

## Age of Saurashtra miliolites by U-Th decay series methods : possible implications to their origin

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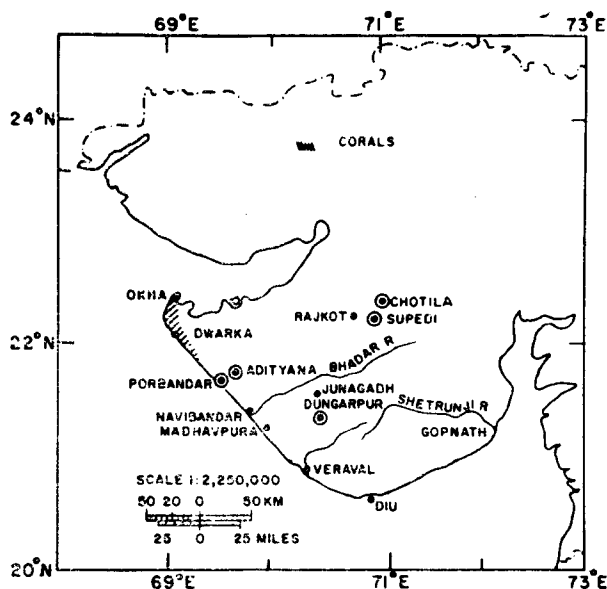
MS received 25 June 1979; revised 25 January 1980

**Abstract.** The miliolite deposits of Saurashtra have been dated by  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$  and  $^{14}\text{C}$  methods. Concordant ages of  $\sim 10^5$  years using the U decay series isotopes are obtained which agree with the ages of the coral reefs of Okha-Dwaraka coast suggesting a contemporaneous origin for both. The lower  $^{14}\text{C}$  ages ( $\leq 40,000$  years) may be due to a recent influx of seawater or ground water. Quartz and clay minerals together constitute only  $\leq 10\%$  by weight, as such the aeolian characteristics of quartz grains may not be relevant to the origin of the miliolites.

**Keywords.** Miliolites; Saurashtra coast; U ages; carbon dating.

### 1. Introduction

Saurashtra in Gujarat is one of the regions where there are corals on the coasts as well as calcium carbonate deposits known as miliolites extending over 100 km inland and upto an elevation of  $\sim 300$  m at Chotila (figure 1). These predominantly calcareous deposits are made up of tests of various littoral forms of foraminifera (mainly Rotalid and Miliolid). Several of these have been identified (Mohan and Bhatt 1968; Kameswara Rao *et al* unpublished results). The coastal deposits are of marine origin and all the previous investigators of this region have agreed on this (Marathe *et al* 1977). However the origin of the inland deposits (figure 1) is very much debated. Two hypotheses exist in this regard: (i) marine and (ii) aeolian. Krishnan (1968) and Lele (1973) argued that these deposits were formed under marine conditions. Krishnan (1968) stated that the presence of miliolite on the top of Chotila hill is a proof for a high sea level stand during that period. The other group consisting of Biswas (1971), Wadia (1975) and more recently Agrawal and Roy (1977) and Agrawal *et al* (1978) favour an aeolian origin for the inland deposits. In most of these arguments regional tectonics was either not taken into account seriously or the region was taken to be tectonically stable (Gupta 1973). The ages of the samples were determined only by  $^{14}\text{C}$  method although the miliolite is not an ideal material for radiocarbon dating (Agrawal *et al* 1978). U-decay series nuclides are by far the most commonly employed for



**Figure 1.** Map of Saurashtra showing the locations of samples (circled dots). Sample M13 (from Tukda) is near Navibandar. The locations of corals are also indicated (slanted lines).

dating corals and other carbonate material (Ku 1976). Hence it was considered worthwhile to try to date these deposits using the U–Th series nuclides which may also provide clues in understanding their origin. With this view in mind attempts have been made to date the miliolites from a few locations (figure 1) using Th and U isotopes. Some of the samples are also measured for  $^{14}\text{C}$  to have a direct comparison.

## 2. Experimental techniques and results

During a field trip conducted in May 1978, several well-preserved samples of miliolite were collected from several locations (figure 1).

Calcium carbonate was determined by dissolution in dilute HCl and the residue which was  $\leq 10\%$  was utilised for mineral identification (table 1). The original material (powder) was also subjected to x-ray diffraction for estimating the calcite and aragonite contents of the carbonate fraction (table 1) using the method of Lowenstam (1954).

### 2.1. Sample preparation

For U–Th analysis clay material was separated from the carbonate as far as possible. Briefly, the procedure is described below: The samples were coarsely ground and put in an ultrasonic vibrator in distilled water for about 30 min. The material was then sieved through a millimeter sieve and the fraction remaining on the sieve was crushed and washed in distilled water and sieved again. The sieved

Table 1. Mineralogy of the miliolite samples

Sample	Location*	CaCO <sub>3</sub> (%)			Quartz + clay minerals (%)
		Calcite	Aragonite	Total	
M6	Porbandar			90.3	9.7
M7	Adityana	81.7	13.9	95.6	4.4
M8	Adityana	94.1	4.2	98.3	1.7
M13	Tukda	77.6	14.0	91.6	8.4
M14	Dungarpur	68.3	21.7	90.0	10.0

\* See also figure 1.

fraction was passed through a 100–200 mesh nylon cloth. The fine fraction mostly consisting of clay material was discarded. The coarse fraction retained on the nylon cloth was again dispersed in distilled water containing  $\sim 1\%$  H<sub>2</sub>O<sub>2</sub> overnight and washed. The carbonate material after washing was dried at 110° C to constant weight.

## 2.2. Chemistry

A known weight of the cleaned material (of the order of 10–15 g) was acidified with 1.5M HCl (AR) in a clean beaker until CO<sub>2</sub> was completely evolved. The solution after centrifugation along with the washings of the residue was used for U, Th and Pa measurements. Yield tracers <sup>232</sup>U, <sup>234</sup>Th and <sup>233</sup>Pa were added to the sample solution after which the chemistry was done using procedures published earlier (Amin 1970; Bhat *et al* 1969; Krishnaswami and Sarin 1976). The Th and U fractions, which were separated and electroplated on platinum planchets, were assayed for their alpha activities using a surface barrier detector coupled to a Nuclear Data 512 Channel pulse height analyser. In the case of two samples, M2 and M13 separate samples of  $\sim 15$  g weight were utilised for <sup>14</sup>C studies. The CO<sub>2</sub> gas evolved on HCl addition to the samples was converted to methane and beta assayed for <sup>14</sup>C activity (Agrawal *et al* 1965).

In this preliminary study five samples were analysed for U, two for Th and <sup>14</sup>C and one for Pa, the results of the U measurements are given in table 2, and those of the Th, Pa and <sup>14</sup>C measurements in table 3.

## 3. Calculation of ages

Essentially three independent methods based on isotope pairs have been employed in addition to the <sup>14</sup>C technique

### 3.1 U isotope method

This method is based on the decay of excess <sup>234</sup>U in the sample. The activity ratio of <sup>234</sup>U/<sup>238</sup>U is determined in the sample and compared with that of the sea water

Table 2. U isotopes in some miliolites.

Sample	U (ppm)	$^{234}\text{U}/^{238}\text{U}^*$ (activity ratio)
M6	$0.71 \pm 0.02$	$1.105 \pm 0.025$
M7	$2.56 \pm 0.04$	$1.088 \pm 0.015$
M8	$1.47 \pm 0.03$	$1.102 \pm 0.022$
M13	$3.89 \pm 0.10$	$1.086 \pm 0.020$
M14	$1.43 \pm 0.04$	$1.108 \pm 0.017$

Mean of all samples  $1.09 \pm 0.02$

Mean U-U age of the miliolites =  $(157 \pm 70) \times 10^3$  years.

\* Corals collected from the Okha-Dwaraka coast also yield a  $^{234}\text{U}/^{238}\text{U}$  activity ratio of  $1.10 \pm 0.01$ .

Table 3. Th, Pa and  $^{14}\text{C}$  ages of some miliolites.

Sample	$^{230}\text{Th}/^{238}\text{U}$ (AR)	$^{231}\text{Pa}/^{235}\text{U}$ (AR)	Ages ( $10^3$ years)*		$^{14}\text{C}$
			Th/U	Pa/U	
M2	..	..	..	..	$\geq 40$
M8	$0.89 \pm 0.03$	$0.94 \pm 0.06$	$177^{+20}_{-15}$	100	18
M13	..	..	..	..	16
M14	$0.65 \pm 0.05$	..	$95 \pm 12$	..	18-20

AR = activity ratio.

\* Th/U and Pa/U ages are calculated using equations (2) and (3) respectively.  $^{14}\text{C}$  ages of M8 and M14 are from Agrawal *et al* (1978). M2 and M13 are measured in the present work.

which is 1.14 (Koide and Goldberg 1965; Krishnaswami *et al* 1970). The  $^{234}\text{U}$  excess (14%) will decay with the half life of  $2.48 \times 10^5$  years. Using the equation

$$[^{234}\text{U}/^{238}\text{U}] = [^{234}\text{U}/^{238}\text{U}]_0 \exp(-\lambda_{234} t), \quad (1)$$

where  $[^{234}\text{U}/^{238}\text{U}]$  is the activity ratio, 234 denotes  $^{234}\text{U}$ ,  $\lambda$  its decay constant and  $t$  is the age of the sample.

3.2.  $^{230}\text{Th}/^{238}\text{U}$  method

This method is based on the growth  $^{230}\text{Th}$  with time in a sample containing U but not Th. Reference is made to Broecker (1963) for a detailed discussion of this technique. Using the equation

$$\left[ \frac{^{230}\text{Th}}{^{238}\text{U}} \right] = \left[ 1 - \exp(-\lambda_{\text{Th}} t) + \frac{^{234}\text{U initial}-^{238}\text{U}}{^{238}\text{U}} \frac{\lambda_{\text{Th}}}{\lambda_{\text{Th}} - \lambda_{234}} \right. \\ \left. \times \exp(-\lambda_{234} t) - \exp(-\lambda_{\text{Th}} t) \right], \quad (2)$$

where  $\lambda$  is the decay constant Th and 234 denotes  $^{234}\text{Th}$  and  $^{234}\text{U}$  respectively and  $t$  is the age.

3.3.  $^{231}\text{Pa}/^{235}\text{U}$  method

Similar to the  $^{230}\text{Th}/^{238}\text{U}$ ,  $^{231}\text{Pa}$  grows into equilibrium with parent  $^{235}\text{U}$  with time.

$$\left[ \frac{^{231}\text{Pa}}{^{235}\text{U}} \right] = [1 - \exp(-\lambda_{231} t)], \quad (3)$$

where  $\lambda_{231}$  denotes  $^{231}\text{Pa}$  decay constant. In all the equations (1, 2 and 3) the measurements indicate activities in units of disintegration per minute (dpm)/g sample.

The calculated ages are also given in tables 2 and 3. It should be pointed out here that a small but definite amount of  $^{232}\text{Th}$  was found in the miliolites (which is due to the presence of clays) in contrast to the ideal case where it should be absent (Tatsumoto and Goldberg 1959). The residues left after HCl digestion were also analysed for Th isotopes and appropriate corrections were made using the  $^{232}\text{Th}$  and  $^{230}\text{Th}$  concentrations of the residue and the  $^{232}\text{Th}$  content of the leachate. The corrected ages are reported in table 2.

## 4. Discussion

The most interesting feature of the data is the  $^{234}\text{U}/^{238}\text{U}$  activity ratios. All the five samples, which are from both coastal and inland locations, have almost identical  $^{234}\text{U}/^{238}\text{U}$  activity ratio which yields an average age of 157,000 years (table 2). The uranium absolute concentrations of the miliolites vary between 0.7-3.9 dpm/g (table 2). Sample M6 which was collected from the shore waters of Porbandar has 0.7 dpm U/g which is most probably due to continuous leaching of U by sea water. All other samples analysed vary between 1.4-3.9 dpm/g. The calcite aragonite contents were measured with a view to see if high aragonite indicate high uranium. No apparent correlation is noticeable from the limited data (table 1). Analyses of more samples from different regions is underway. The  $^{230}\text{Th}/^{238}\text{U}$  ages for the two samples M8 and M14 are found to be  $177 \times 10^3$  and  $95 \times 10^3$  years respectively (table 3).  $^{231}\text{Pa}/^{235}\text{U}$  method yielded  $\geq 100,000$  years for M8 which also falls in the age bracket obtained by  $^{230}\text{Th}$  and  $^{234}\text{U}$  methods. It thus appears that the samples analysed in the present study are in

the age bracket  $(1-1.7) \times 10^5$  years. It is interesting to note that the ages of most of the corals from Saurashtra determined by the same techniques also fall in this range (Broecker *et al* unpublished results).

The carbon-14 ages for some samples are available from literature (Agrawal *et al* 1978). The two samples M2 and M13 which were dated in the present study by  $^{14}\text{C}$  yield  $\geq 40,000$  and 16,000 years respectively. In the case of samples M8 and M14  $^{14}\text{C}$  data are available (Agrawal *et al* 1978) and these are 18,000 years (table 3) which are about 5-10 times lower than the U decay series ages (table 3). In view of the large amount of man-made  $^{14}\text{C}$  still present especially in surface ocean waters and precipitation the young ages may be due to this source. Rainwater does not contain any U and Th to affect the miliolites. However sea water contamination in large amounts can change the  $^{234}\text{U}/^{238}\text{U}$  ratio to 1.14. Ground waters, with  $^{234}\text{U}/^{238}\text{U} > 1.14$ , can also contaminate the sub-surface deposits in which case a further increase in the  $^{234}\text{U}/^{238}\text{U}$  over 1.14 will be expected. Such contaminations from surface ocean waters and ground waters tend to give younger ages. The real ages in such a case will be older than the reported values (table 2). Th and Pa are not present in natural waters to any appreciable extent to contaminate the deposits.

#### 4.1. Tectonic stability

Gupta (1973) discussed in some detail the arguments advanced both for and against the stability of the Saurashtra coast. However, from his own work on the dating of corals, he concluded that tectonics might not have been serious since most of the sea-level stands he obtained agreed well with world-wide sea-level changes. More recently Sood *et al* (1977, 1978) carried out geomorphological studies of the Saurashtra region using Landsat imagery and aerial photography and concluded that this region was subjected to tectonic uplifts during the quaternary. They pointed out that the Saurashtra region had a complex history involving both tectonic activity and eustatism. However, our study shows that corals which grow in shallow waters and miliolite deposits, both coastal and inland, were formed at about the same time  $(1-1.7) \times 10^5$  years before present. It is still not clear whether the sea level was high enough to submerge the Chotila hill or whether there was tectonic uplift after miliolite formation.

Most of the earlier work supporting aeolian origin for the inland miliolite deposits was based on the presentday geomorphological features of the general area. The most recent support for this hypothesis was provided by the work of Agrawal *et al* (1977, 1978) which was based on the structural features of quartz grains separated from the miliolite deposits. Our results in table 1 clearly show that calcium carbonate is the major component ( $\geq 90\%$ ) and that quartz and clay minerals together form  $\leq 10\%$  of the total. Quartz is present in such low concentrations even in deep ocean sediments (Goldberg and Griffin 1964) and it was unequivocally shown by Delany *et al* (1967) that most of the ocean quartz is aeolian in origin. There is no doubt on the origin of quartz in the miliolite deposits. It is aeolian but being a minor component it cannot be used to infer the origin of the major component, i.e., calcium carbonate.

## 5. Conclusions

This work obviously has not answered many of the pending questions, but it has certainly brought to light two observations:

- (i) that miliolites and corals from Saurashtra were formed around the same period  $(1-1.7) \times 10^5$  years before present.
- (ii) that the minor constituents of the deposit like quartz, which display aeolian features, may not have anything to do with the origin of the deposit itself.

Further detailed work on the geomorphology, geochemistry and geochronology on these complex deposits should provide better clues to their origin and their bearing on palaeoclimates.

## Acknowledgements

This work was supported in part by a PL-480 grant. We thank Dr S K Gupta for help in  $^{14}\text{C}$  dating and Dr S Krishnaswami for discussions.

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