VALIDITY OF ^{14}C AGES OF CARBONATES IN SEDIMENTS

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ABSTRACT. This review is based on geologic surveys carried out in Australia and China as well as on more than 300 ^{14}C dates published in *Radiocarbon*. Evaluated are the origins and pathways of carbonate formation, stable isotopic composition, carbonate nodule growth rates and paleo-climatic effects. The three identified $\delta^{13}C$ abundance peaks are unrelated to environment and carbon source whilst ^{14}C ages group themselves into periods corresponding to past humid warm climate. It is concluded that the major error in caliche dating is due to incorporation of old limestone whilst error on nodule dating is related to their slow growth rate. Thus, caliche antedates and nodules postdate the times of their deposition. Delta ^{13}C values cannot be used to correct for limestone or atmospheric contamination effects.

INTRODUCTION

There are various types of carbonate precipitates (authigenic carbonate) in soils, lake deposits, marine sediments, and loess that can be used for ^{14}C dating when there is a lack of organic carbon. However, the validity of authigenic carbonate dates are suspect since the initial ^{14}C concentration is unknown and post-depositional contamination/alteration is often possible. [14]C determinations on this type of material — both in Australia and China — have mostly been interpreted successfully where stratigraphic relationships have been set up with dated sequences and when associated environmental factors have been recognized.

This paper is based on the assessment of the results of geologic surveys carried out in Australia and China and incorporates more than 300 ^{14}C dates, most of which have been published in *Radiocarbon*. It discusses the problems associated with the validity of soil carbonate as a dating material.

CARBON ISOTOPIC COMPOSITION

Soil carbonate formation is generally considered to result from carbonate supersaturation of soil solution due to evaporation, evapotranspiration, and lowered $\rho(CO_2)$. There are four possible carbon sources of soil authigenic carbonate: 1) from soil CO_2, 2) from dissolved carbonate in ground water, 3) from old calcareous dust derived from eroded soil exposure, 4) from limestone or shell detritus in parent sediments (Geyh, 1970; Leamy & Rafter, 1972; Pantin, 1963; Salomons & Mook, 1976).

Stable isotopes in soil carbonates are useful tracers for understanding the process and circumstance of soil carbonate formation (Cerling, 1984; Salomons, Goudie & Mook, 1978). Whether $\delta^{13}C$ values can be used to trace the original carbon in soil carbonate and to correct the "dead" carbon dilution effect is an important concern of ^{14}C dating.

$\delta^{13}C$ values of soil carbonate show values (Fig 1) ranging from 0‰ to −13‰ and falling into three sections, 0‰ to −2‰, −3‰ to −6‰, and −7‰ to −11‰.
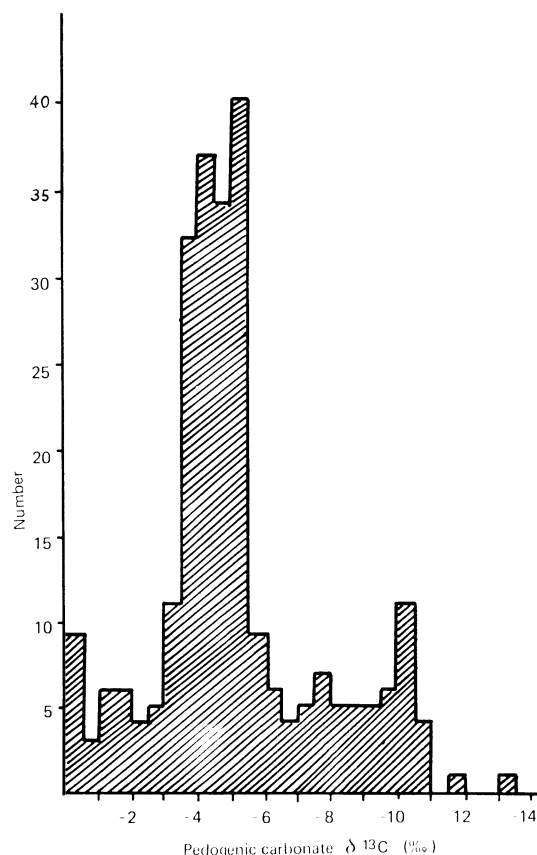
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Fig 1. Distribution of ^{13}C values of caliche and calcareous nodules

δ^{13}C values of soil CO_2 in temperate and semi-arid climate also shows a wide range (Fig 2). In general, the carbon isotopic compositions of soil CO_2 is related to the proportion of biomass using the C_4 photosynthetic pathway and the CO_2 respiration rate of the soil; at low soil respiration rates significant atmospheric CO_2 mixing can occur.

δ^{13}C values of groundwater HCO_3 also show a wide range. δ^{13}C values of rain are generally considered to range from $-14\%_0$ to $-18\%_0$.

In the theoretical calculation, fractionation factors (ϵ) given by Hendy (1971) are adopted for calculating the anticipated δ^{13}C values.

If soil carbonate was formed by weathering of feldspar (Mook, 1976), assuming δ^{13}C values of soil CO_2 range from $-12\%_0$ to $-25\%_0$. Consequently, the anticipated δ^{13}C values range from $-2.5\%_0$ to $-15.5\%_0$ (see Fig 2).

If soil carbonate was formed from the dissolution of limestone detritus (δ^{13}C values of $0\%_0$) by rain, the anticipated δ^{13}C values will range from $-7.9\%_0$ to $-10.9\%_0$.
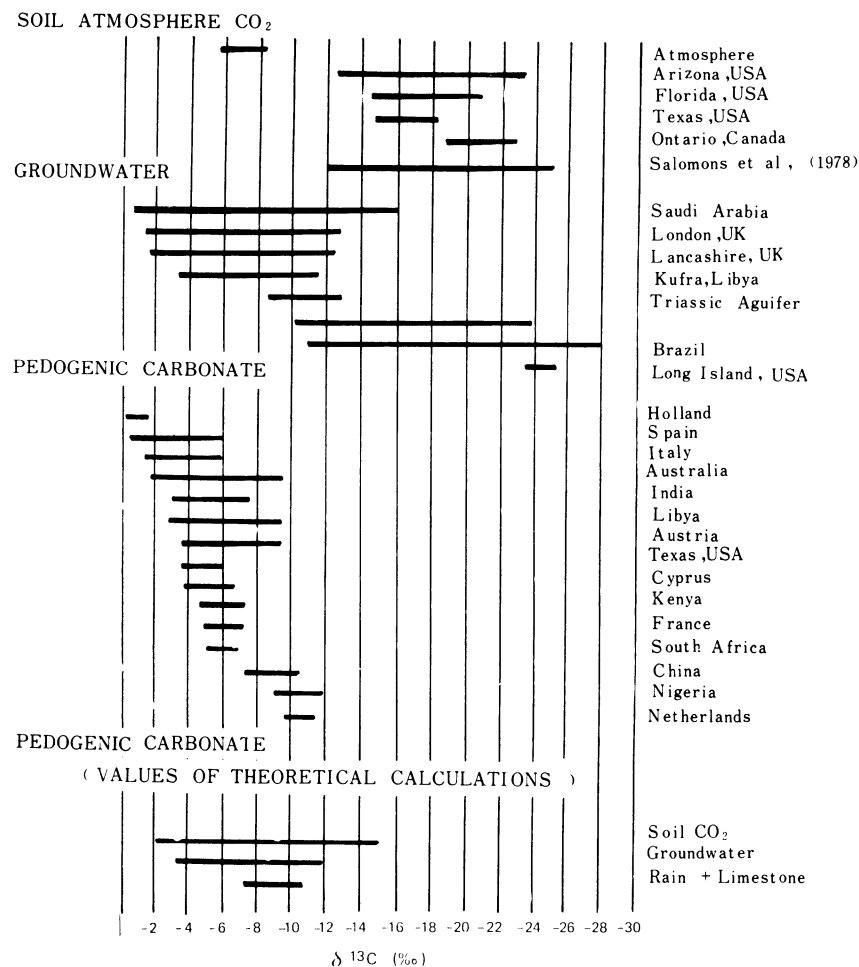
Fig 2. Distribution of ^{13}C values of soil atmosphere CO_2, groundwater HCO_3, and authigenic carbonate in caliche and calcareous nodules

If soil carbonate was formed by reprecipitation of dissolved carbonate in ground water, the anticipated $\delta^{13}C$ values will range from $-3.9‰$ to $12.9‰$.

Because anticipated $\delta^{13}C$ values of different original soil carbonate are analogous, it is impossible to trace carbon sources of soil carbonate from $\delta^{13}C$ values.

In addition, $\delta^{13}C$ values of soil carbonate change while redissolution and reprecipitation occur. Hence, $\delta^{13}C$ values are not suitable for correcting the "dead" carbon dilution effect on soil carbonate dates.

Bowler and Polach (1971) have indicated that $^{13}C/^{12}C$ ratios remain relatively constant despite variations in soil types, carbon sources, vegetative cover, climate, and carbonate mineralogy. This demonstrates that using $\delta^{13}C$ values to trace carbon sources is rather difficult.

AGE COMPARISON WITH ORGANIC CARBON

To test the reliability of authigenic carbonate dates as a time scale, the authigenic carbonate dates are compared with dates determined for those of co-existing organic carbon. Figure 3 shows 82 pairs of dates plotted from determinations carried out by different laboratories around the world. Three important conclusions may be drawn: 1) approximately half of the carbonate dates are older and half are younger than the organic carbon dates, 2) ca 90% of the pairs differ from each other by 1000 to 3000 years and 10% differ from each other by 3000 to 20,000 yr, 3) the majority of dates from drill cores, obtained from lake deposits or marine sediments, differ by <1000 yr.

Williams and Polach (1971) have proposed that the segregation of authigenic carbonate occurs largely after the accumulation of the coexisting organic carbon in the host material; thus, the carbonate dates should be younger than the organic carbon dates. Accordingly, if dates for carbonates are older than those for organics this will suggest that incorporation of carbonate, containing little or no ^{14}C, eg, a "limestone dilution" has occurred
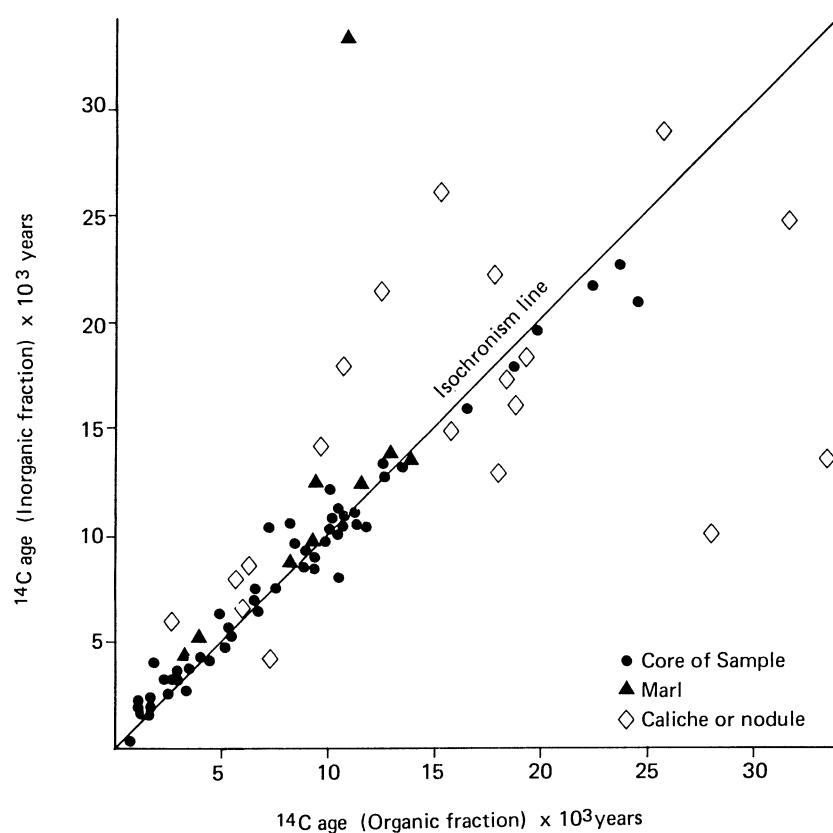

Fig 3. Age comparison of sample pairs of carbonate in sediments and co-existing organic carbon

during formation. The contribution of "dead" carbon to soil carbonate is estimated to be 10%–30% of the total carbon, based on the observed "limestone dilution effect" shown in Figure 3. This is in basic agreement with Goodfriend and Hood (1983) who estimated that the contribution of limestone carbon to snail shell is 0% to 33%.

GROWTH RATE AND APPARENT AGE

The formation of soil carbonate involves a three-stage process: 1) provision of carbonate-rich solution, 2) the movement of that solution, 3) the precipitation of soil carbonate (Salomons, Goudie & Mook, 1978).

Because the provision and movement of carbonate-rich solution in soil are slower than the tufa deposited by a spring or travertine formed in a cave, we assumed that the growth rate of soil carbonate in arid and semi-arid zones is rather slow. Using ^{14}C techniques, Peterson (1966) reported that dolomite crystals in playa deposits grow at the rate of 0.46–0.86 μ/Myr. By measuring caliche profiles in Texas (Fig 4), Valastro, Davies and Rightmire (1968) suggested that the dates closest to the surface are 16,000 to 25,000 yr, changing with increasing depth (to 60cm) to 30,000–35,000 yr. Dating the outer and inner portions of calcareous nodules revealed (Rafter *et al,* 1972) age/time differences of 280–16,400 yr (Table 1). Callen, Wasson and Gillespie (1983) reported that the carbonate segregation in Moko Palaeosol, Australia took at least 4000–15,000 yr to form. This evidence demonstrated that the apparent age of soil carbonate only represents the greatest minimum age. The soil carbonate age is considered younger than the age of parent sediment accumulation, so that the slower the growth rate of the soil carbonate, the greater the deviation from the accumulation time of the parent sediment.

POST-DEPOSITIONAL ALTERATIONS

There are several processes that cause post-depositional alterations: recrystallization, replacement, overgrowth, and dolomitization. Thin-section studies of calcareous nodules (Williams & Polach, 1971) indicated that authigenic carbonate is commonly comprised of microcrystalline calcite, ca 10μ across, which encloses detrital grains of quartz and feldspar. However, in many nodules the carbonate groundmass is significantly coarser grained around the quartz and feldspar as well as in the voids, with individual crystallites attaining 20μ across. The nodules composed of coarser crystallite give anomalously younger ages, showing that recrystallization and contamination with ^{14}C have occurred in the late formation stage.

Chemical and x-ray diffraction analyses of concretions formed in the recent supratidal flats of Broad Sound, Queensland (Cook & Polach, 1973) indicated that concretions up to 20cm are composed of micritic low-magnesium calcite and dolomite. However, poorly crystalline dolomite concentrates mainly in the outer portion of the concretions suggesting that it was formed by post-depositional dolomitization of the calcitic host material.

Bowler and Polach (1971) observed that the percentage of dolomite increases progressively with age in paleosols at Nyah, western Australia. All

TABLE 1

Comparison of ^{14}C ages of calcareous nodules between inner and outer layers

| Species	Sampling site	^{14}C age (yr BP)	Growth time (yr)	Ref
Syngenetic nodule	Atlantic, water depth 73m, 6cm diameter	(1) Inner: 690 ± 50 / Outer: 290 ± 40 / (2) Inner: 1000 ± 45 / Outer: 720 ± 30	400 ± 60 / 280 ± 55	Vogel (1970)
	Atlantic, 91m	Inner: 26,640 ± 600 / Middle: 19,440 ± 600 / Whole: 17,660 ± 450	8980 ± 750	Hubbs, Bien and Suess (1965)
	Atlantic, water depth 89m, 5cm diameter	Inner: 1050 ± 100 / Outer: Modern	1050 ± 100	Delibrias, Guillier and Labeyrie (1972)
	East China Sea, water depth 163m, 6cm in diameter	Inner: 9625 ± 130 / Outer: 6780 ± 110	2845 ± 170	^{14}C dates, Inst Geol, Natl Bur Seismology (ms)
Pedogenic nodule	New Zealand Large nodule	(1) Inner: 9900 / Outer: 8210	1690	Rafter *et al* (1972
	Small nodule	(2) Inner: 7070 / Outer: 6400	670	
	Circular nodule	(3) Inner: 34,400 ± 900 / Outer: 18,000 ± 300	16,400 ± 950	
	Illinois, USA nodule	Inner: 7370 ± 140 / Middle: 5865 ± 80 / Outer: 5030 ± 100	2340 ± 170	Coleman (1974)
	Australia nodule	Rim: 29,000 / Center: 44,000 / Whole: 39,800 ± 3000	15,000	Callen, Wasson and Gillespie (1983)
	Shandong, China nodule	Inner: 29,530 ± 790 / Outer: 20,460 ± 300	9070 ± 850	^{14}C dates, Inst Geol, Natl Bur Seismology (ms)
	Najing, China nodule	Inner: 40,000 ± ? / Outer: 30,600 ± 1100	9400 ± 110	Li and Fang (1983)
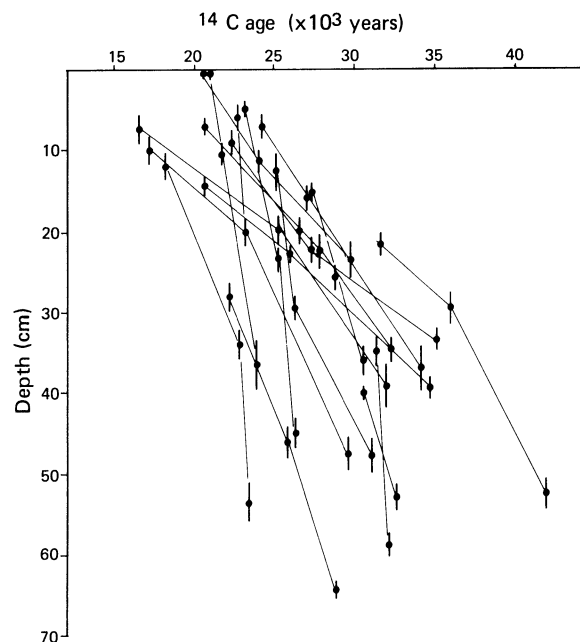
Fig 4. ^{14}C date distribution in caliche from western Texas, (after Valastro, Davies & Rightmire, 1968)

dolomite samples in this area showed considerably higher levels of ^{14}C activity than their true ages would allow, suggesting dolomitization associated with cation/anion exchanges with active carbon.

Both the rarity of rain in arid regions and the impermeability of the dense and hard calcareous nodules seem to be beneficial factors for retarding post-depositional alterations (Williams & Polach, 1969). This is shown by 1) the apparent lack of dates for arid zone soil carbonate younger than 1000 yr (see Fig 5), 2) the existence of soil carbonate with very low ^{14}C content, and 3) the dates of soil carbonate in arid regions seem to relate to the late stages of soil formation. These observations are based on the assumption that the uptake of young carbon occurs more readily under wet conditions.

CLIMATIC INFLUENCE

Soil and paleosols with accumulations of authigenic carbonates are restricted to arid and semi-arid regions. The detailed mechanisms of carbonate formation in soil and loess are not well known, but it is believed that climatic factors play a major role.

Frequency distributions of ^{14}C dates based on 327 determinations on caliches and calcareous nodules in different parts of the world have been plotted in Figure 5. Seven peaks, corresponding to well-established climatic
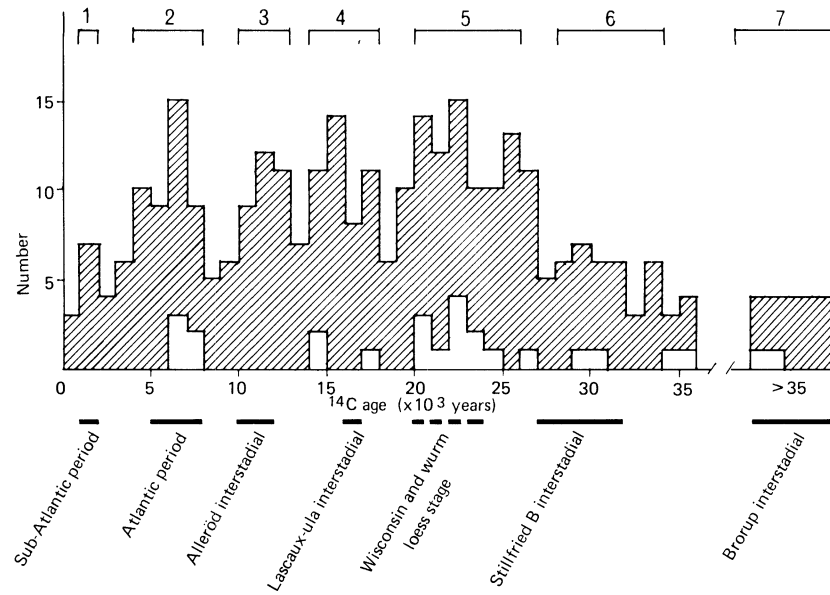
Fig 5. Frequency distributions of ^{14}C ages of caliche (shaded) and calcareous nodules (light area) from different parts of the world

(humid-warm) periods (Cao, 1983), can be identified with the exception of the fifth period showing the Würm and Wisconsin loess deposition period in Europe and North America which are believed to be cold and dry. Studies on paleosols developed in loess reveal that some intermittent humid-warm stage has occurred during this period (Liu, 1964; Ruhe, Miller & Vreeken, 1970). The hypothesis that caliche and calcareous nodules are developed during relatively humid-warm periods seems to be confirmed by the available ^{14}C dates.

CONCLUSIONS

Radiocarbon dates of carbonate from lacustrine or marine sediments generally agree with co-existing organic material, but soil carbonate dates significantly deviate from the co-existing organic carbon dates.

In some cases, soil carbonate is precipitated from a solution in which ^{14}C concentration is not in equilibrium with soil CO_2, so that some "dead" carbon from ground water or older carbon may be incorporated. Age comparison with organic material estimates the contribution of "dead" carbon to soil carbonate at 10%–30% of the total carbon.

In general, the segregation of soil carbonate takes thousands of years. Thus, the ^{14}C age of soil carbonate is younger than its parent sediments and can be regarded as the greatest minimum age of segregation. Consequently, soil carbonate dating does not provide reliable estimates of the age of pedogenesis, but can be useful if its limitations are recognized.

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