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Seasonal variation in the carbon isotope composition and concentration of soil CO_2 gives insight to the formation of modern pedogenic carbonate

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Previous work has shown that the carbon isotope composition of pedogenic carbonate in soils with high respiration rates records the relative abundance of C_3 and C_4 vegetation growing in the soil. Pedogenic carbonate, however, forms in many soils where respiration rates are low and/or the relative magnitude of C_3 and C_4 respiration likely varies seasonally. Low respiration rates could result in anomalously high δ^{13}C values in pedogenic carbonate due to increased mixing of atmospheric CO_2 in the soil. If pedogenic carbonate formation is a seasonal phenomenon, then seasonal variation in the δ^{13}C value of soil-respired CO_2 might induce a bias in the carbonate. The magnitude of these effects are not known and are investigated in this study by comparing the carbon isotope composition of soil CO_2 with that of coexisting, newly formed pedogenic carbonate. The following two questions are addressed: 1) how do low respiration rates affect the carbon isotope composition of pedogenic carbonate? and 2) is there a seasonal bias in pedogenic carbonate formation and if so how does the bias affect the average δ^{13}C value of the carbonate. We have collected pedogenic carbonate from 5 modern soil profiles in central New Mexico, USA. Different vegetation is growing at each site but all the soils are developing in recently abandoned terraces adjacent to active drainages. The δ^{13}C values of the carbonate below 50 cm range from -3 per mil under conifer woodland to -0.5 per mil under Larrea tridentata (a C_3 shrub). These values are higher than expected given the high percentage of C_3 plants growing in these soils. In order to compare the carbonate values with ambient soil CO_2, we have also installed profiles of 8-10 soil gas wells at each site for CO_2 extraction. Soil temperature at several depths is also measured at each site. Fitting the profiles of CO_2 concentration using a steady state production-diffusion model results in estimates of the respiration rate and the average depth of CO_2 production, allowing

us to monitor changes in these variables through time. Values for the respiration rate cannot be uniquely determined unless the diffusivity of CO_2 in the soil is known. A unique value for the carbon isotope composition of soil-respired CO_2 can, however, be calculated by extrapolating regression lines of δ^{13}C soil CO_2 versus 1/CO_2 to the pure CO_2 endmember (keeling plot) and then subtracting the 4.4 per mil diffusional enrichment. Using the measured temperatures, we have calculated the isotopic composition of pedogenic carbonate in equilibrium with soil CO_2. At each site, the calculated δ^{13}C values for carbonate in equilibrium with summer and autumn soil CO_2 are 2-5 per mil lower than actual carbonate values. Much better agreement is observed between spring soil CO_2 and coexisting carbonate for the one site at which spring soil CO_2 has been collected so far. Sustained soil water loss during the dry spring in New Mexico provides a mechanism for pedogenic carbonate formation during this time of year. Low respiration rates and/or seasonal changes in the carbon isotope composition of soil-respired CO_2 may be responsible for the high δ^{13}C values of pedogenic carbonate in these soils. Continued monitoring of these variables will be used to address the relative importance of these two possibilities.