RADIOCARBON ACTIVITY MEASUREMENTS OF OOLITIC SEDIMENTS FROM THE PERSIAN GULF

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ABSTRACT. Radiocarbon activity of successive parts of Pleistocene and Holocene ooids and mollusk shells from the Persian Gulf, Kuwait, was measured. The inner part of the ooids showed the lowest activity and the cement between grains the highest. Radiocarbon activities correspond to the general stratigraphy and to the position of the sediments. Radiocarbon ages of Pleistocene sediments seem to be very low due to recrystallization of aragonite. Higher radiocarbon activity of cement indicates that atmospheric carbon dioxide was involved in the subaerial diagenetic process. The radiocarbon age of well-preserved mollusk shells seems to be lower than their allegedly Pleistocene geologic age.

Oolitic complex

Sediments from the Persian Gulf were submitted to the Radiocarbon Dating Laboratory of Charles University by the Geological Survey, Prague. The samples are oolitic limestone and sandstone of Pleistocene and Holocene ages, and shells of gastropods and lamellibranchs. The ooids of carbonate oolitic rocks are formed by successive concentric layers of calcium carbonate commonly around a nucleus (such as a shell fragment, an algal pellet or a quartz-sand grain) in shallow wave-agitated water (American Geological Institute, 1972).

The studied oolitic samples are from the coastal area in southeast Kuwait, studied by F Pícha and A A M Saleh (Pícha and Saleh, 1977; Pícha, 1978) from whose papers the geological information has been compiled (fig 1).

The oolitic sediments form ridges generally parallel to the coast, representing ancient and recent beaches, barriers and coastal dunes separating the open sea from coastal lagoons and sabkhas. The oldest ridges are found inland, while the younger generations are located progressively closer to the present shoreline. As established by drillings and field observations, the total thickness of Quaternary sediments rarely exceeds 10m; the ridges themselves stand 5 to 15m above the terrain level. The Quaternary sediments are underlain by Tertiary clastic deposits.

Five lithostratigraphic units were distinguished within the investigated complex (from top to bottom):

1) Holocene oolitic sediments on beaches, tidal flats, khors, and coastal dunes. Except for beachrock, all Holocene sediments are unconsolidated.

2) Younger oolitic limestones (Pleistocene) forming ridges along the present coastline. They consist of ooids with highly lustrous hard surfaces little affected by subaerial processes. They are almost completely aragonitic and display the least lithification.

3) Older oolitic limestones (Pleistocene) mostly eolian, forming cross-stratified parallel ridges. They are composed almost entirely of chalky white ooids with only a small admixture of skeletal fragments, pellets, and quartz grains, subaerially cemented by granular sparry

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calcite. The oolites have lost their original luster due to partial dissolution and recrystallization of the cortex under atmospheric conditions.

4) Quartz-oolitic sandstones (Pleistocene) forming a chain of hills and ridges rising to 15m above the average terrain surface. The ridges consist of several sets of cross-stratified marine and eolian sandstones.

5) Oolitic-quartzose sandstones (Pleistocene) exposed along a coastal cliff and found also by drilling at the base of the oolitic complex. The uppermost part is often marked by a fossiliferous horizon, \leq 50cm thick, with abundant skeletal debris dominated by gastropod shells.

Pícha estimates a late Pleistocene age for both the younger and older oolitic limestones, taking into account the superposition of oolitic ridges and comparing their diagenesis with schemes established by Land, Mackenzie, and Gould (1967) in Bermuda, or Gavish and Friedman (1969) in Israel. They can be compared with eolian calcarenites described by Evans (1973) from the Trucial Coast. According to Pícha and Saleh (1977), the heavy mineral assemblages from the oolitic complex show many similarities to those of the Dibdibba Formation of northern Kuwait, and the oolitic-quartzose sandstones of southern Kuwait are contemporaneous facies deposited during a pluvial stage of the Pleistocene.

Eustatic fluctuations of sea level are well documented by the presence of three generations of coastal ridges. There is evidence of



Fig 1. Localities mentioned in the text.

post-Pliocene tectonic movements. The Quaternary tectonics played an important role both in the physiographic and sedimentary development of the area (Pícha, 1978).

The generations of oolitic coastal ridges underwent subaerial diagenetic alterations, the intensity of which gradually increases with age. Diagenesis and recrystallization affected radiocarbon dating of the oolitic sediments.

Methods of processing and measurements of samples

All carbonate samples were converted to CO_2 by acidifying with phosphoric acid. After purification and drying, the CO_2 was placed in a proportional counter with a volume of 727ml under a pressure of 0.3 megapascals. Measurement took 24 hours. ¹⁴C activity of the samples was related to 0.95 activity of NBS oxalic acid.

The results of the measurements appear in table 1 as ¹⁴C activity as well as apparent ¹⁴C age.

The samples of analyzed oolitic sediments consisted of spherical and ovate ooids partly cemented by calcium carbonate. Grain size of the ooids is between 0.1 and 0.5mm, with most of the grains being about 0.25mm in diameter.

Because diagenetic processes affect radiocarbon ages, potential redeposition and mixing of the ooids due to water motion and eolian activity had to be considered. Thus, after the first measurements (table 1, nos. 70, 71, and 73), the calcium-carbonate cement of the remaining oolite samples was separated mechanically and successively; the inner part of the ooids and the cement were measured separately.

Samples of the fossiliferous horizon consisted of shells of *Conus* sp, *Chione* sp, and *Spondylus* sp. Well-preserved specimens of shells were selected. Some of the shells were corroded by boring sponges, probably *Cliona* sp. The surface of shells was mostly aragonitic. To minimize the potential influence of calcite, the samples were dissolved in phosphoric acid to about half their original mass and washed; only the inner part of the shells was converted by renewed acidification to CO₂.

RESULTS

Measurement of ¹⁴C activity of oolites showed lower activity of the inner part of the ooids (table 1, nos. 109 and 110) than that of whole ooids (nos. 97 and 99). On the contrary, the cement showed higher activity (no. 98) than the respective ooids. Samples of the whole oolite including cement showed higher activity in comparison to separated ooids of respective stratigraphic positions (nos. 71 and 72). The ¹⁴C age of the quartz-oolitic sandstone (no. 73) agreed with its Pleistocene geologic age.

Shells of the fossiliferous horizon were collected from two locations. In considering the origin of the fossiliferous horizon, which was discontinuously distributed over a large area, as well as the fact that the samples came from two locations, results of the four measurements agree quite well. They do not, however, agree with ¹⁴C measurements of the

Sample	Measure- ment	Locality	¹⁴ C activity as % of modern standard	Apparent ¹⁴ C age	8 ¹³ C %	Remarks
Shells of living lamellihranchs	74	Al-Khiran	105.07 ± 1.85	modern	+ 1.0	
Recent oolitic sand	70	Al-Khiran	95.41 ± 1.95	380 ± 160	-	ooids including cement
Younger oolitic limestone	11	Al-Khiran	90.67 ± 2.01	790 ± 160		ooids including cement
<i>"</i>	183		91.36 ± 1.19	730 ± 95		inner part of ooids
	*66	:	82.28 ± 1.55	1570 ± 120	+ 4.8	ooids; cement was separated
	109*	:	78.01 ± 1.58	1990 ± 130		inner part of ooids; cement was separated
**		:	83.5 ± 0.9	1440 ± 90	+4.8	measured by M A Geyh
**		:		980 ± 80		measured by Teledyne
		:		2102 ± 105		
Older oolitic limestone	72	coastal cliff	79.52 ± 2.09	1840 ± 170		ooids including cement
"	97*		60.58 ± 1.80	4030 ± 140		ooids; cement was separated
**	110*		55.37 ± 1.77	4750 ± 140		inner part of ooids; cement was separated
**	8 8*	:	68.22 ± 1.64	3070 ± 130	+4.0	separated cement
		, :		3290 ± 95		measured by Teledyne
	186	Al-Khiran	51.61 ± 1.58	5310 ± 130		ooids including cement
**			55.4 ± 0.9	4750 ± 125	+5.0	measured by M A Geyh
				4820 ± 100		measured by Teledyne
Ouartz-oolitic sandstone	73	Al-Khiran	5.81 ± 15.24	$22,850 \pm 1220$		ooids
Shells of fossiliferous horizon	137	Al-Khiran	69.92 ± 1.32	2870 ± 110	+2.9	inner part of shells
"	182	:	78.08 ± 1.28	1990 ± 105	+2.5	, i,
	138	Mena Saud	69.43 ± 1.32	2930 ± 105	+4.1	2
		quarry				
:	181		64.49 ± 1.41	3520 ± 115	+2.5	

 TABLE 1

 Radiocarbon activity measurements of onlitic sediments from the Persian Gulf

* Nos. 99 and 109, and 97, 110, and 98 relate to two respective samples.

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oolitic sediments, because from a stratigraphic point of view they should be Pleistocene in age as well as related to the oldest member of the sedimentary sequence (the oolitic quartz sandstone).

Shells of the living lamellibranchs showed evidence of bomb-effect.

DISCUSSION

Recent oolitic sand (no. 70) demonstrated ¹⁴C activity and apparent ¹⁴C age that reflect its origin and agree with the well-known fact that modern sea water, carbonate sediments, and shells show an apparent age of several hundred years (Broecker and others, 1960; Rafter, 1961; Olsson and Blake, 1962; Olsson and Eriksson, 1965; Olsson, 1973; Mangerud and Gulliksen, 1975). In addition, recent oolites may contain fragments of older reworked material (eg, fragments of shells) as nuclei. Oolites (recent, as well as earlier ones) also may contain redeposited older ooids, as demonstrated by Martin and Ginsburg (1965) at the Great Bahama Bank, so that ¹⁴C-age determination of the entire sample indicates only its average age. At any rate, the ¹⁴C age of the recent oolitic sand agrees with expectations.

Both younger and older oolitic limestones, however, revealed a very low ¹⁴C age which disagrees with their alleged Pleistocene stratigraphic age. The ¹⁴C age of the quartz-oolitic sandstone proves its Pleistocene geologic age.

The young ¹⁴C age of the oolitic sediments is evidently due to recrystallization of the aragonite that was dissolved by water infiltrating from the surface and precipitated to calcite. Since dissolution was connected with admixing of CO_2 of atmospheric origin, the precipitated calcite was enriched with radiocarbon, resulting in a younger ¹⁴C age. Dissolution and recrystallization seem to have been subaerial, as the surface of the earlier ooids was attacked by corrosion.

Pícha and Saleh (1977) suggested that the consolidation as well as recrystallization of oolites increase with the increasing age of the sediments. Thus, ¹⁴C activity of the oldest sediments became higher resulting in a greater shift in ¹⁴C age. Unfortunately, there is no organic carbon available from the sediments for a correction.

Apparent ¹⁴C age of the shells of the fossiliferous horizon indicates a Holocene origin for this layer, which is in sharp contradiction to its stratigraphic position within the lower layers of the Pleistocene. Despite the fact that most of the shells were aragonitic and well-preserved, recrystallization in the form of calcite and corrosion by organisms may have shifted the ¹⁴C activity and ages. As proven by Olsson, Göksu, and Stenberg (1968), atmospheric CO₂ can penetrate into a shell if exposed to the air for a long time. This may be the case for the shells of the fossiliferous horizon, the outcrops of which are exposed to the atmosphere. ¹³C values for the shells are very high compared to those given, eg, by Olsson (1973) from the Ivory coast, or by Mangerud and Gulliksen (1975) from Arctic waters.

Recrystallization of aragonite and shifting of the ¹⁴C age, however, may not be the main reason for the contradiction of ¹⁴C and geologic ages

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of the fossiliferous horizon. This is suggested by comparing these ages with those of the oolitic sediments. From this point of view, additional questions arise about the reliability of ¹⁴C, as well as geologic ages of the oolitic complex.

Geologic dating of oolites is based on stratigraphic position, geomorphologic features, stage of diagenesis and recrystallization, and relation to similar sedimentary sequences and lithic alterations observed in the Persian Gulf, on the Mediterranean coast in Israel, and in Bermuda (Pícha, 1978). Although paleontologic evidence of the Pleistocene age of the oolitic complex does not exist, support for this interpretation comes from the analogy of its mineralogic composition with the Pleistocene Dibdibba Formation in northern Kuwait (Pícha and Saleh, 1977). The stratigraphic succession of oolitic sediments and their relative ages agree with the succession of their 14C ages. The only stratigraphic unit that deviates from this sequence is the fossiliferous horizon. Its 14C ages should be the oldest among all dated samples. Because of the lack of organic carbon, the isotopic effect of recrystallization and of other exogenic processes in carbonate sediments cannot be determined, and the ¹⁴C ages cannot be corrected. The ¹⁴C age of the fossiliferous horizon, however, could enable us to estimate, to a certain degree, reliability of the ¹⁴C ages of the oolites, if the geologic ages were reliable. If contamination by allochthonous carbon from the surface considerably affected the carbonates, and if the stratigraphic position of the fossiliferous horizon is correct, then the shift of the 14C ages should be of a similar order of magnitude in the quartz-oolitic sandstone and in the fossiliferous horizon below it. However, this is not the case. The ¹⁴C age of the quartz-oolitic sandstone is much older although it should be younger. The fact that its sample was measured with cement enriched in ¹⁴C should further increase the activity and decrease the age.

Thus, despite shifting ¹⁴C ages due to recrystallization of aragonite, it is the unclear geologic position of the fossiliferous horizon that causes the contradiction of the ¹⁴C and geologic ages.

CONCLUSION

Cement of the diagenetically consolidated oolites showed a ${}^{14}C$ activity higher than that of the ooids. This indicates a secondary origin of the cement. It also suggests that the cement originated by dissolution of the carbonates at the surface by atmospheric water enriched in CO₂ of atmospheric origin.

Radiocarbon measurements of oolitic sediments have shown that they can contribute to solving problems in Quaternary geology even if they cannot be recalculated to corrected ages, and that they may be applied to the investigation of diagenetic processes.

When considering the ¹⁴C age of the fossiliferous horizon in relation to that of the oolitic complex, the ¹⁴C age of the fossiliferous horizon seems to be more reliable than its geologic age. Its stratigraphic location should be revised in relation to the overlying oolitic layers. Samples of the oolitic complex and of the fossiliferous horizon in clear geologic sections should be dated. Since the comparison of the oolitic complex with the Pleistocene Dibdibba Formation has been the main reason for presuming a Pleistocene age of the major part of oolitic layers, ¹⁴C ages of the fossiliferous horizon in southeastern Kuwait should be compared with those in northern Kuwait.

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