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# Rapid Exchange Between Soil Carbon and Atmospheric Carbon Dioxide Driven by Temperature Change

Susan E. Trumbore,\* Oliver A. Chadwick, Ronald Amundson

Comparison of  $^{14}\text{C}$  (carbon-14) in archived (pre-1963) and contemporary soils taken along an elevation gradient in the Sierra Nevada, California, demonstrates rapid (7 to 65 years) turnover for 50 to 90 percent of carbon in the upper 20 centimeters of soil (A horizon soil carbon). Carbon turnover times increased with elevation (decreasing temperature) along the Sierra transect. This trend was consistent with results from other locations, which indicates that temperature is a dominant control of soil carbon dynamics. When extrapolated to large regions, the observed relation between carbon turnover and temperature suggests that soils should act as significant sources or sinks of atmospheric carbon dioxide in response to global temperature changes.

Two critical questions regarding the role of soils in the global carbon cycle are (i) what is the potential for soils to release carbon from increased decomposition rates in a warmer world and (ii) what is the potential for transient release or sequestering of carbon in soils as a result of interannual climate variability? Soil organic matter (SOM) contains roughly two-thirds of terrestrial carbon and two to three times as much carbon as atmospheric  $\text{CO}_2$  (1). According to estimates based on ecosystem modeling, changes in soil carbon after disturbance, and carbon isotopes, at least half of the organic matter in the 0- to 20-cm layer of soils is in fast-cycling carbon pools with turnover times of decades or less (2-7). Prediction of the short-term effects of climate or land use change on soil carbon storage requires quantification of soil carbon turnover rates and how they vary with factors such as temperature, precipitation, and other soil properties.

To determine the influence of temperature on storage and turnover of soil carbon, we sampled C and  $^{14}\text{C}$  from a series of soils along an elevation transect of the western

slope of the Sierra Nevada range, California, that were previously sampled in the period from 1958 through 1963 (8). All the soils have similar parent material, age, relief, slope, and aspect, although climate and vegetation vary with elevation (9). Thermomolecular weapons testing in the early 1960s approximately doubled the amount of  $^{14}\text{C}$  in atmospheric  $\text{CO}_2$ . Tracing this bomb  $^{14}\text{C}$  through SOM reservoirs over the past 30 years provides a means of determining the size and turnover time of fast-cycling soil carbon pools (5-7, 10, 11).

Mean annual temperature decreases with increasing elevation along the Sierra transect according to the atmospheric lapse rate. Precipitation averages between 90 and 120 cm year $^{-1}$ , except at the lowest elevation site (12). Vegetation changes from oak woodland or savanna in the Sierra foothills to mixed conifer forest at higher elevations (13). Soils vary from Alfisols to Inceptisols with increasing elevation and are developed on unglaciated granodiorite. Vegetation and soil carbon are assumed to have achieved steady state with average Holo-

cene climate conditions and roughly equivalent soil residence times with respect to weathering and erosion (14).

Samples from soils originally collected in the period from 1958 through 1963 were obtained from an archive maintained by the Division of Ecosystem Sciences, University of California, Berkeley. Original field notes and topographic maps were used to relocate and resample the same sites in 1992 (to within 100 m of the original locations). Soil bulk density and C and  $^{14}\text{C}$  amounts were determined from archived and modern soils with the use of standard methods (15). In Table 1, we present data from soil A horizons (16).

We separated bulk (<2 mm) SOM into three fractions (17): low-density organic matter (<2.0 g cm $^{-3}$ ); the portion of dense (>2.0 g cm $^{-3}$ ) organic matter that is hydrolyzable in acids and bases; and the nonhydrolyzable dense residue. Low-density organic matter, consisting of relatively undecomposed vascular plant material mixed with some (<8% by weight) charcoal, made up 50 to 90% of the total carbon in the soil A horizons, with the proportion increasing with elevation (Table 1). The greatest abundance of mineral-associated (>2 g cm $^{-3}$ ) organic matter (40 to 50% of total A horizon carbon) was in soils with  $\geq 10\%$  clay (11). Nonhydrolyzable components made up less than 15% of the total A horizon soil carbon at all sites.

We report  $^{14}\text{C}$  data (Table 1) as  $\Delta^{14}\text{C}$  (18). Negative  $\Delta^{14}\text{C}$  values (less than -50 per mil) indicate that on average, the carbon has resided in the soil long enough to reflect radioactive decay of cosmogenic  $^{14}\text{C}$ . Positive  $\Delta^{14}\text{C}$  values indicate significant amounts of bomb  $^{14}\text{C}$ . SOM fractions with the fastest turnover times have the least negative pre-bomb  $\Delta^{14}\text{C}$  values and show large increases in  $\Delta^{14}\text{C}$  (>100 per mil) over the past 30 years. Refractory organic matter fractions have more negative  $\Delta^{14}\text{C}$  values

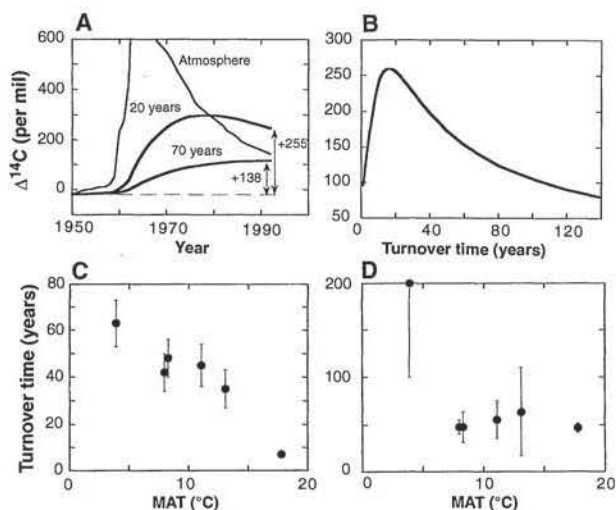
**Table 1.** Carbon inventory and  $\Delta^{14}\text{C}$  values in fractionated SOM for Sierra transect soil A horizons. Soil inventory data are from 1992 collected profiles and represent weighted averages of up to three depth intervals. LF is low-density (<2.0 g cm $^{-3}$ ) organic matter; Hyd. and Res. are the hydrolyzable (in acids and bases) and nonhydrolyzable portions of organic matter, respectively (>2.0 g cm $^{-3}$ ). The amount of carbon in the LF, Hyd., and Res. fractions is expressed as a percent of the total A horizon carbon. The  $\Delta^{14}\text{C}$  values are given for archived (AR) and 1992 soils. The Fallbrook archived soil was sam-

pled in 1962; others were sampled from 1958 through 1959. The Musick2 soil profile was collected approximately 120 km north of the Sierra Nevada Forest in 1959 and 1990. Although not strictly on the temperature transect, it provides a test of the robustness of measuring soil carbon dynamics with  $^{14}\text{C}$  within a soil mapping unit. Fractionation procedures for Musick2 soil differed from those here slightly. Locations of sites (latitude, longitude): Fallbrook, 36°43'N, 119°17'W; Musick, 37°1'N, 119°16'W; Shaver, 37°2'N, 119°11'W; Corbett, 37°5'N, 119°11'W; and Chiquito, 37°18'N, 119°5'W.

Soil series	Elevation (m)	Depth A (cm)	Clay (%)	C (%)	C (kg m $^{-2}$ )	LF	Hyd.	Res.	$\Delta^{14}\text{C}$ LF (per mil)		$\Delta^{14}\text{C}$ Hyd. (per mil)		$\Delta^{14}\text{C}$ Res (per mil)	
									AR	1992	AR	1992	AR	1992
Fallbrook	470	12	10	1.35	2.49	70	26	4	65	+184	-22	+136	-170	+45
Musick1	1240	19	22	3.01	5.81	53	33	12	-47	+142	-54	+25	-74	-74
Musick2	820	23	41	2.32	6.07	50	35	15	-30	+137	-41	+86	-106	-7
Shaver	1780	20	6	3.29	7.40	88	10	2	-31	+127	-62	+81	-173	-143
Corbett	1950	23	6	3.37	7.75	87	11	2	-32	+140	-22	+138	-123	-29
Chiquito	2890	17	6	3.08	5.76	77	29	3	-40	+93	-85	+16	-196	-169

**Fig. 1.** Estimates of turnover time for low-density and hydrolyzable carbon fractions derived from the observed increase in  $\Delta^{14}\text{C}$  between 1959 and 1992 (19). (A) Changes in  $\Delta^{14}\text{C}$  values observed in the atmosphere, compared to the change in  $\Delta^{14}\text{C}$  values expected in steady-state SOM reservoirs with turnover times of 20 or 70 years (19). Double-headed arrows show the  $\Delta(\Delta^{14}\text{C})$  values. (B)  $\Delta(\Delta^{14}\text{C})$  expected for fast-cycling carbon with different turnover times (19). (C) Turnover times for low-density organic matter fractions, assuming that 10  $\pm$  10% of the carbon in the low-density fractions is passive. Uncertainties in turnover time

derived from the overall accuracy of the radiocarbon measurement [about  $\pm 12$  per mil in  $\Delta(\Delta^{14}\text{C})$ ] are of similar magnitude to uncertainties in the amount of passive carbon. (D) Hydrolyzable dense organic matter fraction turnover times do not show a clear trend with altitude. Error bars show the range of turnover times calculated, assuming 0% passive carbon in this fraction (slower turnover) and assuming the amount of passive organic matter needed to explain archived  $\Delta^{14}\text{C}$  values for this fraction (19); MAT, mean annual temperature.



in the 1950s and show little or no increase in  $\Delta^{14}\text{C}$  since 1963. With the use of these criteria, the low-density fraction has the shortest, and the nonhydrolyzable dense residue the longest, average turnover time (Table 1).

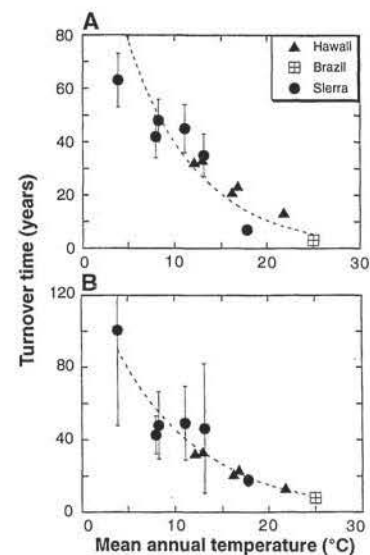
To quantify turnover times for SOM fractions, we compared the observed increase in  $\Delta^{14}\text{C}$  between 1959 and 1992 [defined as  $\Delta(\Delta^{14}\text{C})$ ] with the increase predicted with a time-dependent model (19) (Fig. 1). This approach assumes SOM has remained at steady state over the past 30 years. We believe this is true for Sierra transect sites because land use there has not changed during this time (20) and the carbon inventory and distribution of carbon among fractions are similar between archived and 1992 soils.

The same  $\Delta(\Delta^{14}\text{C})$  value may yield two possible turnover times (Fig. 1B). For example, the Shaver soil (elevation, 1780 m) shows an increase in  $\Delta^{14}\text{C}$  from 1959 to 1992 of +158 per mil (Table 1). This increase could represent an average turnover time of either 5 or 57 years (Fig. 1B). The total amount of carbon stored as low-density organic matter in the Shaver A horizon is  $6.5 \text{ kg m}^{-2}$ . A turnover time of 5 years implies annual steady-state inputs and losses of carbon of  $1300 \text{ g m}^{-2} \text{ year}^{-1}$ , a factor of 10 greater than is reasonable given estimates of litterfall for this site [ $\sim 100 \text{ g m}^{-2}$

$\text{year}^{-1}$  (9)]. We therefore conclude that the turnover time of the Shaver low-density carbon is 57 years (Fig. 1C). Although no flux data are available for the lowest elevation site (Fallbrook), the incorporation of large amounts of bomb  $^{14}\text{C}$  by 1962 indicates fast turnover ( $\leq 10$  years) of the low-density fraction.

Uncertainties in the turnover times shown in Fig. 1, C and D, reflect the degree to which the fractionation scheme fails to separate SOM into homogeneous carbon pools that can be represented by a single, average turnover time. Pre-bomb  $\Delta^{14}\text{C}$  values less than  $-25$  per mil in low-density and nonhydrolyzable fractions indicate that some portion of the carbon is passive and has turnover times longer than 100 years. We estimate the amount of passive carbon to be  $10 \pm 10\%$  of the low-density SOM, on the basis of the abundance of charcoal (up to 8% by weight or 15% of the low-density carbon). The effect of attributing an additional 10% to the passive pool decreases the turnover times derived for the remaining carbon (19) by about 10 years. The importance of carbon that turns over much faster than the average turnover time (for example, a component of low-density carbon cycling on annual time scales) is constrained with estimates of litterfall or net primary productivity (21) to constitute  $< 8\%$  (lowest elevation) and  $< 3\%$  (other sites) of the low-density SOM. This amount is too small to influence the derivation of turnover time from  $\Delta(\Delta^{14}\text{C})$  or the predicted response of the large low-density pool to a disturbance.

Average turnover times for low-density carbon (Fig. 1C) increase from 6 to 8 years



**Fig. 2.** (A) Turnover times for fast-cycling fractions of low-density carbon in the upper 20 cm of soil from the Sierra Nevada transect (this study), Hawaii (7), and eastern Amazonia (22, 23). The exponential curve fit (with 95% confidence intervals) is

$$(151 \pm 47) \exp[-(0.134 \pm 0.02)T]$$

where  $T$  is the temperature in degrees Celsius and the standard deviation of the curve fit is 9. Turnover times derived for the Hawaii sites are inventory-weighted averages of active (1 year turnover) and slow (variable turnover time) carbon pools reported in (7). (B) Carbon inventory-weighted turnover times for combined low-density and hydrolyzable carbon fractions. An exponential curve fit to these data is

$$(138 \pm 18) \exp[-(0.110 \pm 0.09)T]$$

with a standard deviation of 8. Fitting an exponential curve to the data implies constant  $Q_{10}$  values over a range of temperatures [here,  $Q_{10}$  equals 3.8 in (A) and 3.0 in (B)].

at  $17.8^\circ\text{C}$  mean annual temperature (470 m elevation) to 53 to 71 years at  $4^\circ\text{C}$  (2900 m elevation). Average turnover times for fast-cycling components of hydrolyzable carbon (20 to 300 years) are more uncertain and are not related simply to temperature (Fig. 1D). We conclude that temperature is the most important control of low-density carbon turnover times, whereas the amount and turnover time of hydrolyzable carbon may be tied to other soil properties.

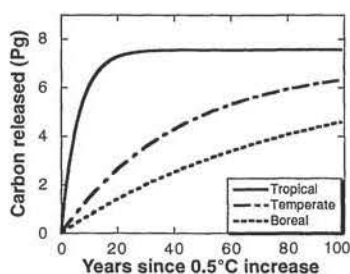
Changes in carbon inventory along the elevation transect arise from combined variations in the rates of carbon input and decay. Maximum carbon concentration and storage occur at mid-elevation. Decay rates of the low-density fraction decreased (and turnover times increased) monotonically with temperature along the Sierra elevation transect, whereas carbon inputs to the soil peak at mid-elevation (21). Thus, increases in the carbon inventory from low to mid-elevation resulted from higher carbon inputs coupled with slower decomposition,

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**Fig. 3.** Estimated change in carbon storage in tropical, temperate, and boreal forest soils after 0.5°C increases in mean annual temperature. We calculated the carbon balance in soil as  $C_{s(t)} = (1 - k)C_{s(t-1)} + I$ , where  $C_{s(t)}$  and  $C_{s(t-1)}$  represent the amount of carbon stored in fast-cycling pools at times  $t$  and  $(t - 1)$ , respectively,  $k$  is the reciprocal of the turnover time, and  $I$  is the annual rate of carbon input. At steady state,  $C_{s(t)} = C_{s(t-1)}$  and  $I = kC_{s(t)}$ . A temperature increase will cause a decrease in turnover time according to the curve fit from Fig. 2A, so that  $I < kC_{s(t)}$ . Assuming inputs do not change, the soil will lose carbon until a new steady state is established. We assumed all three ecosystems have 4 kg m<sup>-2</sup> of fast-cycling carbon in SOM. Areas of tropical, temperate, and boreal forests were assumed to be  $24.5 \times 10^6$ ,  $12 \times 10^6$ , and  $12 \times 10^6$  km<sup>2</sup>, respectively (28), together accounting for ~45% of vegetated land area. Mean annual temperatures were increased 0.5°C from initial values of 24°C (tropical), 11°C (temperate), and 4°C (boreal), causing decreases in turnover time from 6.3 to 5.9 years (tropical), 34.9 to 32.6 years (temperate), and 87.9 to 82.3 years (boreal). These are probably underestimates of the total response of soils because they do not include effects of temperature on decomposition rates of surface detritus.



whereas the decrease in the carbon inventory above 2000 m indicates that inputs declined faster than turnover rates.

The relation observed between mean annual temperature and turnover time along the Sierra Nevada transect is in accord with observations from other locations (Fig. 2). These include an elevation-based temperature transect of Andisols developed on volcanic ash deposits in Hawaii (7) and an Oxisol in seasonal tropical forest in eastern Amazonia, Brazil (22, 23). Because the nature of volcanic ash soils precludes the use of our standard fractionation method (7), we plotted results from the Hawaii transect against both low-density (Fig. 2A) and combined low-density plus hydrolyzable turnover times for Oxisol and Sierra transect soils (Fig. 2B). In all cases, the fast-cycling pools (Fig. 2B) represent >50% of the SOM in the 0- to 20-cm soil layer, with amounts of carbon ranging from 2.5 to 7 kg m<sup>-2</sup> (Sierra transect and Oxisol) to 6 to 12 kg m<sup>-2</sup> (Hawaii). Although the soils differ in vegetation (temperate coniferous forest to tropical forest and pasture), precipitation (90 to 300 cm year<sup>-1</sup>, excepting the Fallbrook soil from the Sierra transect), and soil parent material (volcanic ash to granodiorite), a strong relation between the average turnover time of fast-cycling carbon pools and mean annual (air) temperature was observed. Thus, temperature seems to be a major control of turnover for a large component of SOM in sites where moisture is not a limiting factor, in accord with other modeling and data-based studies (2, 24, 25).

If the relation shown in Fig. 2 between temperature and turnover time of fast-cycling organic matter is general, relatively small changes in temperature ( $\pm 0.5^\circ\text{C}$ ) should cause soils to become significant sources or sinks of atmospheric CO<sub>2</sub> (Fig. 3). Forest soils may release ~1.4 Pg (10<sup>15</sup> g) of carbon (25% of the annual fossil fuel addition of carbon to the atmosphere) in the first

year after a 0.5°C temperature increase, with most of the response occurring in the tropics. A 0.5°C warming would result in a ~6% overall decrease in fast-cycling carbon reservoirs at steady state. This change is too small to measure directly in soil profiles. All else remaining equal (26), changes in decomposition rates of SOM with temperature suggest two consequences important for the global carbon cycle. First, warming documented over the past century should have increased decomposition rates in SOM, causing a (continuing) net transfer of carbon from fast-cycling pools to the atmosphere. Second, large, short-term temperature anomalies, such as the cooling after the eruption of Mount Pinatubo (27), should result in significant transient sequestration of carbon in SOM. Our results suggest that tropical regions will dominate that response.

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- Temperature decreases linearly with elevation, from 17.8°C at 470 m to 3.9°C at 2900 m. Precipitation is 31 cm year<sup>-1</sup> at 470 m (Fallbrook), 90 to 100 cm year<sup>-1</sup> at 1200 to 1900 m, and 127 cm year<sup>-1</sup> at 2900 m. Precipitation is primarily in late fall, winter, and early spring. Above 1000 m elevation, precipitation falls as a mixture of rain and snow.
- Vegetation is mixed conifer at all but the Fallbrook site, which is dominated by oak trees and annual grasses. At 1200 m, the dominant tree species are ponderosa pine, incense cedar, and manzanita. At 1800 to 1900 m, white fir, ponderosa, and sugar pine dominate, whereas at 2900 m, Sierra juniper, western white pine, and lodgepole pine dominate.
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- Soils collected in 1992 were channel-sampled by horizon to match archived samples. Bulk density was determined from the oven-dry weight of known-volume samples for each soil horizon, corrected for gravel content. The percentage of carbon was determined from either CO<sub>2</sub> evolution on combustion [D. L. Buchanan and B. J. Corcoran, *Anal. Chem.* **31**, 1635 (1959)] or with a Carlo Erba 1500 N combustion analyzer. <sup>14</sup>C was measured on graphite targets [J. S. Vogel, *Radiocarbon* **34**, 344 (1992)] with the use of accelerator mass spectrometry (AMS) at the Center for AMS at Lawrence Livermore National Laboratory, Livermore, California [J. R. Southon et al., *Radiocarbon* **34**, 473 (1992)].
- We chose the genetic soil A horizon (total depths ranging from 12 to 23 cm; Table 1), rather than a standard depth interval, because the properties of A horizon organic matter differ from those of the horizons below. The total inventory of carbon in the soil A horizon roughly equals that of surface detritus (surface litter) and is between 50 and 90% of the total SOM integrated to 80 cm.
- We separated bulk soil (sieved to <2 mm) into fractions less than or greater than 2.0 g cm<sup>-3</sup>, using sodium polytungstate (23). Further treatment of the dense fractions (>2.0 g cm<sup>-3</sup>) with a sequence of acids and bases (0.5 N HCl; 0.1 N NaOH-Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub>; and 6 N HCl) isolated a residue that was always depleted in <sup>14</sup>C relative to the starting material. The amount and  $\Delta^{14}\text{C}$  value of the organic carbon removed during hydrolysis were calculated by mass balance of C and <sup>14</sup>C from measurements in the dense, untreated and dense, hydrolysis residue fractions.
- $\Delta^{14}\text{C}$  is the per mil difference in the <sup>14</sup>C/<sup>12</sup>C ratio between the sample and an absolute standard (oxalic acid decay) corrected to 1950 values [M. Stuiver and H. Polach, *Radiocarbon* **19**, 255 (1977)]. We assumed a value of -25 per mil for <sup>13</sup>C corrections.
- For each year ( $t$ ) from 1950 through 1992, we computed the fraction modern carbon,  $F_{s(t)}$ , equal to  $\Delta^{14}\text{C}_{(t)}/1000 + 1$ , as

$$F_{s(t)} = [C_{s(t-1)} F_{s(t-1)}(1 - k - \lambda) + (I F_{\text{atm}(t)})]/C_{s(t-1)}$$

where  $F_{s(t-1)}$  is the fraction of modern carbon in the SOM fraction in the previous 1-year time step,  $k$  and  $\lambda$  are constants representing decomposition and radioactive decay of <sup>14</sup>C, respectively (both in year<sup>-1</sup>),  $F_{\text{atm}(t)}$  is the fraction modern for carbon fixed from the Northern Hemisphere atmosphere in year  $t$  [from A. Burcholadze et al., *Radiocarbon* **31**, 771 (1989)],  $I$  is the annual addition of carbon to the soil (grams per square meter), and  $C_{s(t-1)}$  is the steady-state carbon inventory in the SOM fraction (grams per square meter per year). The  $\Delta^{14}\text{C}$  of the SOM fraction in year  $t$  is then  $1000(F_{s(t)} - 1)$ , and the turnover time of the SOM fraction is  $k^{-1}$ .  $\Delta(\Delta^{14}\text{C})$  is calculated by subtracting the predicted 1992  $\Delta^{14}\text{C}$  value from the 1959 value (or the 1962 value, for the Fallbrook soil). To account for the presence of passive carbon (which does not change its  $\Delta^{14}\text{C}$  value during the period from 1950 through 1992 and therefore acts to dilute the <sup>14</sup>C signal), we divided the observed  $\Delta(\Delta^{14}\text{C})$  by the fraction of fast-cycling organic matter and used the new, larger  $\Delta(\Delta^{14}\text{C})$  value to estimate the turnover time. We estimated the maximum and minimum turnover time for hydrolyzable carbon by (i) assuming 0% passive carbon (maximum turnover time) and (ii) assuming hydrolyzable carbon is a mixture of passive carbon with a value of  $\Delta^{14}\text{C}$  equal to that of the nonhydrolyzable residue (-70 to -170 per mil; Table 1) and of fast-cycling carbon with turnover times of about 50 years ( $\Delta^{14}\text{C}$  values of 0 per mil in 1959). The amount of passive carbon is derived from observed  $\Delta^{14}\text{C}$  values for pre-bomb samples; these values ranged from 2 to 62% of the hydrolyzable carbon. The second approach gives the minimum turnover time.

- The Fallbrook site has been in continuous pasture since the late 1950s. The Shaver site was logged between 1959 and 1992; we sampled in an un-



- logged stand of trees.
21. Litterfall data, from (9), indicate that litterfall inputs of carbon are between about 50 and 120 g m<sup>-2</sup> year<sup>-1</sup> for coniferous forests of the Sierra transect above 1200 m elevation. We estimated carbon productivity for grasses at the Fallbrook site by assuming that their values are similar to those for other grassland soils in California (between 50 and 100 g m<sup>-2</sup> year<sup>-1</sup> [R. Valentini *et al.*, *Ecology* **76**, 1940 (1995)]).
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  26. The estimates of carbon change in Fig. 3 ignore important factors, such as probable changes in carbon inputs to the soil by plants and feedbacks be-

tween SOM decomposition and plant productivity. In addition, the climate transects studied in Hawaii and the Sierra Nevada integrate long-term adjustment of ecosystems to average climatic conditions, and transient responses may not be predictable from the temperature-turnover relations derived here. However, soil incubations and soil respiration measurements have shown that on short time scales, carbon fluxes from soils are strongly dependent on temperature, with  $Q_{10}$  values ranging from 2 to 5 [J. W. Raich and W. H. Schlesinger, *Tellus* **44B**, 81 (1992); D. W. Kicklighter *et al.*, *J. Geophys. Res.* **99**, 1303 (1994)] (25), in accord with values, derived from Fig. 2, of 3.0 to 3.8. [ $Q_{10}$  is the rate of a biological process (here, decomposition) at one temperature divided by the rate of the process at a temperature 10°C cooler.]

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## Engineered Interfaces for Adherent Diamond Coatings on Large Thermal-Expansion Coefficient Mismatched Substrates

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Adhesion of thin or thick films on substrates is a critical issue in systems where the thermal-expansion coefficients of the coating and bulk material are significantly different from each other. The large mismatch of the expansion coefficients results in the generation of very high stresses in the coating that may lead to delamination, cracking, or other deleterious effects. A method to increase the adherence of diamond coatings on tungsten-carbide and stainless steel substrates is reported based on a substrate-modification process that creates a three-dimensional thermally and compositionally graded interface. Scratch and indentation tests on diamond-coated steel and tungsten-carbide samples did not exhibit film fracture at the interface and concomitant catastrophic propagation of interfacial cracks.

There has been a considerable effort in recent years to develop adherent coatings, especially in systems in which there is a large mismatch between the thermal-expansion coefficients (1-6). During heating or cooling, very high stresses are induced in the coating when the thermal-expansion coefficients of the films and the substrate vary significantly from each other. These stresses frequently crack or delaminate the coating from the substrate material. A number of techniques have been developed to increase adhesion strength so that coatings remain adherent even when subjected to large compressive or tensile stresses. Some of the methods used include roughening of the surface for mechanical interlocking and the use of chemically compatible interlayers having intermediate expansion coefficients (1-4). These methods to enhance adhesion have been successful in some material systems; however, in very large thermal-mismatched systems, cracking or debonding of the coating can still occur.

Diamond coatings on substrates like

steel and tungsten-carbide (WC) with cobalt (WC-10% Co) are thermally mismatched but are expected to have applications in cutting tools and corrosion- and erosion-resistant coatings. Many techniques have been applied to improve adhesion in this case but have met with very limited success (1). The main problem for the deposition of diamond thin films on these materials is the large thermal stress generated during the deposition process. Besides thermal stresses, other complicating problems such as the diffusion of carbon species and the graphitization of diamond species by iron or cobalt can reduce the adhesion strength substantially.

Several methods to improve the adhesion of diamond coatings have been investigated (1-7). One of the most common methods to enhance adhesion is to apply interlayers having intermediate thermal-expansion coefficients. The interlayers are expected to decrease the effect of interfacial stresses and reduce the graphitization and diffusion of carbon species during deposition. However, these methods have been only partially successful chiefly because the residual stresses are still high enough to

debond from the intermediate film.

We have observed that creation of a three-dimensional (3D) thermally and compositionally graded interface between diamond and the substrate material leads to improved adhesion of the diamond film (8). A schematic diagram of the nature of the film in sharp and 3D chemically and thermally graded interfaces is shown in Fig. 1. The diamond film was subjected to biaxial compression while the metallic substrate was under tension. Figure 1A shows an idealized representation of the normal stresses across the cross section of the homogeneous coating and freestanding substrate at a point far from the edge. The stress distribution in the film is determined by the requirements that the normal forces, and the bending moments, over the total cross section should be zero (9). From the first requirement, stresses of opposite sign must form in the substrate to balance those in the film. Thus, the stress reverses sign at the interface. Because of the much larger thickness of the substrate, the magnitudes of the stresses are much lower in the substrate than in the film. The second require-

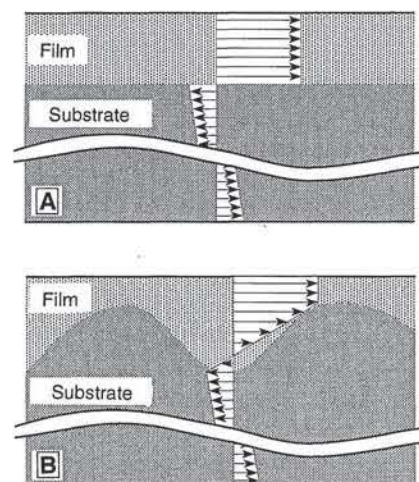


Fig. 1. Schematic diagram showing the nature of stresses present for (A) a planar interface and (B) a 3D thermally and compositionally graded interface.