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The North Atlantic Marine Reservoir Effect in the Early Holocene: Implications for Defining and Understanding MRE Values.

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Abstract

The marine reservoir effect (MRE) is a ¹⁴C age offset between the oceanic and atmospheric carbon reservoirs. The MRE is neither spatially nor temporally constant and values may deviate significantly from the global model average provided by the MARINE04 curve. Such a deviation is calculated as a ΔR value and modern (pre-bomb) values show considerable spatial variations. There is also considerable evidence for temporal variability linked to paleoenvironmental changes identified in paleoclimatic proxy records. Seven new ΔR values are presented for the North Atlantic, relating to the period c. 8430–3890 cal. BP (c.6480–1940 BC). These were obtained from ¹⁴C analysis of multiple samples of terrestrial and marine material derived from seven individual archaeological deposits from Mainland Scotland, the Outer Hebrides and the Orkney Isles. The ΔR values vary between 143 ± 20 ¹⁴C yr and -100 ± 15 ¹⁴C y with the positive values all occurring in the earlier period (8430–5060 cal BP), and the negative values all coming from later deposits (4820–3890 cal BP). The nature of MRE values and the potential for spatial and temporal variation in values is the subject of current research interest and these data are placed in the context of (i) other estimates for UK coastal waters and (ii) important questions concerning current approaches to quantifying the MRE.

Keywords

Marine reservoir effect, ΔR , North Atlantic, paired samples, Scotland, Holocene.

Introduction

The marine reservoir effect (MRE) is a temporally and spatially variable ^{14}C offset between the atmospheric and oceanic carbon reservoirs where the ^{14}C activity of the oceans shows depletion relative to the contemporaneous atmosphere as well as greater spatial variability. This means that the MRE has crucial implications for ^{14}C measurements made on samples containing marine-derived carbon. In order to relate measurements made on marine-derived material to those made on terrestrial samples, the offset in activity between contemporaneous marine and terrestrial samples must be reliably quantified. A time-dependant quantification of the offset for the global average surface oceans is provided by the MARINE04 curve [1] using model-derived values of the oceanic response to atmospheric production-driven $\Delta^{14}\text{C}$ variations. However, the depletion in ^{14}C for a specific geographic ocean area may deviate from the MARINE04 global average, due to the heterogeneity of ^{14}C distribution in both the lateral and vertical structure of the oceans. While rapid mixing results in a relatively uniform global atmosphere with respect to ^{14}C , variations in activity occur in the marine reservoir as a function of local oceanographic and climatic variables including temperature, wind speed, sea ice cover and the locations of deep water upwelling [2-4]. For example, in an upwelling zone, a water body that is depleted in ^{14}C due to separation from the atmosphere-ocean interface during thermohaline circulation is introduced to the surface ocean thereby increasing the atmosphere-ocean ^{14}C offset. The resulting deviation from the global average surface ocean activity, as defined in MARINE04, is known as ΔR , a region-specific ^{14}C offset between the local and world surface ocean layers. ΔR therefore incorporates ^{14}C shifts from differences in local ocean processes to the parameters used in the marine calibration curve model [5].

The distribution of known, modern (i.e. pre-bomb) regional average ΔR values is available from the on-line marine reservoir correction database [6,7]. These values show great geographic variability, for example, from $\Delta\text{R} = 1312 \pm 55$ ^{14}C yr for Inexpressible Island, Antarctica [8] to $\Delta\text{R} = -216 \pm 37$ ^{14}C yr for Guayaquil, Ecuador [9], and reflect the global influence of the environmental variables mentioned above.

A large body of research exists showing that the climate and ocean variables (mentioned above) that influence local ocean ^{14}C content have not remained static

through time. If changes in these variables occur that are of sufficient magnitude and duration then a change in the MRE of an area within the global ocean may occur that is reflected in ^{14}C measurements of marine samples. For example, there is significant evidence that deglacial changes in ocean circulation in the Northeast Atlantic, with fluctuating input from North Atlantic Deep Water and Antarctic Bottom Water resulted in changes in the ^{14}C content of deep waters over this time period [10].

In samples younger than 12,400 cal BP, temporal variability can be expressed in terms of ΔR , however it is important to note that beyond the end of the INTCAL04 tree-ring data, the term ΔR has limited value as INTCAL04 data prior to this were obtained from marine records (measurements of corals and foraminifera) converted into an 'equivalent' atmospheric age using a site-specific MRE correction [11].

The potential for temporal variability in MRE values at a specific location is important due to the effect this would have upon the apparent timing and correlation of palaeoenvironmental and archaeological changes that are dated using samples containing marine-derived carbon. Within the North Atlantic region this is highly relevant due to apparent correlations in the timing of observed variations in MRE values and significant environmental fluctuations. Here, if the modern regional average MRE is taken as c.400 ^{14}C yr, values of more than double this have been identified during the last glacial period. In the West Iceland Sea, surface MRE values of c.950 yr are observed at c.25,000 cal yr BP and c.2240 yr at c.18,000 cal yr BP, with later values in this area of between c.630 and c.1160 yr at 14,600–18,100 cal yr BP, and these are attributed to the influence of an increase in sea ice cover [12,13]. Increased glacial MRE values are not observed in all oceans, for example, values for the glacial Mediterranean Sea of 350 ± 150 yr [14] are close to the present value for this area of 390 ± 80 yr [15]. Higher MRE values for the Mediterranean of 820 ± 120 yr are however observed at c.17,000 cal. yr BP and 810 ± 130 yr at c.15,700 cal yr BP. These have been attributed to variations in ocean circulation during Heinrich event 1 [14]. Similarly, the impact of increasing input of ^{14}C -depleted Southern Ocean source waters during this time has been proposed as a potential mechanism for a rapid increase in the age of western North Atlantic intermediate water (of c.670 ^{14}C yr), recorded at 15,410 cal. yr BP in corals situated at 40°N [16]. In addition to these values, much higher surface-water MRE values, relative to modern, of 1630 ± 600

and 2340 ± 750 yr have been derived at c.15,000 cal. yr BP from marine cores in the Atlantic between $37\text{--}55^\circ\text{N}$ [17].

Assessments of the pre-Holocene North Atlantic MRE are not uniformly higher than present. Bondevik *et al.* [18] estimated a value during the Bølling/Allerød for the West Norwegian coast of 380 ± 32 yr at 12,300–11,000 ^{14}C yr BP. This is indistinguishable from the present value for Southern Norway of 379 ± 20 yr [18]. In contrast, North Atlantic MRE values in the pre-Holocene appear to be significantly raised relative to present values at a range of sites identified using samples from the Vedde Ash layer. The Vedde Ash is dated in terrestrial deposits to $10,310 \pm 50$ ^{14}C yr BP [19] and for this time, MRE values around the West Norwegian coast are 610 ± 55 yr [20]. Across the North Atlantic, MRE values at the Vedde Ash layer of 700–800 yr have been determined for four marine cores [21], 700–800 yr on the Hebridean Shelf off the northwest coast of Scotland [22], between 700 and 1100 yr off the Norwegian coast [21,23] and 750–800 yr on the North Icelandic Shelf [21]. Variability in North Atlantic MRE, relative to present, has been identified as extending into the Holocene period, with early Holocene values of 690 yr off the west coast of Norway, and 730 yr off the North Icelandic coast at c.9000 ^{14}C yr BP [24].

Figure 1: A compilation of North Atlantic MRE assessments for the last glacial to early Holocene, incorporating Mediterranean data [14]. The modern-day estimated value for the North Atlantic (c.400 ^{14}C yr) is indicated by the dashed line.

Assessments of MRE and ΔR for subsequent Holocene periods also show variations relative to present, although the scale of these variations appears to be of a lower intensity than for the pre-Holocene, probably due to increased climatic stability relative to periods such as the transition from the last glacial. On the North Iceland shelf over the past 4600 cal yr, significant fluctuations are observed in MRE and ΔR values, which appear to fluctuate between with varying dominance of the Irminger and East Iceland Currents [25,26]. An assessment of ΔR values for UK coastal waters at various periods during the past 6000 years did not provide evidence for time-dependence in ΔR , although such a variation could not be ruled out [27]. However, subsequent research covering the last 2000 years has demonstrated significantly lower ΔR values relative to modern [28].

Overall therefore, there is considerable evidence that MRE values within the North Atlantic have not remained constant over extended time periods, indicating that further investigation of potential variations is desirable. Large variations in values have been identified from the last glacial to the early Holocene (Fig 1), and there is also evidence that this variability continued after the Holocene transition. At present there is a growing effort to characterize the MRE over extended time periods in the North Atlantic, in order to apply effective corrections to ^{14}C measurements made on samples containing marine carbon. Here, we present data from six Scottish coastal sites that enable us to examine ΔR values for the period c.6480–1940 cal BC (c.8430–3890 cal BP). This new dataset enables an examination of features of the MRE for this ocean area from the early to mid Holocene and places the ΔR values in the context of previously available MRE studies and palaeoenvironmental data for the North Atlantic.

Methodology

Seven deposits were selected from six Scottish coastal archaeological sites where the resolution of the stratigraphy allowed the application of a rigorous selection protocol [29] to obtain marine and terrestrial material for ^{14}C measurement that was reliably of the sample calendar age. The sites were situated in three areas; Mainland Scotland, the Outer Hebrides and the Orkney Isles (Figure 2), where at one site (Skara Brae), two deposits were selected from which to obtain samples.

Figure 2: Location of the sampling sites within Mainland Scotland, the Outer Hebrides and the Orkney Isles.

Multiple samples of terrestrial and marine material (minimum 4 of each) were obtained from each deposit for ^{14}C measurement. The samples consisted of single entities (i.e. individual organisms) that represented a relatively short growth interval. The marine samples were mollusc shells (*Patella vulgata*) and the terrestrial samples were either carbonised plant macrofossils (cereal grains or hazelnut shells) or terrestrial mammal bones (cattle or red deer). Pre-treatment of marine carbonates involved inspection of the shell surface and selection of only hard, non-porous shells

for analysis [30,31]. Physical contaminants were removed by abrasion and cleaning in an ultrasonic bath and then the outer portion (20% by mass) was removed by etching in 1 M HCl [32]. A 0.1g homogenised sample of the shell structure was obtained by crushing. Prior to CO₂ extraction, a further 20% of the sample was removed with 1M HCl to extract any further surface contamination that had occurred during the storage period following pre-treatment. Carbonized plant material was pre-treated using the standard procedure for removal of carbonates by acid hydrolysis with HCl and of organic acids with alkali solution (NaOH) in a series of successive extractions. Mammal bones were pre-treated using a modified Longin method [33], where the sample surface was cleaned with a Dremmel® drill, weighed and roughly crushed before immersion in 1M HCl for c.18 hours. After dissolution of the bone phosphate, the phosphate and organic contaminants were decanted/filtered and the residue heated gently to denature and solubilize the collagen, after which the solution was filtered and the collagen freeze-dried.

CO₂ was obtained from the pre-treated carbonised plant material and bone samples by combustion in pre-cleaned sealed quartz tubes [34]. CO₂ was obtained from the marine shell by complete hydrolysis of the carbonate using HCl, under vacuum. Sample CO₂ was cryogenically purified using a sequence of traps containing solid CO₂/ethanol for removal of water vapour and liquid N₂ to trap the CO₂ with removal of non-condensing gaseous contaminants by pumping. Three sub-samples of the purified CO₂ were taken; one 2 ml sample was converted to graphite [35] for subsequent AMS analysis, a second sub-sample was collected and sealed in a clean glass vial for subsequent $\delta^{13}\text{C}$ analysis while any remaining sample CO₂ was similarly collected and sealed for possible future analysis. The sample ¹⁴C/¹³C ratios were measured on the SUERC AMS, which is a NEC 5 MV terminal voltage instrument operated at 4.5 MV, with carbon in the 4+ charge state. Wherever possible during measurement, samples from a single context were measured on the same sample wheel to reduce variability introduced by random machine error. The $\delta^{13}\text{C}$ value of the sample CO₂ was determined on a VG SIRA 10 stable isotope mass spectrometer using NBS standards 22 (oil) and 19 (marble) to determine the 45/44 and 46/44 mass ratios, from which a sample $\delta^{13}\text{C}$ value could be calculated.

The consistency of each terrestrial or marine group of measured ages from individual contexts was assessed using the chi-squared (χ^2) test [36] to determine whether the internal variability of a measurement group was consistent with the errors associated with the individual measurements. To avoid biasing the test towards samples that had been measured more than once, multiple measurements of a single sample that were not significantly different from one another were combined to produce a weighted mean age and appropriate error for that sample. The χ^2 test critical value was compared with the T value calculated for each group of ages to determine whether the variability within the measurement groups exceeded what could occur by chance. Where the T -statistic was lower than the critical value, the ages within that group were considered to be contemporaneous. Where the T -statistic exceeded the critical value, the ages within the group were considered significantly different, and the measurements were examined to determine the source of variation. The ^{14}C measurements that most accurately reflected the age of terrestrial or marine material at the time of context deposition were identified using repeat measurements and reference to other available chronological data.

ΔR was calculated for a terrestrial and marine sample pair using the Intcal04 atmospheric calibration data and the Marine04 modelled ^{14}C ages [1,11]. The terrestrial ^{14}C age $\pm 1\sigma$ was converted to an equivalent Marine04 modelled marine ^{14}C age from which ΔR was calculated as the offset between the modelled age and a measured marine ^{14}C age. The 1σ error for the ΔR determination was obtained by combining the errors on the modelled and measured marine ^{14}C ages.

The groups of terrestrial and marine measurements from a single context that gave a T -statistic lower than the critical values were used to assess ΔR for each context. An empirical assessment was made of the variation in ΔR that could be produced over all the terrestrial and marine samples from the context. This was achieved by considering all possible estimates of ΔR for the group of measured samples from that context by calculating a ΔR value for each possible pairing of terrestrial and marine ^{14}C ages. The distribution of ΔR values was summarised by the weighted mean and appropriate standard error for prediction. In this way it is possible to account for any additional variability due to uncertainty about the precise pairing of terrestrial and marine

samples. To assess the calendar age range that was represented by the measured contexts, the terrestrial measurements for each context that were statistically the same on the basis of a χ^2 test were combined to produce a weighted mean. This was then converted to a calibrated range using the INTCAL04 atmospheric dataset [11] and the OxCal v3.10 calibration program [37-39].

Results

The results of ^{14}C measurements on all samples is given in Table 1. The χ^2 test results (Table 2) showed that for three individual deposits the variability in measurements for a group of terrestrial or marine samples exceeded that which would be expected from random measurement variability. These were **SA-013** (terrestrial samples), **CMB-XIII** (terrestrial samples), and **SkB-68** (terrestrial and marine samples). These groups of measurements were examined to determine the likely cause of the variation and to identify the most representative ^{14}C ages from the group.

Table 1: Results of ^{14}C measurements, showing sample details, ^{14}C age (yr BP $\pm 1\sigma$) and $\delta^{13}\text{C}$ for all samples.

Table 2: Results of χ^2 test on all ^{14}C ages for terrestrial and marine samples from each context.

For **CMB-XIII** and **SkB-68** (marine), the variation was due to a single measurement that could not be combined legitimately with the remainder of the group, while in the case of **SkB-68** (terrestrial), two measurements were not consistent with the remainder of the group or with each other. In these instances, exclusion of the outlying data point(s) before repetition of the χ^2 test showed that the measurements were indistinguishable at 5% level. Therefore, for these cases the larger group of consistent measurements was taken as a more accurate representation of the ^{14}C age of the deposit.

For **SA-013** (terrestrial), the measurements span c.500 ^{14}C yr where SUERC-3543 (7600 \pm 40 BP) and SUERC-3544 (7600 \pm 35 BP) are consistent with each other. SUERC-3567/4957 (7405 \pm 28 BP) and SUERC-3566/4953 (7139 \pm 26 BP) are not

consistent with these measurements or each other. SUERC-3543 and SUERC-3544 were chosen as the most accurate representation of the deposit ^{14}C age as these are consistent on the basis of a χ^2 test with previous measurements of deer bone and charcoal submitted by the site excavators from contexts that underlay **SA-013** [40-42].

Table 3: Data for contexts that contained inconsistent measurements on the basis of a χ^2 test. Consistent measurements were used to calculate values of ΔR and the T -statistics for consistent measurement groups are shown.

The calibrated ages of the seven contexts discontinuously cover a time period from c. 8430–3890 cal. BP (c.6480–1940 BC) (Table 4).

Table 4: Calibrated age ranges and ΔR values for measured contexts.

As a group, the ΔR values from the seven deposits show significant differences ($T = 117.23$ ($\chi^2_{:0.05} = 12.59$)). When compared to the current regional mean ΔR for the British Isles (17 ± 14 ^{14}C y) the values within this study are similar to the regional mean with the exception of the highest value of 143 ± 20 for **CMB-XIII** ($T = 26.64$ ($\chi^2_{:0.05} = 3.84$)) and the lowest value of -100 ± 15 for **LO-6** ($T = 32.52$ ($\chi^2_{:0.05} = 3.84$)).

Discussion

As discussed above, a range of MRE values are available for UK waters, covering an extended time period. A MRE value of c.700 ^{14}C yr at the Vedde Ash layer (c. 10,300 ^{14}C yr BP) on the Hebridean Shelf off Northwest Scotland [22] indicates that prior to the Holocene, the ^{14}C activity of the surface ocean, in proximity to the UK, was similar to other North Atlantic sites. The ΔR values assessed by Reimer *et al.* [27] for UK waters used pairs of single terrestrial and marine samples of various types and amounts of material that were derived from archaeological deposits. This showed a large variation in ΔR values, ranging from -208 ± 75 ^{14}C to 207 ± 73 ^{14}C yr where the samples discontinuously cover a period of c.6100 yr. From this, an overall recommendation of a $\Delta R = -33 \pm 93$ ^{14}C yr was made because time-dependency in

ΔR could not be identified from the data. For a more constrained time period (c.400 BC–60 AD), using measurements of multiple individual terrestrial and marine samples, Ascough *et al.* [28] carried out assessments of ΔR from 6 individual contexts at 3 separate sites. The ΔR values were indistinguishable, giving a weighted mean value of -79 ± 17 ^{14}C yr, which is significantly different to the modern regional average ΔR for British waters of 17 ± 14 ^{14}C yr [7].

The ΔR determinations presented in this paper show different values for UK waters over a c.4500 yr span, with the highest value ($\Delta R = 143 \pm 20$ ^{14}C yr) occurring at 5600–5470 cal BP (**CMB-XIII**) and the lowest ($\Delta R = -100 \pm 15$ ^{14}C yr) at 4140–3970 cal BP (**LO-6**). It is interesting to note that the positive ΔR values all occur in the earlier period (8430–5060 cal BP), and those that have negative values are from the later deposits (4820–3890 cal BP). If changes in the ocean ^{14}C content, relative to the atmosphere, occurred in UK waters between the early Holocene and the present, then the data offered here may indicate that in addition to the higher present-day ΔR values relative to c.400 BC–60 AD [28], values from the earlier to mid Holocene were also higher relative to 400 BC–60 AD. Thus, the similarities between the majority of the ΔR values presented in this paper and the current regional mean ΔR for the British Isles shows that the ^{14}C offset between atmosphere and ocean for this region was comparable at points during the early and mid- Holocene to that of today. In contrast, at other points during the Holocene, lower ΔR values appear to be a feature of this North Atlantic region. The potential effect is one of higher ΔR values for the earlier part of the time period covered by the data illustrated here, reducing to ΔR values nearer 0 ^{14}C yr in the mid-Holocene. However, a greater density of data is required before any temporal trend can be confidently ascribed. In the measurements made by Reimer *et al.* [27], the potential for a similar trend in early ΔR values was also observed. Here, a linear regression of data for the period c. 6500–3800 cal. BP showed the possibility of a time-dependence in the values. However, similar to this study, this evaluation could only be based upon a limited number of available samples (11 individual sample pairs) for the early time period. This highlights the problem of data availability when attempting to examine pre-modern (i.e. prior to the existence of samples for which a calendar age is recorded) MRE values. Within the data presented here, the significant gaps in coverage between 6480 and 1940 cal BC are due to a

more limited availability of suitable sample material that met the selection criteria, which were imposed in order to increase reliability of determinations.

This feature raises another important aspect of MRE determinations in general and in particular for earlier time periods. At present, a variety of approaches have been adopted to determine MRE and ΔR values, and one issue raised is the use of rigorous selection protocols in order to obtain samples for ^{14}C measurements from which ΔR values are obtained. The utility of making multiple ^{14}C measurements on separate individual samples from a single context is highlighted by the variation observed in the measurements from single archaeological deposits at **SA** and **CMB**. If single measurements had been made to determine ΔR from one of these contexts, a wide range in potential values could have been obtained where material that is apparently intrusive would have remained unidentified. This variability in ^{14}C ages within a single deposit means that it is more difficult to obtain a reliable ΔR value from a single marine / terrestrial pair. It is possible that in these instances, more effective application of sample selection protocols and multiple measurements might allow more accurate ΔR assessments and enable the removal of some of the uncertainty associated with MRE determinations. One aspect of both modern and palaeo- studies that seek to investigate MRE and ΔR values is that of the methodology applied to determine the values. Improvements in methodological approaches, including multiple sampling, will have the result of improving the precision to which MRE and ΔR values can be assigned, but more importantly, they will enable improved accuracy. At present, there is a growing interest in investigating MRE offsets in a range of global locations and this provides the opportunity to apply rigorous selection protocols to obtain sample material that will give a realistic assessment of MRE for a given time period and geographic location. Existing data can then be incorporated into a framework within which it is important to assess the methodological approaches used to determine individual MRE/ ΔR values in a critical manner.

Leading from this discussion is a question that is important to address; namely, that of how accurately it is practically possible to determine MRE values through time and space, given the various methods of determination. For example, it is difficult to interpret the differences between ΔR values at **LO-6** (-100 ± 15) and **BB-XF** (-13 ± 18) that relate to the period 2190-1940 BC. It is possible that such differences in ΔR

values might be observed between relatively small distances at a single point in time (the sites are located <50 km apart), and it is also possible that the data from the two sites relate to different points within the calibrated age range of c.110 cal yr that is common to both contexts. In this instance it could be that both ΔR values were experienced at **LO-6** and **BB-XF**, where one is the ΔR that applied during the earlier part of the age range, and one to the later. It may be that this was a period of rapid fluctuations in surface water ^{14}C at the sites that has resulted in the apparent differences in ΔR values from the two contexts. Therefore, the difference in ΔR values may be either a reflection of differences in the ^{14}C content of the surface water at the two sites, or may be a product of the resolution to which the methodology can determine ΔR in this instance. In the former case, this could result from local circulation differences or variation in the input of terrestrial water components to surface water around the site. Again, these questions require more intensive data coverage and investigation before they are likely to be adequately resolved.

An improved critical awareness should also extend to the assignment of potential forcing mechanisms for proposed temporal and geographic variability in MRE, and caution should be used when suggesting causal links between evidence of palaeoclimatic changes and evidence of MRE variations, when the two appear to coincide. It is important to consider the implication that many of the palaeoclimatic variations, which can provide potential forcing mechanisms for MRE change, are themselves placed on an absolute timescale using ^{14}C measurements of marine material (e.g. from marine cores). An important difficulty for paleoclimate investigation is often that of the most accurate and precise correction that can be applied to marine samples. The accuracy of the paleoclimate chronology constructed from these measurements depends upon several factors, including the accuracy of the correction for the MRE. The implication is that an inaccurate MRE correction may lead to inaccuracies in correlation of paleoclimate events and interpretations involving forcing mechanisms and their effects. The timing of events that is inferred from paleoclimatic proxy data for the early Holocene is often relatively rapid. For example, during the climate transition from the Younger Dryas to the Holocene, factors such as wind speed, precipitation, temperature, and sea ice appear to have changed significantly throughout the Northern Hemisphere on sub-decadal time scales [43]. Although a calendrical chronology can be confidently ascribed with c.1% precision to

ice core data for this period [44], identification of coinciding rapid changes in marine cores highlights the need for both accurate and precise ^{14}C measurements of marine material to support interpretations. The use of unsuitable data in an attempt to define the MRE for this important paleoclimatic period would be counter-productive and merely serve to increase uncertainty. The question therefore remains over the most practical approach to take towards integrating paleoclimatic evidence that is dated using marine material within a wider framework that includes terrestrial and ice-core records. It is conceivable that some of the interpretations and correlations that have been proposed on the basis of ^{14}C measurements made on marine material for the early Holocene (and previous periods) may contain additional chronological uncertainties that have not yet been accounted for.

Conclusions

The results of this study indicate a fluctuating MRE for UK coastal waters during the early to mid-Holocene. Most of the ΔR values are not significantly different from the modern-day value of 17 ± 14 ^{14}C yr with 2 exceptions. At 3650-3520 BC there is a significantly increased ΔR value of 143 ± 20 . At one location (**LO-6**) during 2190-2020 BC the value is significantly reduced (-100 ± 15) compared to the modern value but indistinguishable from ΔR determinations made for this area during the periods c.400 BC–60 AD and c.1000 AD [28,45]. Several issues are identified which are important considerations for determining MRE values. These include repeat measurements of separate individual samples from single deposits and the adoption of criteria designed to ensure that measured terrestrial and marine sample material is likely to be of the same actual calendar age. If samples that do not meet the various criteria are used in assessments then the potential uncertainty associated with determinations is increased. There is a need to investigate the underlying mechanisms behind MRE values in a quantitative manner in specific ocean areas, for example, to what extent would a particular environmental variable (such as deep ocean water upwelling) have to change in order to effect a variation in MRE at a location. At present there is a need to coordinate research strategies in order to produce useful assessments of the MRE and to have an agreed approach to correction.

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Figure captions

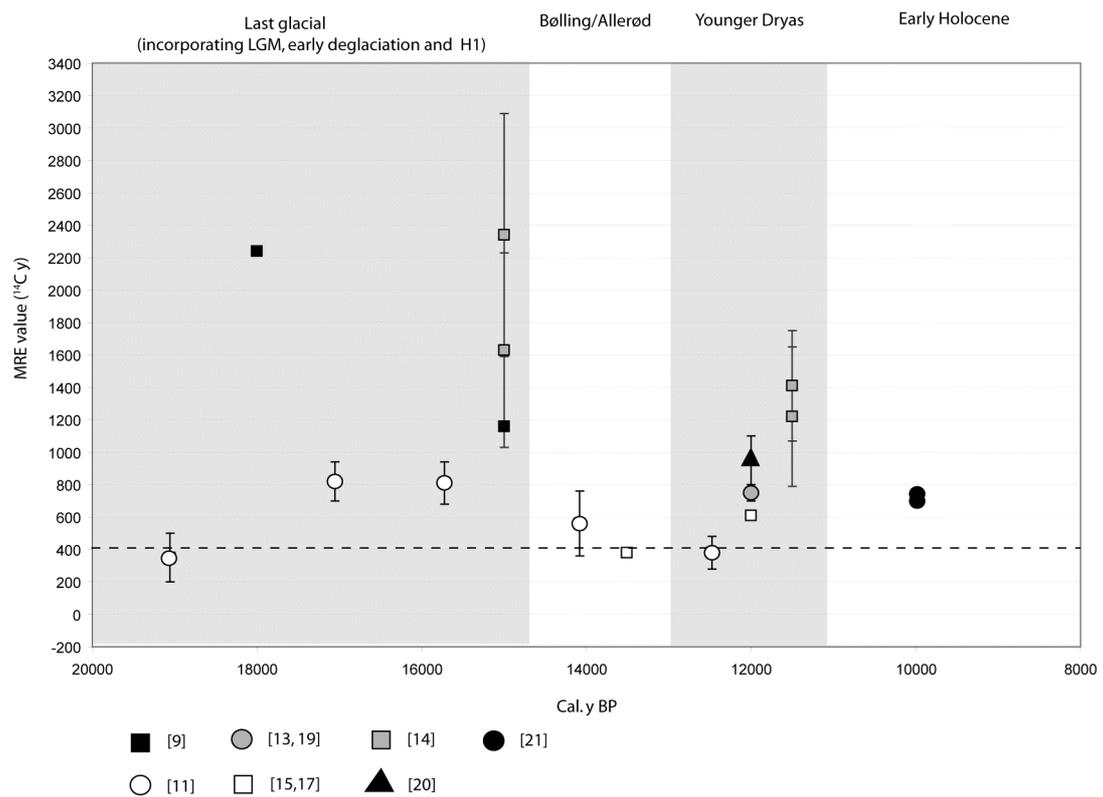


Figure 1: A compilation of North Atlantic MRE assessments for the last glacial to early Holocene, incorporating Mediterranean data [11]. The modern-day estimated value for the North Atlantic (c.400 ^{14}C yr) is indicated by the dashed line.

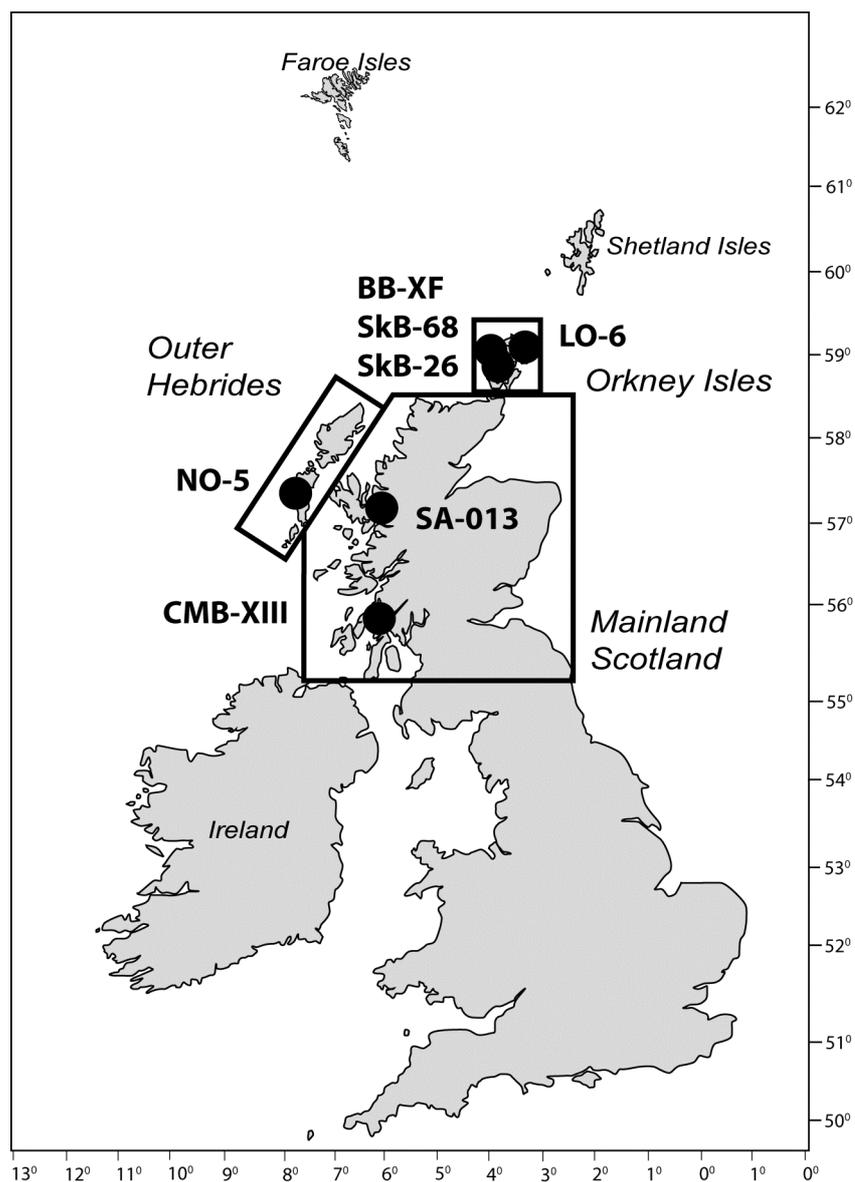


Figure 2: Location of the sampling sites within Mainland Scotland, the Outer Hebrides and the Orkney Isles.

Tables

Deposit	Sample ID	Measurement ID	Material	^{14}C age (yr BP $\pm 1\sigma$)	$\delta^{13}\text{C}$
SA-013	13-01A	SUERC-3566* ¹	Red deer	7135 \pm 35	-21.8
SA-013		SUERC-4953* ¹	Red deer	7145 \pm 40	-21.8
SA-013	13-01B	SUERC-3567* ²	Red deer	7400 \pm 40	-22.3
SA-013		SUERC-4957* ²	Red deer	7410 \pm 40	-22.3
SA-013	13-01C	SUERC-3543	Red deer	7600 \pm 40	-21.9
SA-013	13-01D	SUERC-3544	Red deer	7600 \pm 35	-22.0
SA-013	13-02E	SUERC-241	Marine mollusc	8025 \pm 60	1.7
SA-013	13-02F	SUERC-242	Marine mollusc	8028 \pm 60	1.1
SA-013	13-02G	SUERC-3167	Marine mollusc	7975 \pm 40	0.7

SA-013	13-02H	SUERC-3168	Marine mollusc	8045 ± 40	0.9
CMB-XIII	XIII-01A	SUERC-3587	Hazlenut	4775 ± 35	-22.7
CMB-XIII	XIII-01B	SUERC-3588	Hazlenut	4785 ± 45	-25.7
CMB-XIII	XIII-01C	SUERC-3592* ³	Hazlenut	4785 ± 40	-26.6
CMB-XIII		SUERC-4951* ³	Hazlenut	4840 ± 35	-26.6
CMB-XIII	XIII-01D	SUERC-4952* ⁴	Hazlenut	5070 ± 40	-23.1
CMB-XIII		SUERC-3593* ⁴	Hazlenut	5035 ± 40	-23.1
CMB-XIII	XIII-02E	SUERC-4947	Marine mollusc	5330 ± 35	1.4
CMB-XIII	XIII-02F	SUERC-4948	Marine mollusc	5310 ± 40	1.3
CMB-XIII	XIII-02G	SUERC-4949	Marine mollusc	5325 ± 40	0.6
CMB-XIII	XIII-02H	SUERC-4950	Marine mollusc	5335 ± 40	0.7
NO-5	C5-01A	AA-50332	Hazlenut	7525 ± 80	-24.4
NO-5	C5-01B	AA-50333	Hazlenut	7395 ± 45	-23.7
NO-5	C5-01C	AA-50334	Hazlenut	7420 ± 45	-24.1
NO-5	C5-02E	AA-53250	Marine mollusc	7860 ± 45	1.5
NO-5	C5-02F	AA-53251	Marine mollusc	7880 ± 45	1.1
SkB-68	68-01A	SUERC-3126	Cereal grain	4270 ± 40	-24.2
SkB-68	68-01B	SUERC-3127	Cereal grain	4735 ± 40	-24.2
SkB-68	68-01C	SUERC-3128	Cereal grain	4555 ± 40	-24.5
SkB-68	68-01D	SUERC-3129	Cereal grain	4605 ± 40	-24.2
SkB-68	68-01E	SUERC-4119	Cereal grain	4525 ± 40	-21.8
SkB-68	68-01F	SUERC-4121	Cereal grain	4530 ± 35	-21.3
SkB-68	68-02E	SUERC-3130	Marine mollusc	4975 ± 40	-0.5
SkB-68	68-02F	SUERC-3131	Marine mollusc	4995 ± 40	1.2
SkB-68	68-02G	SUERC-3132	Marine mollusc	4960 ± 45	0.9
SkB-68	68-02H	SUERC-4122* ⁵	Marine mollusc	4790 ± 40	-0.7
SkB-68		SUERC-4959* ⁵	Marine mollusc	4745 ± 40	1.0
SkB-26	26-01A	SUERC-3576	Cow	4140 ± 40	-22.0
SkB-26	26-01B	SUERC-4958	Cow	4015 ± 40	-21.4
SkB-26	26-01C	SUERC-3578	Cow	4110 ± 35	-21.6
SkB-26	26-01D	SUERC-3582	Cow	4145 ± 45	-21.3
SkB-26	26-02E	SUERC-232	Marine mollusc	4440 ± 50	1.6
SkB-26	26-02F	SUERC-233	Marine mollusc	4370 ± 45	0.6
SkB-26	26-02G	SUERC-234	Marine mollusc	4445 ± 50	0.9
SkB-26	26-02H	SUERC-235	Marine mollusc	4405 ± 45	0.9
BB-XF	XF-01A	SUERC-3588	Red deer	3640 ± 35	-22.0
BB-XF	XF-01B	SUERC-3572	Red deer	3645 ± 40	-22.4
BB-XF	XF-01C	SUERC-3573	Red deer	3625 ± 40	-22.3
BB-XF	XF-01D	SUERC-3575	Red deer	3685 ± 40	-22.1
BB-XF	XF-02E	SUERC-221	Marine mollusc	3920 ± 50	0.6
BB-XF	XF-02F	SUERC-222	Marine mollusc	3980 ± 50	1.2
BB-XF	XF-02G	SUERC-223	Marine mollusc	4000 ± 50	1.5
BB-XF	XF-02H	SUERC-224	Marine mollusc	3956 ± 55	1.5
LO-6	6-01A	SUERC-1837	Cereal grain	3735 ± 40	-23.1
LO-6	6-01B	SUERC-1838	Cereal grain	3690 ± 35	-24.0
LO-6	6-01C	SUERC-3228	Cereal grain	3690 ± 35	-24.9
LO-6	6-01D	SUERC-1839	Cereal grain	3685 ± 40	-24.7
LO-6	6-02E	SUERC-1840	Marine mollusc	3960 ± 40	1.3

LO-6	6-02F	SUERC-1841	Marine mollusc	3915 ± 35	1.2
LO-6	6-02G	SUERC-3137	Marine mollusc	3950 ± 35	1.0
LO-6	6-02H	SUERC-3139	Marine mollusc	3880 ± 45	1.0

Table 1: Results of ^{14}C measurements, showing sample details, ^{14}C age (yr BP $\pm 1\sigma$) and $\delta^{13}\text{C}$ for all samples. **n* indicates repeat measurements of a single sample. Where these were statistically indistinguishable the two measurements were combined in a weighted mean for subsequent analysis.

Deposit	χ^2 test result (terrestrial samples)	χ^2 test result (marine samples)
SA-013	156.46; ($\chi^2_{:0.05} = 7.81$)	1.64; ($\chi^2_{:0.05} = 7.81$)
NO-5	2.02; ($\chi^2_{:0.05} = 5.99$)	0.10; ($\chi^2_{:0.05} = 3.84$)
CMB-XIII	57.25; ($\chi^2_{:0.05} = 7.81$)	0.22; ($\chi^2_{:0.05} = 7.81$)
SkB-68	72.28; ($\chi^2_{:0.05} = 11.1$)	16.59; ($\chi^2_{:0.05} = 7.81$)
SkB-26	6.60; ($\chi^2_{:0.05} = 7.81$)	1.64; ($\chi^2_{:0.05} = 7.81$)
BB-XF	1.24; ($\chi^2_{:0.05} = 7.81$)	1.42; ($\chi^2_{:0.05} = 7.81$)
LO-6	1.06; ($\chi^2_{:0.05} = 7.81$)	2.31; ($\chi^2_{:0.05} = 7.81$)

Table 2: Results of χ^2 test on all ^{14}C ages for terrestrial and marine samples from each context.

Context	Consistent measurements	Age BP $\pm 1\sigma$	Inconsistent measurements	Age BP $\pm 1\sigma$	<i>T</i> value
SA-013 (Terrestrial)	SUERC-3543 SUERC-3544	7600 \pm 40 7600 \pm 35	SUERC-3567/4957 SUERC-3566/4953	7139 \pm 26 7405 \pm 28	0.00 ($\chi^2_{:0.05}$ = 3.84)
CMB-XIII (Terrestrial)	SUERC-3587 SUERC-3588 SUERC-3592/4951	4775 \pm 35 4785 \pm 45 4816 \pm 27	SUERC-3593/4952	5053 \pm 28	0.96 ($\chi^2_{:0.05}$ = 5.99)
SkB-68 (Terrestrial)	SUERC-3128 SUERC-3129 SUERC-4119 SUERC-4121	4555 \pm 40 4605 \pm 40 4525 \pm 40 4530 \pm 35	SUERC-3126 SUERC-3127	4270 \pm 40 4735 \pm 40	2.61 ($\chi^2_{:0.05}$ = 7.81)
SkB-68 (Marine)	SUERC-3130 SUERC-3131 SUERC-3132	4975 \pm 40 4995 \pm 40 4960 \pm 45	SUERC-4122/4959	4768 \pm 28	0.35($\chi^2_{:0.05}$ = 5.99)

Table 3: Data for contexts that contained inconsistent measurements on the basis of a χ^2 test. Consistent measurements were used to calculate values of ΔR and the *T*-statistics for consistent measurement groups are shown.

Context	Terrestrial weighted mean age BP $\pm 1\sigma$	2σ cal. range	ΔR
SA-013	7600 \pm 26	6480-6420 BC	64 \pm 19
NO-5	7424 \pm 30	6390-6230 BC	79 \pm 32
CMB-XIII	4798 \pm 19	3650-3520 BC	143 \pm 20
SkB-68	4552 \pm 19	3370-3110 BC	26 \pm 24
SkB-26	4101 \pm 29	2870-2500 BC	-20 \pm 21
LO-6	3699 \pm 19	2190-2020 BC	-100 \pm 15
BB-XF	3648 \pm 19	2130-1940 BC	-13 \pm 18

Table 4: Calibrated age ranges and ΔR values for measured contexts.