be much higher. So, how are we creating a good model for paleo-application by testing the model with these arid to hyper-arid sites? Seasonal patterns of precipitation and carbonate formation are likely different in these sites vs. higher MAP sites.

What if we attempt to use data only from MAP > 400 mm that still have carbonate in the modern envr? There may not be many of them, but maybe would be a better analog, even if they don’t have clumped isotope temps. There could be a significant difference or “tipping point” of when sites precipitate carbonate in the summer vs. fall/spring controlled by MAP/soil water balance (which is temp, soil texture dependent as well).

Could be a target of future work: find some sites that are higher MAP, C3 dominant, and also have pedogenic carbonate with the target paleoapplication being paleosols that indicate higher MAP and are older than mid Cenozoic (C3 plants only).