Preliminary modeling was undertaken with the bulk and respired $\Delta$^14^C data. We used bulk soil ^14^C observations from 2001, 2009, and 2019, and $\Delta$^14^C-CO~2~ measured in laboratory soil incubations of soils collected in 2001 and 2019. Previous work indicated that carbon stocks at these sites are likely in equilibrium with inputs, so we assumed steady-state for the models.

One pool models have been shown repeatedly to be inadequate for describing soil carbon dynamics. We started with two-pool parallel and two-series models, as these are the simplest model system beyond the single pool approach and simpler models are easier to constrain. However, we were unable to successfully fit the bulk and respired radiocarbon time series data with only two pools. We were able to expand to a three-pool model system using the density and thermal fractionation data as additional constraints. The key benefit of this more complex model structure is that enables us to model the dynamics of the fast cycling component of mineral-associated soil C explicitly.

The three pools in the model correspond to:

1. fast cycling particulate organic matter (POM~fast~)

2. fast cycling mineral-associated organic matter (MOM~fast~)

3. slow cycling organic matter (SOM~slow~)

Inputs are split between POM~fast~ and MOM~fast~, and C then passes sequentially into SOM~slow~ from both pools (\*\*Fig. \@ref(fig:mod-scheme-3p)\*\*)). The POM~fast~ pool corresponds directly to the free light fraction isolated by density separation. The MOM~fast~ pool does not directly correspond to an empirical fraction, but rather to a hypothesized pool of actively cycling mineral-associated organic matter. The SOM~slow~ pool is comprised of a mixture of organic matter pool cycling on centennial to millenial time scales, and includes both slowly cycling mineral-associated organic matter and charcoal.

(ref:mod-scheme-4p-cap) Schematic for a compartmental model of soil C with four pools (fPOM, oPOM, MOM~fast~, MOM~slow~). Inputs and transfers between pools are drawn with gray arrows and heterotrophic respiration fluxes are drawn with purple arrows. Relative sizes of pools and fluxes are respresented by box size and arrow weights. The transfer coefficients $\alpha$~POM~ and $\alpha$~MOM~ represent the proportion of inputs transfered from the fast to the slow pools for POM and MOM respectively. The coefficient $\gamma$~in~ gives the proportion of C inputs partitioned to the fPOM and MOM~fast~ pools, while $\gamma$~MOM~ gives the propotion of C in the heavy fraction partitioned to the MOM~slow~ pool.

This three-pool model requires the following parameters:

\* input partitioning coefficient ($\gamma$~in~)

\* decomposition constants for each soil C pool (\*k\*~POMfast~, \*k\*~MOMfast~, \*k\*~SOMslow~)

\* transfer coefficients ($\alpha$~POM~, $\alpha$~MOM~)

Constraints for the model include:

\* C stocks

\* $\Delta$^14^C of density fractions in 2001, 2009, and 2019 (n = 9)

\* $\Delta$^14^C of heterotrophic respiration in 2001 and 2019 (n = 4)

\* $\Delta$^14^C of thermal fractions in 2019 (n = 3)

The central issue with such a complex model is that the number of unknown parameters (6) is high relative to the available data constraints. The parameters that we know the least about and that therefore may be most appropriate to fit with the model are the turnover rates (\*k\*s) for the pools and the transfer coefficients ($\alpha$s). In order to reduce number of unknown parameters we will use a combination of reference data from the literature and empirical measurements made in the laboratory to determine $\gamma$~in~ and \*k\*~SOMslow~, respectively. This leaves 4 unknown parameters to be estimated.

The input partitioning coefficient, $\gamma$~in~, determines the proportion of the inputs going into POM~fast~ versus MOM~fast~. The dominant precursors to MOM are low molecular weight (LMW, < 600 Da) molecules that can be dissolved in the soil solution and transported as dissolved organic matter (DOM) (Lehmann & Kleber, 2015; Sokol et al., 2019). A study by Uselman et al. (2007a) in a similar setting (Mt. Shasta) to that of our study sites provides some insight into the production of dissolved versus particulate organic matter from both leaf and fine root inputs into the soil. Following 47 d of simulated snowmelt, the authors observed that 13.4% of the leaf litter input at the soil surface was translocated in the soil as DOM, and for fine roots added to the soil at a depth of 10 cm, they observed 88.6% of the root material remained as POM, 5.2% was transformed to DOM, and 6.2% was lost via respiration or leaching. Using the data from these study and disregarding the losses, we may assume that a ballpark estimate for $\gamma$~in~ could be calculated as the sum of DOM production from litter and fine roots divided by the sum of litter DOM and both POM and DOM from fine roots. Using data from a companion study from the same authors (Uselman et al. 2007b) in which they measured litter fall and fine root production from the A horizon, the estimate for $\gamma$~in~ using this procedure would be 0.13.

Inputs are relative to the C stocks at steady state, and can be adjusted after parameter fitting so that C stocks are realistic. Alternatively, inputs could be estimated from data obtained from flux towers near to the cool climate sites for the granitic and andesitic parent materials. However, we do not have a similar data source for the basaltic soils. Other potential data sources for inputs are remotely sensed GPP data or downscaled GPP estimates from global models. While inputs could be assumed to be a function of climate and not vary among parent materials, this is a strong assumption that could limit the inferential power of the models regarding temperature sensitivity.

We can calculate the value of \*k\*~SOMslow~ using the relationship between input, carbon stock, and turnover rate at steady-state (\*\*Eq. 1\*\*). The amount of C in the SOM~slow~ pool will be determined a priori using the proportion of C in the oPOM fraction and the most thermally resistant component of the heavy fraction, while the amount of C going into the SOM~slow~ pool is a function of the turnover rates of the MOM~fast~ and POM~fast~ pools and the transfer coefficients $\alpha$~POM~ and $\alpha$~MOM~.

>\*\*Eq. 1\*\*

$$In = (k\_{1} \cdot C\_{1}) + ... + (k\_{n} \cdot C\_{n})$$

>where \*k~1~\* and \*k~n~\* and \*C~1~\* and \*C~n~\* are the decomposition rates and carbon stocks of the first and \*n\*th model pools, respectively.

The thermal fractionation data measured from the heavy fraction samples provides a distribution of carbon content and $\Delta$^14^C across operationally defined subpools of mineral-associated C. Previous studies on the relationship between the temperature of oxidative combustion and $\Delta$^14^C have shown that the carbon oxidized at highest temperatures is consistently the most depleted in $\Delta$^14^C. While oxidative combustion is an imperfect proxy for microbial decomposition \*in situ\*, it is clear that the majority of the organic matter lost at high temperatures is highly persistent. Using the proportion of C lost from the two highest temperature cuts (> 390° C) allows us to calculate the mineral-associated organic matter contribution to SOM~slow~.

Thermal fractionation was only performed for a subset of samples, specifically the heavy fraction samples from the 20-30 cm depth of the cool climate soil profiles collected in 2019. However, we expect the amount of C partitioned to the oldest component of the mineral-associated C pool to be largely controlled by lithology, rather than climate. Under this assumption, we will determine the mineral-associated organic matter contribution to SOM~slow~ by parent material, i.e. this value will differ within a climate zone among parent materials, but not among climate zones within a parent material.

We did not directly measure charcoal content of our samples, so the contribution of charcoal to SOM~slow~ is more challenging to estimate. However, through a combination of visual inspection and $\Delta$^14^C measurements, we have determined that charcoal must make up a substantial of the occluded light fraction (oPOM). The $\Delta$^14^C values for the oPOM fraction were below zero for almost all of the sites, indicating that these fractions are dominated by pre-bomb C cycling at centennial or greater time scales. We also observed charcoal in the free light fraction. However, both visual assessment and $\Delta$^14^C measurements indicate that the contribution of centennial to millenial-aged charcoal is minimal for the fPOM. Accordingly, we are considering the charcoal contribution to SOM~slow~ to be equivalent to the values measured for the oPOM fractions.

## Initial conditions

The problem of determining initial parameter values prior to optimization is non-trivial. Sensitivity to initial values can lead the optimization algorithm to stop at local minima before finding the global minima. Values for decomposition rates (\*k\*) are related to the amount of ^14^C in a pre-bomb system (fraction modern, \*F\*) at steady-state by \*\*Eq. 1\*\* (cf. Schuur, Druffle, and Trumbore, 2016), making this a useful relationship for determining initial \*k\* values. However, the use of this relationship requires knowledge of pre-bomb values for $\Delta$^14^C.

We obtained $\Delta$^14^C values from samples collected in 1959 from sites adjacent to the three granitic soil sites. These soils were fractionated with both physical (density) and chemical means. Initial values for \*k~MOMfast~\* and \*k~SOMslow~\* were determined with \*\*Eq. 2\*\* using the $\Delta$^14^C values measured for the acid-hydrolyzable and non-acid-hydrolyzable fractions of heavy fraction samples collected in 1959. We used the same initial values of \*k~MOMfast~\* and \*k~SOMslow~\* at all sites. Free light and occluded light fractions were not measured separately for the 1959 samples, so we calculated the initial value for \*k~POMfast\* using a one pool model fit to the observations of $\Delta$^14^C for the free light fraction in 2001 and 2019. The one pool model assumption is valid for the POM~fast~ pool as this pool only receives external inputs and therefore \*k~POMfast\* is not affected by turnover rates of the other pools.

>\*\*Eq. 2\*\*

$$k = \frac{\lambda \cdot F}{1 - F}$$

>where $\lambda$ is the radioactive decay constant (8267^-1).

## Workflow

A Monte-Carlo Markov chain approach will be used for parameter estimation in combination with an initial optimization algorithm run to determine an optimal initial parameter set. Initial parameter optimization was performed using turnover times constrained to be between 1 and 50 years for for POM~fast~ (\*k~POMfast~\* = [0.02, 1]), between 1 and 100 years for MOM~fast~ (\*k~MOMfast~\* = [0.01, 1]), and between 100 and 100,000 years for SOM~slow~ (\*k~SOMslow~\* = [0.00001, .01]). The values for $\alpha$~POM~ and $\alpha$~MOM~ were not constrained. We used the function "modFit" (R package FME) with the the Nelder-Mead algorithm for the initial parameter optimization. The best set of parameters found by modFit was then used as the input to a Monte Carlo Markov Chain (MCMC), using the function "modMCMC" (R package FME). The number of iterations for the MCMC optimization was set at 5000 intially, with delayed rejection employed to increase efficiency.