LETTERS
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Widespread coupling between the rate and temperature sensitivity of organic matter decay

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Microbial breakdown of soil organic matter influences the potential for terrestrial ecosystems to sequester carbon, and the amount of carbon dioxide released to the atmosphere[1–4]. Predicting the sensitivity of microbial decomposition to temperature change is therefore critical to predicting future atmospheric carbon dioxide concentrations and feedbacks to anthropogenic warming[5]. According to enzyme kinetics, the more biogeochemically recalcitrant the organic matter, the greater the temperature sensitivity of microbial respiration[6–8]. Here, we measured the temperature sensitivity of microbial respiration in soils from 28 sites in North America, ranging from Alaska to Puerto Rico, to test the generality of this principle. We show that the lower the rate of respiration at a reference temperature of 20 °C—and thus the more biogeochemically recalcitrant the organic matter—the greater the temperature sensitivity of soil respiration. We compiled our findings with those from other studies, encapsulating a range of environments, and show that this relationship holds across multiple scales and soil types. Although physico-chemical protection of soil organic matter and substrate availability will also influence the temperature sensitivity of decomposition, we suggest that biogeochemically recalcitrant organic matter will respond the most sensitively to anticipated warming.

Like many chemical reactions, the rate at which microbial enzymes decompose organic matter increases with temperature. However, the fundamental drivers and basic patterns of the temperature sensitivity of microbial decomposition have yet to be quantified[6,9,10], rendering it difficult to improve predictions of the fate of the largest terrestrial pool of C—soil organic matter (SOM)—as climate warms[3,11–13]. On the basis of fundamental principles of enzyme kinetics associated with the Arrhenius equation (1), the carbon-quality temperature (CQT) hypothesis[6–8] predicts that the temperature sensitivity of microbial decomposition should increase with increasing activation energy (E_a) of a reaction. Therefore, the enzymatic decomposition of biochemically recalcitrant substrates, that is, those that require a high activation energy to degrade, generally should be more sensitive to changes in temperature than the decomposition of more labile substrates. Past research has supported relationships that follow the CQT hypothesis for the decomposition of a range of plant biomass over time[8,14], across soils at the continental and landscape scales[15,16] and for soils incubated over time[14,17]. Despite these individual results, no general relationship between temperature sensitivity of respiration and biochemical recalcitrance has yet emerged. If such a general relationship exists, it would parallel previously described scaling relationships between plant nitrogen concentration and respiration[18,19], litter decomposition and nitrogen (N) mineralization[20,21], and body size and metabolic rates[22], which have become key components of comprehensive theories of the functioning of ecosystems.

To better understand how the temperature sensitivity of microbial decomposition of SOM changes as decomposition proceeds, we report the latest of a series of parallel experiments[8,15,16,23] aimed at examining the relationships between biochemical recalcitrance of organic matter and the temperature sensitivity of its decomposition. Here, we analysed microbial decomposition of SOM for a diverse set of surface soils from 28 sites in North America, ranging from Alaska to Puerto Rico, to test the CQT hypothesis across a wide variety of soils. In calculating the E_a of microbial respiration from the periodic short-term manipulations of temperature, we test two corollaries of the CQT hypothesis. First, if biochemical recalcitrance limits the rate at which soil C is respired, soils with organic matter that is respired at a lower rate should be associated with a higher E_a. Second, as incubations proceed and the overall lability of the respired C pool decreases, E_a should increase over time.

Across the 28 soils, the response of microbial respiration to variation in temperature consistently supported the CQT hypothesis. The average coefficient of determination across all soils and all time points of the relationship between temperature and respiration rates was 0.96 using the Arrhenius equation ($n = 420$). Early in the incubations (day 15), E_a varied by a factor of 2.7, from 51.3 kJ mol^{-1} (Ordway Prairie, Florida) to 139.1 kJ mol^{-1} (Florida Coastal Everglades). This is the equivalent of a range of Q_{10} from 2.0 to 6.6 (here and hereafter expressed between 20 and 30 °C). Consistent with predictions from the Arrhenius equation, soils with low relative respiration rates at 20 °C (R_{20}) initially had higher E_a than soils with high respiration rates. Forty-three per cent of the variation in log-transformed E_a among sites at this time could be explained by log-transformed R_{20} as the two scaled negatively with one another ($\log E_a = 2.17–0.28 \times \log R_{20}$; 95% confidence interval (C.I.) $= -0.46–(-0.17)$; $r = -0.66$, $P < 0.001$). On average, E_a decreased with increasing R_{20} (Fig. 1c) across the 28 sites over the 365-day incubation period.

Comparisons of E_a as SOM decomposition proceeds also support the CQT hypothesis. Over the course of the 365-day incubations, R_{20} had declined 85% (20.0 to 2.93 μg C g C^{-1} h^{-1}) and the average E_a had increased 9% from 81.9 kJ mol^{-1} at day 1 to 88.9 kJ mol^{-1} (Fig. 1d). This is the equivalent of Q_{10} increasing from 3.03 to 3.33. All other things equal, on the basis of the Arrhenius equation, organic matter with an E_a that was 7.0 kJ mol^{-1} greater than another substrate would be respired at a rate that was 94% lower, which is similar to the observed 85% decline.

Beyond the relative respiration rates at 20 °C (R_{20}), no other soil characteristics that we measured correlated with E_a, either early or late in the incubation. The fraction of soil carbon resistant

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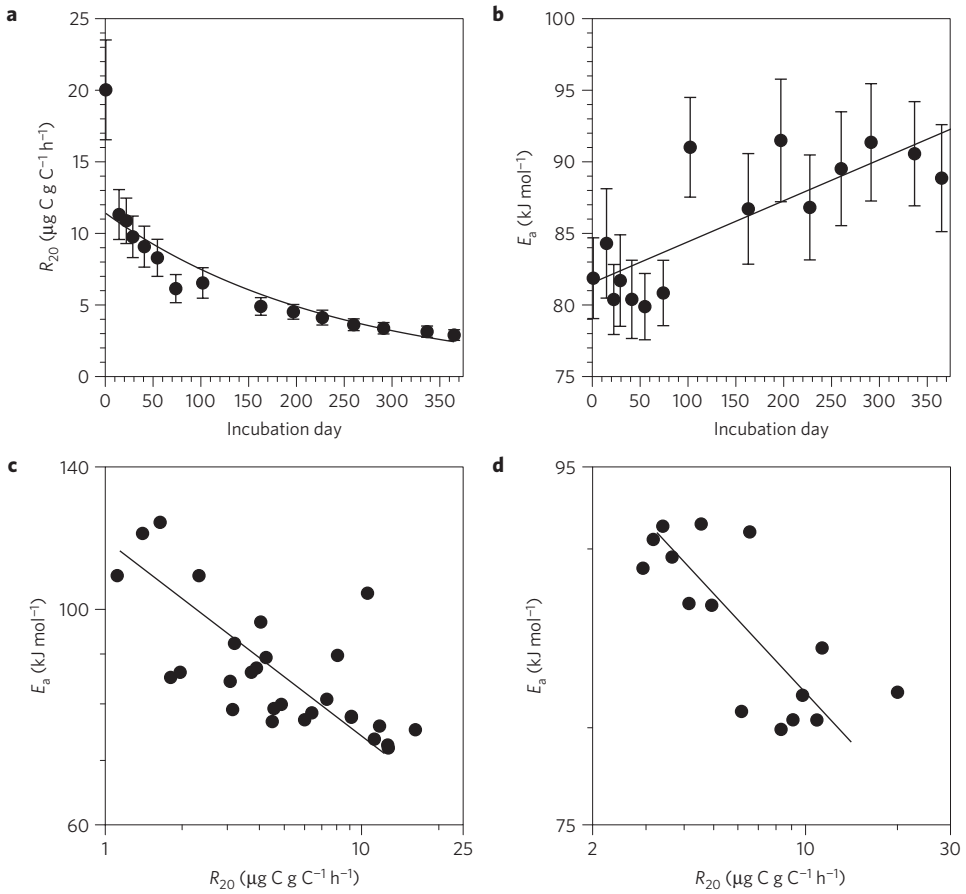

Figure 1 | Changes in respiration rate and apparent activation energy over time for 28 soils. a,**b**, Respiration rates at 20 °C (R_{20}; $\log(y) = 2.43 - 0.0042x$, $r^2 = 0.88$, $P < 0.001$) (**a**) and the activation energy (E_a) of decomposition ($y = 81.6 + 0.028x$, $r^2 = 0.63$, $P < 0.001$; s.e. shown) (**b**) over the 365-day incubations averaged across 28 soils. **c**,**d**, The orthogonal relationships between R_{20} and E_a across the 28 soils averaged for all the measurement dates ($\log(y) = 10.27 - 4.96 \times \log(x)$; $r = -0.70$, $P < 0.001$) with each point representing one of the 28 soils (**c**) and across the 15 measurement dates averaged for all 28 soils ($\log(y) = 2.01 - 0.094 \times \log(x)$; $r = -0.75$, $P = 0.001$) with each point representing one of the 15 measurement dates (**d**).

to acid hydrolysis did not correlate with variation in average E_a or R_{20} or with E_a or R_{20} at any time during the incubations ($P > 0.4$). Soil fractionation techniques such as acid hydrolysis typically quantify the sizes of labile and recalcitrant pools as opposed to the characteristics of one pool[24]. Future research into the chemical nature of E_a among sites would probably require recently developed analytical techniques, such as pyrolysis gas chromatography mass spectrometry[25], that can quantify a diversity of molecular structures. At present, there are still no chemical indices that consistently indicate differences in the quality of a given SOM pool for microbes. Site mean annual precipitation and temperature, soil C and N, pH and texture did not explain any additional variation in E_a after R_{20} ($P > 0.05$).

When joined with the results of a series of parallel experiments that used similar methods to determine E_a and R_{20} (refs 8, 15,16,23), a general relationship between temperature sensitivity of organic matter (both SOM and plant litter) decomposition and biochemical recalcitrance emerges (Fig. 2). Among 206 soils examined, R_{20} varied by a factor of 70 (0.8–55.5 μg C g C^{-1} h^{-1}) and E_a by 2.9 (51.4–146.8 kJ mol^{-1}). As seen in each study, E_a decreased with increasing R_{20} and there were no differences in the scaling coefficients between E_a and R_{20} among four independent surveys of the temperature sensitivity of SOM ($P > 0.07$; Fig. 3). With one of these additional studies at the continental scale[15], one at the landscape scale[16] and one examining patterns with soil depth[23], the fundamental drivers of the temperature sensitivity seem robust across multiple scales and soil contrasts. For the larger

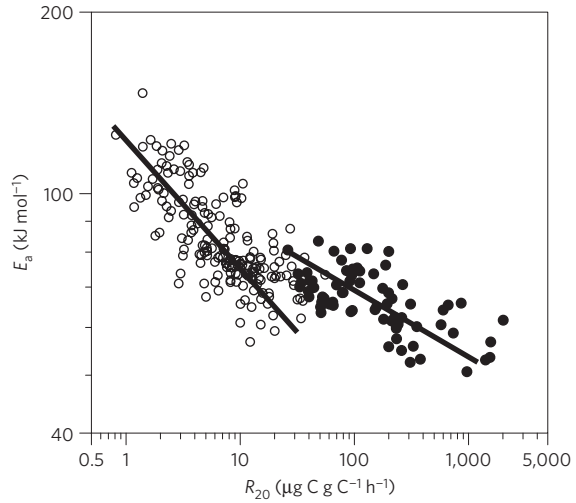

Figure 2 | General scaling of biochemical recalcitrance and temperature sensitivity of decomposition for plant and SOM. Relationships between the respiration rate of microbes at 20 °C (R_{20}) and the activation energy (E_a) of decomposition for SOM (open circles) and plant biomass (filled circles). The lines represent orthogonal regressions for log-transformed data. For SOM, $\log(y) = 2.09 - 0.21 \times \log(x)$; C.I. $= -0.25 - (-0.18)$; $r = -0.66$, $P < 0.001$. For plant biomass, $\log(y) = 2.06 - 0.11 \times \log(x)$; C.I. $= -0.15 - (-0.08)$; $r = -0.64$, $P < 0.001$.

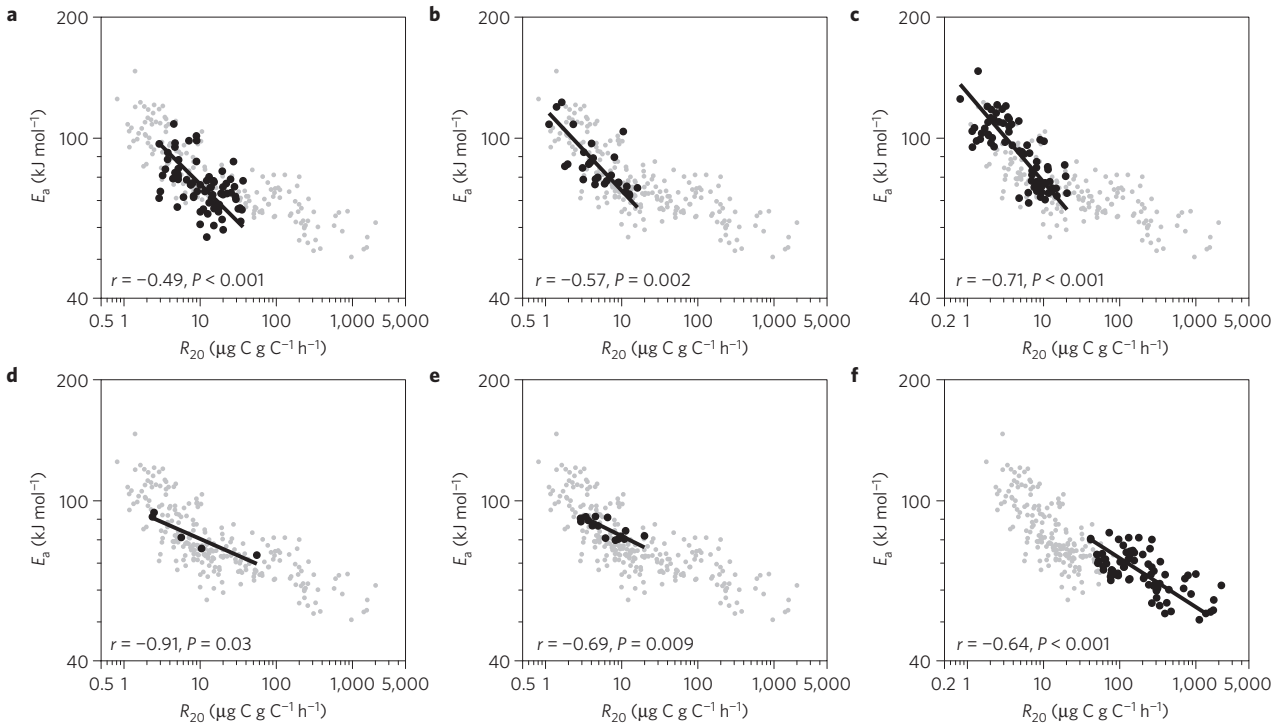

Figure 3 | Scaling of biochemical recalcitrance and temperature sensitivity of decomposition compared across contrasts. a–f, Relationships between the respiration rate of microbes at 20 °C (R_{20}) and the activation energy (E_a) of decomposition of SOM observed across different individual studies (black circles): at the continental scale primarily for North America[15] (**a**), among soils for this study (**b**), at the landscape scale[16] (**c**), across soil depths for a given soil[23] (**d**), over time for soils in this study (**e**) and for plant biomass[8] (**f**). For reference, the unified data set from Fig. 2 is shown in grey in each panel.

SOM data set, E_a continued to decrease as respiration increased (Fig. 2) with a large range of variability among samples in the temperature sensitivity of SOM decomposition. E_a was predicted to be as high as 110.0 kJ mol^{-1} ($Q_{10} = 4.44$) for the lowest observed R_{20} (0.81 kJ mol^{-1}) and as low as 57.7 kJ mol^{-1}($Q_{10} = 2.17$) for the highest observed R_{20} (55.5 μg C g^{-1} h^{-1}).

Joining the plant litter and SOM data sets extends the range of R_{20} by a factor of 33 (new maximum of 2,012 μg C g C^{-1} h^{-1}), although the lowest E_a observed for litter decomposition (50.7 kJ mol^{-1}) was only slightly less than the lowest observed for SOM (51.4 kJ mol^{-1}). When the relationships between E_a and R_{20} for SOM and litter are assessed jointly (Fig. 2), there is evidence for a general relationship between temperature sensitivity and lability among substrate types that is probably modified by the physico-chemical protection of organic matter in soils[26]. For SOM and plant litter with the same E_a, the microbial decomposition respiration rate is lower for SOM than litter. For example, SOM with an E_a of 59 kJ mol^{-1}, which is the lowest predicted SOM E_a in our data set, would have an R_{20} of 31.5 μg C g C^{-1} h^{-1}. Yet, biomass with the same E_a would be respired at a rate that was more than an order of magnitude greater: 420.9 μg C g C^{-1} h^{-1}. The offset in decomposition rates between SOM and biomass at a given E_a could be ascribed to physico-chemical protection of SOM lowering the relative respiration rate of SOM. Desorption of organic matter from soil minerals is only weakly affected by temperature[27], and therefore unlikely to be generating observed relationships between R_{20} and E_a. Without estimates of physico-chemical protection and/or chemical lability that are independent of microbial utilization rates, a more highly resolved general relationship between biochemical recalcitrance and temperature sensitivity will be difficult to describe.

Although the CQT hypothesis is probably the most parsimonious explanation for the observed relationship between SOM decomposition rates and its temperature sensitivity, other processes are probably influencing observed patterns in ways that have yet to be quantified directly. For example, physico-chemical protection of SOM by minerals can increase the temperature sensitivity of SOM decomposition, and the microbial communities of soils are likely to differ in their short-term responses to temperature changes independent of substrate biochemical recalcitrance (see Supplementary Discussion). In addition, the longer-term responses of SOC to changes in temperature might be more complicated than short-term responses. Several factors, including changes in the quantity and quality of organic matter pools over time, changes in nutrient availability, the influence of plants in supplying labile C to fuel co-metabolism of organic matter[28], and the activity and structure of microbial communities, will increase in importance as altered temperatures are maintained for longer periods of time[10]. Incorporating these factors requires the establishment of additional first principles that can be combined with the CQT relationships for more accurate predictions.

Establishing the generality of the CQT hypothesis is an important step in predicting the ultimate response of present organic matter pools to increases in temperature. For example, present coupled climate–carbon cycle models often use a Q_{10} of 2 to describe decomposition responses to increased temperature[4]. It might be possible to not only generate a better average temperature sensitivity to use in these models through more extensive sampling, but to include continuous recalcitrance–temperature sensitivity functions that better describe temperature responses of decomposition. If enzyme kinetics continue to govern extracellular decomposition with longer temperature increases, then responses would continue to follow CQT scaling relationships. As such, decomposition of the most biochemically recalcitrant organic matter would respond the most to anticipated warming, probably generating a positive feedback to climate change.

Methods

At each of 28 sites, mineral soil was collected from the top 10 cm of the soil profile, generally restricted to the A horizon. Soils were then mailed to Kansas State University where they were passed through a 2 mm sieve and maintained at 5 °C for 10–60 days until incubations began. For each soil, we measured texture using the hydrometer method, C and N concentrations on a Leco CHN analyser, water-holding capacity, pH in a 1:1 mixture of soil and water[29], and acid-hydrolysis-resistant C (ref. 30). We adjusted seven replicates of 20 g dry-equivalent soil to 35% water-holding capacity and placed them in 50 ml polyethylene centrifuge tubes. Replicates were then incubated at 20 °C. Periodically, the five replicates for each soil were sealed with a cap containing a rubber septum, and then distributed over five temperatures (10, 15, 20, 25 and 30 °C). Two additional replicates were maintained at 20 °C. These soils were incubated for 18–72 h and then respiration rates for each determined by removing 4 ml of gas. They were then injected in-line into a N_2 gas stream and the peak heights measured with a Licor 6252 infrared gas analyser. Using a set of calibrations, peak heights were converted to CO_2 concentrations in the tubes and then to respiration rates that were scaled relative to soil organic C. The respiration rates of the two replicates at 20 °C (R_{20}) were used as an index of lability. The five replicates incubated from 10 to 30 °C were used to generate an E_a that was mathematically independent of R_{20}. We used the Arrhenius equation to calculate the apparent activation energy of the chemical reactions that contributed to respiration (E_a) where the rate of respiration relative to total SOC (k) is described by:

$$k = Ae^{-\frac{E_a}{RT}} \quad (1)$$

where T is temperature in Kelvin, R is the gas constant (8.314 J K^{-1} mol^{-1}) and A is the frequency factor that is specific to each reaction and generated independently for each set of five replicates. Specifically, E_a was calculated as the slope of the relationship between $-1/RT$ and the natural logarithm of relative respiration rates. This process was repeated 15 times over 365 days with replicates for a given soil rotated among the five temperatures for each measurement period.

To assemble a common data set of R_{20} and E_a, we compiled data from four other experiments that used the same methods to examine temperature sensitivity. To minimize the influence of inorganic carbon release, no soils were used with pH > 8. For each soil, we recalculated E_a and extracted R_{20} from the original respiration data. For SOM, the studies measured temperature sensitivity at only one time point, or were averaged between two time points. From the present study, we included only the average R_{20} and E_a for each soil (145 d), although we later compare relationships over time to the larger data set (Fig. 3). For the temperature sensitivity of leaves and roots, we include the temperature sensitivity measurements at each of the three time points originally reported. Scaling relationships between R_{20} and E_a were assessed with orthogonal regression, that is, standardized major axis regression, on log-transformed data. All data were analysed in JMP 8.0.1 (SAS Institute, Cary, North Carolina, USA).

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References

1. Denman, K. L. *et al.* in *IPCC Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (ed. Solomon, S.) (Cambridge Univ. Press, 2007).
2. Schuur, E. A. G. *et al.* The effect of permafrost thaw on old carbon release and net carbon exchange from tundra. *Nature* **459,** 556–559 (2009).
3. Trumbore, S. E. & Czimczik, C. I. Geology—An uncertain future for soil carbon. *Science* **321,** 1455–1456 (2008).
4. Friedlingstein, P. *et al.* Climate-carbon cycle feedback analysis: Results from the (CMIP)-M-4 model intercomparison. *J. Clim.* **19,** 3337–3353 (2006).
5. Kirschbaum, M. U. F. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* **27,** 753–760 (1995).
6. Davidson, E. A. & Janssens, I. A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* **440,** 165–173 (2006).
7. Bosatta, E. & Ågren, G. I. Soil organic matter quality interpreted thermodynamically. *Soil Biol. Biochem.* **31,** 1889–1891 (1999).
8. Fierer, N., Craine, J., McLauchlan, K. & Schimel, J. Litter quality and the temperature sensitivity of decomposition. *Ecology* **85,** 320–326 (2005).
9. van der Meer, J. Metabolic theories in ecology. *Trends Ecol. Evol.* **21,** 136–140 (2006).
10. von Lützow, M. & Kögel-Knabner, I. Temperature sensitivity of soil organic matter decomposition—what do we know? *Biol. Fertil. Soils* **46,** 1–5 (2009).
11. Fang, C. M., Smith, P., Moncrieff, J. B. & Smith, J. U. Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature* **433,** 57–59 (2005).
12. Knorr, W., Prentice, I. C., House, J. I. & Holland, E. A. Long-term sensitivity of soil carbon turnover to warming. *Nature* **433,** 298–301 (2005).
13. Giardina, C. P. & Ryan, M. G. Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature. *Nature* **404,** 858–861 (2000).
14. Conant, R. T. *et al.* Sensitivity of organic matter decomposition to warming varies with its quality. *Glob. Change Biol.* **14,** 868–877 (2008).
15. Fierer, N., Colman, B. P., Schimel, J. P. & Jackson, R. B. Predicting the temperature dependence of microbial respiration in soil: A continental-scale analysis. *Glob. Biogeochem. Cycles* **20,** GB3026 (2006).
16. Craine, J. M., Spurr, R., McLauchlan, K. K. & Fierer, N. Landscape-level variation in temperature sensitivity of soil organic carbon decomposition. *Soil Biol. Biochem.* **42,** 373–375 (2010).
17. Conant, R. T. *et al.* Experimental warming shows that decomposition temperature sensitivity increases with soil organic matter recalcitrance. *Ecology* **89,** 2384–2391 (2008).
18. Wright, I. J. *et al.* The worldwide leaf economics spectrum. *Nature* **428,** 821–827 (2004).
19. Reich, P. B., Tjoelker, M. G., Machado, J. L. & Oleksyn, J. Universal scaling of respiratory metabolism, size and nitrogen in plants. *Nature* **439,** 457–461 (2006).
20. Manzoni, S., Jackson, R. B., Trofymow, J. A. & Porporato, A. The global stoichiometry of litter nitrogen mineralization. *Science* **321,** 684–686 (2008).
21. Parton, W. *et al.* Global-scale similarities in nitrogen release patterns during long-term decomposition. *Science* **315,** 361–364 (2007).
22. West, G. B., Woodruff, W. H. & Brown, J. H. Allometric scaling of metabolic rate from molecules and mitochondria to cells and mammals. *Proc. Natl Acad. Sci. USA* **99,** 2473–2478 (2002).
23. Fierer, N., Allen, A. S., Schimel, J. P. & Holden, P. A. Controls on microbial CO_2 production: A comparison of surface and subsurface soil horizons. *Glob. Change Biol.* **9,** 1322–1332 (2003).
24. McLauchlan, K. K. & Hobbie, S. E. Comparison of labile soil organic matter fractionation techniques. *Soil Sci. Soc. Am. J.* **68,** 1616–1625 (2004).
25. Janos, P. Separation methods in the chemistry of humic substances. *J. Chromatogr. A.* **983,** 1–18 (2003).
26. Thornley, J. H. M. & Cannell, M. G. R. Soil carbon storage response to temperature: An hypothesis. *Ann. Bot.* **87,** 591–598 (2001).
27. von Oepen, B., Kordel, W. & Klein, W. Sorption of nonpolar and polar compounds to soils—processes, measurements and experience with the applicability of the modified OECD-guideline-106. *Chemosphere* **22,** 285–304 (1991).
28. Gershenson, A., Bader, N. E. & Cheng, W. X. Effects of substrate availability on the temperature sensitivity of soil organic matter decomposition. *Glob. Change Biol.* **15,** 176–183 (2009).
29. Robertson, G. P., Sollins, P., Ellis, B. G. & Lajtha, K. in *Standard Soil Methods for Long-Term Ecological Research* (eds Robertson, G. P., Coleman, D. C., Bledsoe, C. S. & Sollins, P.) 106–114 (Oxford Univ. Press, 1999).
30. Paul, E. A., Morris, S. J. & Bohm, S. in *Assessment Methods for Soil Carbon* (ed. Lal, R.) 193–206 (Lewis, 2001).

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Author contributions

All authors designed the experiment. J.M.C. and K.K.M. carried out the measurements. J.M.C. analysed the data and wrote the manuscript, to which all authors contributed discussion and text.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://npg.nature.com/reprintsandpermissions. Correspondence and requests for materials should be addressed to J.M.C.