Climate and the association of soil organic matter with minerals play key roles in soil organic persistence. However, the relevance of parent material for explaining soil organic matter persistence in soils with mixed mineralogies is still poorly explained. In the current study we illuminate how parent material interactions with climate via weathering lead to the development of distinct mineral assemblages, which in turn control the dynamics of soil C cycling at timescales ranging from annual to centennial. Our key finding is that soil mineral characteristics mediate climatic controls on soil C cycling, and that mineralogical controls on soil C cycling are not limited to soil C persistence on centennial timescales, but are also relevant for C cycling on shorter timescales as well.

Our results challenge the primacy of climate control on soil carbon persistence, insofar as we observed the most depleted $\Delta$^14^C~\*bulk\*~ in soils of the cool climate zone, not the cold climate zone. We found that climate is still a critical factor for explaining the dynamics of both persistent and more transient soil C pools, as measured by proxy with $\Delta$^14^C~\*bulk\*~ and $\Delta$^14^C~\*respired\*~, respectively, but our results indicate that soil mineral characteristics moderate the strength of the climate effect. This is particularly apparent at depth. These results are supported by a recent study in which the authors used a depth-resolved model with energy and substrate limitation proscribed by Michalis Menten kinetics to model profiles of $\Delta$^14^C~\*bulk\*~ (Ahrens et al. 2020). The authors found that site mean annual temperature could only explain a minimal amount of variation in the observed radiocarbon profiles, while varying sorption potential in the model allowed for a superior fit.

Previous work at our study sites showed that poorly crystalline minerals were key to explaining both soil C accumulation and bulk soil C ages in these soils (Rasmussen et al., 2018). Our results confirm these findings and extend them to demonstrate a significant negative correlation between poorly crystalline mineral content and $\Delta$^14^C~\*respired\*~. However, the interpretation of this relationship is complicated by the bomb-C peak, as C fixed from the atmosphere in the past 5 years now has the same $\Delta$^14^C as C fixed in the latter half of the 19th century (Graven et al., 2017). Instead, we focus here on the relationship between poorly crystalline mineral content and the difference between $\Delta$^14^C~\*respired\*~ and $\Delta$^14^C~\*bulk\*~.

We would expect the greatest differences between $\Delta$^14^C~\*respired\*~ and $\Delta$^14^C~\*bulk\*~ to be found in soils with a pool of old soil C protected from decomposition in some way, and another pool of soil C that is readily decomposed. In contrast, the smallest differences should occur for soils lacking strong soil C protection mechanisms, in which the majority of soil C has an equal probability of being decomposed by microbes. We observed the smallest differences between $\Delta$^14^C~\*respired\*~ and $\Delta$^14^C~\*bulk\*~ in the soils with the lowest concentration of poorly crystalline minerals, while we observed the largest differences in the soils with the highest concentrations of these minerals. We interpret these findings as providing strong evidence for the role of poorly crystalline minerals in protecting soil organic matter from decomposition. $\Delta$^14^C~\*bulk\*~ in the soils with low poorly crystalline mineral content was still depleted relative to the atmosphere at depth, but the similarity between $\Delta$^14^C~\*respired\*~ and $\Delta$^14^C~\*bulk\*~ in these soils suggests that soil C persistence in these soils is due to physical decomposition constraints that are alleviated under laboratory incubation conditions, such as transport or isolation.

The soils with the largest difference between $\Delta$^14^C~\*respired\*~ and $\Delta$^14^C~\*bulk\*~ were those that had both highly depleted $\Delta$^14^C~\*bulk\*~ values and $\Delta$^14^C~\*respired\*~ values that were enriched relative to the atmosphere. This combination provides evidence for the presence of an intermediate age soil C pool in these soils, one dominated by decadally cycling C. If we interpret this finding in terms of a compartmental model, a possible scenario would involve one pool of centennial to millennially cycling soil C whose signal dominates the $\Delta$^14^C~\*bulk\*~ signal, and second pool of soil C enriched with C fixed from the atmosphere in the years immediately following the bomb-C spike, e.g. 1964 to 1990, whose signal dominates the $\Delta$^14^C~\*respired\*~ signal. More complex model structures could potentially be fit to these data, but the data provide clear evidence for the presence of at least two distinct pools with highly depleted C largely inaccessible to the microbial community, and another pool enriched with bomb-C dominating the respiration flux.

Laboratory studies on soil organic matter associations with poorly crystalline minerals such as goethite show that only a portion of the organic matter is so tightly bound as to resist desorption (Kaiser and Guggenberger, 2003). Further studies have demonstrated that a portion of the organic matter can be mobilized by exchange with DOC (Leinemann et al., 2018). In this scenario the highly depleted $\Delta$^14^C~\*bulk\*~ values observed in the soils with high concentrations of poorly crystalline minerals may derive from organic matter that is strongly sorbed or trapped in micropores, while the bomb-C enriched decadally cycling C observed in the respiration flux could derive from the more microbially accessible and DOC-exchangeable mineral associated soil C pool. However, the rates of change over time we observed for $\Delta$^14^C~\*respired\*~ indicate that annually cycling C is also an important component of soil organic matter at all of our sites.

Our finding that parent material explains more of the variation in $\Delta$^14^C~\*respired\*~ at depth than does climate suggests the role of soil minerals in regulating annually to decadally cycling soil C is of particular importance in deeper soil layers. DOC has been shown to move downward through the soil profile via preferential sorption of new soil C inputs and corresponding desorption of older DOC, which is then available to the microbial community (Kaiser and Kalbitz, 2012). While we did not test this directly, mineral control of this process could be one explanation for the increasing importance of parent material and the interaction of climate and parent material for explaining $\Delta$^14^C~\*respired\*~ trends with depth.

In contrast to what we observed for the poorly crystalline minerals, the lack of correlation we observed between crystalline minerals and soil radiocarbon suggests that these minerals do not play an important role in explaining soil C persistence, at least in these soils. Other studies have shown that crystalline minerals do protect soil C from microbial decomposition, but that the overall sorption capacity of these mineral species is low. We observed a large increase in the amount of iron dissolved from crystalline minerals at the warm sites relative to the cool or cold sites, along with a corresponding decrease in soil C concentration and relative enrichment in both $\Delta$^14^C~\*bulk\*~ and $\Delta$^14^C~\*respired\*~. This increase in crystalline iron was also associated with a corresponding decrease in the amount of poorly crystalline minerals. Together these trends suggest that these soils have lost poorly crystalline minerals through weathering, via leaching and transformation into crystalline species. The patterns of carbon stocks, $\Delta$^14^C~\*bulk\*~, and $\Delta$^14^C~\*respired\*~ observed across the weathering gradient suggest that the consequences of this mineral weathering is a reduction in soil carbon stocks caused by losses of older, $\Delta$^14^C depleted carbon that is independent of parent material.

The sensitivity of decomposition to temperature is of particular interest for understanding how soil C dynamics may change under a warming climate. Comparing the change in $\Delta$^14^C~\*respired\*~ over time for the different climate zones across the different lithologies provides some insight into this question. Focusing on the near surface soils (0-10 cm), where climate effects are strongest, we observed that the rate of change in $\Delta$^14^C~\*respired\*~ were correlated with poorly crystalline mineral content. For example, rates of change were linearly related to temperature in the granitic soils with lower poorly crystalline mineral content. In contrast, the basaltic and andesitic had higher rates of change in the coldest climate zone than in the cool climate zone where poorly crystalline mineral concentrations were highest, but had similarly rapid rates of change as the granitic soils in the warm climate zone where crystalline mineral concentrations were highest. These findings provide evidence that the temperature sensitivity of soil organic matter decomposition may be attenuated in the presence of poorly crystalline minerals. If this is true, we would expect that potential increases in decomposition rates due to climate warming and accompanying carbon losses would be greater in soils dominated by crystalline mineral assemblages than those enriched in poorly crystalline minerals.

# Conclusion

Our study shows clearly that parent material and climate interact to control soil C dynamics. This interaction was the key to explain trends in $\Delta$^14^C~\*bulk\*~, which is a proxy for the mean age of soil C, and additionally in $\Delta$^14^C~\*respired\*~, which reveals the relative contributions of faster or more slowly cycling soil C to respiration. We observed that the trends in both $\Delta$^14^C~\*bulk\*~ and $\Delta$^14^C~\*respired\*~ were best explained by climate at the soil surface, but best explained by parent material in deeper soil layers. This importance of climate was reflected in the changes in $\Delta$^14^C (both bulk and respired) 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 the expected temperature-decomposition relationship, we saw the most depleted $\Delta$^14^C~\*bulk\*~ in the cool climate andesitic soil, which is also where we saw the least change over time at all depths.

The effect of the interaction between parent material and climate on soil C dynamics is best explained by the development of distinct mineral assemblages via weathering, in particular the formation and subsequent loss of poorly crystalline secondary minerals. We confirm the findings of other studies that poorly crystalline minerals are highly correlated with the age of soil C, as measured by proxy with $\Delta$^14^C~\*bulk\*~. We extend this finding to show that it is specifically the poorly crystalline mineral content that is correlated with $\Delta$^14^C~\*bulk\*~, while crystalline mineral content is not. Furthermore, we provide mechanistic evidence for the protective effect of mineral-association on decomposition of soil organic matter by demonstrating that the difference between $\Delta$^14^C~\*bulk\*~ and $\Delta$^14^C~\*respired\*~ is more strongly correlated with poorly crystalline mineral content than $\Delta$^14^C~\*bulk\*~ alone. Finally, the time series data for $\Delta$^14^C~\*respired\*~ provides preliminary evidence that the association of soil organic matter with poorly crystalline minerals attenuates the temperature sensitivity of decomposition.

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. With this modeling framework we also hope to explore hypotheses regarding mineral association and temperature sensitivity further.