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Controls on the rate of oxygen isotope exchange between soil waters and carbon dioxide

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The oxygen isotope composition (δ^{18}O) of CO_2 can be used to separate net land-atmosphere CO_2 exchanges into photosynthesis and respiration. This requires a good understanding of the contributions of these two large and opposite fluxes to variations in the δ^{18}O of atmospheric CO_2. Global scale photosynthetic estimates are particularly sensitive to the δ^{18}O of CO_2 exchanged between the soil and atmosphere. Soils influence the δ^{18}O of CO_2 in the atmosphere as respired CO_2 or atmospheric CO_2 invading the soil profile dissolves and undergoes hydration in soil water. Owing to the relative abundance of molecules, the exchange of oxygen atoms during hydration imparts the δ^{18}O of water to CO_2. The degree to which CO_2 exchanged between the soil and atmosphere is labelled by the δ^{18}O signature of soil water depends on the residence time of CO_2 in the soil profile and the rate of the hydration reaction. It has been shown that soil microbes, like plants, express carbonic anhydrases that catalyse this process. However, the variability and environmental controls on this enzymatic activity are poorly understood in soils. Here we investigate variations in the rate of hydration through controlled laboratory gas exchange measurements on soil microcosms. To understand the drivers of these variations we measured soils, with different chemical and physical properties, sampled from 44 sites across western Europe and northeastern Australia. Observed hydration rates exceeded theoretical uncatalysed rates for the incubation conditions by up to three orders of magnitude highlighting the importance of the role played by catalysts such as carbonic anhydrase. Variations in the rate of hydration were best explained by positive relationships with soil pH and microbial biomass, and a negative relationship with nitrate availability under acidic conditions. These results reinforce the emergent view of pH as the principal driver of carbonic anhydrase expression by soil microbial communities and for the first time we show the sensitivity of this activity to nitrate availability in soils. This work highlights the need for a better understanding of interactions between the rate of hydration and nutrient availability in order to refine modelling efforts aimed at accounting for the influence of soils on the δ^{18}O of atmospheric CO_2.