

Climate and topographic controls on soil organic carbon cycling in southern Arizona, USA

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The objective of this research was to understand how climate and topography control soil organic carbon (SOC) sequestration across the Santa Catalina Mountain Critical Zone Observatory in southern Arizona, USA. The CZO spans significant range in mean annual temperature (>10°C) and precipitation (>50 cm yr⁻¹). SOC distribution was examined using density and aggregate separations to obtain the free, occluded, and mineral SOC pools for surface and subsurface granitic soils from divergent and convergent landscape positions. Radiocarbon analyses demonstrated that free fractions typically contained the youngest and the mineral or occluded the oldest C depending on the ecosystem. Desert scrub soils sequestered relatively little (<1%), dominantly fast-cycling SOC where the oldest C was mineral associated, indicating organo-mineral interactions as the dominant sequestration mechanism. In contrast, the conifer systems stored more SOC (>3%) and preserved the oldest C through physical occlusion mechanisms. Conifer SOC was 2x greater in the convergent site versus the adjacent divergent site. The age and chemistry of SOC in conifer convergent landscapes suggest downslope transport and burial of SOC in convergent surface soils as an important topographic control on SOC cycling. Bulk soil measurements at the mixed conifer convergent soil-weathered rock interface (~120 cm in depth) indicated a modern $\Delta^{14}\text{C}$ signal (0.0‰, -16.3‰), suggesting downward transport of dissolved organic carbon in the soil pedon. The data confirms shifts in SOC sequestration mechanisms across climatically distinct ecosystems of the southwestern U.S.

O-MIF and S-MIF effects in photolysis of CO and SO₂

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CO Photolysis

O-MIF during CO photolysis in the solar nebula has been suggested as the origin of the slope-1 solar system O isotope line. Photolysis experiments have demonstrated a wavelength-dependence to the $\delta^{17}\text{O}/\delta^{18}\text{O}$ ratio of photoproduct O that seems to rule out a slope-1 trend. Simulations of the experiments using synthetic isotopic CO spectra and ALS synchrotron spectra reproduce the data well, but require an isotope dependence in the dissociation probability, ϕ , such that $\phi_{\text{C180}} \sim 0.5 * \phi_{\text{C170}}$ for the CO E(0) band at 107 nm. Solar nebula model calculations of CO photolysis using OB stellar spectra, synthetic CO spectra, and the new values for ϕ for the E(0) band yield $\delta^{17}\text{O}/\delta^{18}\text{O}$ values close to unity, so that inclusion of the revised ϕ value improves the agreement between the nebular photolysis model and the solar system O isotope line. Direct evidence for a reduced value for ϕ_{C180} can be made by high-resolution linewidth measurements of the E(0) band for C¹⁸O. The cause of the isotopic differences in ϕ are the mismatch of energy levels in an indirect predissociation process, such as occurs in CO photolysis.

SO₂ Photolysis

Could isotopic dissociation probability effects play a role in S-MIF generation during SO₂ photolysis? Self-shielding has been shown to be important in photolysis experiments in optically-thick SO₂ columns, but a pressure effect is also seen such that the S-MIF signature in photoproduct sulfur is reduced at pressures approaching ~1 atmosphere. The pressure effect could arise from either 1) pressure broadening of the SO₂ rovibronic lines in the dissociation regions, or 2) from collisional deactivation of coupled (bound) SO₂ excited states. At the Soleil synchrotron we have measured pressure broadening in ³²SO₂, and see broadening ~ 0.2 – 0.3 cm⁻¹ atm⁻¹ for N₂ and CO₂ gases. Such broadening appears to be insufficient to explain the pressure effect seen in photolysis experiments. We therefore consider it possible that isotopic variations in dissociation probability also occur during SO₂ photolysis. Optically-thin model simulations for the known non-unity dissociation probability region for SO₂ (~210-220 nm) show that maximum $\Delta^{33}\text{S}$ values of ~ 10‰, with $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -1$ for elemental sulfur are possible (but far from proven) for this mechanism.