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**Mineral control of soil organic carbon storage and turnover**

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A large source of uncertainty in present understanding of the global carbon cycle is the distribution and dynamics of the soil organic carbon reservoir. Most of the organic carbon in soils is degraded to inorganic forms slowly, on timescales from centuries to millennia. Soil minerals are known to play a stabilizing role, but how spatial and temporal variation in mineralogy controls the quantity and turnover of long-residence-time organic carbon is not well known. Here we use radiocarbon analyses to explore interactions between soil mineralogy and soil organic carbon along two natural gradients—of soil-age and of climate—in volcanic soil environments. During the first ~150,000 years of soil development, the volcanic parent material weathered to metastable, non-crystalline minerals. Thereafter, the amount of non-crystalline minerals declined, and more stable crystalline minerals accumulated. Soil organic carbon content followed a similar trend, accumulating to a maximum after 150,000 years, and then decreasing by 50% over the next four million years. A positive relationship between non-crystalline minerals and organic carbon was also observed in soils through the climate gradient, indicating that the accumulation and subsequent loss of organic matter were largely driven by changes in the millennial scale cycling of mineral-stabilized carbon, rather than by changes in the amount of fast-cycling organic matter or in net primary productivity. Soil mineralogy is therefore important in determining the quantity of organic carbon stored in soil, its turnover time, and atmosphere–ecosystem carbon fluxes during long-term soil development; this conclusion should be generalizable at least to other humid environments.

Our primary gradient was a chronosequence of six sites (300 yr to 1,400 kyr) located at the same elevation and climate in areas dominated by native Metrosideros polymorpha trees and Cibotium tree ferns (Table 1). The soils formed from volcanic ash overlying either lava or a lava-ash mixture. Soil organic carbon and radiocarbon

Figure 1 Chronoclines: a. carbon in soil organic matter (SOM) versus depth; b. Δ14C of soil organic matter versus depth. Key for both panels in a. The depth shown is the midpoint of each horizon. See Methods for details of analysis and modeling. For the four youngest sites, modelled SOM turnover items are slow relative to substrate age. They indicate that the soils are not at steady state and are still accumulating C. At 300 yr, carbon and 14C content were best explained by assuming a constant C accumulation rate and infinitely slow turnover (the C stabilized on minerals had effectively no turnover over 300 yr). The best fit for the 150-kyr site, assuming constant C inputs, was turnover of 175,000 yr. The C turnover much less than substrate age, can be assumed to be at steady state. The third horizon (Bhs) at Kauai is a plinthe (stable iron oxide) layer with sharply depleted radiocarbon content.
content were measured by horizon down to the depth at which relatively unweathered parent material was encountered (Table 1). Soil depth remained nearly constant to 1 Myr, as a result of soil collapse due to congruent dissolution of minerals. At the 4,100-kyr site, however, the weathered lava extended >3 m deep. Between 1.2 and 1.3 m, organic content fell by nearly 100-fold to 0.01%, and we stopped sampling at 1.5 m.

At all sites, carbon (C) content declined with depth, with the steepest decline from the surface to 20–30 cm depth (Fig. 1a). Nevertheless, a significant fraction of each site's soil organic matter (SOM) was below 20 cm, ranging from 33% at the two youngest sites to 70% at the two intermediate-aged sites.

Radiocarbon content decreased with depth at all sites, with slope depending on soil age (Fig. 2). To estimate average turnover time of SOM (the reciprocal of the decomposition rate), we used 14C/12C ratios to constrain a non-equilibrium model of carbon stocks and flows (see Methods). The surface horizons were dominated by fast-cycling organic matter, shown by positive ('bomb') Δ14C values (Fig. 1b, Fig. 2b). In the subsurface horizons, soil C was depleted in 14C, yielding modelled turnover times slower than 10,000 yr at the 20-kyr, 1,400-kyr and 4,100-kyr sites, and slower than 20,000 yr at the 150-kyr site (Fig. 1b). The mineral horizons were clearly dominated by long-residence-time C, often referred to as the passive fraction of SOM. At the youngest site, radiocarbon content in the lowest soil horizons was consistent with C accumulating at a constant rate with virtually no turnover.

The total stock of organic C in soil increased with substrate age up to 150 kyr, to 60 kg m⁻², and then decreased to 31 kg m⁻² at the oldest site (Fig. 2a). Carbon inventory in the surface horizons (O and A horizons) reached its maximum at 20 kyr, and varied less with age than did deep soil C. A similar pattern was observed in the top 50 cm of these soils, based on 10 replicate soil pits per soil age. Most of the carbon sequestered after the first few thousand years of soil development accumulated below 20 cm, in the passive fraction. Similarly, most of the organic C lost in later soil development was from the subsurface soil.

The decline in the quantity of soil C stored on older substrates could result from a decline in productivity and/or an increase in turnover. Net primary productivity does peak at 150 kyr, but is only 15% less at 4,100 kyr (ref. 8)—too small a decrease to explain the 50% loss of soil C. The profile-integrated turnover rate, however, doubles between 150 and 4,100 kyr. Most of the decrease in soil organic C late in soil development therefore can be attributed to faster turnover of passive C, rather than to a decrease in plant productivity.

What controls these changes in the storage and turnover of soil organic C? Volcanic soils undergo dramatic changes in mineral composition as they develop. Young volcanic soils are characterized by high organic content and an abundance of non-crystalline minerals (allophane, imogolite and ferrihydrite), which are the primary weathering products. These relatively amorphous minerals have a high degree of hydration, extensive surface area, and variable charges. As a result, they can form stable organic– mineral bonds through anion and inner-sphere ligand-exchange reactions, and their geometry may be well suited for physically protecting organic matter. Non-crystalline minerals are metastable. Given enough

**Figure 3** The quantity and turnover of soil C versus non-crystalline mineral content for the six chronosequence sites. **a**, Soil C versus non-crystalline content of mineral horizons (that is, excluding O and A horizons) from the chronosequence sites, \( R^2 = 0.44, n = 35 \). Plotting symbols as in Fig. 1a. **b**, \( \Delta^{14}C \) versus non-crystalline content of all horizons from the chronosequence sites. The solid line shows the regression between mineral abundance and \( \Delta^{14}C \) with chronosequence data, excluding 4,100-kyr site; \( R^2 = 0.62, n = 39 \); model: \( \Delta^{14}C = 184 - 20 \) (noncrystalline %). The dashed line shows the regression for the soil-age and precipitation gradients combined (precipitation gradient \( n = 16 \), described in Table 1); model: \( \Delta^{14}C = 119 - 17 \) (noncrystalline %); \( R^2 = 0.63 \) for data from all sites except 4,100 kyr, \( n = 55 \). Plotting symbols for chronosequence data as in Fig. 1a; symbols for precipitation gradient data are ∇, 150 kyr, and ○, 400 kyr.

**Figure 2** Soil inventory of carbon in soil organic matter (SOM; **a**), \( \Delta^{14}C \) of SOM (**b**), non-crystalline minerals (**c**), and crystalline minerals (**d**) versus age of soil substrate. Filled circles, total profile; filled triangles, surface (O and A) horizons. See Methods for details of soil inventory determinations.
time, they dehydrate to crystalline clays, including halloysite, kaolinite, gibbsite, goethite and haematite,\textsuperscript{10,11}, that have a lower surface area and charge density, and consequently a lower affinity for SOM.

Mineral composition varied substantially with site age along the chronosequence. The amount of non-crystalline minerals increased up to 150 kyr and then declined with greater age (Fig. 2c). In contrast, the amount of crystalline minerals remained low until 150 kyr, then increased steeply between 1,400 and 4,100 kyr (Fig. 2d), tracking the transition from Andisol to Oxisol.

We found that the abundance of non-crystalline minerals accounted for >40\% of the variation in organic C content across all the mineral horizons, substrate ages, and soil orders (excluding the O and A horizons dominated by fast-cycling plant litter; Fig. 3a). Non-crystalline minerals also strongly influenced turnover of SOM. Organic-matter $\Delta^{14}$C was highly and negatively correlated with abundance of non-crystalline mineral ($R^2 = 0.62$) except in the oldest site, which had <10\% non-crystalline content (Fig. 3b). In contrast, there was no discernible correlation between the abundance of crystalline minerals and C content or turnover across sites. The amount of C stabilized per gram was much greater for non-crystalline than for crystalline minerals.

Can this relationship between non-crystalline minerals and organic C be used to predict turnover at other sites? To test this, we analysed soil samples from a precipitation gradient of eight sites formed on volcanic soils on the Island of Hawaii. Due to the effects of climate on weathering processes, the six drier sites of this gradient differed substantially in soil development and mineral composition from the chronosequence soils. The amount of non-crystalline minerals increased with precipitation across the precipitation gradient (data not shown). We sampled 16 horizons (Table 1) and found that the relationship between non-crystalline minerals and $\Delta^{14}$C along the precipitation gradient was nearly identical to that along the chronosequence (Fig. 3b). A linear regression from the chronosequence accounted for 46\% of the variance in $\Delta^{14}$C on the precipitation gradient; a regression with the two data sets combined ($n = 55$) yielded a coefficient of determination $R^2 = 0.63$ (Fig. 3b).

We conclude that the ability of these soils to retain C is due to the capacity of non-crystalline minerals to stabilize large quantities of organic C for thousands of years. The mechanisms identified here may be generalizable to many soils of humid environments, where weathering initially produces metastable, reactive minerals that later transform to stable, less-reactive products. In such environments common parent materials—such as granite, siltstone, sandstone and basalt—that contain feldspar, olivine, pyroxene or glass initially weather to non-crystalline minerals. In addition, in cool, wet environments, pedogenic processes create spodic horizons which have high concentrations of non-crystalline minerals and organic matter, on a wide variety of coarse-textured parent materials. In both cases, the non-crystalline minerals transform over time to weakly reactive crystalline kaolin and sesquioxide minerals\textsuperscript{13} that have a much lower capacity to stabilize C.

The weathering of other common minerals follows a similar sequence of reactivity in humid environments. Biotite and muscovite micas initially weather to 2:1 clays such as vermiculite and smectite; these in turn weather to kaolin (1:1 clay) and gibbsite with large losses of mineral surface area and reactivity. These changes are not as large as those observed in volcanic soils (Fig. 3)—globally, as well as on our chronosequence, Andisols contain twice as much organic soil C per m$^2$ as do Oxisols or any other soil order except Histosols\textsuperscript{14}—but the pattern of change in C storage and turnover should be similar in kind to that shown here\textsuperscript{15}. As mineral stability increases over time, soil minerals lose capacity to stabilize SOM.

These results allow prediction of the direction and magnitude of C fluxes caused by mineralogical changes associated with millennial timescales of soil development. For example, ~25\% of the world’s SOM is stored in soils that began developing after the last major deglaciation\textsuperscript{16,17}; the capacity of the mineral soils to store C will change as they undergo further development, and they may eventually become long-term sources of atmospheric CO$_2$.

Among the big uncertainties in our understanding of the global carbon cycle are the current distribution of soil organic C, and how much of this large reservoir of C exchanges with the atmosphere on centennial and shorter timescales compared with millennial timescales. An understanding of mineral control over SOM storage and turnover can improve our ability to model terrestrial carbon cycling. In addition to the influence on long-term storage and turnover shown here, C stabilization by non-crystalline minerals also influences nutrient availability\textsuperscript{7} and decomposition of labile

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Table 1 Site descriptions

| Site     | Age of parent material (yr) | Soil order | Elev. (m) | Mean annual temp. (°C) | Mean annual precip. (mm) | Dominant vegetation       | Horizons | Depth (cm) |
|----------|-----------------------------|------------|-----------|------------------------|--------------------------|---------------------------|----------|------------|
| Chronosequence sites |                            |            |           |                        |                          |                           |          |            |
| Thurston | 300                         | Inceptisol | 1,76      | 16                     | 2,500                    | Metroxeris forest         | Oe-4Bvb  | 0–38       |
| Olaa     | 2,100                       | Inceptisol | 1,200     | 16                     | 2,500                    | Metroxeris forest         | Oe-C3    | 0–64       |
| Laupahoehoe | 20,000                  | Andisol   | 1,770     | 16                     | 2,500                    | Metroxeris forest         | Oe-2CR   | 0–115      |
| Kohala   | 150,000                     | Andisol   | 1,122     | 16                     | 2,500                    | Metroxeris forest         | Oe-6CR1  | 0–98       |
| Kokee    | 4,100,000                   | Oxisol    | 1,134     | 16                     | 2,500                    | Metroxeris forest         | Oe-6CR    | 0–125      |
| precipitation gradient sites |                     |            |           |                        |                          |                           |          |            |
| Kohala-A | 170,000                     | Andisol   | 77        | 23                     | 160                      | Buffelgrass pasture       | Bw3      | 69–104     |
| Kohala-B | 170,000                     | Mollisol  | 185       | 23                     | 180                      | Buffelgrass pasture       | Bw2      | 37–65      |
| Kohala-E | 170,000                     | Andisol   | 674       | 20                     | 570                      | Buffelgrass pasture       | Bw3      | 44–62      |
| Kohala-H | 170,000                     | Andisol   | 992       | 18                     | 1,060                    | Kikuyu pasture            | Bw3      | 42–71      |
| Kohala-J | 170,000                     | Andisol   | 1,158     | 18                     | 1,380                    | (Pennisetum clandestinum) | Bw3      | 47–67      |
| Kohala-L | 170,000                     | Andisol   | 1,254     | 17                     | 3,000                    | Metroxeris forest         | Bw1      | 25–40      |
| Amalu    | 400,000                     | Andisol   | 1,494     | 14                     | 2,000                    | Metroxeris forest         | Bw2      | 40–56      |

All the sites were located on the Island of Hawaii, except the 1,400-kyr (Kokee, Kauai) and 4,100-kyr (Kokee, Kauai) chronosequence sites, and were on undisturbed shield surfaces or broad ridge tops.
substrates in surface soils. Ecosystem models at present represent the mineral soil environment with a soil-texture parametrization which is used to partition flows of organic C into fast- and slow-cycling pools. We suggest that these models should include mineralogical and textural parameters as well as textural influence on carbon storage and turnover times, based on the varying influence of different minerals. Soil mineral composition can be estimated from soil maps tied to soil classification schemes, which reflect climate, parent material and developmental stage of soil.

Our results show that across landscapes and over long timescales, the largest changes in the quantity and turnover of soil organic carbon may be due to variation in passive (mineral-stabilized) carbon deep in the soil. Passive carbon pools in turn are controlled by soil mineralogy, which exerts an influence on soil carbon storage of the same magnitude as that attributed to climate or vegetation in other studies. The predictability of soil mineralogy, as it varies spatially as a function of climate and parent material and temporally as a function of soil development, means that an understanding of how minerals influence soil carbon dynamics should yield significant improvements to our understanding of the role of the global carbon cycle.

Methods

Carbon analysis and turnover calculation. Soils for carbon analysis were oven-dried at 110 °C for 48 h, sieved (2 mm), ground, and analysed with a Carlo Erba NA1500 autoanalyzer. Radiocarbon content of SOM, measured by Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory on targets prepared by sealed-tube, zinc reduction, is expressed as Δ14C, calculated as (R – 1) × 1000, R or fraction modern, is the per mil deviation from 14C/12C ratio of oxalic acid in 1950. Analytical error averaged 8‰ for values close to modern. Carbonate was removed from Kola B soils with dilute HCl before radiocarbon analysis. Fast-cycling C (turnover time, years–century) has positive Δ14C because it has incorporated a significant proportion of the 14C that was released by atmospheric nuclear weapons testing from 1959 to 1963. Before weapons testing, atmospheric Δ14C was approximately zero. Slow-cycling C (century–millennia) has negative Δ14C owing to extensive radioactive decay relative to 14C inputs from more recently photosynthesized organic material. We used a non–steady-state model to estimate turnover from our measurements of C and radiocarbon content, and substrate age. Carbon accumulation was modelled as (C(t) = IT/1 + e^(-x*G)(1 + T)(1 + e^(-x*G))(1 + T)(1 + e^(-x*G)(1 + T)), where T is turnover time, G is fraction modern, and T is the time of soil development. We assume that C loss due to erosion is negligible relative to the rate of decomposition.

Soil inventory determination. The C inventory is the sum of (% C)(bulk density)/thickness for each horizon. An analogous formula was used for inventory of the mineral groups. The profile-total radiocarbon content is the sum of (% C)(bulk density)/thickness for each horizon divided by total C content of the profile, where B is fraction modern, defined above. Bulk density of wax-coated clods was determined by displacement. Soils for mineral analysis were air-dried, sieved (<2 mm), ground and subject to sequential extractions, with mass balance at each step, before analysis of Al, Fe, Si, and mineral structure. Organic matter was removed with hydrogen peroxide and acetone. Non-crystalline mineral content was estimated by ammonium oxalate extract and KCl sky-water fraction and Fourier-transform infrared spectroscopy. Coarse fraction was negligible in the chronosequence soils. To quantify collapse of the soil during weathering, zirconium was used as a conservative element.

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Eclogite xenoliths in west African kimberlites as residues from Archaean granitoid crust formation

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Eclogites are a comparatively rare but petrologically important member of kimberlite xenolith suites. Their broadly basaltic chemistry has led many authors to propose that they represent ancient, subducted ocean crust. Recent studies, however, have suggested an alternative origin and propose that kimberlitic eclogites are residues from the process of Archaean granitoid crust formation. Geochemical arguments in support of this new