in La$_2$Mo$_2$O$_9$ form a lattice of slightly distorted parallelepipeds whose corners are occupied alternately by La and Mo cations, thus defining buckled alternated (LaMo) planes perpendicular to the three main crystallographic axes (Fig. 4a). Such an arrangement is reminiscent of that observed in the monazite structural type (LnPO$_4$), and can be described as a micro-twinning of the cationic arrangement of the monazite structure (Fig. 4b). In La$_2$Mo$_2$O$_9$, the relatively large shortest Mo–Mo distances (4.58 Å) make electron conduction improbable, as effectively measured.

The structural and electrical results reported above show that oxide-ion conductivity is strongly indicated in La$_2$Mo$_2$O$_9$. A more direct way to unequivocally demonstrate oxide ion transport is to perform concentration or permeation measurements on fully densified materials. These experiments are planned, and will be reported at a later stage.

A way to consider the high-temperature form of the La$_2$Mo$_2$O$_9$ structure is through its relationship with that of β-SnWO$_4$ (ref. 14). Both compounds crystallize in the same space group, P2$_1$3, with identical cationic positions. Divalent tin is a 5+ lone-pair element, and it is well known that a lone pair occupies a volume equivalent to that of an oxide ion O$^{2-}$. La$_2$Mo$_2$O$_9$ can thus be viewed as β-SnWO$_4$ where tin has been replaced by lanthanum (with identical size but without a lone pair), and tungsten by iso-element molybdenum. As lanthanum is trivalent, an extra oxygen atom is necessary to fulfil its oxidation state, so that the formal substitution starting from Sn$_2$W$_2$O$_8$E$_2$ leads to La$_2$Mo$_2$O$_9$↓ (here we use E to indicate a lone pair, and ↓ to indicate a vacancy). Two lone pairs are thus replaced by one oxygen atom and one vacancy, through which oxygen diffusion can progress, which suggests the origin of oxide-ion conduction in La$_2$Mo$_2$O$_9$. Oxygen localization with large thermal factors of ~10 Å$^2$, and strongly modulated background with characteristic O–O distances as obtained from neutron diffraction data, are consistent with both the conduction property and its interpretation. The substitution of lanthanum by bismuth, although it significantly increases the cell volume and stabilizes the high-temperature form, does not increase the oxide-ion conductivity because Bi$^{3+}$ substitution reintroduces a lone pair in the system, which tends to block the conduction path.

These stereochemical considerations suggest a way to design new oxide-ion conductors: starting from a mixed oxide of a lone-pair element (like Ti$^{4+}$, Ge$^{4+}$, Sn$^{4+}$, Pb$^{2+}$, Sb$^{3+}$, Bi$^{3+}$, Se$^{4+}$, I$^{5+}$…), and substituting the lone-pair element with oxidation state (n$^+$) by a non-lone-pair element of the same size and oxidation state (n+1$^+$). For each two substituted cations, this would create one extra oxygen and one vacancy, which is a favourable situation for oxygen diffusion. As far as possible, the counter-cation should withstand a variation of coordination (as does Mo$^{4+}$).

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Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature

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It has been suggested that increases in temperature can accelerate the decomposition of organic carbon contained in forest mineral soil (C$_s$) and, therefore, that global warming should increase the release of soil organic carbon to the atmosphere. These predictions assume, however, that decay constants can be accurately derived from short-term laboratory incubations of soil or that in situ incubations of fresh litter accurately represent the temperature sensitivity of C$_s$ decomposition. But our limited understanding of the biophysical factors that control C$_s$ decomposition rates, and observations of only minor increases in C$_s$ decomposition rate with temperature in longer-term forest soil heating experiments brings these predictions into question. Here we have compiled C$_s$ decomposition data from 82 sites on five continents. We found that C$_s$ decomposition rates were remarkably constant across a global-scale gradient in mean annual temperature. These data suggest that C$_s$ decomposition rates for forest soils are not controlled by temperature limitations to microbial activity, and that increased temperature alone will not stimulate the decomposition of forest-derived carbon in mineral soil.

To examine the long-term influence of temperature on the decomposition of C$_s$ in forest soils, we assembled results from studies that used one of two standard methods for estimating C$_s$ loss from soil. Method 1 studies estimate C$_s$ loss by measuring in situ changes in the $^{13}$C/$^{12}$C ratio and total C$_s$ content of soil after existing vegetation is replaced with vegetation that uses a different photosynthetic pathway (for example, C$_3$ forest to C$_4$ pasture). The
change in vegetation alters the $^{13}C/^{12}C$ ratio of new detritus, allowing an estimate of the loss of $C_s$ formed before conversion. Method 2 studies estimate $C_s$ loss by incubating soils in the laboratory for 1 yr at temperatures representative of field conditions, and quantifying the $CO_2$ evolved$^{17,18}$. The 82 sites examined here span 8 soil orders and the global range of mean annual temperature (MAT) for forests (see Supplementary Information).

Calculated $C_s$ turnover times for method 1 studies were unrelated to MAT ($R^2 = 0.01, P = 0.50$; Fig. 1); turnover times under moist tropical conditions were similar to those in cool temperate soils. In these studies, soil clay content, which is thought to control $C_s$ storage$^1$, did not explain the lack of a relationship between $C_s$ decomposition rates and MAT. For soils with similar ($15-27\%$) clay content, $C_s$ turnover was still unrelated to MAT ($R^2 = 0.05, P = 0.28$). In method 2 studies, $C_s$ turnover time was positively related to incubation temperature, with $C_s$ decomposing more slowly at higher temperatures ($R^2 = 0.14, P = 0.02$; Fig. 2). The $C_s$ lost from method 1 and method 2 soils is the most active, and therefore the most temperature-sensitive, carbon in mineral soil$^{2,19}$. However, the decomposition rates of forest-derived $C_s$ reviewed here are insensitive to temperature, unlike the response predicted by models$^{1-6}$.

In our calculations of turnover time, we assumed a single-pool model for soil carbon. To test whether this assumption affected the results, we compared $C_s$ mass loss per year across MAT, with method 1 sites segregated by time since conversion. For method 1 studies, $C_s$ mass loss per year decreased with increasing MAT for sites sampled <11 yr after conversion ($R^2 = 0.66, P < 0.01$), and was unrelated to MAT for sites sampled 11–45 yr after conversion ($R^2 = 0.01; P = 0.72$) or >45 yr after conversion ($R^2 = 0.15; P = 0.35$). Despite a 20 $^\circ$C gradient in MAT, $C_s$ mass loss as a function of time since conversion was insensitive to temperature (Fig. 3). $C_s$ mass loss was roughly constant with time until about 30 years or about 60% mass loss. After this time, $C_s$ decomposition appears to slow dramatically or stop. For method 2 studies, $C_s$ mass loss for the 1-yr incubations decreased with incubation temperature ($R^2 = 0.19, P < 0.01$). We conclude that our choice of a single-pool model did not cause the lack of a relationship between $C_s$ decomposition rates and temperature.

Our results conflict with those of Trumbore et al.$^2$, who used $^{14}C$-based estimates of light-fraction $C_s$ age (separated from generally smaller quantities of heavy-fraction $C_s$ during density fractionation of total $C_s$) to model the decomposition of light-fraction $C_s$ across a gradient in MAT. These authors found that decomposition rates of light-fraction $C_s$ increased exponentially with increasing temperature. An explanation for the discrepancy with our findings may be that in the study of Trumbore et al., other factors that alter $C_s$ decomposition (moisture, disturbance, and litter quality$^{12,21}$) were highest at sites with the highest decomposition rates. The warmer sites were generally wetter, more disturbed, and supported vegetation that produced higher-quality litter.

Although many short-term studies of $C_s$ or litter decomposition show that decomposition rates increase with temperature$^{8,10}$, transient responses to increasing global temperature are unlikely to represent the response of most detrital carbon in forests. First, detrital carbon in forests resides primarily in the mineral soil (up to 70% in boreal forests$^{13}$ and 95% in the lowland tropics$^{2,12,23}$), and in situ $C_s$ mass loss rates are much slower than losses of fresh litter or forest-floor material$^{12,23}$. Second, all method 2 studies show large, rapid declines in decomposition rates in the first weeks of incubation, during which <5% of total $C_s$ is typically released$^{8,12,14,21}$. These declines indicate either the depletion of a very small, active pool of $C_s$, or—because soils are processed before incubation—a return to pre-disturbance conditions. Third, long-term incubations of forest soils$^{12,13}$, and in situ comparisons of $C_s$ content in heated and unheated soil$^8$ or $C_s$ turnover along gradients in MAT$^{13,15}$, show responses to increased temperature that are small, ephemeral or non-existent (that is, $Q_{10}$ values of 1.0–1.4, where $Q_{10}$ = reaction rate at $T + 10^\circ$C/reactio reaction rate at $T$ and $T$ is temperature). Taken together, these data and the data presented in Figs 1 and 2 suggest that sustained, temperature-related increases in the decomposition rate of forest-derived $C_s$ should not be expected.

A global-scale relationship between $C_s$ decomposition rates and MAT is central to predictions that global warming will accelerate the release of carbon stored in mineral soil$^{1-6}$. However, decomposition is performed by enzymes, and enzyme activity is limited by ...
temperature only when the supply rate of substrate exceeds the reaction rate for that substrate. Therefore, the most tenable explanation for the apparent temperature insensitivity of Cs decomposition is that heterotrophic microbes in mineral soil (those organisms responsible for decomposing Cs) survive on a supply of substrate that is sub-optimal for growth\textsuperscript{21,24}. Soil clay content, available moisture, and Cs quality are three factors that may influence substrate availability\textsuperscript{1,21}.

The binding of Cs to clay particles and physical protection within soil aggregates are thought to lower Cs availability\textsuperscript{1,21}. At a given location, where variations in climate and biota are more uniform, turnover times are longer for Cs associated with clay than with sand\textsuperscript{20,25}. If clay controls substrate availability, we would expect Cs turnover times to increase as clay content increases. However, data from method 1 and method 2 studies provide only weak support for clay limitations to substrate availability. For both method 1 and method 2 studies, Cs turnover time was nearly constant across sites, and variation among soils within a region was similar to global variation. For method 1 studies, where clay varied from 7\% to 84\%, there was no relationship between Cs turnover time and soil clay content ($R^2 = 0.05, P = 0.14$; see Supplementary Information). In method 2 studies, Cs mass loss was weakly related to clay content in soils with 7\%–30\% clay ($R^2 = 0.15, P = 0.05$; Supplementary Information). For clay $>30\%$, Cs mass loss decreased with increased clay ($R^2 = 0.41, P = 0.06$; Supplementary Information). While these results conflict with established modelling assumptions\textsuperscript{1}, other studies have also found weak relationships between clay content and Cs decomposition rates\textsuperscript{17,26}.

Available moisture exerts a large influence on soil microbial activity\textsuperscript{21}, and low soil moisture probably reduces microbial populations. However, available moisture did not affect substrate availability in method 2 studies because soils were maintained at or near field moisture capacity for the length of the incubation. Although we have no information on differences in soil moisture among method 1 sites, method 1 data were taken primarily from sites that had previously supported closed-canopy forests, which indicates moisture regimes that are at least adequate for decomposition.

Low Cs quality may limit substrate availability for microbes, and perhaps also limit microbial populations\textsuperscript{21}. Forest-derived Cs consists of lignin-dominated remnants and precipitated by-products of plant and microbial residue decomposition. These compounds are poor carbon sources for microbes, because energy yields are low for the energy expended to digest them\textsuperscript{21}. Evidence that low quality of Cs limits Cs decomposition rates in mineral soil includes low Cs decomposition rates compared with rates for fresh litter\textsuperscript{25} and rapid increases in CO$_2$ release from non-rhizosphere soils that are amended with labile substrate\textsuperscript{24}. 13C nuclear magnetic resonance analyses of forest-derived Cs show that the relative abundance of Cs functional groups (for example, alkyls, O-alkyls, aromatics and carbonyls) varies minimally across global-scale gradients in MAT (ref. 27). If Cs quality limits decomposition rates, then low global-scale variation in Cs decomposition rates may reflect low variation in the chemical composition of Cs.

Whether Cs decomposition is controlled by temperature or by substrate availability will change predictions for the effect of global warming on the large quantity of Cs stored in tropical soils\textsuperscript{1,2,24} and in soils that are frozen for most of the year\textsuperscript{26,29}. If temperature limits Cs decomposition, as assumed in most current ecosystem models, then tropical soils would provide the main source of additional carbon released in a warmer climate because Cs decomposition rates in high-latitude soils would be constrained by perennially low soil temperatures\textsuperscript{12}. In contrast, if substrate availability limits Cs decomposition rates, increased global temperatures alone would have little influence on Cs decomposition rates in the tropics. Warming at high latitudes, however, would expose larger amounts of Cs to microbial activity by lowering the depth of frozen soil, lowering the water table, and extending the duration of thawed conditions\textsuperscript{29}. Once these soils are thawed or the water table lowered, Cs decomposition rates would be constrained by substrate quality and moisture rather than by low temperatures.

The turnover of Cs in forest soils appears to be remarkably constant on a global scale, and insensitive to differences in MAT. However, the relationship between Cs turnover and MAT presented here serves only as a proxy for the changes that will occur in situ in response to global warming. The influence of temperature on Cs decomposition rates needs to be directly examined across a range of sites to better constrain predictions of the effects of warming on carbon release from soil.

### Methods

Method 1 studies primarily examined the loss of forest-derived Cs. All sites were disturbed during conversion, but land management varied during and following conversion. Details on methodology for a typical method 1 study are given in ref. 16. For method 2 studies, all soils were sampled from closed-canopy forests, similarly processed, and maintained at constant moisture levels near field capacity for the length of the incubation period. We used studies in which soils were incubated for at least 1 yr, because long-term incubations provide information on the mineralization potential of both the small labile Cs pool and the larger intermediate Cs pool\textsuperscript{1}. Microbial activity and Cs decomposition rates also may be less sensitive to sampling disturbance in long-term incubations than in short-term incubations. Method 2 studies have some important limitations. Soil macro-structure is altered during sampling and processing. Soils are incubated at a constant temperature and high moisture, whereas field environments fluctuate and are generally drier. Finally, incubations eliminate carbon inputs, which can shift microbial populations\textsuperscript{46}. Although
incubation-derived indices of C₃ decomposition rates will probably differ from those developed in the field, relative differences among sites are presumably real12,13,27.

We used single-pool exponential decay models to estimate C₃ turnover time in method 1 and method 2 studies. Single-pool models are widely used to describe C₃ turnover, but they may over-estimate rates because the approach assumes that all C₃ will behave as did the C₃ released during the study13. It is unlikely, however, that our single-pool approach masked a relationship between the turnover of a large, temperature-sensitive C₃ pool and temperature. In method 1 studies, we would suspect masking if C₃ mass loss per year increased with temperature early in the decomposition sequence. However, for sites with <11 yr since conversion, C₃ mass loss per year was higher for cool sites (9.5% yr⁻¹) than for warm (4.5% yr⁻¹) climates (P < 0.01). In method 2 studies, we would suspect masking if the total quantity of C₃ released per gram of soil increased with temperature because the release of this C₃ is independent of total C₃ pool size. However, C₃ released per kilogram of soil in one year declined with increasing incubation temperature (R² = 0.11, P = 0.04). Further, for masking to have occurred, the proportion of total C₃ that is temperature sensitive or fast-cycling must decline steeply with increasing temperature. Using this approach, techniques available, Trumbore et al.1 found no relationship between the proportion of fast-cycling C₃ (from 50% to 80% of total C₃) and MAT. Nonetheless, we tested the potential for masking by assuming that all C₃ released in method 2 studies was fast cycling and that 50%, 65% and 80% of total C₃ in tropical, temperate and subalpine soils, respectively, was fast cycling. We then recalculated turnover times for fast-cycling C₃ alone. Overall, patterns of C₃ decomposition were unchanged.

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Supplementary information is available on Nature’s World-Wide Web site (http://www.nature.com) or as paper copy from the London editorial office of Nature.

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