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Relationships between soil water oxygen isotope composition and the oxygen isotope composition of soil-atmosphere carbon dioxide exchange

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The oxygen isotope composition ($\delta^{18}O$) of CO_2 can be used to separate net land-atmosphere CO_2 exchange into photosynthesis and respiration. This requires a good understanding of the contributions of these two large and opposite fluxes to the atmospheric $\delta^{18}O$-CO_2 budget. Global scale photosynthetic estimates are particularly sensitive to the $\delta^{18}O$ of CO_2 exchanged between the soil and atmosphere. Soils influence the atmospheric $\delta^{18}O$ of CO_2 as respired CO_2 or atmospheric CO_2 invading the soil profile dissolves and undergoes hydration in soil H_2O. Owing to the relative abundance of molecules, the exchange of oxygen atoms during hydration imparts the $\delta^{18}O$ of H_2O to CO_2. Typically CO_2 has been expected to inherit the $\delta^{18}O$ of "free" soil H_2O. However, recent evidence of isotopic fractionation between "free" and "bound" soil water pools, and uncertainty about the micro-pore distribution of carbonic anhydrases that catalyse the hydration reaction call this assumption into question. Here we investigate the relationship between the $\delta^{18}O$ of CO_2 and H_2O in soils through laboratory gas exchange measurements and H_2O extractions. To understand the influence of diffusion and hydration rate on this relationship we consider soils with different chemical and physical properties, and treatments where the hydration rate has been artificially increased or decreased through enzyme and inhibitor additions. We consider the implications of these findings for effectively modelling soil-atmosphere $\delta^{18}O$-CO_2 exchange and better understand the distribution of H_2O isotopes in the critical zone.