





ESR dating of raised coral reefs from Kish Island, Persian Gulf

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Abstract

Electron spin resonance (ESR) dating of raised coral reefs from Kish Island, Persian Gulf, Iran, was used for the calculation of uplift rates. From the methodological point of view, it has been demonstrated that concentrations of uranium, as needed for the calculation of dose rates, determined by instrumental neutron activation analyses were significantly lower than the results of inductively coupled plasma—mass spectrometry and are probably systematically underestimated. The ESR ages for the corals show no increase with elevation as was expected due to field observations. This apparent discrepancy is explained by the dicyclic nature of the palaeo-reef. Average uplift rates for Kish Island are between ~0.13 and ~0.24 mm a⁻¹. This is consistent with previous estimates based on ²³⁰Th/²³⁴U dating of raised marine deposits from the nearby Iranian mainland and Qeshm Island, Strait of Hormuz, but contrary to results based on ¹⁴C dating that predicted uplift rates as high as 3 mm a⁻¹ in that area. It is once more demonstrated that ¹⁴C dates > 20 ka from this context often have to be interpreted as minimum ages.

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1. Introduction

The coastal area of southern Iran is part of the southern Zagros Mountains geological structure. This area has been tectonically active since the Tertiary and remains active. Uplift of the region during the Pleistocene is indicated by the presence of raised marine sediments. These consist of reef and beach deposits from near shore or shallow water environments. From the altitude and age of the raised sediments the uplift rate of a specific area can be reconstructed. Corals that are frequently found in the shallow water deposits can be dated by various methods. Suitable ways of age determination beyond the limits of radiocarbon dating are provided by the ²³⁰Th/²³⁴U and electron spin resonance (ESR) methods.

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A first set of ¹⁴C ages for corals from raised beaches along the Iranian coast has been reported by Little (1970). Further dates mainly older than 20 ka led to the calculation of uplift rates as high as 3 mm a⁻¹ for the Makran coast (Vita-Finzi, 1979, 1980, 1981) and up to 2.6 mm a⁻¹ for Qeshm Island (Haghipour and Fontugne, 1993). From the comparison of ¹⁴C and ²³⁰Th/²³⁴U dating results it was concluded, however, that ¹⁴C ages older than 20 ka have to be considered as minimum ages (Page et al., 1979). A revised chronology of raised marine deposits along the Persian Gulf and Makran Coast of Iran based on ¹⁴C and ²³⁰Th/²³⁴U dating was later established by Fontugne et al. (1997) and Reyss et al. (1998). Both studies demonstrated that most of the samples investigated were not suitable for ²³⁰Th/²³⁴U dating due to significant re-crystallisation of Aragonite to Calcite. The few ²³⁰Th/²³⁴U results available indicate a much smaller uplift rate of about 0.2 mm a⁻¹ for the Makran coast/Persian Gulf area. Due to the re-crystallisation problem, it was however not possible to expand the dating beyond the limits of last interglacial deposits. In contrast to ²³⁰Th/²³⁴U, the

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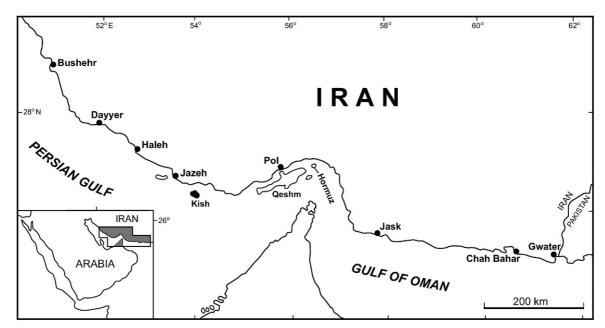


Fig. 1. Map of the Persian Gulf area indicating the location of Kish Island and relevant sites mentioned in the text.

ESR method is less vulnerable to re-crystallisation and may allow a dating as far back as 500–600 ka (Pirazzoli et al., 1991; Schellmann and Radtke, 2001). The present study seeks to establish an absolute chronology for the so far non-investigated island of Kish, Persian Gulf, and to extend the age control on raised coral reefs from southern Iran beyond the limits of ²³⁰Th/²³⁴U dating by using the ESR method.

A set of 25 ESR ages determined for raised coral reefs from Kish Island, Iran (26°29′N; 54°01′E) is presented in this work. Kish is an island of about 77 km² in the southeastern Persian Gulf, a few kilometres south of the Iranian mainland (Fig. 1). Coral reefs and shallow marine deposits are found all over Kish and were expected to give relevant information about age, uplift rate and geomorphologic history of the island. Altogether, 27 samples were taken at elevation between 1.5 and 32 m above mean sea level (MSL) (Fig. 2). From field observations different levels of reef deposits were identified. The lowest level found ~1.5 m above MSL was expected to be of Holocene age.

2. Methods

The inner parts of the coral samples were collected and sieved to a particle size of $125-250\,\mu m$. Prior to dating, all samples were tested by X-ray diffraction and ESR screening and two samples had to be rejected due to an almost complete re-crystallisation of Aragonite to Calcite. 20 aliquots of each sample were γ -irradiated using a 60 Co source with a dose rate of $\sim 2.5\,\mathrm{Gy\,min}^{-1}$ to a maximum dose of 330 Gy. ESR intensities were measured using a Bruker ESP 300E. The following

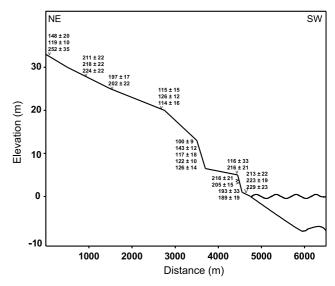


Fig. 2. Schematic cross section of Kish Island showing the location of samples and ESR ages. (Note: due to the flat morphology of Kish Island the vertical scale is enlarged by a factor of 100.)

measurement parameters have been used: $25 \,\mathrm{mW}$ microwave power; $0.5 \,\mathrm{G}$ modulation amplitude; $22.972 \,\mathrm{s}$ sweep time; $40 \,\mathrm{G}$ scan width; 1024 points resolution; accumulation of 5–10 scans. The ESR peak at g = 2.0006 has been used since it is most suitable for the dating of corals (Schellmann and Radtke, 2001). In the present study, no significant disturbance of that signal due to the influence of Mn-lines originating from calcite was detectable. It was thus possible to date even heavily re-crystallised coral species. However, ESR results for corals showing low calcite contents are expected to be more reliable. $D_{\rm e}$ determination was

carried out using the "Fit-sim (version 1993)" program by R. Grün (Canberra).

Dose response curves of the dating signal from corals can contain inflexion points and minor oscillations that complicate the $D_{\rm e}$ determination. Fitting single exponential function through all data points of such a "disturbed" growth curve can result in a significant overestimation of the calculated $D_{\rm e}$. Used here was the $D_{\rm e}-D_{\rm max}$ approach of Schellmann and Radtke (1999, 2001) that reduces the effect of inflexion points on $D_{\rm e}$ determination.

Isotopes of the uranium decay chains are the main contributors to the natural radiation dose (D') in corals. As the coral species sampled on Kish Island are generally small, some contribution of gamma irradiation from the surrounding material needs to be considered. Unfortunately, it was not possible to carry out in situ gamma measurements. For the calculation of dose rates it was assumed that the corals and the surrounding material have similar uranium contents. This seems to be permissible since the later is mainly build up of carbonate debris, mostly consisting of bioclasts like coral rubble. The uncertainty associated with this assumption is believed to be not more than about 10%, even when the possibility of significant differences in uranium contents is taken into account.

The determination of uranium was carried out by both instrumental neutron activation analyses (INAA; by a commercial laboratory) and inductively coupled plasma—mass spectrometry (ICP-MS; at the Cologne laboratory). It was expected that a comparison of both methods would allow a more reliable dose rate determination as using one technique only. For ICP-MS, microwave high pressure/temperature decomposition of samples (230°C, 7.0 MPa; Paar Physica Multiwave sample preparation system) was carried out using in all stages Merck Suprapur® grade reagents (HF, HClO₄, HNO₃, and HCl). Measurements were made on a Sciex/Perkin-Elmer ELAN 6000 ICP-MS (quadrupole mass spectrometer). Determinations of element concentrations were performed using an internal standard to minimise drift effects and two calibration solutions (high purity chemical reagents). A batch of 5–7 samples was bracketed by two calibration procedures. Accuracy and precision of determinations were checked with certified reference material (CRM) such as CCH-1 (limestone) and DWA-1 (dolomite) (Roelandts and Duchesne, 1994).

The contribution of cosmic rays to the total dose rate was calculated using present day depth. It is considered that due to unknown erosional processes in the past a precise determination of the cosmic dose rate is barely possible. However, the effect on age determination due to this uncertainty is rather negligible compared to the problems that are encountered with the accurate measurements of uranium concentrations. Age calcula-

tion was carried out using the "DATA VII (version 1999)" program by R. Grün (Canberra) using an alphaefficiency (*k*-factor) of 0.05.

3. Results and discussion

There is an obvious discrepancy for the concentrations of uranium as determined by INAA and ICP-MS, respectively (Table 1, Fig. 3). For concentrations of 2–3 µg g⁻¹ the results of INAA are significantly lower than those determined by ICP-MS. The performance of ICP-MS was confirmed by routinely running CRMs simultaneous to the samples used for dose rate determination. The excellent correspondence of ICP-MS results with CRM-values gives strong indication of the reliability of the method (Table 2). It is thus concluded that the INAA results are systematically underestimated. Hence, ages were calculated based on ICP-MS determinations only. Further investigations are needed to explain the systematic shortfall of uranium concentrations as measured by INAA.

The ESR dating results show two distinct clusters of ages indicating formation of coral reefs on Kish Island during sea level highs in Marine Isotope Stages (MIS) 7 and 5e (Fig. 4). It is remarkable that MIS 7 (186–242 ka, Bassinot et al., 1994) deposits are found at both the lowest (1.5 m above MSL) and the highest elevation (32 m above MSL) on the island (Fig. 2). This is contradictory to the first assumption based on field observations that corals close to present MSL should be of Holocene age. In a temporary pit on the coastal flat $(\sim 6 \text{ m above MSL})$ a green mud horizon separating two layers of reef deposits could be observed. Coral growth was obviously interrupted by clastic sedimentation. This indicates that reef development on Kish Island was at least dicyclic. Corals started to grow on the slowly emerging remains of a pre-existing older reef. The presence of old corals at low elevation is interpreted to represent the lower part of that older palaeo-reef. The hypothesis of at least dicyclic reef growth on Kish Island is supported by identifying coral of different age at the same elevation on two sites (6 m above MSL, samples 0KI 3-4; 32 m above MSL, samples 0KI 23-25).

It is important to note that all samples taken at altitudes > 18 m were taken from debris on the island flat and not from corals in living position, in contrast to samples from lower altitudes, due to the lack of suitable outcrops. A post-sedimentary dislocation of the sample material in the highest part of the island by man must thus be considered, although no valid evidence of such an anthropogenic impact exists. For the calculation of uplift rates it is, however, essential to determine the exact elevation of the top of the last interglacial reef. Consequently, two different scenarios considering this uncertainty will be presented. If the samples from

Table 1 Summary data of ESR dating giving the equivalent dose (D_e) , concentrations of uranium as determined by instrumental neutron activation analysis (INAA) and inductively coupled plasma—mass spectrometry (ICP-MS), dose rate based on the ICP-MS measurements and resulting ESR ages

Sample	Lab. no.	Calcite (%)	Altitude (m asl)	D _e (Gy)	U INAA (μg g ⁻¹)	U ICP-MS (μg g ⁻¹)	$D' (\mu \text{Gy a}^{-1})$	Age (ka)
0KI-01	K-4215	50	3	165.93 ± 25.99	2.10	2.34	862±63	193 ± 33
0KI-02	K-4216	0.5	3	209.55 ± 14.55	2.70	3.26	1111 ± 83	189 ± 19
0KI-03	K-4217	2	6	99.14 ± 27.10	2.26	2.81	854 ± 61	116 ± 33
0KI-04	K-4218	9	6	241.59 ± 14.71	2.52	3.13	1117 ± 86	216 ± 21
0KI-05	K-4219	12	4	215.06 ± 26.53	2.58	2.96	1052 ± 80	205 ± 15
0KI-06	K-4220	1.5	4	256.39 ± 11.02	2.62	2.89	1075 ± 83	239 ± 21
0KI-07	K-4221	20	1.5	208.74 ± 13.94	2.46	2.68	982 ± 75	213 ± 22
0KI-08	K-4222	20	5.2	116.68 ± 9.82	2.75	3.01	923 ± 67	126 ± 14
0KI-09	K-4223	25	6.1	No sol.	_	_	_	_
0KI-10	K-4224	12	6.7	97.32 ± 3.62	2.01	2.51	798 ± 56	122 ± 10
0KI-11	K-4225	13	8.1	102.93 ± 13.57	2.30	2.90	878 ± 63	117 ± 18
0KI-12	K-4226	8	8.4	125.40 ± 6.06	2.45	2.69	880 ± 63	143 ± 12
0KI-13	K-4227	16	9.2	No sol.	_	_	_	_
0KI-14	K-4228	9	11.6	85.1 ± 4.84	2.54	2.96	849 ± 60	100 ± 9
0KI-15	K-4229	10	18	146.30 ± 18.60	4.72	4.64	1275 ± 58	115 ± 15
0KI-16	K-4230	14	18	110.75 ± 6.30	2.46	2.82	878 ± 64	126 ± 12
0KI-17	K-4231	16	18	105.96 ± 12.78	2.63	3.18	932 ± 68	114 ± 16
0KI-18	K-4232	1	25.5	208.65 ± 8.41	2.35	3.02	1058 ± 79	197 ± 17
0KI-19	K-4233	8	25.5	204.07 ± 16.26	2.73	2.82	1009 ± 76	202 ± 22
0KI-20	K-4234	8	28	202.27 ± 14.97	2.20	2.60	958 ± 73	211 ± 22
0KI-21	K-4235	7	28	223.85 ± 15.11	2.61	2.82	1029 ± 78	218 ± 22
0KI-22	K-4236	7	28	215.00 ± 13.22	2.31	2.56	961 ± 74	224 ± 22
0KI-23	K-4237	6	32	127.82 ± 14.35	2.45	2.59	864 ± 63	148 ± 20
0KI-24	K-4238	0	32	161.98 ± 4.53	4.88	4.99	1362 ± 104	119 ± 10
0KI-25	K-4239	5	32	322.37 ± 36.19	3.33	3.51	1277 ± 104	252 ± 35
0KI-26	K-4240	0.7	1.5	231.56 ± 8.46	2.63	2.84	1041 ± 79	223 ± 19
0KI-27	K-4241	0	1.5	243.32 ± 14.60	2.61	2.89	1063 ± 83	229 ± 23

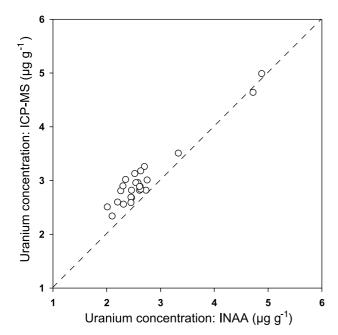


Fig. 3. Comparison of the concentration of uranium as determined by instrumental neutron activation analysis (INAA) and inductively coupled plasma—mass spectrometry (ICP-MS).

elevation 32 m above MSL are in situ, the very top of Kish Island was at least temporarily below sea level during the last interglacial. This leads by using a mean

age of 125 ka and assuming a 4 m higher than-present sea-level for MIS 5e (Stirling et al., 1995, 1998) to an uplift rate of $\sim 0.24 \,\mathrm{mm\,a^{-1}}$. Alternatively, if the elevation of 18 m (where in situ corals have been sampled) is interpreted to represent the uppermost part of the last interglacial reef the resulting uplift rate would be $\sim 0.13 \,\mathrm{mm\,a^{-1}}$.

Nevertheless, both alternative scenarios for Kish Island are very similar to the 0.2 mm a⁻¹ uplift rate as calculated for nearby mainland Iran (Haleh, Jazeh) and Qeshm Island, Strait of Hormuz. These uplift rates are based on ²³⁰Th/²³⁴U dating (Fontugne et al., 1997; Reyss et al., 1998). All these findings are significantly lower than predicted average uplift rates of $\sim 3 \,\mathrm{mm \, a^{-1}}$ for the nearby Makran coast and Qeshm Island (Vita-Finzi, 1980; Haghipour and Fontugne, 1993). This discrepancy is caused by the different interpretation of ¹⁴C ages > 20 ka. As demonstrated by the comparison of ¹⁴C and 230 Th/ 234 U ages, 14 C ages of corals > 20 ka have to be considered as minimum ages (Page et al., 1979). Although this interpretation has not generally been accepted. The unreliability of 14 C ages of ~ 23 and ~ 30 ka for corals from this area (Snead, 1993) is additionally confirmed when considering that the Persian Gulf, due to its waterdepth of mainly less than 40 m, dried out (Uchupi et al., 1999) and was thus no suitable place for coral growth during most of the last glacial cycle.

Table 2
Comparison of the results of ICP-MS measurements (n = number of determinations) with CRM values (after Roelandts and Duchesne, 1994)

Sample	n	ICP-MS U $(\mu g g^{-1})$	CRM U ($\mu g g^{-1}$)	Ratio U	ICP-MS Th $(\mu g g^{-1})$	CRM Th $(\mu g g^{-1})$	Ratio Th
CCH-1 DWA-1	32 11	3.6 ± 0.1 1.4 ± 0.04	3.7 1.4	0.97 1.00	$\begin{array}{c} 0.28 \pm 0.02 \\ 0.09 \pm 0.01 \end{array}$	0.29 0.08	0.97 1.13

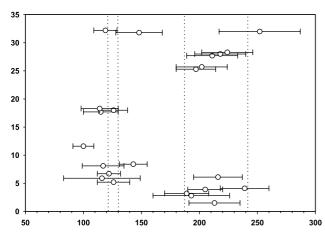


Fig. 4. Plot of ESR ages versus altitude. The limits of marine isotope stages 5e and 7 are indicated by the dashed lines following the chronology of the low-latitude isotope stack from the Maldives area (Bassinot et al., 1994).

4. Conclusion

The present data set demonstrates that ESR dating of corals can be advantageous in comparison to the ²³⁰Th/²³⁴U method when samples show re-crystallisation. Determination of dose rate relevant elements might be an underestimated error source when performance of analytic methods is not regularly verified. Running CRMs parallel to samples used for dating is a good possibility to check the reliability of the measurements of dose rate relevant elements. The coral reefs found on present Kish Island developed during MIS 7 and MIS 5e. Most of the present islands surface was probably below water level during the maximum of the last and penultimate interglacial. The ages of corals do not increase with elevation and reef development is interpreted to have been at least dicyclic. From age and elevation of the corals the calculated uplift rate is very similar to previous estimates based on ²³⁰Th/²³⁴U dating for the Iranian mainland and Qeshm Island. These results are lower by an order of magnitude to uplift rates based on ¹⁴C dating which did consider ages of > 20 ka as reliable. Consequently, Upper Pleistocene average uplift on the southern edge of the Zagros Mountain was much lower than previously expected which is an important consideration to be recognised when assessing the potential seismic risk of that area.

Acknowledgements

We thank the Geological Survey of Iran for organising and financing the field trip along the Persian Gulf coast. Further travel expenses for F.P. were provided by the Universität zu Köln. We are grateful for the comments of C. Murray–Wallace on an earlier version of the manuscript.

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