Toward non-destructive, semi-continuous monitoring of calcite precipitation/dissolution in soils

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Pedogenic carbonates are an important component in dryland soils. In modern surface soils, pedogenic carbonates are known to influence soil hydrology, nutrient dynamics, and soil fertility. In paleosols, pedogenic carbonates serve as an archive of past environmental factors, including vegetation, elevation, and atmospheric $p\mathrm{CO_2}$. However, the factors controlling the seasonal timing of pedogenic carbonate formation and dissolution are only partly understood, limiting our ability to predict nutrient availability in surface soils and interpret geochemical compositions of paleosol carbonates.

A commonly held assumption when studying pedogenic carbonate is that soil pore spaces behave as an open system in which the soil gas composition controls the geochemical composition of soil water and calcium carbonate that precipitates from it. However, dissolution/precipitation of pedogenic carbonate consumes/produces CO_2 gas, which could significantly affect the concentration and isotopic composition of soil CO_2. If such effects are detectable, they could be used to monitor calcium carbonate dissolution and precipitation in soils.

To explore the utility of this approach, we designed a series of experiments during which soil pore space O_2 and CO_2 concentrations were monitored in calcium carbonate-amended soils and carbonate-free control soils. Soil gas measurements were made using a Sable Systems Field Metabolic System allowing for high precision monitoring of both soil O_2 and CO_2. Measurement of soil O_2 enables soil CO_2 changes driven by carbonate dissolution/precipitation to be separated from changes in CO_2 driven by soil respiration. When water was added to stimulate soil respiration rates, comparable decreases in O_2 were observed in the soil pore space gas in both carbonate-amended and control soils. However, the increases in soil CO_2 were demonstrably lower in the carbonate-amended soils compared to the control, likely due to calcite dissolution. We also developed a numerical production-diffusion model in which water-gas equilibration occurs in a closed system in the soil pore spaces at each time step to compare with empirical and experimental results.