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Marine ^{14}C Reservoir Age and Suess Effect in the Indian Ocean

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Abstract

Apparent radiocarbon (^{14}C) ages of marine biogenic samples that derive their carbon from surface seawater dissolved inorganic carbon are on the average about 400 years older than contemporary terrestrial woods or global atmospheric CO_2. This age offset is due to mixing of old carbon from the deep ocean and is referred to marine ^{14}C reservoir effect. Both regional and temporal variations of ocean circulation pattern causes significant spatial and temporal variations in marine ^{14}C reservoir ages and hence of biogenic surface marine samples. Knowledge of reservoir age is very important to accurately calibrate ^{14}C-ages of biogenic carbonates and sediment organic matter from marine sediments that are frequently used in paleoceanographic studies. Here the concept of marine ^{14}C reservoir ages and their quantification are discussed and data for the Indian Ocean region are reviewed. Regional variations of marine ^{14}C reservoir ages and fossil fuel Suess effect for the Indian Ocean and the South China Sea are analyzed.

Introduction

The only naturally occurring radioactive isotope of carbon is ^{14}C, commonly known as radiocarbon. ^{14}C is introduced in the environment through its production in the upper atmosphere by the reaction of atmospheric nitrogen with thermal neutrons that are produced form cosmic ray spallation reaction on other atmospheric components.

$$^{14}N_7 + {}^{1}n_0 = {}^{14}C_6 + {}^{1}H_1 + \textit{(energy)}$$

The energetic ^{14}C atoms freshly produced in the atmosphere are soon oxidized in presence of atmospheric oxygen to form carbon monoxide which eventually oxidises to carbon dioxide.

$$^{14}C_6 + O = {}^{14}CO$$
$$^{14}CO + O = {}^{14}CO_2$$

Radioactive carbon dioxide $^{14}CO_2$ being indistinguishable from other forms of CO_2 ($^{12}CO_2$ or $^{13}CO_2$), it eventually enters the biosphere through photosynthesis by terrestrial plants, and then to the entire food chain through herbivorous animals. ^{14}C activities of most terrestrial living organisms are therefore in equilibrium with that in the atmosphere, through continuous exchange of ^{14}C by photosynthesis or food intake and respiration. When an organism dies the ^{14}C exchange halts, and the ^{14}C in the dead tissues start to decrease exponentially through radioactive decay. ^{14}C forms stable nitrogen through beta decay and half-life of 5730±40 years.

$$^{14}C_6 = {}^{14}N_7 + \beta^-$$
$$(T½ = 5730\pm40 \text{ years})$$

There are various conventions for expressing ^{14}C concentrations in natural samples (Stuiver and Polach, 1977; Mook and van der Plicht, 1999). ^{14}C concentration in a sample can be expressed either as age in years before present or BP, where 'present' is actually the year AD 1950. For geochemical applications ^{14}C is commonly expressed as $\Delta^{14}C$ which is permil (‰) deviation of $^{14}C/^{12}C$ ratio of the sample with respect to a modern ^{14}C standard (whose ^{14}C activity equal to that of pre-industrial wood of AD 1890), the ratios being normalised for isotopic fractionation of the ^{13}C isotope and corrected for decay of ^{14}C. Old carbon containing samples (such as foraminifers from

deep sea cores) have less ^{14}C than that present in a modern sample and therefore have positive ^{14}C-ages in BP and negative $\Delta^{14}C$ ‰ values; whereas most present day terrestrial wood samples with higher ^{14}C than the modern ^{14}C standard show negative ^{14}C-ages in BP and positive Δ14C ‰ values. Geologically old carbon samples (such as marble or old limestone, coal and other fossil fuels) are '^{14}C-dead' from which nearly all ^{14}C got decayed away. Such samples have infinite ^{14}C-age and $\Delta^{14}C$ close to –1000‰.

Oceans are important reservoir of exchangeable carbon (40,000 Gt), most of which are present as dissolved inorganic carbon (DIC). The natural steady-state concentration of ^{14}C in the DIC of surface ocean waters is in quasi-equilibrium with atmospheric ^{14}C production, air-sea exchange of atmospheric CO_2, and mixing with deeper ocean water (Fig.1). The mixing time-scale of the global oceans through large-scale thermohaline circulation is about 1000 years. This causes aging of a given water mass during its residence in the ocean since its last equilibration with the atmosphere when it was closer to the surface, and results in ^{14}C-ages of deep ocean water close to 1000 BP ($\Delta^{14}C$ about –200‰) (Bien *et al.,* 1965; Stuiver and Quay, 1983). Diffusive and advective mixing with ^{14}C-depleted deep ocean waters causes the ^{14}C concentration for the surface oceans to be 5% lower on the average than in the contemporary atmosphere. Hence, the ^{14}C-ages of surface ocean waters are apparently older than contemporary terrestrial plants by about 400 years (Taylor and Berger, 1967; Bard, 1988; Hughen *et al.,* 2004). This phenomenon is known as marine ^{14}C reservoir effect. While the long-term temporal variations of surface ocean ^{14}C-ages are a function of the contemporary atmospheric ^{14}C levels and vertical mixing rates of the global ocean, their spatial variations also depend on the regional circulation patterns within the thermocline and regional air-sea CO_2 exchange rates. Local variations of marine ^{14}C-ages can take place due to input of hard water whose DIC is depleted in ^{14}C. Sources of hard water include rivers draining a geologically old carbonate terrain or ground water flowing through old carbonate aquifer. All these factors cause considerable spatial variations in the steady-sate (or natural) distribution of ^{14}C in the surface oceans and regional offsets of marine reservoir ^{14}C-ages from the global mean value, and make it difficult to use a common ^{14}C calibration curve for ^{14}C-dating of all marine samples. This is unlike ^{14}C-dating of terrestrial samples, which depends on past ^{14}C levels of rapidly mixing global atmosphere with a small difference between the two hemispheres.

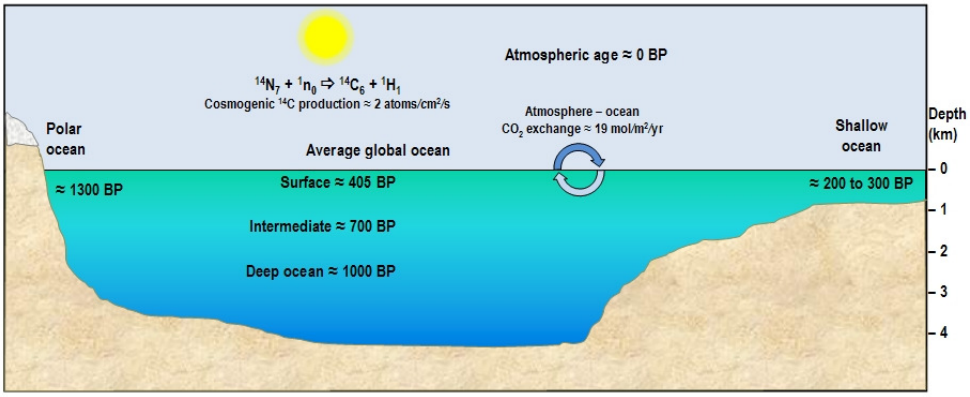

Fig.1: Natural radiocarbon age distribution in the marine environment

The introduction of anthropogenic ^{14}C produced from atmospheric nuclear tests of the late 1950's and early 1960's had nearly doubled the ^{14}C levels of the atmosphere CO_2, which eventually transferred to other exchangeable carbon reservoirs as the biosphere and the oceans (Rafter and Fergusson, 1957). Mixing of bomb-^{14}C contaminated atmospheric CO_2 resulted in steady increase of the level of ^{14}C in the surface oceans. This injection of bomb ^{14}C in surface waters though obliterated the natural (pre-nuclear) ^{14}C signatures and its inventory in the water column provided a means of determining the air-sea exchange rates of CO_2. The results of state-of-the-art ocean general circulation models (GCMs), which predict the future rise of greenhouse gases in the atmosphere, must be verified through observations before they can be used for planning of policies to control anthropogenic CO_2

emissions. Such models can be also used to simulate steady state distributions of pre-nuclear $\Delta^{14}C$ for the global oceans (Maier-Reimer, 1993; Toggweiler *et al.,* 1989). Comparison of these model results with direct measurements of ^{14}C in surface dwelling marine calcareous organisms from the pre-nuclear era offer a way to check the validity of these models and testing their predictive capabilities.

Knowledge about the natural (or pre-nuclear) level of ^{14}C in the surface ocean waters is necessary to determine:

(i) Offsets of regional reservoir ages from the modelled global mean—to calibrate the ^{14}C-ages of marine calcareous fossils, which grew during the pre-nuclear period and used for dating of marine sediments

(ii) Temporal variations of bomb-^{14}C in water column and its inventory—to assess the air-sea CO_2 exchange rates and decadal circulation in the thermocline

First oceanic measurements of ^{14}C started during the mid 1950's—about the same time when bomb-^{14}C started penetrating the world oceans. Soon, it was realized that bomb-^{14}C can be used as a powerful tracer to study air-sea exchange rates of CO_2 and mixing in the thermocline region on decadal time scales, utilizing the temporal variations of ^{14}C concentrations (Rafter and O'Brien, 1973; Broecker *et al.,* 1978; Broecker and Peng, 1982; Broecker *et al.,* 1995). The need for information about the pre-nuclear surface ocean ^{14}C levels was felt, while attempting to determine the increase of the surface ^{14}C levels from the pre-nuclear values. To determine the penetration depth and inventory of bomb-^{14}C in oceans, it is essential to have knowledge about the surface pre-nuclear ^{14}C (Broecker *et al.,* 1985). Several approaches have been made to determine these pre-nuclear surface ocean ^{14}C values from the analyses of suitable marine samples from the pre-nuclear era. Broecker *et al.,* (1985) estimated the pre-nuclear $\Delta^{14}C$ values for different oceanic regions of the world within ±10‰. These values range from a minimum of –140‰ in the polar oceans to –50‰ in the mid latitudes. However, the surface ocean circulations for the global oceans are far from simple to adopt a uniform scheme for meridional pre-nuclear $\Delta^{14}C$ variations for different oceans.

Chronological applications of ^{14}C

Since carbon is ubiquitous in all living beings, the radioactive decay of ^{14}C can be conveniently used for age determination of organic or biogenic samples. The science of ^{14}C-dating was established by Prof. Willard Frank Libby of the University of Chicago, who for the first time demonstrated the potential of ^{14}C in dating of archaeological artefacts (Libby *et al., 1949;* Libby, 1955), and was awarded the Nobel Prize in Chemistry in 1960 for this pioneering discovery. The half-life of ^{14}C (5730±40 years) is suitable for dating of samples that are within 50,000 years old, thus making it the most widely used dating method in Quaternary geochronology. To determine accumulation rates of marine sediments, the most common method in use is ^{14}C-dating of planktonic foraminifers. Adult species (250 to 500 μ) of surface dwelling foraminifera, such as *Globigerinoides ruber*, *Globigerinoides sacculifer*, *Neogloboquadrina dutertrie* and *Orbulina universa* are best suited for ^{14}C-dating, which grow within the top 100 m of the seawater column. In special cases such as in near shore areas where planktonic species are scarce, calcareous benthic foraminifera species may also be used. Marine organic matter may also be used for ^{14}C-dating of sediments when calcareous fossils are totally absent. However, as will be discussed later the last two methods may need special attention for their ^{14}C-age calibration. All samples chosen for analysis are carefully scrutinized and are thoroughly cleaned from all forms of contamination which may potentially alter their ^{14}C-age. Since the amount of datable carbon from sediments are usually small—typically few tens of milligrams from a gram of sediment, accelerator mass spectrometry (AMS) method is essential for ^{14}C analysis of these samples. For accurate calibration of marine ^{14}C-dates their initial ^{14}C-ages must be well known, that depend on regional marine reservoir effect.

Concept of marine ^{14}C reservoir age and ΔR correction values

For a given oceanic region at any given time, the ^{14}C reservoir age is defined as the difference between the measured conventional ^{14}C-age of the reservoir (seawater) and that of the contemporary atmospheric CO_2 (derived from tree-rings). ^{14}C reservoir ages can be determined from ^{14}C analysis of pre-nuclear (pre-1950s) marine calcareous samples of known calendar age. Considerable spatial variability is seen in the regional marine reservoir ^{14}C-ages from the global mean value, mainly due to variations in local ocean circulation patterns and regional exchange rates of CO_2 with the atmosphere. For a given region at any given time, the difference between the regional marine ^{14}C-age and that of the modelled global surface ocean is expressed by the term ΔR, which account for regional deviations of reservoir ages from the global mean value (Stuiver and Braziunas, 1993). The regional ΔR correction values can be determined from the difference of regional ^{14}C reservoir age and that of the modelled global ocean.

Marine reservoir ^{14}C-ages exhibit considerable spatial variations due to change in ocean circulation regimes. In those oceanic regions where favourable conditions exist for mixing with deeper ocean water (with older ^{14}C-ages) through wind induced upwelling, surface marine reservoir ^{14}C-ages will be higher than the global average value. Therefore, ΔR for such regions will have a positive value. Examples of such region in the Indian Ocean are the eastern and the western Arabian Sea, where upwelling takes place through seasonal monsoon induced winds. DIC inputs from rivers that leach geologically old carbonate rocks may result in large regional reservoir ^{14}C-ages (Little, 1993). On the other hand, ^{14}C in seawater DIC are higher than the average global ocean in shallow oceanic regions or in enclosed lagoons, where mixing with ^{14}C depleted water from deeper ocean is limited. Such regions have negative ΔR values, examples of which include the Gulf of Kutch in the northeastern Arabian Sea, and the Chilika Lake in the northern Bay of Bengal. Shallow oceanic regions of the western Pacific such as the southern part of the South China Sea also have negative ΔR values, where the water depth is less than 600 m. According to the latest compilation of Global Marine Reservoir Correction Database (Reimer and Reimer, 2001), ΔR values for the global oceanic regions excluding the Southern Ocean vary from –200 year to +800 year, and majority of them fall between –50 years to +250 years. As discussed later, rapid vertical mixing off the Antarctica coast causes unusually high ΔR values for the Southern Ocean.

The Marine 04 calibration curve (Hughen *et al.,* 2004), is shown in Fig.2(a) which has been determined using the decadal tree-ring ^{14}C data and the carbon cycle model after Oescheger *et al.,* (1975). Regional ΔR correction values must be added to this curve in Fig-2(a) to obtain the regional marine ^{14}C calibration curves shown in Fig.2(b). Reconstruction of regional marine ^{14}C-age calibration curves for three hypothetical oceanic regions are shown in Fig-2(b). The Marine04 calibration curve extends back to 26,000 years BP. For calibrating older ^{14}C-dates up to 50,000 years BP one may use the calibration curve after Fairbanks *et al.,* (2005), which uses high-precision ^{14}C data of very old unaltered corals absolute dated with U-Th series isotopic method.

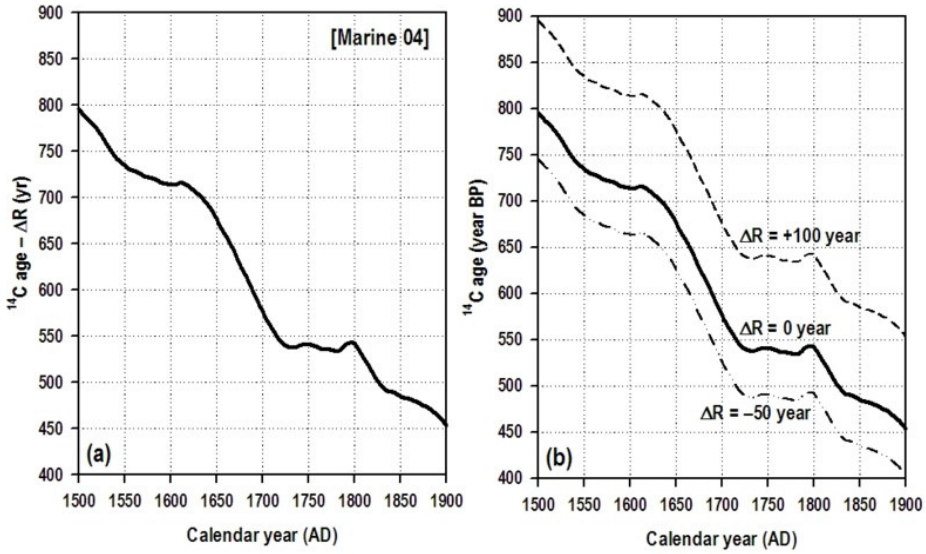

Fig.2: Illustration of the concept of marine reservoir effect and ΔR correction values. (a) The Marine04 calibration curve (Hughen *et al.,* 2004). (b) Reconstructed marine ^{14}C-ages at three hypothetical oceanic regions. Top curve: in an upwelling region for which reservoir ^{14}C-age is older than the global mean (ΔR = +100 years). Middle curve: in an oceanic area that resembles the average world ocean (ΔR = 0 year). Bottom curve: an oceanic area with lower vertical mixing with deeper waters where reservoir ^{14}C-age is younger than the global mean (ΔR = –50 years)

Knowledge of regional ΔR values is necessary for accurate calibration of ^{14}C-ages of marine samples. It is implicit in the definition of ΔR, that temporal variations of regional reservoir ages will parallel those of the global ocean, thus ΔR is assumed to be time independent for any given region (Stuiver *et al.,* 1986, 1998). The reservoir ^{14}C-ages and ΔR correction values reported from various oceanic regions are valid for the modern state of ocean circulation, since these were usually derived from samples that grown within past few hundred years or so. Since climate induced changes in ocean circulation may effect both mixing with deep water and atmosphere-ocean CO_2 exchange, regional reservoir ^{14}C-ages may respond to major shifts in climate, thus temporal variations of ΔR is inevitable. Reservoir ^{14}C-ages change at glacial-interglacial time scales, due to major shifts in ocean circulation pattern. Model simulations of past reservoir ^{14}C-ages have indicated that 30% reduction in Atlantic meridional circulation may enhance reservoir ages in high latitudes by 500 years (Franke *et al.,* 2008). If the changes in regional reservoir ^{14}C-ages are significantly different from that of the global modelled ocean, the ΔR values would also change. Thus, the assumption that ΔR values are constant for a given region is not strictly valid. Staubwassar *et al.,* (2002) and Ascough *et al.,* (2004, 2006) reported such changes indeed took place during the Holocene in the Arabian Sea and in the north Atlantic Ocean.

Determination of marine ^{14}C reservoir effect and regional ΔR values

An ideal approach to determine the ^{14}C-age of seawater is to measure directly ^{14}C in its DIC (Fonselius and Östlund, 1959). However, direct measurements of ^{14}C in oceans began too late—only after the onset of nuclear weapons testing in the early 1950's (Rubin and Suess, 1955). Therefore, nearly all the seawater samples collected for ^{14}C determinations were contaminated with bomb ^{14}C. To determine pre-nuclear surface ocean Δ^{14}C, reservoir ^{14}C-ages and ΔR correction values, one must rely on the analysis ^{14}C in marine samples of known age, which were grown or collected before 1950. Some of the commonly used methods for determination of marine ^{14}C reservoir ages and ΔR correction values are described here.

(a) Marine shells:

Measurement of ^{14}C in archived marine calcareous shells (*e.g.,* bivalves or gastropods) collected prior to the nuclear-testing era is the most common approach to determine marine ^{14}C reservoir ages or pre-nuclear levels of surface water $\Delta^{14}C$ (Stuiver *et al.,* 1986; Siani *et al.,* 2000; Dutta *et al.,* 2001). Short-lived and epifaunal (non-burrowing) mollusc species are preferred with well-documented collection dates. One can also measure ^{14}C in long-lived giant calms (*e.g., Tridacna gigas* or *Arctica islandica*), which form well-developed annual growth bands (Weidman and Jones, 1993). Shell derived marine ^{14}C reservoir ages often yield anomalous old ages due to incorporation of geologically old detrital carbonates in the shells (Dye, 1994). Several studies have indicated that ^{14}C-ages of various mollusc species differ due to difference in their habitat and diet. However, Ascough *et al.,* (2005a) concluded that any mollusc species may be suitable for the purpose if no geologically old carbonate rocks or sources of hard water are present.

(b) Corals:

Hermatypic or reef building corals form annual growth bands made of aragonite ($CaCO_3$) with $^{14}C/^{12}C$ in equilibrium with the ambient seawater DIC. Once deposited these aragonite bands do not exchange their carbonate with external source unless they are very old causing recrystallisation. In a live collected coral these bands can be precisely dated back in time by counting them just as in tree-rings. Past changes in $^{14}C/^{12}C$ ratio of the DIC of surface-oceans can be determined from ^{14}C measurements in coral growth bands. Some of the earliest ^{14}C measurements in coral skeletons were reported by Moore *et al.,* (1973), Moore and Krishnaswami (1974) and Buddemeier *et al.,* (1974). Continuous records of ^{14}C variations in surface oceans can be deciphered from long corals, extending back to several hundred years in the pre-nuclear era (Nozaki *et al.,* 1978; Druffel and Linick, 1978; Druffel, 1981; Druffel and Suess, 1983; Druffel and Griffin, 1993; Grumet *et al.,* 2002; Hua *et al.,* 2004). The major disadvantage of using corals is their restricted geographical distribution. Their habitat is confined mainly within the tropical or limited sub-tropical oceanic regions.

(c) Charcoal and marine shell pairs:

Direct determination of the atmosphere-ocean ^{14}C-age difference can be obtained from ^{14}C measurements in co-existing terrestrial charcoal and marine shell pairs collected from same stratigraphic horizon, thus capturing the oceanic and terrestrial events simultaneously (Southon *et al.,* 1990, 1992; Talma, 1990; Little, 1993; Ingram, 1998). This method has potential to determine past variations of regional reservoir ages in response to the ocean circulation changes for longer timescales. To measure past reservoir ages, Bard (1988) had suggested comparing the ^{14}C-age of a short and well-defined marker or event both on the land and in the deep-sea sediments (*e.g.,* deposition of a volcanic ash layer).

(d) Otoliths:

Otoliths are hard calcareous deposits that grow within the inner ears of teleost or bony fish, which primarily function as gravity and auditory receptors. Similar to corals, otoliths are made of aragonite and form annual growth layers. AMS ^{14}C measurements in otoliths of known age marine fishes can be used for reconstructing the ^{14}C evolution in surface water (Higham and Hogg, 1995; Kalish, 1993; Kalish *et al.,* 2000). Advantage of using fish otoliths over other methods is their large geographical range. Fish being nektonic (or free swimming), their otoliths can integrate the past ^{14}C signals over much wider oceanic region, unlike other archives as in shells or corals that record oceanic ^{14}C variations only at their growth location.

Most of the methods described above have their own merits and demerits, and are often fraught with problems. Ascough *et al.* (2005b) reviewed on various intricacies involved in determination of marine reservoir ^{14}C-ages. Reservoir ages and ΔR correction values are usually applicable for surface marine samples, but may not be valid for samples such as benthic foraminifers which live at the sediment surface. However, the same ΔR correction values may be applicable for benthic samples too, if the water depth of their occurrence is within 50 m or so as often the case for near shore samples. Reservoir ages derived from surface marine biogenic carbonates are also applicable to marine organic matter, since they derive their carbon from the same reservoir (seawater DIC). However, complications may arise if the organic matter is a mixture of terrestrial and marine

organic matters. Organic molecules of purely marine origin will register the marine reservoir effects in their ^{14}C-ages, while terrestrial organic matters may show a range of ages that can be either too old or too young. In such cases, it may be beneficial to assess the contribution of each organic matter types from geochemical (C/N wt.) or isotopic ($\delta^{13}C$) ratios, or even better to isolate individual organic compounds of purely marine origin. All reservoir ^{14}C-age estimates are long-term average, ignoring any seasonal DIC ^{14}C changes that may occur due to seasonal change in ocean circulation pattern. Most known age marine biogenic carbonate samples used for regional reservoir age determinations are usually collected from coastal locations or small islands, which are then extrapolated for use with open ocean samples. Reservoir age corrections as derived using samples from small islands found to match fairly well to that derived from nearby coastal locations, since the surface waters of the coastal ocean are normally get replenished by the open ocean water in a short time scale.

In spite of the availability of several established methods, pre-nuclear surface water ^{14}C data for many key oceanic regions are still sparse mainly due to scarcity of suitable known-age marine samples. The Indian Ocean region is an area of considerable interest from the perspective of paleoclimate and paleoceanographic studies. Unfortunately spatial data of ^{14}C reservoir ages for this region is too meagre, essential for reporting reliable ^{14}C chronologies crucial for such studies.

Studies of reservoir ^{14}C-ages and ΔR correction values for the Indian Ocean

The earliest seawater DIC ^{14}C measurements in the tropical Indian Ocean region were done during the expeditions named Monsoon (10°S, 99°E; November, 1960), Lusiad (8°N, 71°E; October, 1962) and Dodo (6°S, 55°E; September, 1964) by the Scripps Institute of Oceanography, USA (Linick, 1975). The surface ocean Δ14C values measured during these periods ranged from –38 to –24‰, for the latitude band of 24°S to 11°S during the Monsoon expedition. These results, however, could not provide pre-nuclear $\Delta^{14}C$ values for the region. These values are significantly higher than those obtained from pre-nuclear $\Delta^{14}C$ in biological archives—indicating the penetration of bomb ^{14}C even during early 1960s. More extensive studies of surface water $\Delta^{14}C$ measurements were made between 1977 and 1978 as a part of the international GEOSECS Indian Ocean expedition (Stuiver and Östlund, 1983). To calculate the bomb ^{14}C inventories from the GEOSECS ^{14}C measurements, Broecker *et al.,* (1985) assumed pre-nuclear surface $\Delta^{14}C$ values of –60 to –65‰ for the northern Indian Ocean. In a later report, Broecker *et al.,* (1995) assumed surface natural $\Delta^{14}C$ –59‰ in the equatorial Indian Ocean (GEOSECS 448), and a steadily decreasing $\Delta^{14}C$ trend was followed towards the north, assuming minimum $\Delta^{14}C$ value of –68‰ for the northern Arabian Sea (GEOSECS 416). Moore and Krishnaswami (1974) first reported measurement of ^{14}C in the growth bands of corals from the Gulf of Kutch. $\Delta^{14}C$ of coral growth bands grown during or before 1950s have been reported for corals from the Red Sea and Gulf of Aden (Cember, 1989), the Gulf of Kutch (Chakraborty, 1993) and the western Indian Ocean (Grumet *et al.,* 2002).

First systematic studies of marine ^{14}C-reservoir ages and ΔR correction values for the northern Indian Ocean were reported by Dutta *et al.,* (2001), from ^{14}C measurements in archived marine mollusc shells collected between 1930 and 1954. The ΔR correction values were calculated from the ^{14}C data of annual growth bands of corals from the Gulf of Kutch (Chakraborty, 1993; Bhushan *et al.,* 1994), and AMS ^{14}C dates of annually laminated sediments in the northeastern Arabian Sea (von Rad *et al.,* 1999). Southon *et al.,* (2002) reported ΔR correction values for several locations in the Indian Ocean and the South China Sea mainly using museum archived marine shells. Hua *et al.,* (2004) reported ΔR correction values for the Cocos (Keeling) Islands in the eastern Indian Ocean using annual coral bands.

Spatial and temporal variations of marine ^{14}C reservoir ages in the Indian Ocean

The data of marine ^{14}C reservoir ages and ΔR correction values for the Indian Ocean and South China Sea are compiled here and shown in Fig-3. The ^{14}C-reservoir ages for the open eastern Arabian Sea range from 622 to 390 years, which are in general higher when compared to the open Bay of Bengal values which range from 315 to 474 years. Reservoir ages in the shallow marine areas of the Gulf of Kutch and the Chilika Lake lagoon are 241 years and 229 years, respectively (Dutta *et al.,* 2001). One sample collected near Pondicherry in the western Bay of Bengal yield anomalous high reservoir age of 831 years, possibly due to incorporation of geological carbonate (Southon *et al.,* 2002). These two shallow marine samples and the anomalous old sample from Pondicherry were excluded for determining regional ΔR correction values of the Indian Ocean. The reservoir ages are younger in the shallow marine areas of the South China Sea. The Red Sea, the Persian Gulf, the western Arabian Sea and the western Indian Ocean near Madagascar have rather narrow range of reservoir ^{14}C-ages, mostly lying between 400 and 500 years. The eastern Indian Ocean south of Indonesia and west of Australia has reservoir ^{14}C-ages between 323 and 377 years, similar to the Bay of Bengal values.

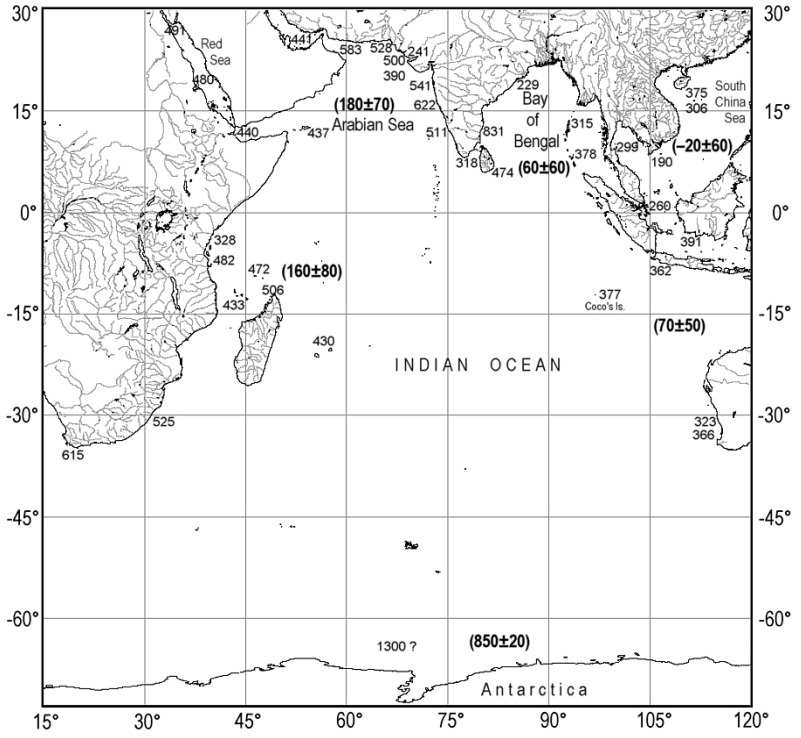

Fig. 3: Spatial variation of marine ^{14}C reservoir ages for the entire Indian Ocean obtained from Global Marine Reservoir Correction Database (Reimer and Reimer, 2001). Reservoir ^{14}C-ages (in years) reported from selected locations are shown, while regional average ΔR values (in years) are in given bold with 1-σ standard deviation. Indian Ocean reservoir ^{14}C-age data compiled from Bowman (1985a, 1985b), Cember (1989), Bhushan *et al.,* (1994), von Rad *et al.,* (1999), Dutta *et al.,* (2001), Southon *et al.,* (2002), Grumet *et al.,* (2002), and Hua *et al.,* (2004). Values for the southern Indian Ocean south of 60°S (in parentheses) have been estimated from Berkman and Forman (1996).

The observed pattern of ^{14}C reservoir ages in the Indian Ocean can be explained in terms of regional variation of circulation patterns within the thermocline. In the northeastern Arabian Sea vertical mixing is favoured by (i) seasonal upwelling during southwest monsoon and (ii) convective processes associated with winter cooling (Madhupratap *et al.,* 1996). The average reservoir ^{14}C-ages for the Arabian Sea is older than that of the modelled world ocean (mean ΔR ~ 180 years), due to upwelling induced mixing with deeper ^{14}C-depleted water derived from Antarctic Bottom Water from the south. The Bay of Bengal, which receives large amount of fresh water from several major rivers

(Milliman and Mead, 1983) has steep gradients of the isopycnal (equal density) surfaces within the top 200 m. Steep isopycnal gradient in the Bay of Bengal may greatly impede the vertical mixing rate, retarding the advection of deeper ^{14}C depleted water. This resulted in relatively younger reservoir ^{14}C-ages (ΔR ~ 60 years) for the Bay of Bengal compared to the Arabian Sea. Input of riverine DIC depleted in ^{14}C may tend to counteract the effect of reduced mixing (Little, 1993), due to the hard water effect. Higher reservoir ages in the Arabian Sea compared to the Bay of Bengal shows that greater vertical mixing is the dominant process, which determines the observed pattern of ^{14}C reservoir ages in the northern Indian Ocean. Interestingly, the modelled pre-nuclear surface ocean ^{14}C distribution by Toggweiler *et al.,* (1989) and Guilderson *et al.,* (2000) predicts younger ^{14}C-ages in the Arabian Sea than in the Bay of Bengal. This is in contrary to the pattern observed from the ^{14}C data of pre-nuclear marine carbonates.

These ΔR values would be useful in calibrating the ^{14}C-ages of marine microfossils for dating marine sediments and also for dating coastal calcareous archeological samples from the Indian Ocean region. The regional average ΔR correction values given in Fig.3 have taken into account all valid reservoir ^{14}C-age data, and are only indicative of the large scale pattern. In order to calibrate a given marine ^{14}C date, ΔR data from the nearest locations must be chosen. Pooled mean (error weighted) ΔR correction values from these locations must be used for the calibration.

Significant climate induced changes in the northern Indian Ocean circulation took place during the glacial and interglacial periods (Duplessy, 1982). Since the marine ^{14}C reservoir age of the northern Indian Ocean, particularly in the Arabian Sea is controlled by summer monsoon upwelling, winter monsoon convection and the reservoir age of the Arabian Sea thermocline water which is derived from Antarctic Bottom Water (Staubwasser *et al.,* 2002), variations in any of these factors due to global climate shifts can potentially alter the regional reservoir ^{14}C-ages. Staubwasser *et al.,* (2002) reported that the surface Arabian Sea reservoir ages were more than 1000 years during the deglaciation, and they varied between 780 and 1120 years during the early Holocene.

Marine ^{14}C reservoir ages of the southern Indian Ocean off Antarctica

The southern Indian Ocean is a region for which knowledge of pre-nuclear surface water ^{14}C is too meagre. The earliest seawater ^{14}C measurements in the southern Indian Ocean region were compiled by Delibrius *et al.,* (1980). Reports of marine reservoir ^{14}C-ages close to Antarctica range from 932 BP to 1632 BP, corresponding to mean ΔR of 849±13 year (n=14). Till date, no systematic study on marine reservoir ^{14}C-ages had been done specifically for the Southern Indian Ocean near Antarctica. This oceanic region is an area of considerable interest from the perspective of paleoclimate studies from multi-proxy geochemical analyses of marine sediments. Such studies must rely on firm ^{14}C-chronology, for which accurate knowledge on reservoir ^{14}C-age is essential. Berkman and Forman (1996) recommended use of reservoir ^{14}C-ages of 1300±100 year for the Southern Ocean region. However, it is unlikely that reservoir age of the Southern Indian Ocean off Antarctica coast are significantly different than in other areas of the Southern Ocean, due to fast zonal mixing by the circum-polar currents.

Marine ^{14}C Suess effect in the northern Indian Ocean and the South China Sea

Following the beginning of industrial era during the late 19th century and before the onset of large scale atmospheric tests in the late 1950's, ^{14}C in the atmospheric CO_2 steadily decreased by about –25‰ through dilution by ^{14}C depleted fossil fuel CO_2. Invasion of fossil fuel CO_2 to the oceans caused significant depletion of surface ocean $\Delta^{14}C$ values between 1900 and early 1950s, an phenomena known as marine Suess effect (Druffel, 1981; Druffel and Suess, 1983; Toggweiler *et al.,*

1989). The observed depletion was typically few permil per decade, but variable among different oceanic areas (Druffel and Griffin, 1993). The $\Delta^{14}C$ values of the samples reported from the northern Indian Ocean and the South China Sea are analyzed in this study, which also show a decreasing trend between AD 1900 and 1955 (Fig.4). The results show the magnitude of marine ^{14}C Suess effect of –3.0±1.8‰ per decade for the Arabian Sea, –2.1±0.5‰ per decade for the Bay of Bengal, and –2.0±1.3‰ per decade for the South China Sea.

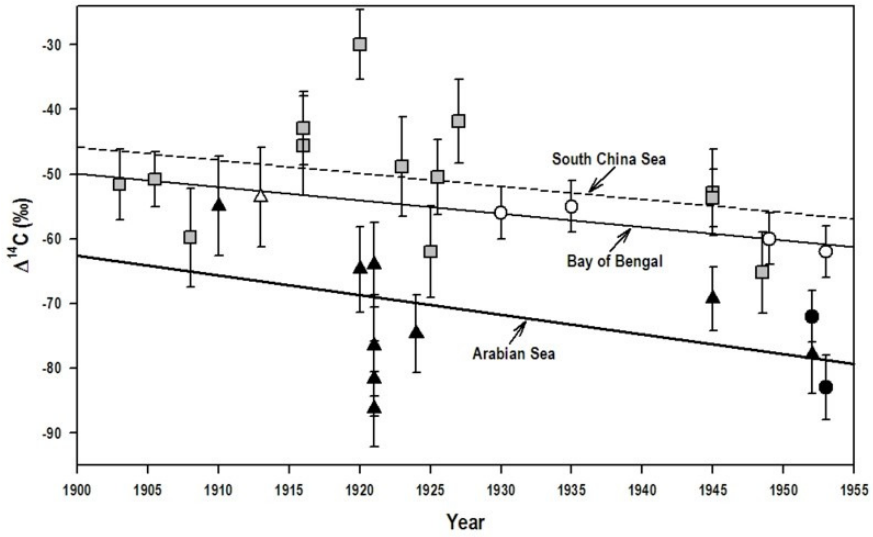

Fig. 4: Suess effect in the Northern Indian Ocean and the South China Sea. Data from Dutta *et al.,* (2001) plotted as circles and from Southon *et al.,* (2002) plotted as triangles and squares. Symbol fills: white – Bay of Bengal, black – Arabian Sea; and grey – South China Sea. Straight lines indicate linear fit to the $\Delta^{14}C$ data between 1900 and 1955.

Even though the uncertainties in individual reservoir age estimates are of the order of ±5‰, several samples were considered to evaluate the Suess effect for a large oceanic area. Thus, the small values of the Suess effect (2 to 3±1‰) reported in this study are statistically significant. Magnitude of Suess effect for various ocean basins depends mainly on the penetration of anthropogenic CO_2 to the ocean. The present analysis shows similar magnitude of Suess effect for the Arabian Sea and the Bay of Bengal, as indicated by the parallel trends of the linear fits, though the vertical scales of these lines are offset depending on their reservoir ages.

Further measurements from the Indian Ocean region are needed to assess and reduce the uncertainty in marine ^{14}C Suess effect. This can be better understood from ^{14}C analysis in long coral cores dating back to the pre-industrial era. Druffel (1981) reported post-industrial and pre-nuclear $\Delta^{14}C$ recorded in corals from the Urvina Bay, Galapagos Island, in the eastern equatorial Pacific Ocean, which also show similar magnitude of Suess effect of about – 6‰ between 1930 and 1953.

Conclusions

^{14}C is commonly used for dating of marine sediments that are up to 50,000 years old. Initial ^{14}C-ages depend on regional marine ^{14}C-ages of surface oceans and any variations thereof must be known to accurately determine ^{14}C-dates of marine samples. Information on natural or pre-bomb ^{14}C in surface oceans is also important for studies of oceanic carbon cycle that use anthropogenic or bomb-^{14}C as a tracer. Reservoir ^{14}C-ages has been reported from many places in the Indian Ocean analyzing known age marine biogenic carbonates, but data on its spatial and temporal variability is still not adequate. The $\Delta^{14}C$ values between 1900 and 1955 from the Indian Ocean and the South

China Sea show a decreasing trend, indicating marine ^{14}C Suess effect in the Bay of Bengal. The average magnitude of this Suess effect is –3±2‰ per decade for the Arabian Sea and –2±1‰ per decade for the Bay of Bengal and the South China Sea.

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