In this paper we discuss the limitation of radiocarbon dates on the pedogenic calcic nodules formed in situ within the vertisols in the upland region of Coimbatore, Tamil Nadu. The radiocarbon ages were obtained using low level scintillation counters and the ages range from ~24 Ka to ~31 Ka. The ages correlate well with the marine isotope stage of Late MIS3. Since the calcic nodules are pedogenised and formed in a terrestrial open system we express caution in the interpretation of the radiocarbon ages obtained on pedogenic carbonate nodules. The radiocarbon dates represent maximum ages and hence the ages measured should only be considered as age estimates and not absolute geologic ages. Multiple sub-mm size subsamples could provide more reliable estimates of soil chronology.
Introduction

Soils provide key evidence in reconstructing long-term landscape evolution and paleoenvironmental change (Birkeland, 1999). Calcrete nodules or calcic nodules in soils are a postdepositional, pedogenic accumulation of calcium carbonate that represents an ancient, buried, soil B-Bk horizon (Goudie, 1983). The sediment's permeability, porosity, primary bedding structures, internal stratification, and vertical distance from the modern ground surface and water table determines the vertical position of the carbonate horizon. A carbonate accumulation zone can occasionally parallel a depositional stratum and give a Bca/Bk horizon the appearance of a time stratigraphic unit. Minimum five factors are responsible for the calcium carbonate formation in the soils and these are: (1) climate, (2) lithology of carbonate parent material, (3) depth under the soil surface, (4) clast size, (5) bulk density and composition of cutans (Pustovoytov, 2003).

Vertisols offer opportunities for paleoecological studies, indicated by their characteristic accumulation of organic matter and calcium carbonate nodules within the soil horizons. However, it is important to understand the chronostratigraphy of vertisols and calcic nodules formed within them. Therefore, radiocarbon dating of calcic nodules in geologically recent soils is necessary. Deutz et al., (2002) suggested that radiocarbon ages of the carbonates allow assessment of the degree of isotope variations in contemporaneous carbonates and temporal isotopic trends.

Calcretes occurring around Coimbatore region, Southern India, have not been age dated. Calcrete deposits are locally known as Chunambu kal/ Odai kal and are often used locally as a raw material for painting houses and laying temporary rough roads. In this paper we present the radiocarbon ages on the calcic nodules and discuss the constraints on the radiocarbon ages.

Study Area

Coimbatore is a plateau region, lying towards the eastern approach to the Palghat Gap (the major pass through the Western Ghats mountains) and falls in the northwestern part of Tamil Nadu (at an altitude ranging between 200 and 500 m above sea level) (10° 26′ N and 11° 45′ N and 76° 61′ E and 77° 56′ E; Fig. 1). The plateau is bounded by the Nilgiri hills to the north and the Palani and Anaimalai hills to the south and the altitude decreases progressively to the east. The geomorphic units of the study area are residual hills, linear ridges, buried pediments, erosional plains and valley fills. The higher elevations (~ 440 m) are typically covered with soil and calcic horizons whereas in the plains, the topography is dominated by hardpan calcretes formed over the bedrock supporting a thin veneer of soil cover. The bedrock consists of a wide range of high grade metamorphic rocks of
the peninsular gneissic complex. The geology of the area is represented by the Precambrian rocks consisting of biotite and hornblende rich gneiss, exposures of charnockite (i.e. plagioclase and orthopyroxene rich granulites) and dolomitic limestone. There are biotite gneiss, augene gneiss, garnetiferous biotite gneiss and hornblende gneiss. In addition minor occurrences of magnetite, corundum, mica, semi-precious stones like moonstone, beryl and different types of quartz have also been reported from various parts of this area (Navin Shankar and Achyuthan 2007).

This region receives an average annual precipitation of 500-800 mm during the Indian summer southwest monsoon (June-August) and also the northeastern rains between October to December. The highest and lowest annual average temperatures are respectively 32ºC and 21ºC. The climate is characterized by recurrent but non-periodic droughts. Three major rivers that drain the study area are Noyal, Bhavani and Amaravati. The main drainage basin is carved by the Noyal River flowing east towards the Tamil Nadu plain and the area to the west is dissected by a network of channels flowing through the Palghat gap (Fig. 1). The net recharge of the water table is ~30 mm yr\(^{-1}\) (Jacks and Sharma, 1982). The water table levels vary from 10 to 20 m below the ground surface. The general vegetation cover around this region belongs to the families of *Artemisia*, *Acacia* and *Chenopodiacea*.

**Soils**

Vertisols with calcic horizons cover nearly one third of the study area in the upland region. These deposits are naturally exposed along the road cuttings, canal cuttings and railway cuttings. The soil profiles were studied for their color, texture, structure and distribution pattern within the profiles using the classification schemes developed by World Reference Base for Soil Resources (FAO, 1998), and calcrete formation following Gile et al., (1966, 1981) and Goudie, (1983) (Fig. 2).

**Materials and methods**

For radiocarbon dating, samples were collected from the Bk horizons and the radiocarbon dates for three calcretes nodules from Ramanathapuram (Section C) (2 samples) and Vellakinur (Section D) (1 sample) are presented in Table 1. Radiocarbon dates were obtained using liquid scintillating counting technique at the Isotope Geochemistry laboratory of Dipartimento di Scienze Geologiche, Ambientali e’ Marine, University of Trieste in Italy (Table 1). The samples for radiocarbon dating were cleaned by using ultrasonic bath with deionized water for 10 minutes. CO\(_2\) was obtained by acidification of the samples with HCl diluted 1:1 in a glass reactor attached to a vacuum system.
The evolved CO₂ was purified cryogenically; LiC₂ was synthesized in a stainless steel reactor at high temperature (over 700°C) and under vacuum, hydrolyzed into acetylene (C₂H₂), and then polymerized into benzene (C₆H₆). ¹⁴C concentrations were performed using the Quantulus low level scintillating counter. Samples were converted to calendar ages using a calibration that incorporates variations of the ¹⁴C concentration in the atmosphere and the marine reservoir effect (Hugen et al., 2004). This effect was estimated to be ΔR=101 and was input to the calibration program calib 5.0 (Table 1).

**Results**

The radiocarbon ages obtained for two calcrete nodule samples from the Ramnathapuram vertisol section (Section C) and one sample from the Vellakinur (Section D) range in age from 23,957±580 to 30,965±110. The radiocarbon ages are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Calibrated radiocarbon Age (years BP) after Polach (1976); Stuiver and Polach (1977)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramnathapuram</td>
<td>1.30-1.50 m</td>
<td>23,957±580</td>
</tr>
<tr>
<td>Ramnathapuram</td>
<td>2.30-2.50 m</td>
<td>25,959±570</td>
</tr>
<tr>
<td>Vellikinaru</td>
<td>3-3.2 m</td>
<td>30,965±110</td>
</tr>
</tbody>
</table>

**Discussion**

**Calcrete formation and source of cations**

Field studies and observations of the soil sections around Coimbatore region reveal that the calcic (Bk) horizons formed insitu within the vertisols are important factors in shaping the landscape. These horizons protect the underlying older soil units from denudation processes. There have been multiple episodes of calcrete precipitation and redissolution. Field evidence in the Coimbatore region is consistent with our observations. Evidence includes features such as calcrete coatings around the detritus sediments, infillings within cavities and along the soil peds and fractures. Calcrete is also commonly found as post-sediment infillings and as cementing matrix of the sediments. The geochemistry of the calcic horizons in soils indicates process of intense pedogenesis that has taken place in phases and bears signatures of differential weathering and calcic nodule forming processes (Navin Shankar and Achyuthan, 2007).
The development of the calcic nodules is controlled by three factors: climatic changes, type of parent material and tectonics. The repeated changes from semi-arid to humid climate are the main controlling factor, in the formation of calcic horizons in vertisols. During humid periods descending water carried the dissolved carbonates downward as bicarbonates, while the carbonate rich solutions were carried upwards by capillary action during the arid periods (Goudie, 1983). The source of the cations concentrated in calcrete can be either bedrock or transported materials (such as wind blown dust, aerosols and rainwater). Cations accumulate in groundwater during weathering and chemical leaching. The predominant bedrocks in the Coimbatore region are the gneissies, dolomite limestone and granites. These rocks that make up the Coimbatore Basin typically have <3% CaO and <4% MgO. Mafic and genissic lithologies in the Archaen group can have higher CaO and MgO. The overlying soils, which have a significant aeolian dust component generally, contain more Ca and Mg with 5-12% CaO and 2-4% MgO. Sr concentrations and isotopic compositions by thermal ionization mass spectrometry (TIMS) of the calcrete samples from Coimbatore and sites from Karnataka were determined by Durand et al., (2003) and the results indicate Sr isotopic ratios of 0.715647±0.000022 for the hardpan and 0.718294±0.000020 for a nodule from a nodular horizon that are close to ratios known for Quaternary seawater (0.7092). The modern marine 87Sr/86Sr is 0.70918; implying advection of Ca-rich dust that exudes from the carbonate platforms during low sea stands rather than a bedrock source (Durand et al., 2003). This suggests that the Sr and geochemically associated Ca have probably been introduced in dust, aerosols or rainwater from seawater or marine-derived carbonate accumulations (Dart et al., 2005). Calcium carbonate in atmosphere dust is the main source of carbonate found in desert soils that have non-calcareous parent materials (Gile et al., 1966). Dust flux also contributes the amount of carbonate that can accumulate in a weathering soil. Trace elements have probably also been introduced with these materials accounting for some of their background content in the calcrete. Significantly elevated levels of many trace elements in the known bedrock concentrations clearly indicate that the weathered bedrocks are also a source of cations. A correlation of the atmospheric dust in marine sediments and glacial deposits and pedogenic events (Owen et al. 2002, 2005; Pourmand et al., 2004, Srivastava et al., 2009) with marine oxygen isotope record indicates that both SW and NE monsoon weakened during the cooling intervals of MIS3 (Imbrie et al., 1984) and the sea level (Lambeck and Chappell, 2001) was nearly 120 m low (Fig. 3).
Age of the calcic horizon (Bk)

Radiocarbon dates have been obtained on the three representative calcic nodule samples and the dates range from ~23 Kyrs to ~31 K yrs BP (Late MIS3 period). These are for nodular and soft calcrites in a pedogenic sequence of soil formation representing the maximum age. 14C data is attributed to a more complex mixture and these dates represent a maximum age. The radiocarbon dates suggest a late MIS3 period indicating a wetter and cooler conditions and this inference also conforms to the palaeoclimate studies carried out in the peninsular India and western India (Mishra et al., 2003, Achyuthan et al., 2007). 14C dating of calcrete can be speculative, given the limited time range of the 14C method (<50 Ka) and uncertainties related to potential contamination by both modern and dead carbon (Chen et al., 2002). Obtaining an age on the calcrete nodules implies that the dated microfabric has remained stable within its environment since it formed, and this can be used as a tool to make inferences either about geomorphic history, microfabric formation and processes or about palaeoclimate. In all these cases, great care is needed as the radiogenic isotope values reflect varying degrees of over printing of the pedogenic carbonates (Deutz et al., 2001). In this study, dating soil calcrete nodules that are ~24 Ka – ~31 kyrs BP old means that the radiometric system did not reopen since that time and so it is tempting to conclude that climate has never since then been sufficiently humid to dissolve and reprecipitate the calcite. It is also tempting to conclude that soil erosion has been extremely limited for ca 30,000 kyrs BP, otherwise the topsoil would have been eroded and the nodules would have been exposed or removed. Occurrence of calcic nodules in the soils dated to ~31 Ka provides a signal of wetter conditions. The release of calcium into the slope system through rock weathering is an indication of greater moisture availability during Late MIS3 than today. This is important as the arrest of the calcium within the local slope system places an upper limit to long term climatic humidity and to the capacity of the hydrological system to export solutes. Thus the carbonates can have either an older or younger 14C age than the soil itself. The deviation of the carbonate’s age from that of the soil can be estimated, judging from the carbonate accumulation rate during the dry phases. Carbonate dissolution and redeposition rates is during the humid phases of the Late MIS3 phase. Therefore the current calcrete fabrics are the result of short range redistributions, effected since Late MIS3, of a stock of Ca that was released predominantly during the interstadial period. This may contain Ca inherited from earlier as well as from more recent periods. The exact proportions are impossible to establish quantitatively although further dating of microfabrics may reveal a finer succession of carbonate precipitation phases. The most striking aspect in terms of the timing of CaCO3 precipitation is that it
occurred during an interstadial period. Durand et al., (2007) explained the calcrete formation phenomenon occurring around Gundlupet and the Palladam area which are in the lee ward side of the Western Ghats escarpment.

**Limitations of radiocarbon dating on pedogenic carbonates**

There are at least two sources of ancient carbonate in the study area; one source is the meso Proterozoic dolomite limetstone Formation, which contains carbonate content and the second, includes dust. Either source would contribute carbon that contains $^{14}$C. The reservoir effect alters the calcic nodule’s radiocarbon age because geological limestone carbon used to calcic CaCO$_3$ contains significantly less radiocarbon than the atmosphere. "Less radiocarbon" means that the $^{14}$C/$^{12}$C ratio in stream waters is smaller than that ratio in the atmosphere. This disequilibrium between water and atmosphere $^{14}$C sources causes calcrete to have less radiocarbon than terrestrial calcium carbonate forming at the same time. The net effect is that $^{14}$C dates on shells can be "older" than the nodules true geological age. This geochemical condition is the "reservoir effect". Second, nodules from the carbonate-bearing sediments or from sediments where pedogenic or groundwater carbonate are common are susceptible to post-mortem exchange of their indigenous carbonate with foreign (exogenous) carbonate. This secondary carbonate can have radiocarbon contents ranging from modern values to undetectable, the latter representing carbon from geologically ancient carbonates. Because modern rainwater and ancient groundwaters can mix in varying proportions, the apparent age of the secondary carbonate is unknown unless there are independent age determinations available for the calcrete nodules. It is widely known that radiocarbon measurements on calcrete nodules from soil system often differ by thousands of years from radiocarbon dates on charcoal associated with calcretes. Reservoir effects and diagenetic factors preclude the calcrete dates from being used as absolute geologic ages. Thus excess radiocarbon ages may be due to a combination of a) ancient carbon being incorporated into the sediment during deposition, b) unrecognized bioturbation of soil sediments and calcic nodules, c) groundwaters circulating unknown quantities of ancient and modern soluble carbon, d) continuous immersion of the soil sediments in reservoir waters of unknown radiocarbon content, and e) variations in the apparent geological ages of the different chemical phases comprising the total soil sediment.

Petrographic and stable ($\delta^{13}$C and $\delta^{18}$O) and radiogenic ($^{14}$C) isotope study of pedogenic carbonates from late Quaternary soils around Coimbatore region (Navin Shankar and Achyuthan 2007) documents that carbonate formation in vertisols occurs principally by overprinting and is a
result of a complex petrographic and isotopic record. This makes the studied soils ideal for evaluating the radiocarbon dates obtained for the use as paleoenvironmental proxies. Specific implications of this study include the following: (1) Pedogenic carbonates that form by overprinting are a cumulative record of the soil conditions present during their accumulation; thus, the date result in "time averaging" of paleoenvironmental, and paleoecologic conditions. (2) Carbonates may record only a fraction of the duration of development of their host profile. (3) There is a high level of uncertainty associated with using the sequence of morphologic development of carbonate as a function of time or maturity in paleosols (Stafford Jr., 1998, Chen et al., 2002). Furthermore, the actual chemical fraction dated could be any of at least five different chemical fractions, including: a) total sediment, b) total humates, c) humic acids, d) fulvic acids, or e) humins. Different chemical fractions from the same sediment can yield very different radiocarbon measurements (Stafford Jr., 1998). These individual \(^{14}\text{C}\) measurements can be drastically different from other sediment fractions (Stafford Jr., 1998). A problem for additional dating of the carbonate horizon is that accurate radiocarbon ages cannot be obtained from the calcium carbonate phase that forms the carbonate concretions. The reason for this is that the initial \(^{14}\text{C}\) activity, expressed as fraction modern (Fm), is unknown for the CO\(_3\) in the Bk or BCa carbonate nodules. It is unknown how much of the total CO\(_3\) in the carbonate horizon is represented by modern carbon or carbon having no detectable \(^{14}\text{C}\). Post depositional alteration (carbonate exchange) can alter the carbonate's original \(^{14}\text{C}\) content (Chen et al., 2002). This carbonate alteration can be by modern carbon, ancient carbon, or a combination of carbon from different sources. Consequently, a radiocarbon date based on total carbon is only a weighted average of \(^{14}\text{C}\) from all sources contributing to the sample's \(^{14}\text{C}\) content. Thus such a radiocarbon measurement does not establish the geologic age of the sediment from which the carbon was derived until the relationship is known between a specific carbon phases \(^{14}\text{C}\) content and the time-of-deposition. Because of these factors, radiocarbon measurement should not be considered anything other than a preliminary, and very tentative, chronological estimate moreover further testing of the area is needed. It is imperative that multiple radiocarbon dating must be carried out. Multiple dates from the same horizon, and from carbonates in vertical sequence in the same exposure, should be used to test the reliability of those dates. There can be reversals and inconsistencies along single horizons, and it was found that carbonate fragments in cores of nodules may give older dates as some recrystallization of carbonate has taken place and more than one generation of micrite was present (Callen et al., 1983). Dates from soil carbonates in the semi arid zone are not reliable estimates of the age of pedogenesis, but can be useful if their limitations are
recognized (Callen et al., 1983). From the radiocarbon ages that we have studied on the calcic nodules we conclude that the radiocarbon ages on pedogenic carbonate nodules determined represent maximum ages and that multiple sub-mm size subsamples could provide more reliable estimates of soil chronology than methods employing larger samples, chemical enhancement of, or isochrones and further radiocarbon testing of the samples from these soil sites are needed. Until this is done, the radiocarbon ages measured can only be considered age estimates, not absolute geologic ages.

Conclusions
Pedogenic carbonates from the upland vertisols of Coimbatore region have been radiocarbon dated from 23 kyrs BP to 30 Kyrs BP. Dissolution of limestone and dolomites supplied calcium carbonates to form calcic nodules. Tectonic factor manifested in faults and lineaments in the study area provided the topographic lows that enabled preservation of runoff water and inturn more water infiltration rose by capillarity carrying calcium carbonate rich solutions followed by precipitation of CaCO₃ and formed calcic units (Navin Shankar, 2007). Since pedogenic carbonates have been formed in an terrestrial, open system, the radiocarbon ages represent maximum ages and these ages measured should only be considered as age estimates.

Acknowledgments
This work was done within the framework of the Associateship Scheme of the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy. The authors thank Dr. Jeff Pigati, USGS, USA, for critically going through the manuscript that helped in the presentation of the paper.

References


Fig. 1. Location map of the study area.
Fig. 2. Lithosection of soil profiles.
Fig. 3. Figure showing the calcic nodule formation in the soils during the late MIS3 period when the sea level was low.