A potential new proxy for paleo-atmospheric pO_2 from soil carbonate-hosted fluid inclusions

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We have developed a new proxy for ancient atmospheric pO_2 based on the composition of soil carbonate-hosted fluid inclusions, which form in equilibrium with the soil pore space gas. The concentration of O_2 in soil gas is controlled by diffusion from the atmosphere and respiration at depth. Therefore, profiles of fluid inclusion compositions can be used with production-diffusion modeling to reconstruct atmospheric O_2. Here we show that carbonate hosted fluid inclusions faithfully record soil gas concentrations, and that soil pO_2 can be derived from the total gas contents of the inclusions. Carbonate nodules collected from profiles of two modern Vertisols near Dallas and Fairfield, TX, are used as test cases. Inclusion compositions are compared to direct soil pore space gas measurements at the Fairfield site, which were collected in septum-capped vials flushed with soil gas through PVC and stainless steel gas wells. At UT Austin lab we separate CO_2 from air and O_2 from Ar using He carrier gas in an Agilent GC and measure each gas individually using a TCD. Fluid inclusions are measured at RPI by an online crushing technique that physically ruptures inclusions into a custom-built quadrupole mass spectrometer where all the gases are measured simultaneously. We quantify pO_2 using a matrix-matched calibration, and define each species as a partial pressure of the total gas released. Total CO_2 is corrected for carbonate speciation assuming inclusions are in equilibrium with the micrite host, verified by measuring the relative abundance of each species by Raman Spectroscopy. When corrected for aqueous solubility using Henry's Law, the soil-carbonate hosted gas concentrations agree with the soil pore space gas concentrations to within <1% for N_2, O_2 and CO_2. The diffusion-production model predicts atmospheric pO_2 of 21%, validating the method.