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Carbon isotopes in soils and palaeosols as ecology and palaeoecology indicators

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THERE are few quantitative techniques in use today for palaeoecological reconstruction in terrestrial depositional systems. One approach to such reconstructions is to estimate the proportion of C_3 to C_4 plants once present at a site using carbon isotopes from palaeosol carbonates[1-3]. Until now, this has been hampered by an inadequate understanding of the relationship between the carbon isotopic composition of modern soil carbonate and coexisting organic matter. Here we have found that the two systematically differ by 14–16‰ in undisturbed modern soils. This difference is compatible with isotopic equilibrium between gaseous CO_2, and aqueous and solid carbonate species in a soil system controlled by diffusive mass transfer of soil CO_2 derived from irreversible oxidation of soil organic matter. Organic matter and pedogenic carbonate from palaeosols of Pleistocene to late Miocene age in Pakistan also differ by 14–16‰. This indicates that diagenesis has not altered the original isotopic composition of either phase, thus confirming their use in palaeoecological reconstruction.

Stable carbon isotopes in pedogenic carbonate[1-4] and soil organic matter[5,6] can be used as palaeoecological indicators. A critical assumption, however, in the use of pedogenic carbonate is that of isotopic equilibrium between the carbon species—soil CO_2, dissolved carbonate species, and solid carbonate—in the soil system buffered by an effectively infinite soil CO_2 reservoir. Other studies in recent years have invoked processes such as 'Rayleigh' distillation[7,8], kinetic fractionation[8], and partial exchange or inheritance[8,9] to describe carbon isotope systematics in soils. The principal drawback of the latter models is that little isotope data on co-genetic organic carbon and soil carbonate was collected. Instead, the isotopic composition of the organic matter was usually assumed[7-9]. Where measured, the results were considered unreliable because of the vegetation changes resulting from cultivation[8]. Many of the studied soils have complex vegetational histories attributable to either the effects of cultivation and extensive grazing[7-9] or, in the case of calcretes[7], to long periods of development in the presence of pre-Holocene vegetation. These complexities make interpretation of the soil isotope system exceedingly difficult.

Our approach is to study ten soils in North America with simple pedogenic histories (Table 1). All the soils are latest Pleistocene or, in most cases, entirely Holocene in age. In all but one case, vegetation cover can be assumed to have been constant and similar to that of today. The six mid-western soils are located on national prairie preserves where the vegetation shows little or no post-settlement impact. The Nevada soils come from remote mountain settings that are unsuitable for grazing, in which vegetation remains entirely native. Vegetation at the New York site, though disturbed, must always have been 100% C_3 in character given the forested nature of the region.

The isotopic composition of plants using the C_3 and C_4 photosynthetic pathways have $\delta^{13}C$ values averaging ~ -27 and -13‰, respectively[10]. We have examined ten soils the biomasses of which span the range from nearly 100% C_3 to 100% C_4 and have analysed coexisting bulk-soil organic matter and pedogenic carbonate in each. The soil carbonates were present as nodules and as pendants on pebble undersides. We confined our studies to areas where the rainfall exceeds 35 cm yr^{-1} because modelling of soils shows that pedogenic carbonate from soils with very low respiration rates, such as in deserts, can be isotopically enriched because of diffusional mixing with the atmosphere[1,11]. We sampled carbonates at depths >30 cm because the near-surface carbonate could be affected by diffusional mixing with atmospheric CO_2, irrespective of the soil respiration rate. Nearly all the soils studied contained carbonate in the parent alluvium, loess or till.

The diffusion coefficients for $^{12}CO_2$ and $^{13}CO_2$ differ, producing a 4.4‰ enrichment in the plant-derived component of soil CO_2 compared with respired CO_2 (refs 1, 11, 12). At equilibrium, the isotopic equilibrium factor $10^3 \ln \alpha_{CO_2\text{-calcite}}$ is -9.8 to -12.4 for the temperature range 25–0 °C (ref. 13). Pedogenic carbonate precipitated in equilibrium with soil CO_2 should, therefore, be $\sim$14‰ (25 °C)–17‰ (0 °C) enriched relative to respired CO_2. At low soil respiration rates, carbonates precipitated in equilibrium with soil CO_2 would have an even greater enrichment as a result of the atmospheric effects mentioned above.

The isotopic composition of pedogenic carbonate from a single soil in the Konza Prairie of Kansas is constant in the soil from depths of 40 to 103 cm, and it is 14.5‰ more positive than the co-existing organic material in the soil (Fig. 1). This difference supports the model of a diffusion-controlled soil CO_2-$CaCO_3$ system in isotopic equilibrium. The patterns displayed by this soil and those described below are not consistent with kinetic or Rayleigh distillation processes resulting in isotopic disequilibrium between soil CO_2 and precipitated carbonate. Similarly, modern soil organic matter and coexisting pedogenic carbonate from nine other North American soils differ by $\sim$14–16‰ (Fig. 2), as predicted for high-respiration-rate soils. All soils we studied, including palaeosols from Pakistan, show strong leaching and contain well developed organic horizons, thus indicating high respiration rates[14,15]. In low-respiration-rate soils, such as in deserts, diffusional mixing of atmospheric CO_2 and plant-derived CO_2 can produce up to 2‰ enrichment in the $\delta^{13}C$ of soil carbonate at 50-cm depth[11]. No systematic trend in

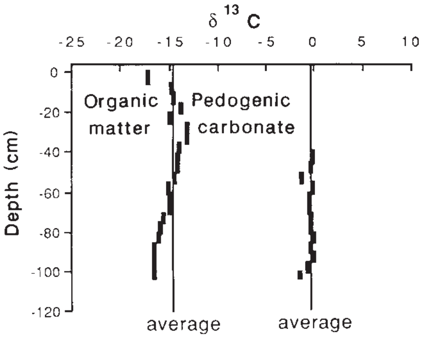

FIG. 1 The isotopic composition of soil organic matter and pedogenic carbonate as a function of depth in a prairie soil from Kansas, USA.

TABLE 1 General features of soil sites

Locality	Soil series	Soil type	$\delta^{13}C$ (PDB*) org. matter	$\delta^{13}C$ (PDB*) carbonate	MAP†	MAT‡	Carbonate sample depth (cm)	Parent material	Vegetation
Manhattan, Kansas	Dwight	Natrustoll	−15.7§	−1.6 ± 0.4	81	13.3	50–86	loess	native prairie
Manhattan, Kansas	Tully	Argiustoll	−14.9 ± 1.1‖	−0.4 ± 0.3	81	13.3	40–103	colluvium	native prairie
Lincoln, Nebraska	Burchard	Argiudoll	−17.3§	−2.4 ± 0.7	68	11.4	94–129	till	native prairie
Pocahontas, Iowa	Clarion	Hapludoll	−18.5§	−3.4 ± 0.9	73	8.7	106–171	till	native prairie
Watertown, South Dakota	Barnes	Haploboroll	−17.3 ± 1.1‖	−2.0 ± 0.4	53	6.2	35–65	till	native prairie
Saskatoon, Saskatchewan, Canada	Elstow	Haploboroll	−24.2 ± 0.7‖	−7.9 ± 0.6	35	1.6	40–75	lake deposits	native prairie
Binghamton, New York	Howard	Hapludalf	−25.6¶	−9.4 ± 0.2	92	7.7	100–125	outwash gravel	mixed woodland
Spring Mountains-4, Nevada	—	Calciorthid	−23.4#	−6.8 ± 1.1	55	8.8	40-60	alluvial gravel	pigmy conifer woodland
Spring Mountains-5, Nevada	—	Calciorthid	−23.7#	−8.6 ± 0.2	61	7.3	40-60	alluvial gravel	conifer woodland
Spring Mountains-6, Nevada	—	Calciorthid	−23.9#	−8.5 ± 0.5	68	5.7	40-60	alluvial gravel	conifer woodland

* PDB = the Peedee-belemnite standard CO_2 for carbon and oxygen isotopic composition.

† MAP = mean annual precipitation (cm).

‡ MAT = mean annual temperature (T °C).

§ ~5 g soil from 5–10 cm intervals over whole profile except surface litter, mixed together, analysis on a single homogenized sample.

‖ ~5 g soil from 5–10 cm intervals over whole profile except surface litter, analysed separately, results averaged.

¶ Soil sample from 15–35 cm only, homogenized before analysis.

\# Soil sample from 40-60 cm only, homogenized before analysis.

Fig. 2 would be expected for soils in which the vegetation has been altered by agricultural or pastoral practices or, in the case of old surface soils, by major climatic change. The isotopic compositions of all the soils studied are compatible with a diffusion-controlled system in which all oxidized carbon species are in isotopic equilibrium. Therefore, the isotopic composition of soil organic matter or pedogenic carbonate in high-respiration-rate soils is a direct indicator of the fraction of the biomass using the C_3 or C_4 photosynthetic pathways.

Obtaining palaeoecological information from palaeosol carbonates and organic matter requires that the sampled palaeosols bear the imprint of time spans during which vegetation remained undisturbed by humans or by major climate change, as in the case of the modern soils we selected for study. Clearly, buried pre-Holocene palaeosols of any type should not have experienced anthropogenic modification. We estimate that the length of pedogenesis for Pliocene and Pleistocene soils in Pakistan to have been <10,000–15,000 yr, and probably much less in most cases. Thus, the carbonate build-ups in these palaeosols should not be, in most instances, polygenetic. Palaeosol humus probably represents organic matter from the last few hundred years before burial, given the short residence times typical for humus in most modern soils[15].

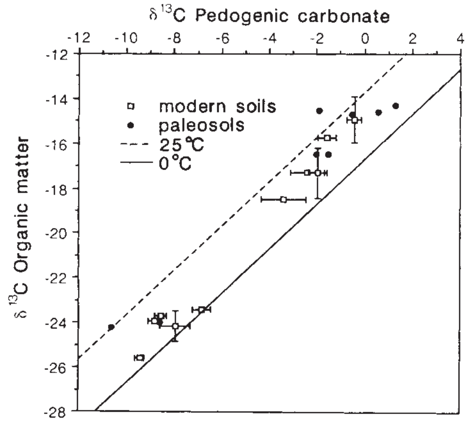

FIG. 2 The isotopic composition, relative to the PDB standard, of co-existing organic matter and pedogenic carbonate from ten modern North American soils, and from eight late Miocene-to-Pleistocene palaeosols in Pakistan. Solid lines represent isotope values for pedogenic carbonates in isotopic equilibrium with soil CO_2 derived from irreversible oxidation of soil organic matter in a diffusion-controlled soil system[1,11] at 0 and 25 °C.

Figure 2 also shows the isotopic composition of co-existing palaeosol organic matter and pedogenic carbonates from palaeosols in the Siwalik sequence of Pakistan. The concordance with the modern trend indicates that the pedogenic carbonates in the palaeosols have not been isotopically altered during diagenesis, notwithstanding several kilometres of burial. The isotope results from two Pakistani palaeosols indicate the highest soil temperatures of any soil or palaeosol studied. Mean annual temperatures and maximum soil temperatures (at 50-cm depth) for the Potwar Plateau of Pakistan are ~24 and 33 °C, respectively, much higher than for any North American site. Although this is interesting, we feel that use of co-existing carbonate-organic matter in palaeosols as a palaeotemperature indicator is premature, given the small sample size. Further evidence against diagenetic alteration is that modern soils and Miocene-to-Pleistocene palaeosol carbonates both range from −11 to +2‰, whereas coexisting organic matter for both range from ~−25 to −13‰.

Carbon isotope analysis of coexisting organic matter and pedogenic carbonate constitutes a simple test of the state of preservation of the original palaeoecological signal in soils. □

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