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U-series and radiocarbon dates on mollusc shells from the uppermost layer of the archaeological site of KHB-1, Ra's al Khabbah, Oman

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Abstract

The archaeological site of KHB-1, Oman, has been investigated in order to improve the chronological knowledge of the site, which is dated to the beginning of the fourth millennium B.C. on the basis of the archaeological context. Mollusc shells of the genus *Anadara*, coming from the uppermost layers of the site, have been dated using two different methods, radiocarbon and U-series technique. The results of the two techniques date the last occupational phase of the site from the end of the fourth millennium B.C. to the beginning of the third millennium B.C.

Keywords: Radiocarbon dating; U-series dating; Shells; Isochron technique; Oman; Neolithic

1. Introduction

It is well known that the absolute dating of mollusc shells is a difficult task, independently on the applied technique. This observation is even more important if we consider that shells are generally the most abundant remains in many kinds of settlements and are found in a variety of contexts such as ancient shorelines and paleosoils. Moreover, in a number of circumstances, shells are the only available remains that could be used for radiometric measurements.

Shell is deposited in the form of calcium carbonate crystals bonded in an organic matrix with a protein called conchiolin. This comprises an outer layer of quinone-tanned protein (periostracum), a columnar crystalline layer usually consisting of either calcite or aragonite, and an inner, nacreous layer of thin crystalline sheets. The most often used fraction in radiocarbon dating is the calcium carbonate, which is the inorganic fraction of the shell, and it is the largest percentage fraction.

The carbon for the shell building is obtained from two sources: organic or metabolic carbon from marine or terrestrial plant material Little, 1993) and inorganic carbon from ocean water bicarbonate, atmospheric carbon dioxide and fresh water bicarbonate (Keith et al., 1964).

Fractionation during the geochemical transfer of carbon in nature produces variation in the equilibrium distribution of the isotopes of carbon (^{12}C, ^{13}C and ^{14}C) (Craig, 1953) and then has to be taken in account in the age determination. The extent of isotopic fractionation on the $^{14}C/^{12}C$ ratio which radiocarbon daters are seeking to measure accurately, is approximately double that for the measured $^{13}C/^{12}C$ ratio. If isotopic fractionation occurs in natural processes, a correction can be made by measuring the ratio of the isotope ^{13}C to the isotope ^{12}C in the sample being dated. The isotopic composition of the sample

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being measured is expressed as delta13C ($\delta^{13}C$) which represents the parts per thousand difference (per mille) between the sample carbon 13 content and the content of the international PDB standard carbonate (Keith et al., 1964). In summary, then, isotopic fractionation refers to the fluctuation in the carbon isotope ratios as a result of natural biochemical processes as a function of their atomic mass.

The $\delta^{13}C$ value for a sample can yield important information regarding the environment from which the sample comes, because the isotope value of the sample reflects the isotopic composition of the immediate environment (Head et al., 1989; Keith et al., 1964).

Keith et al. (1964) measured typical $\delta^{13}C$ values in shell from marine, lacustrine and riverine environments. Marine shells possess a $\delta^{13}C$ between +4.2 and −1.7 per mille wrt PDB, river shells between −8.3 and −15.2 per mille and shells from large clear lakes between −2.4 and 6.0 per mille. One of the principal advantages of dating shell is that the "lag" or dilution effect of the oceanic reservoir upon the Suess "wiggles" makes the calibration curve smoother than for terrestrial samples.

The dissolution of primary aragonite, which forms the major crystalline carbonate fraction in most shells, and the subsequent re-precipitation in a calcite-type carbonate, which is called the *post-depositional re-crystallisation*, may alter the isotopic ratio of the carbonate and affect the "true" age because bicarbonates of different age may be present in the post-depositional matrix. This exchange usually occurs on the exterior shell surfaces in terrestrial environments. Recrystallised shells may often show a "chalky" or powdery exterior (Aitken, 1990; Taylor, 1987).

On the other hand, the application of U-series dating technique to mollusc shells has often led to consider that this method is generally unreliable. Kaufman et al. (1971) reviewed over 400 mollusc shells ages obtained using this technique and concluded, on the basis of internal consistencies and by comparison with ^{14}C and stratigraphic ages, that the $^{230}Th/U$ ages of molluscs were generally unreliable due to the *post mortem* uptake and migration of uranium isotopes into mollusc shells. The ideal assumption for the applicability of the method foresees the U-uptake in the shell from sea water during mollusc's life, followed by a *post mortem* closed system behaviour, but few evidences of this hypothesis have been shown until now. Later works led to similar conclusions regarding the non-applicability of the $^{230}Th/U$ technique to mollusc shells (McLaren and Rowe, 1996; Szabo, 1979). Szabo (1979) showed discrepancies comparing $^{230}Th/U$ mollusc ages with the apparently reliable ages of coeval coral samples and McLaren and Rowe (1996) demonstrated the evidence of open system behaviour of *S. latus* and other molluscs and consequently the unreliability of mollusc U-series dates. A more recent work suggested the possibility of dating shells as closed system because buried in arid and hyper-arid environments (Labonne and Hillaire-Marcel, 2000). Shell samples from the site of KHB-1 located in the Sultanate of Oman and dated in this work with radiocarbon and U-series methods, show this peculiarity: a *post mortem* maintenance in an arid environment. In fact a study of the chronology of climate change over the Arabian Sea, conducted by Sirocko (1996), which results can be inferred on surrounding countries in Asia and Africa, demonstrated that during the mid-Holocene (about 5500 cal-yr PB), after a humid period in the Early Holocene, the eolian flux from Arabia increased indicating desertification on the Arabian peninsula and a southward shift of precipitation on the Arabian Sea. Since then these conditions on land have not changed showing persisting arid climatic conditions in the area.

Another problem to deal with when applying U-series technique to carbonate samples is the presence of detrital contamination on the samples which cannot be removed with chemical procedures and can consequently alter the age results. Detrital contamination, often clay or sand, contains unpredictable amount of U and Th isotopes, leading therefore to erroneous dating. It is easy to verify the presence of contamination by detecting the ^{232}Th that is present only in the detrital fraction. Several analytical methods, based on the evaluation of the amount of contamination, have been developed to correct for detrital contamination (Kaufman, 1992).

2. Archaeological setting

The site of KHB-1 lies about 1.5 km north of the village of Khabbah and less than 1 km from the Ra's al Khabbah headland in the Ja'lān region, the eastern province of the Sultanate of Oman (Fig. 1). It is situated on a ridge adjacent to a cliff, which is a marine erosion terrace, that starts at the headland, and continues in a northerly direction ending about 3 km south

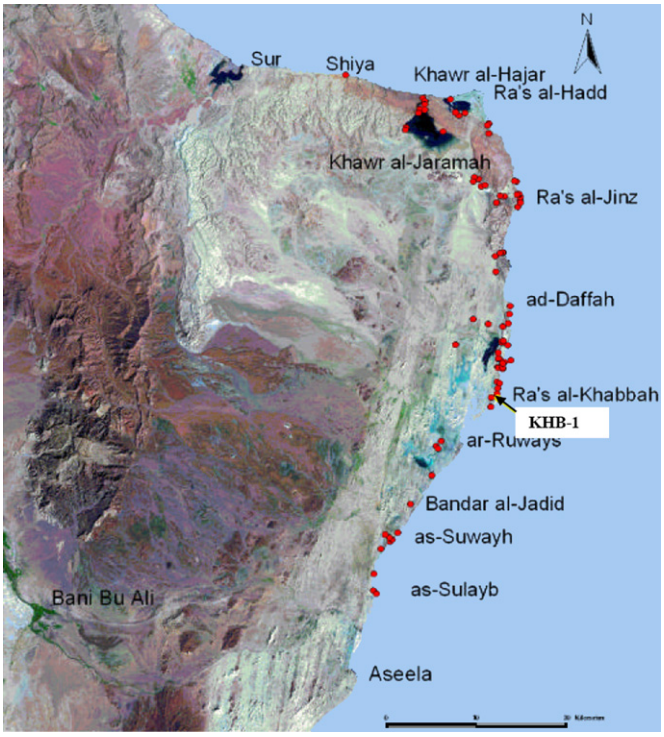

Fig. 1. View of the Ja'lān region with indication of the location of the KHB-1 archaeological site.

of the village of Ra's al Hadd. Since 1985 this area has been explored by the Joint Hadd Project formed by the ''Istituto Italiano per l'Asia e l'Oriente'' (IsIAO) of Rome, the ''Maison de l'Archéologie et de l'Ethnologie'' of the French CNRS and the Universities of Bologna and Trento.

The archaeological deposit is characterised by grey sand and a good quantity of artefacts.

The archaeological findings, including the large-bladed flint tools (mainly scrapers), a large amount of flat limestone and quartz net sinkers, borers, shell and stone beads, hooks in *Pinctada margaritifera* and stone tools, place the site between the end of the fifth or early fourth millennium cal. B.C.

Wind erosion strongly affected the surface of the deposit, taking away the sand of the uppermost layers. As a result the heavy material, mainly artefact and shells, are packed on the top of the site.

The investigation of the deposit permitted to distinguish five different phases built up by hearths, stone features, artefacts and shells in thin sandy loose layers.

Working on the stratigraphic diagrams (Harris matrix), the aeolian layers were interpreted as stratigraphic pauses and were treated as events that divide the various occupation phases. Strictly speaking, these light-coloured, loose, semi-sterile layers, could or maybe should constitute a phase in themselves. For convenience, however, they were considered simply as period interfaces, especially as their chronological significance is still unclear. This question will be discussed below in connection with issues concerning the deposit:

- *Phase 0*, the natural pre-occupation situation (bedrock).
- *Phase I* corresponds to the oldest occupation of the site, situated on top of the reddish and compact breccia. Area E was occupied by small feature complexes (huts). There are five fairly small contemporary huts with diameters varying between 2 and 3.5 m. All the huts, constructed in a similar way, have their own particularities in finding distribution or interior arrangements. These were probably domed or conical shaped structures with a slightly off centre hearth or other combustion features. The entrances are commonly orientated south or northeast. The foundations of standing structures consist of a trench excavated in sterile ground with vertical sides and a concave base and a small breccia embankment. The breccia embankment follows the same circular shape as the hut. It is the material excavated from the trench and deposited on the outer edge. The organic elements, completely disappeared today, were most probably flexible wooden stakes, bent into an arc shape and fixed into the small channel. The stakes were sometimes held by a system of stone wedges. They probably came from the marsh vegetation of the nearby lagoon and would have formed a dome shaped structure with no distinction between the walls and roof. Judging from the small trench, this framework must have been fairly dense and was probably covered by vegetation or animal hide to make it resistant to rain and sun. The breccia embankment may have been used to fix these elements into the ground to prevent the wind blowing the top off the structure. The post holes that are usually found outside the huts may also have been used to stabilise the cover, as is suggested in ethnographic comparisons (Cataldi, 1986; Cataldi et al., 1982).
- *Phase II* is characterised by some shallow pits and a few hearths, which are relatively indistinct and lack noticeable features. The accompanying layers are very dark with scattered finds.
- *Phase III* is clearly marked by a layer of semi-sterile loose sand. This phase contains feature complexes that appear to be open semi-circular shelters with hearths at the front. The breccia material is arranged in such a way that it appears to have been used to stabilise the inner floor surface. Four feature complexes were found (one of these is rather fragmentary), which build up an interesting sequence of features, with clear superimpositions. The construction of a new shelter would have inevitably resulted in the destruction of the preceding feature.
- *Phase IV* corresponds to a relatively short occupation period, which although not especially articulate, developed through time. In this phase the occupation was not sufficiently intense to form a consistent, compact organic soil. The occupation is within a thick layer of light-coloured, loose sterile sand that contained little besides some faint features. The stone circles with an evanishing hearth at the centre and artefacts around it may be interpreted as tents or lightweight tent-like shelters in which the circle of stones would anchor the vegetation or animal skin covering of the structure to the ground.
- *Phase V* follows what may be interpreted as a long period of abandonment, if the thickness of the aeolian layer is seen as an indicator of time depth. This phase is the most recent period of activity, although it does not contain any standing features (Cavulli, 2004).

At this early stage of research, considering the archaeological evidence and the morphology of the surrounding territory, only a cautionary settlement model of the area can be proposed. The community who lived in the cliff area around Ra's al Khabbah must have been of nomadic character, moving from the inner mountainous area to the lagoon and the sea following the *awdiya (widian)*. The occupation that started at the beginning of fourth millennium B.C. was possibly seasonal, probably occurring in the winter months when fish is abundant along the coast.

It is still unclear if the purpose of the settlement was for habitation or work. It could have been used for the preparation of fishnets and fish products, or maybe as a specialised site serving a larger settlement located somewhere else, may be, near the lagoon.

3. Experimental procedure

Mollusc shells from KHB-1, collected in 2000, have been dated using two different dating techniques, radiocarbon and U-series. The shells, all of the genus *Anadara*, came from the upper stratigraphic layers (named US. 1, in square E102

of the grid) situated on the topmost part of the deposit of the excavation.

For ^{14}C dating we selected hard, non-porous, thick shells with fresh surfaces and preserved textures to minimise the possibility of post-depositional isotopic exchange. Shells have been cleaned in an ultrasonic bath with deionised water, and shell surfaces have been scraped with a metallic scrub. 70 grams of sample were first pre-treated chemically with 30 ml of 5.8 M hydrochloric acid in order to remove the superficial calcite layer which may contain contamination, then rinsed and dried.

The samples were crushed prior to hydrolysis with 3 M hydrochloric acid. Hydrolysis was performed under vacuum and the CO_2 generated was collected and converted through acetylene to benzene. Teflon vials (Plastino et al., 2001) filled with benzene volumes of 3 ml were used. The scintillation cocktail comprised 15 mg butyl-PBD/ml benzene (Gupta and Polach, 1985). 1220 Quantulus™ (Perkin Elmer) was used as LSC beta counter, while Carrara marble and ANU sucrose were used as background and modern standard, respectively. All dates were $^{13}C/^{12}C$ adjusted according to Stuiver and Polach (1977) to correct for mass-dependent fractionation. In this case, we assumed $\delta^{13}C$ values of 0‰. ^{14}C ages were calibrated to calendar ages using OxCal 3.10 (Hughen et al., 2004). The local marine reservoir correction (ΔR) used to calibrate shell dates was 200 ± 60 years (Southon et al., 2002).

Eight *Anadara* shells from the same stratigraphic layer (US. 1, E102) have been selected to be analysed by U-series technique. The shells were separated from the evident detrital component, mainly clay, using a surgical lancet and then burned at 800 °C for 12 h to remove organic contamination. The total sample dissolution method (TSD) followed by the isochron approach, as proposed by Bischoff and Fitzpatrick (1991) or by Luo and Ku (1991), was applied. In TSD, the sample (authigenic part plus detritus) is completely dissolved in an acid solution and the leachate used for the radiochemical analyses. We dissolved each sample in 8 M HNO_3, then added Al nitrate carrier and ^{232}U and ^{228}Th tracer solution. U and Th isotopes were separated using an ion exchange column. The radiochemical procedure followed for thorium and uranium separation is described by Choukri et al. (1994). After the separation, thorium and uranium were plated on aluminium foil and counted by Silena Alphaquattro alpha-spectrometer. The ages of the samples were calculated using an iterative computer program (Ivanovich and Harmon, 1992). Then the isochron correction technique was applied to compensate for the detrital component and to find the ''true'' age of the samples, as described below.

4. Results and discussion

The radiocarbon dates of eight *Anadara* shell samples are shown in Table 1, where CRA-Conventional Radiocarbon Ages (Stuiver and Polach, 1977), 1σ calibrated dates without and with additional regional correction (ΔR) are reported. It is well known that original radiocarbon content of shells is highly affected by the so-called reservoir effect (Stuiver et al., 1986). In fact, isotope exchanges take place more easily in carbonates than in other inorganic or organic residues. Hence, shell dates have a certain tendency to deviate from true ages. Uerpmann (1992) declared that Oman radiocarbon dates from shells were quite consistent with the chronological expectations provided by the analysis of the stratigraphy, geomorphology and typology of the sites, even if he applied a ΔR of 800 years to the radiocarbon ages of shells taken in Ra's al-Hamra (RH) sites.

Table 1
Conventional radiocarbon ages (CRA), 1σ calibrated ages and 1σ calibrated ages with reservoir effect of eight shell samples

Sample	CRA, (BP)	Calibrated ages (B.C.)	Calibrated ages with reservoir effect proposed by Southon et al. (2002) (B.C.)
ENEA-635	4920 ± 80	3380–3120	3170–2870
ENEA-655	4850 ± 80	3320–3080	3090–2780
ENEA-658	5120 ± 120	3640–3370	3470–3100
ENEA-683	4810 ± 60	3260–3040	3000–2750
ENEA-688	4610 ± 50	2940–2820	2740–2490
ENEA-690	4870 ± 50	3320–3130	3060–2860
ENEA-691	4860 ± 50	3310–3120	3050–2850
ENEA-737	4890 ± 50	3340–3170	3080–2870

More recently, same author applied a reservoir effect correction of 400 years to the same ages in order to justify the differences between Oman shell dates and charcoal dates (Uerpmann and Uerpmann, 2003). The same approach was used to calibrate the dates reported by Biagi (1994) who found no systematic difference between shell and charcoal dates from defined contexts at the site of RH5 and RH6. Biagi also reported dates of samples coming from the KHB-1 site (Biagi, 1994). In Table 2 these dates are reported with in addition the correction due to the reservoir effect proposed respectively by Uerpmann and Uerpmann (2003) and Southon et al. (2002), in order to put in evidence a strong correlation between our radiocarbon dates and dates reported by Biagi (1994) when a ΔR of 200 years is used.

Charpentier et al. (2000) proposed for the Ja'lān region (Oman) a ΔR of 235 ± 30 years, a value calculated comparing ^{14}C shell dates to the ''correct'' age of the archaeological context. The age of the archaeological context was determined by dating ceramics artefacts. The value proposed by Charpentier et al. (2000) is strictly in agreement with the one estimated by Southon et al. (2002) and the dates of the shells coming from KHB-1 site seems to confirm that a local marine reservoir correction (ΔR) of 200 ± 60 years is the most correct value among those reported in literature. More recently, this value was also confirmed by Saliege et al. (2005) who found that a value of $\Delta R = 215 \pm 15$ can be used from the present to 4560 cal B.C.

The uranium-series analyses results of eight *Anadara* shell samples are shown in Table 3, where uncertainties are reported at 1σ. Uranium isotope activities are expressed in disintegrations per minute per gram of sample, while all ratios refer to specific activities. In the last column the calculated ages without detrital corrections are reported. It is possible to consider

Table 2
Dates of KHB-1 reported by Biagi (1994) and in addition the correction due to the reservoir effect proposed by Uerpmann and Uerpmann (2003) and Southon et al. (2002)

Sample collected by Biagi (1994)	CRA (BP)	Calibrated ages (B.C.)	Calibrated ages with reservoir effect proposed by Uerpmann and Uerpmann (2003) (B.C.)	Calibrated ages with reservoir effect proposed by Southon et al. (2002) (B.C.)
Bin-3642/I	4850 ± 80	3320–3080	2830–2560	3080–2780
Bin-3642/II	4690 ± 80	3070–2870	2560–2340	2860–2600

a sample sufficiently pure to be dated without detrital correction if the amount of the non-radiogenic ^{230}Th is smaller than the statistical error of the total ^{230}Th measured. Bischoff and Fitzpatrick (1991) showed that this is possible if the ^{230}Th/^{232}Th activity ratio is greater than 16, considering errors normally obtained with traditional alpha spectrometry. All the samples measured show a low ^{230}Th/^{232}Th activity ratio, less than 16, indicating a relative abundance of ^{232}Th and hence a presence of detrital contamination that cannot be neglected in calculating the age of the samples. The age of each sample in the last column of Table 3 has therefore to be corrected. It is possible to apply the isochron correction procedure under the hypotheses that all the samples considered must be coeval and containing a different amount of the same detritus. We applied the isochron technique as proposed by Ludwig and Titterington (1994) who described a method for determining the best-fit line to isochron data. Following this procedure the isochron should be fitted by a technique that weights the data points according to their analytical errors and error correlations and that uses a single three-dimensional *XYZ* diagram ($X = {}^{230}\mathrm{Th}/{}^{238}\mathrm{U}$, $Y = {}^{234}\mathrm{U}/{}^{238}\mathrm{U}$, $Z = {}^{232}\mathrm{Th}/{}^{238}\mathrm{U}$). The intersection of the best-fit line with the *XY* plane (it is the ^{232}Th-free plane) defines the corrected ratios (meaning the ^{232}Th-free ^{230}Th/^{238}U and ^{234}U/^{238}U activity ratios) to be used in estimating the age and the age error of the authigenic part. Ludwig and Titterington (1994) also developed the equations to calculate the isotopes-ratio errors and error correlations and implemented a computer program, called *Isoplot*, which carries out the calculations. In this work we used the program version 2.33a. The input parameters of the program are $X = {}^{230}\mathrm{Th}/{}^{238}\mathrm{U}$, $Y = {}^{234}\mathrm{U}/{}^{238}\mathrm{U}$ and $Z = {}^{232}\mathrm{Th}/{}^{238}\mathrm{U}$ activity-ratios, their errors and the error-correlations $\rho(X,Y)$, $\rho(Y,Z)$, $\rho(Z,X)$ calculated following the equations for alpha spectrometric data (Ludwig and Titterington, 1994). To calculate the activity-ratio errors we used the expression:

$$s^2_{(a/b)} = s^2_a + s^2_b \tag{1}$$

valid for ratios of isotopes of the same element (^{234}U/^{238}U), where a and b refer to the two isotopes and s is the percent relative error in a measurement ($s_a = 100\sigma_a/a$). For ratios of different isotopes (^{230}Th/^{238}U) the error is expressed as:

$$s^2_{(a/b)} = s^2_a + s^2_b + s^2_{\mathrm{ThSpike}} + s^2_{\mathrm{USpike}} \tag{2}$$

where USpike is the uranium spike-isotope (^{232}U in our case) and ThSpike is the thorium spike-isotope (^{228}Th in our case). The error correlations $\rho(X,Y)$, $\rho(Y,Z)$, $\rho(Z,X)$ for each of the isochron's data used are expressed as:

$$\rho\left(X = {}^{230}\mathrm{Th}/{}^{238}\mathrm{U},\ Y = {}^{234}\mathrm{U}/{}^{238}\mathrm{U}\right) = s^2\left({}^{238}\mathrm{U}\right)/s_X s_Y \tag{3}$$

$$\rho\left(Y = {}^{234}\mathrm{U}/{}^{238}\mathrm{U},\ Z = {}^{232}\mathrm{Th}/{}^{238}\mathrm{U}\right) = s^2\left({}^{238}\mathrm{U}\right)/s_Y s_Z \tag{4}$$

expressions valid for ratio pairs where one of the ratios is for two isotopes of the same element, and:

$$\rho\left(Z = {}^{232}\mathrm{Th}/{}^{238}\mathrm{U},\ X = {}^{230}\mathrm{Th}/{}^{238}\mathrm{U}\right) = \left(s^2_{\mathrm{ThSpike}} + s^2_{\mathrm{USpike}} + s^2\left({}^{238}\mathrm{U}\right)\right)/s_X s_Z \tag{5}$$

valid for ratio-pairs where both contain isotopes of different elements.

Table 4 shows the input values to *Isoplot* program. These data were used as input parameters to the program *Isoplot*, while the main outputs were the corrected activity ratios ^{230}Th/^{238}U, ^{234}U/^{238}U, the corrected activity ratio $(^{234}\mathrm{U}/^{238}\mathrm{U})_{t=0}$ at time zero, the calculated age with its error and the MSWD parameter (Mean Square of Weighted Deviates) which represents the degree to which the observed amount of scatter of the U-series data points from the isochron line can be explained by the assigned analytical errors and error correlations (if it is small, between 0.01 and 0.2, it means that the analytical errors have been significantly underestimated or that does not exist any analytical cause of scatter from a straight line).

Table 3
U-series measurement results and calculated ages for eight shell samples (1σ errors, n.d. = not determined)

Sample	^{238}U (dpm/g)	^{234}U/^{238}U	^{230}Th/^{234}U	^{230}Th/^{232}Th	Age (years)
K-1	0.048 ± 0.003	1.16 ± 0.09	0.31 ± 0.04	1.0 ± 0.2	40000 ± 6000
K-2	0.089 ± 0.002	1.18 ± 0.05	0.08 ± 0.01	4.8 ± 1.2	8500 ± 800
K-3	0.076 ± 0.002	1.12 ± 0.05	0.03 ± 0.01	n.d.	3000 ± 700
K-4	0.102 ± 0.004	1.06 ± 0.06	0.06 ± 0.01	6.2 ± 4.0	7000 ± 1000
K-A	0.079 ± 0.002	1.12 ± 0.05	0.055 ± 0.004	3.8 ± 0.6	6100 ± 400
K-B	0.112 ± 0.004	1.16 ± 0.06	1.0 ± 0.2	1.16 ± 0.09	5800 ± 600
K-U	0.066 ± 0.002	1.16 ± 0.05	0.052 ± 0.004	4.6 ± 0.8	5800 ± 400
K-P	0.058 ± 0.002	1.10 ± 0.47	0.06 ± 0.01	n.d.	6600 ± 1.100

Table 4
Activity isotope-ratios, associated errors and correlation errors calculated according to the equations developed by Ludwig et al. (1994) for alpha-spectrometric data (1σ errors)

Sample	$X = {}^{230}Th/{}^{238}U$	1σ %err	$Y = {}^{234}U/{}^{238}U$	1σ %err	$Z = {}^{232}Th/{}^{238}U$	1σ %err	$\rho(X,Y)$	$\rho(Y,Z)$	$\rho(Z,X)$
K-1	0.3000	12.83	1.1603	5.92	0.2909	13.16	0.2461	0.2798	0.2399
K-2	0.0877	9.14	1.1811	2.80	0.0182	23.65	0.1655	0.0575	0.0640
K-3	0.0299	25.22	1.1168	3.77	0.0023	228.55	0.0786	0.0020	0.0087
K-4	0.0649	16.64	1.0548	4.63	0.0104	62.51	0.1426	0.0182	0.0379
K-A	0.0602	7.21	1.1221	2.67	0.0159	15.32	0.1964	0.0975	0.0924
K-B	0.0599	10.71	1.1625	4.10	0.0098	39.80	0.2075	0.0379	0.0558
K-U	0.0591	7.25	1.1554	2.48	0.0128	16.16	0.1834	0.1133	0.0822
K-P	0.0630	16.12	1.0982	4.99	0.0019	339.15	0.1624	0.0039	0.0077

Our output results were: ${}^{230}Th/{}^{238}U = 0.047 \pm 0.009$; ${}^{234}U/{}^{238}U = 1.13 \pm 0.04$; $({}^{234}U/{}^{238}U)_{t=0} = 1.14 \pm 0.04$ (errors at 2σ). On the basis of these values, the corrected age of all the coeval shells could be determined as 2600 ± 500 years B.C. (1σ error) with MSWD = 1.6.

The value MSWD = 1.6 indicates that our hypothesis were correct, that is all the shells were coeval and the detritus was homogeneous. The initial ${}^{234}U/{}^{238}U$ activity ratio is consistent with the world-wide accepted oceanic ${}^{234}U/{}^{238}U$ ratio, 1.14 ± 0.02 (Chen et al., 1986), meaning that during the mollusc's life the uranium incorporated had an oceanic origin and after death shells behaved, in this specific case, as closed systems.

5. Conclusions

The results place the uppermost stratigraphic layers of KHB-1 from the end of the fourth millennium B.C. to the beginning of the third millennium B.C., in agreement with previous CRA obtained with the radiocarbon technique applied to the same site and to the same stratigraphic layer (Biagi, 1994).

Considering the material culture found at KHB-1 and that no consistent variations occur on it during the five phases, we can reasonably date the beginning of the settlement to the end of the fifth millennium B.C. or the beginning of the fourth, and was occupied for no more then 500 years. This time span has been suggested by cross-site comparisons with the site of RH-5 (Ra's al-Hamra, Oman) whose chronology was deduced by many radiocarbon dates as reported by different authors (Biagi, 1994; Uerpmann, 1992; Uerpmann and Uerpmann, 2003).

Because of the samples dated with ${}^{14}C$ and U/Th have been taken from the surface of the deposit, which was exposed to air and to deflation effects, the results give new information on the last occupation phase of the site that has probably seen a new occupation at the end of the fourth millennium, which we could not recognise by findings.

The U-series isochron dating technique on shells from KHB-1 gave a reliable age as compared to radiocarbon age. This can be explained by a closed system behaviour of shells due, probably, to their *post mortem* permanence in an arid environment where the lack of water has inhibited the U-uptake and migration from and into the shells.

As far as we know this is the first example of U/Th isochron technique applied to shells and the result is encouraging because in this specific case it seems to work. In general it is not possible to apply the technique to shells, as it would be necessary to have a protocol to be able to verify *a priori* the applicability of the method. Unfortunately such a protocol is not yet available, and the only way to verify the goodness of the technique is to compare the result with independent information such as radiocarbon dating or archaeological context.

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