**Parent material and climate interact to control actively cycling and microbially inaccessible soil C**

**Outline**

Question:

1. What factor best explains the variation observed in bulk and respired 14C? Parent material or temperature? Or is the interaction more important? [interaction suggests a role for MAOM...]

* Hypotheses: *Temperature controls respired 14C, parent material controls bulk 14C*

1. How do we quantify this interaction?

Climate change and shifting patterns of land-use will determine whether or not soils will continue to be a sink for atmospheric carbon or become a source in the coming decades. Understanding the response of soil carbon to these changes requires insight into the mechanisms of soil carbon protection. This study compares soils developed on different parent materials across a climate and weathering gradient in order to quantify the relative importance of mean annual temperature and soil lithology for explaining patterns in soil C stocks and carbon persistence.

Climate is the most important explanatory factor for the variation observed in both soil carbon accumulation and persistence globally, due to the strong effect of both temperature and moisture on decomposition rates. However, association of soil organic matter with minerals in the soil has been show to attenuate the effects of climate.

* example of soils with different parent materials under similar climates that have different C stocks and ages
* weathering

(Holding mean annual temperature/MAP constant...) soils rich in poorly crystalline minerals tend to have higher carbon stocks and more depleted 14C than soils with more crystalline minerals, as well as young soils with more primary minerals.

Emerging understanding of the associations formed between soil organic matter and soil minerals demonstrates that neither clay nor parent material alone are adequate for determining soil carbon stocks and soil carbon ages (Beyond bulk, Shi et al, Beyond clay, etc.).

The accumulation and persistence of carbon in soils is a function of both decomposition rates and the accessibility of soil organic matter to the decomposer community present in the soil. Climate is the most important explanatory factor for the variation observed in both soil carbon accumulation and persistence globally.

Global trends in soil carbon stocks and soil carbon ages are well-explained by climate and parent material lithology.

The degree to which one of these factors is more important than the other or the nature of their interaction in governing soil C storage potential

The degree to which these two factors control rates of soil carbon cycling is not clear, however, and

The amount of carbon stored in soil is a function of the carbon inputs relative to the losses. In a steady state system, where inputs and losses are equal, the amount of carbon stored in the soil and the duration of storage are determined by chemical and thermodynamic constraints on decomposition rates, as well as the physical availability of organic matter to decomposer organisms in the soil.

In an ecosystem in which carbon inputs to the soil are balanced by carbon outputs, the amount of carbon stored by a soil is

and the length of time that carbon persists in the soil is determined by the balance f

Direct effects, such as temperature increases, are likely to increase decomposition rates of soil carbon [cite], as is suggested theoretically by the Q10 relationship and empirically in soil warming experiments. Indirect effects, such as pH shifts with changes in precipitation patterns, or alteration of weathering rates, may lead to either increases or decreases of soil carbon stocks as well as potentially redistribute carbon within the soil profile.

Globally, the age of soil carbon is well explained by two main factors: parent material, and climate.

For example, radiocarbon values of carbon in volcanic ash soils tends to be older on average than carbon in soils developed on sedimentary parent materials.

The explanation for this relationship is that parent material has a key influence on mineral organic associations, which are known to protect soil organic matter from decomposition.

The effect of temperature on decomposition rates is thought to control the accumulation of carbon in regions with cooler mean annual temperatures, leading to older mean ages of carbon in these areas

In general, positive values indicate the presence of bomb-radiocarbon, derived from atmospheric testing of nuclear weapons in the 1960s.

In panel B I’ve plotted 14C by mean annual temperature, and here you can see that 14C increases with increasing temperature.

Again, the interpretation here is that on average, soil carbon is older in colder climates and younger in warmer climates.

Of course, climate is more than just mean annual temperature, but looking at MAT alone we still see a strong relationship with 14C.

The simplest explanation for the temperature relationship is the speed of reaction rates. Given the same inputs, a soil at steady state with a slower rate of decomposition will accumulate more organic matter than a soil with a faster decomposition rate.

I should mention that both of these plots use data from the international soil radicoarbon database, ISRaD, which is freely available for anyone to use.

Of course, the simple explanation doesn’t tell the whole story.

The formation of mineral-organic associations that protect soil carbon from decomposition is a function of the mineral assemblage, which in turn, is a function of how the parent material weathers over time.

What you are looking at here are three soils developed on basalt that show progressively more weathering, moving from right to left.

Chronosequence studies have found that oldest carbon tends to be found in soils that are in intermediate stages of weathering.

*[introduce mineral characterization]*

The amount and persistence of soil organic matter found in association with soil minerals varies depending on the physical and chemical properties of the minerals present. While we can infer differences in soil mineral assemblages from parent material, selective dissolution of iron and aluminum provides a quantitative measure of the crystalline and poorly crystalline minerals thought to be most important in protecting soil organic matter from decomposition. These extractions also give insight into how mineral assemblages change over geologic time through weathering. We compared selective dissolution data from our sites (Rasmussen et al. 2018) to the radiocarbon measured in bulk soils and heterotrophically respired CO~2~ (this study) in order to assess the relationship between mineral assemblage and potential mineral protection of soil C.

Oxalate extracts poorly crystalline (short range ordered, SRO) iron oxyhydroxides, e.g. ferrihydrite, as well as SRO aluminosilicates, e.g. allophane and imogolite (Parfitt and Childs, 1988). These minerals have high surface area and variable charge that facilitates the formation of strong innersphere bonds with soil organic matter. The SRO minerals are additionally characterised by a high degree of hydration and are able bind to soil organic matter through both electrostatic attraction and surface complexation (Berhe et al., 2012). Extraction of iron with the dithionite-citrate reagent dissolves poorly crystalline minerals as well as crystalline minerals such as goethite and hematite (Parfitt and Childs, 1988). The crystalline minerals are also capable of binding soil organic matter, but have smaller specific surface area than the poorly crystalline minerals (Kaiser and Guggenberger, 2003).

So the take home message here is that the parent material effect that drives the 14C trends we observe in soils, is actually a function of the interaction of parent material and climate over time.

Which leads us to the central question we set out to answer in this study. We wanted to know if we see different effects on carbon dynamics, as revealed by 14C, across a parent material by climate gradient.

[OK, so this is the sort of relationship between climate and parent material we might expect if climate was not an important predictor of bulk soil 14C, but parent material was. Here we might expect that granite soils would have the youngest carbon, then basalts, and then andesites.

On the other hand, if only climate was important and parent material did not have an effect, we might expect something like the relationship shown on the right, with the oldest carbon at the coldest sites and the youngest carbon at the warmest sites.

If climate and parent material were both important, but had additive effects, we might see a linear decrease in 14C with temperature, but with different intercepts for the different parent materials.]

the 14C content of the bulk soil only tells part of the story.

Most of the carbon that enters the soil does not stick around. But some carbon gets stuck, caught in aggregates, for example, or sorbed to soil minerals. We can represent these dynamics with a simple two pool model, with one pool of fast cycling carbon and one pool of more slowly cycling carbon.

In a multiple pool system, bulk 14C is weighted by the mass of carbon in each pool.

In contrast, the 14C of respired CO2 is weighted by the flux of carbon from each pool.

We can see in a diagram like this how bulk 14C could give us a skewed sense of how soil carbon stocks might respond to changes in inputs due to climate change, or how vulnerable soil carbon stocks might be to changes in climate or landuse.

This is because the amount of C stored in the soil is dependent on the turnover rate of the fast pool, the turnover rate of the slow pool, and the transfer of carbon between the two pools.

The 14C of respired CO2 provides important insight into the mechanisms of carbon protection because by definition, the flux of carbon leaving the soil must be derived from carbon that is both accessible to and decomposable by the microbrial community.

This leads us to the observation that if bulk and heterotrophically respired 14C are different from one another, it indicates that there is a mixture of both fast and more slowly cycling carbon.

Furthermore, there must be some mechanism of physiochemical protection responsible for slowing down the decomposition rate of the more slowly cycling carbon.

**Methods**

*Site descriptions*

We collected samples from 9 sites across a combined gradient of parent material and climate in the Sierra Nevada Mountains of California (Table 1). These mountains are a perfect setting for this study as they make up a natural gradient of parent material and mean annual temperature (MAT). Moving from north to south along the cordillera the parent material changes from basalt to andesite to granite, while the change in elevation headed eastward from the Central Valley leads to a decrease in MAT that is consistent for each parent material.

Total mean annual precipitation is relatively constant with elevation, but falls mainly as rain at lower elevations, and mainly as snow at higher elevations. There is a slight precipitation gradient running north to south, with MAP of xxx mm yr-1 averaged across the basalt sites in the north, xxx mm yr-1 for the andesitic sites, and xxx mm yr-1 for the granodiorite sites in the south.

Vegetation at the study sites is typical of the Sierra Mixed Conifer habitat (*Parker, I., and W. J. Matyas. 1981. CALVEG: a classification of Californian vegetation. U.S. Dep. Agric., For. Serv., Reg. Ecol. Group, San Francisco.)*. All of the sites are forested and dominated by conifers, although the species composition changes along with climate. Tree species at the lowest elevation, “warm”, sites are predominantly *Pinus ponderosa* mixed with lesser amounts of *Quercus* spp. The canopy species at the mid-elevation cool sites is comprised primarily of *Abies concolor* and *Pinus lambertiana*, while *Abies magnifica* is the dominant species at the highest elevation “cold” sites. Species present at all sites include *Calocedrus decurrens* in the canopy, the shrubs *Arctostaphylos* spp., *Chamaebatia foliolosa*, and *Ceanothus* spp. to varying degrees, and ground cover of grasses and forbs.

*Sample collection*

Site locations were initially established in 2001 by C. Rasmussen (Rasmussen et al., 2006), and resampled in 2009 (Rasmussen et al., 2018). We returned in late September of 2019 to collect samples for this study. Sites were located using GPS and geospatial coordinates recorded during site establishment. At each site we dug three replicate pits down to a depth of 0.3m. Prior to sample collection we compared the soil profiles to the pedon descriptions from the previous sampling campaigns. After confirming profiles were comparable we collected samples from the pit sidewalls in 0.1m increments for each of the three pits. We also measured the depth of the litter layer and collected representative litter samples from each site.

*Spline fitting*

Soils collected in 2001 and 2009 were sampled by horizon, while soils collected in 2019 were sampled by depth. We were motivated to use consistent depth increments across sites because of the strong correlation between depth and 14C. In order to make the horizon and depth-based measurements comparable, we fit a mass-preserving quadratic spline to the 2001 and 2009 profiles in order to convert soil property data to the equivalent depth increments sampled in 2019 (Bishop et al., 2001). We used the mpspline function of the GSIF package in R, with a lamba value of 0.1 (Hengl 2019).

*Incubations*

Laboratory soil incubations were performed on composite samples from the three replicate pedons sampled at each site. We composited and incubated each depth increment (0-10cm, 10-20cm, 20-30cm) separately in 1 L glass mason jars fitted with sampling ports in the lids. Incubations were performed in duplicate. Prior to the start of incubations we adjusted the soil moisture content to 60% of water holding capacity (WHC). We defined WHC as the gravimetric water content of water-saturated soil placed in mesh-covered (50µm) tubes (50ml) weighed after draining for 30 minutes on a bed of fine sand. Following rewetting we allowed the soils to respire for one week before closing the jars. Incubations proceeded until CO2 concentrations in the jar headspace reached approximately 10,000 ppm, at which point we collected a 400ml gas subsample for radicocarbon analysis. Gas samples were collected with pre-evacuated stainless-steel (Restec) vacuum canisters. All incubations were performed in the dark at 20°C.

*Soil Physical Analyses and Mineral Characterization*

Data on soil particle size distributions, bulk density, and mineral characterization were obtained from previously published analyses of samples collected at the study sites in 2001 and 2009 (Rasmussen et al. 2006, Rasmussen et al., 2018). Both qualitative and quantitative approaches were used to characterize soil mineral assemblages, including X-ray diffraction (XRD) for the clay (<2µm) fraction, atomic absorption spectroscopy, and non-sequential selective dissolution. Details on these analyses are provided by Rasmussen et al. (20XX). In this study we use the amount of iron selectively dissolved from bulk soils by acid ammonium-oxalate and citrate dithionite as proxies for the quantity of poorly crystalline and crystalline minerals, respectively.

*Carbon, Nitrogen, and Radiocarbon Analysis*

Total carbon and nitrogen content was determined by dry combustion (Vario Max, Elementar Analysensysteme GmbH) on finely ground soils (Retch MM400). For radiocarbon analysis, we first purified CO2 from incubation flask samples and combusted soil samples on a vacuum line using liquid N2. Following purification, samples were graphitized with an iron catalyst under an H2 enriched atmosphere at 550°C. Radiocarbon content was then measured by accelerator mass spectrometry (Micadas, Ionplus, Switzerland) at the Max Planck Institute for Biogeochemisty (Steinhof, 2017).

We report radiocarbon values using units of ∆14C, defined as the deviation in parts per thousand of the ratio of 14C–12C from that of the oxalic acid standard measured in 1950. This unit also contains a correction for the potential effect of mass-dependent fractionation by normalizing sample δ13C to a common δ13C value of 25 per mil (Stuiver & Polach, 1977).

*Statistical analysis*

We used a linear modeling approach to assess the relative explanatory power of climate versus parent material on the observed variation in 14C, as well as potential interactions between these two factors. We constructed separate models for bulk soil 14C and respired 14C-CO2. For each model we considered the two-way interaction between parent material and climate as well as the three-way interaction with time. For ease of interpretation, we considered the effect of depth by modeling each depth layer separately (0-10 cm, 10-20 cm, 20-30 cm). We also made pairwise comparisons of bulk 14C and respired 14C-CO2 across sites and within years, as well as comparisons of individual sites across years. We corrected for multiple comparisons using Tukey’s honestly significant mean difference.

We assessed the relative importance of poorly crystalline versus crystalline iron minerals in protecting soil C from microbial decomposition by regressing the difference between bulk soil 14C and respired 14C-CO2 against the concentrations of ammonium-oxalate extractable iron, ammonium-oxalate extractable aluminum, pyrophosphate extractable aluminum, and dithionite-citrate extractable iron. We did not observe a significant relationship between the bulk and respired 14C difference and time, so we used 14C data from both 2001 and 2019 in the model. Selective dissolution was performed on splits of the soils collected in 2001. Extracted mineral concentrations did not change substantially by horizon, so in order to simplify data interpretation we conducted regressions for the entire 0-30 cm depth. We computed carbon mass-weighted means for bulk soil 14C data and flux-weighted means for the respired 14C-CO2 data.

**Results**

*Bulk soil radiocarbon: Parent material and climate effects*

Both parent material and climate had strong effects on the distribution of bulk soil 14C, but climate explained more of the variance for the uppermost soil layer (0-10cm) whereas parent material explained more in the bottom two layers (10-20cm, 20-30cm). Focusing on the overall climate effects, soils at the cool climate sites tended to be more depleted in 14C than soils at the cold climate sites, while soils at warmest sites tended to be the most enriched in 14C. Comparing parent materials within climate zones, andesite soils tended to be the most depleted in 14C, while the granites tended to be the most enriched.

14C declined with depth for all sites, regardless of parent material or climate. However, linear models for bulk soil 14C revealed significant two-way interactions between parent material and climate at all depths. Accordingly, differences in bulk 14C among parent materials were greatest at the warm and cool sites. In contrast, bulk 14C at the coldest sites was similar across the three parent materials.

*Bulk soil radiocarbon: Temporal trends*

As with the trends in bulk soil ∆14C within years, parent material and climate interacted to control the change in ∆14C observed over time. However, we observed the greatest change in the warm climate sites, while bulk soil ∆14C at the cold climate sites remained relatively unchanged over time. Temporal trends in bulk soil ∆14C were greater in magnitude at the surface than in the deeper soil layers. For the uppermost soil layer we observed significant changes in both warm and cool climate granitic soils, as well as in the warm climate andesitic soils. In the deeper soil layers (10-20 cm and 20-30 cm) the only significant change over time was observed in the cool climate basalt and granite soils. Bulk soil ∆14C of the cool climate andesitic soils remained essentially unchanged between 2001 and 2019. Additionally, bulk soil ∆14C at this site was the most depleted relative to the atmosphere in 2001, 2009, and 2019.

In 2001, the warm climate sites were the only sites where the basaltic and andesitic soils were enriched relative to the atmosphere, and even then only in the A horizon. Granitic soil A horizons were enriched relative to the atmosphere at both the cool and warm sites in 2001, while the bulk 14C of all three lithologies were depleted relative to atmospheric 14C for both A and B horizons at the cold climate sites. For the 2019 samples, surface soil 14C (0-10 cm) was enriched relative to the atmosphere at all sites except for the cool climate andesite soils. At two of the sites bulk soil 14C remained enriched relative to the atmosphere down to 30cm in 2019: the warm climate granite soil and cold climate basalt soil.

*Heterotrophically respired radiocarbon: Parent material and climate effects*

The trends in respired 14C-CO2 were distinct from what we observed in the bulk soil. 14C-CO2 was enriched relative to the bulk soil at all sites, although bulk and respired 14C were not significantly different from one another for the majority of the granitic soils. While 14C-CO2 declined with depth at some of the sites, the decrease was always less than what we observed in the bulk soil. The andesitic soils did not show much of a decline in 14C-CO2 with respect to depth at all, whereas the granitic soils tended to follow the trend in bulk 14C closely.

The interaction between parent material and climate explained more of the variance in 14C-CO2 data than in the bulk 14C data. For the andesitic soils there were no significant differences between respired 14C-CO2 between the different climate zones at any depth. In contrast, 14C-CO2 respired by the basaltic and granitic soils diverged substantially between climate zones, particularly for the 10-20 cm and 20-30 cm depth layers. Overall, 14C-CO2 across sites was most similar at the soil surface, and most divergent at the intermediate depth (10-20 cm).

*Heterotrophically respired radiocarbon: Temporal trends*

Respired 14C-CO2 was almost always either enriched or indistinguishable from atmospheric 14C-CO2. However, we did measure respired 14C-CO2 that was clearly depleted relative to the atmosphere for the 20-30 cm depth layer at the cool basalt site. Additionally, we observed extremely depleted 14C-CO2 (-396.7 per mil) for one of the laboratory replicates of the cold granite site soils in the 10-20 cm depth layer (the other replicate measured -23.5 per mil). Yet we do not believe this extremely depleted 14C-CO2 is due to laboratory error, as we measured similarly depleted 14C-CO2 in the 20-30cm layer from soils collected in 2001 at the same site. Previous work on the effects of drying and rewetting on 14C-CO2 measured in laboratory incubations suggests this disturbance can mobilize older C than would otherwise be respired (Beem-Miller et al., 2021). However, while it may be a very real effect, it appears from our dataset that this effect is limited to only a couple of samples from the deeper soil layers at the granitic sites, which we feel justifies excluding these highly depleted samples from our analysis.

*Bulk and respired 14C differences*

Respired 14C-CO2 was enriched relative to bulk soil 14C for all sites with the exception of the soils at the cold granite site. When comparing differences between bulk and respired 14C across sites, the effect of parent material is immediately evident (table?). Depth profiles of bulk and respired 14C are very similar for the granitic soils, slightly offset for the basaltic soils, and most divergent for the andesitic soils. We also observed a clear climatic effect on the difference between bulk and respired 14C. When compared across parent materials, differences between bulk and respired 14C were smallest for the warm sites and typically greatest at the cool sites in both 2001 and 2019. However, we observed the greatest overall differences at the cool andesitic sites.

The difference between bulk and respired 14C did not change substantially with depth for the granitic or basaltic soils, although it was slightly greater at depth for the andesitic soils. Changes in the bulk and respired 14C difference between 2001 and 2019 were within a single standard deviation of the mean at all sites except for the cold climate basaltic soil, where the difference was 97.9 ± 13.3 per mil in 2001 and 26.2 ± 6.2 per mil in 2019.

*Mineral assemblages*

We saw a strong correlation between the difference in bulk and respired 14C and poorly crystalline mineral content, but not with crystalline mineral content. Specifically, as concentrations of oxalate extractable iron, oxalate extractable aluminum, and pyrophosphate extractable aluminum increased, so did the absolute value of the difference between bulk and respired 14C. In contrast, we did not observe a significant relationship between dithionite-citrate extractable iron and this difference.

Note that we excluded the data from the cold granite site in this analysis, as the respired 14C-CO2 from the deeper layers in those soils was more depleted than what we measured at the other sites by two orders of magnitude. The fact that these were the only soils for which the respired 14C-CO2 was more depleted than the bulk 14C suggests that there is a different mechanism involved in the release of this extremely depleted 14C-CO2, and thus warrants exclusion from this analysis.

**Discussion**

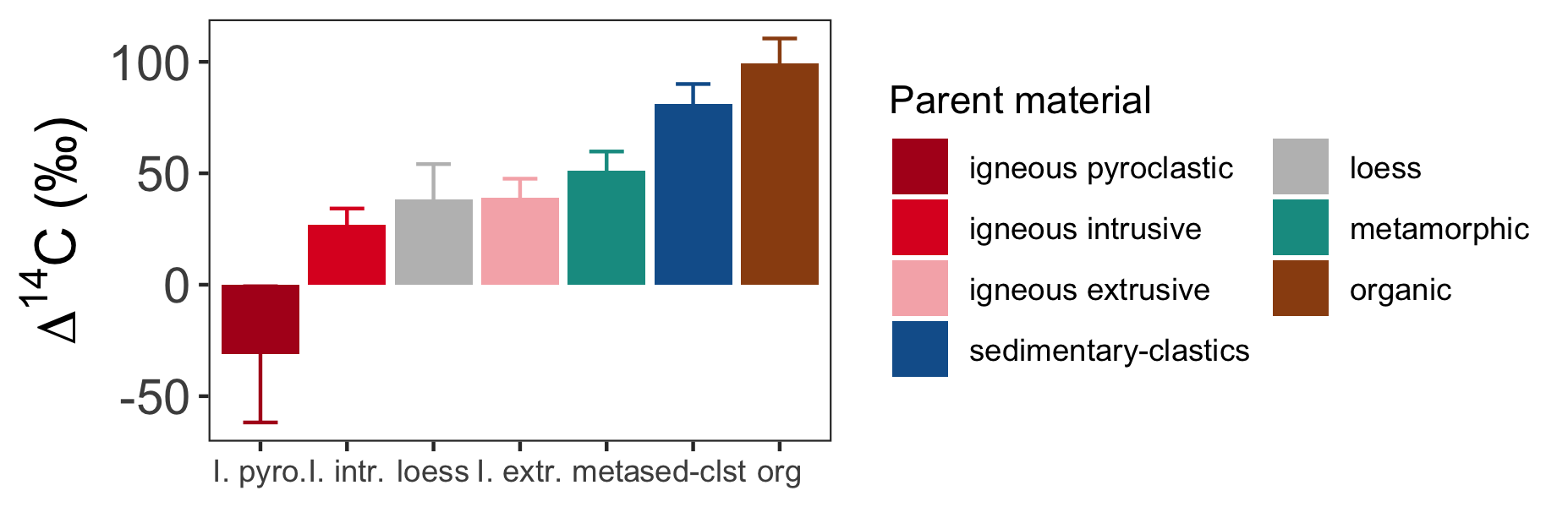
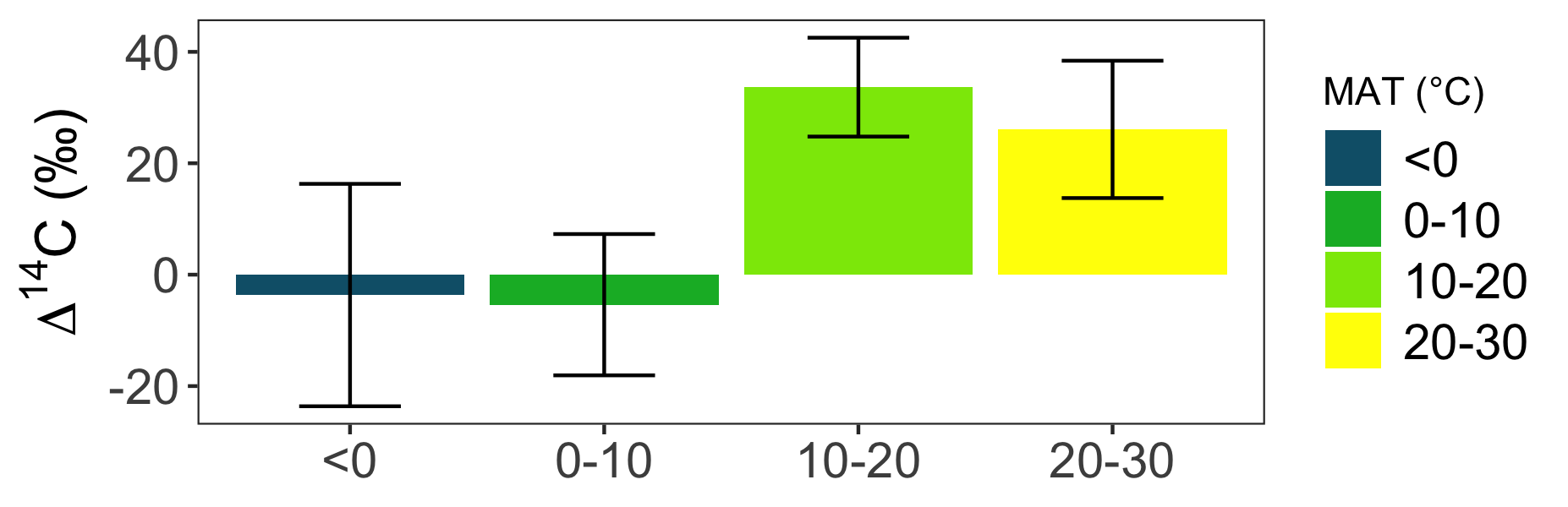
**Conclusion**

Our study shows clearly that parent material and climate interact to control soil C dynamics. This interaction was the key to explaining trends in both bulk ∆14C, which we use a proxy for age of carbon in the soil, and respired ∆14C-CO2, which tells us about the relative contribution of faster or more slowly cycling soil C to respiration. We observed that the trends in both bulk and respired ∆14C at the soil surface were best explained by climate, but best explained by parent material in deeper soil layers. This importance of climate was reflected in the changes in ∆14C we observed over time, which were greater for surface soils than deeper soils, and greater for the highly weathered soils at the warm sites than the poorly developed soils at the cold sites. Yet contrary to expectations, we saw the most depleted bulk soil ∆14C in the cool climate andesitic soil, which is also where we saw the least change over time at all depths.

The interaction between parent material and climate can be characterized by the effects of weathering on the development of the soil mineral assemblage through formation and subsequent loss of secondary minerals. We confirm the findings of other studies that specific mineral assemblages are highly correlated with the age of soil C, as measured by proxy with bulk soil ∆14C. We extend this finding to show that it is specifically the poorly crystalline mineral content that is correlated with bulk soil ∆14C, while crystalline mineral content is not. Finally, we provide mechanistic evidence for the protective effect of mineral-association on decomposition of soil organic matter by demonstrating that the difference between bulk soil ∆14C and respired ∆14C-CO2 is even more strongly correlated with poorly crystalline mineral content than bulk ∆14C alone.

In future work we intend to quantify the timescales of soil carbon cycling in mineral and non-mineral associated pools with a compartmental modeling approach, using the radiocarbon time series presented here in addition to radiocarbon measurements of soil density and thermal fractions as constraints.

Figures



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| --- | --- | --- | --- |
|  | SOC stocks | | |
|  | Parent material | | |
| Climate | Basalt | Andesite | Granite |
|  |  | *kg m-2* |  |
| Cold | 10.1 | 12.9 | 8.1 |
| Cool | 7.0 | 12.5 | 4.2 |
| Warm | 7.9 | 10.5 | 4.4 |



