volume of the sample fluid was 10 times higher than that of the cell solution.

After 10-fold preconcentration, the cell solution was washed with distilled water from reservoir I. At a 10-fold volume of filtrate referred to the cell fluid >98% of Hg, Cd, and Cu were retained by poly(ethyleneimine-methylthiourea), whereas poly(ethyleneimine) retained 75-95% of Cu, Ni, Zn, Cd and Cu. Note that the concentration of Na in the cell was as low as 3-5 p.p.m. after the washing. This means that the Na concentration decreased by 10^4 times and that a factor of 10^5 (relative preconcentration factor) for the metals retained is achieved when taking into account the first preconcentration step (absolute preconcentration). Another absolute preconcentration step (up to one order) can be applied by reduction of the cell solution volume using conventional ultrafiltration. In addition, it is an advantage for the analysis that the sample can be handled in the homogeneous phase

In conclusion, these polymeric reagents in combination with membrane filtration allow the enrichment and separation of trace elements in the presence of comparable and large excess quantities of sample constituents which could interfere with subsequent analysis.

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Evidence for an increase in cosmogenic ^{10}Be during a geomagnetic reversal

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Reversals in the geomagnetic field, which occur every few hundred thousand years, represent a dramatic change in the Earth's environment. Although there is no satisfactory theory for such reversals, it is generally accepted that the dipole field intensity decreases to <20% of its 'normal' value for a few thousand years during the change in direction[1]. Because the galactic and solar cosmic rays which impinge on the Earth's atmosphere are charged, a significant fraction (about half) of them are deflected by the geomagnetic field[2]. At the time of a reversal, this magnetic shielding is greatly reduced, and it has been suggested that the increased flux of high-energy particles could have effects on evolutionary[3] or climatic[4] processes. For example, the statistically significant coincidence in levels of some marine faunal extinctions and reversal boundaries in ocean sediments[5] could be caused, directly or indirectly, by the decreased geomagnetic intensity during the reversal. We report here evidence in marine sediments for an increase in cosmogenic ^{10}Be production in the Earth's atmosphere during the Brunhes–Matuyama reversal 730,000 yr ago. In addition to confirming an increase in cosmogenic isotope production, the results provide information on the magnitude and duration of the geomagnetic intensity decrease during such an event, and the depth at which remanent magnetism is acquired in marine sediments.

In previous work, we found no significant evidence for increased ^{10}Be (half-life 1.5 Myr) at a reversal boundary[6]. Among the explanations we gave for this negative result was that the sedimentation rate of the core studied (1.13 cm kyr^{-1}) was not high enough to retain a significant signal. We have thus looked at a core having a sedimentation rate of ~2.5 cm kyr^{-1}. This core, V16-58, was taken at 46°30′ S, 31°16′ E at a depth of 4,731 m. The material near the reversal zone is mostly diatomaceous lutite with thin interspersed layers of calcareous ooze[7]. The identification of the reversal level at ~1,129 cm as the Brunhes–Matuyama boundary, and the estimation of the sedimentation rate at this level are based on the biostratigraphy of Hays[7], with more recent studies putting the 425,000-yr extinction level of the radiolarian *Stylatractus universus*[8] at 420 cm (J. Morley, personal communication). The top part of the core has apparently suffered from a reduced sedimentation rate, hiatus or erosion.

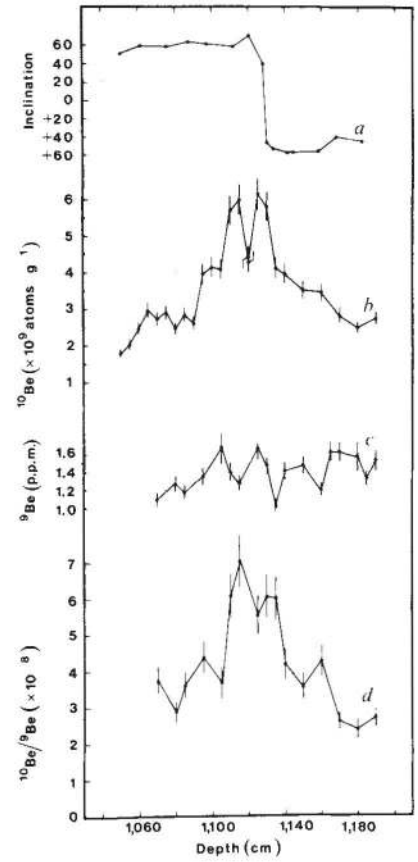

Fig. 1 *a*, Magnetic inclination; *b*, ^{10}Be concentration; *c*, ^{9}Be concentration; *d*, ^{10}Be/^{9}Be ratio as a function of depth in core V16-58.

Initial magnetic measurements, indicating a reversal level at ~1,129 cm, as shown in Fig. 1, were carried out using procedures described in ref. 9. After the ^{10}Be results became available, the core was resampled and the position of the reversal confirmed. A more detailed palaeomagnetic investigation around the reversal level is now in progress.

For the ^{10}Be measurements, samples of 0.3-1 g were dissolved in the presence of 0.5 mg of ^{9}Be carrier, and chemical purification carried out as described earlier[6]. The ^{10}Be measurements were made on a Tandetron accelerator mass spectrometer facility, using the procedure described in ref. 10. Several thousand ^{10}Be events were recorded for each sample, and the estimated uncertainties are due to instrumental variations, as deduced from replicate measurements of standards[10]. The results are shown in Fig. 1. The low value at 1,120 cm during the initial series of measurements was so surprising that we processed and measured a second portion of the same sample. The good agreement between the two results both confirms the low value for this sample, and gives us added confidence that our assigned uncertainties are realistic.

As can be seen in Fig. 1, the ^{10}Be concentration increases by a factor of ~2 for samples near the reversal level. Before

ascribing this to a production increase, it is useful to consider other possible factors which could effect a change in ^{10}Be concentrations. For example, a change in the biological productivity, possibly associated with the reversal, could give rise to a variable biogenic component (opal or calcium carbonate) in the sediments; this would probably give a variable dilution of the ^{10}Be. Another possibility is that some change in environmental conditions might lead to an 'enrichment' of beryllium compared with other components in the sediment. To examine these alternatives, we have measured the stable isotope ^{9}Be over the same interval as the ^{10}Be. The ^{9}Be was measured by flameless atomic absorption spectrometry. Uncertainties in the ^{9}Be concentrations are estimated from the reproducibility of the measurements (in all cases except one, the results are the average of at least two determinations). The decision to measure ^{9}Be was made after the completion of the ^{10}Be measurements. Unfortunately, this meant we did not have material remaining for some of the levels, including the critical minimum at 1,120 cm, in which ^{10}Be had been determined.

Although there are variations in the measured ^{9}Be, these do not parallel those of ^{10}Be. In fact, the ^{10}Be/^{9}Be ratio, also given in Fig. 1, shows a peak similar to ^{10}Be alone. Unfortunately, this normalization may not be completely satisfactory. Although the oceanic geochemistry of ^{9}Be is still poorly known, we believe[11,12], contrary to Measures and Edmond[13,14], that a significant fraction of ^{9}Be may be deposited in marine sediments without coming to equilibrium with ^{10}Be. In such a case, the ^{9}Be would be an imperfect tracer for ^{10}Be, although it still should compensate for a variable biogenic component.

While the ^{10}Be/^{9}Be evidence strongly supports the interpretation of the observed increase of ^{10}Be concentration as being due to increased production, it is not necessarily a better monitor of ^{10}Be production variations. However, because of the similarity in the two curves (except for the minimum at 1,120 cm), the conclusions that follow are relatively insensitive to which one is used.

We also note that both ^{10}Be concentration and ^{10}Be/^{9}Be are of potential interest as dating tools[11,15]. The strong variation in these parameters observed here demonstrates that caution must be exercised when dating by such procedures near reversal levels. In a preliminary study, Ku *et al.*[15] have also observed a high ^{10}Be concentration in a single sample near the Brunhes–Matuyama reversal level. However, they also found an abnormally low concentration in a sample nearby, so the origin of their variations is not clear.

The ^{10}Be (or ^{10}Be/^{9}Be) signal is not expected to reflect directly the geomagnetic palaeointensity profile for two reasons. First, the effect of the magnetic field on production rate is a function of geomagnetic latitude[2]. The degree to which mixing in the atmosphere and the ocean average out this variation is not yet established. However, the mid-latitude location of V16-58, in a region of significant input of stratospheric aerosols, means that its sediment probably should reflect a reasonably 'average' production effect. Second, once the ^{10}Be is incorporated in the sediment, it is subject to mixing processes by benthic organisms. To illustrate the potential effect of this bioturbation, we adopt a model[16] in which the sediment is assumed to be completely homogenized over a given depth, called the mixed layer, with no mixing below this depth. A more sophisticated model has been proposed which treats the mixing process explicitly by diffusion[17]. However, we do not have independent information on the appropriate diffusion constant for this core. For diffusion constants >100 cm^2 kyr^{-1} the uniform mixing assumption is a good approximation to the diffusion model.

Adopting a mixed-layer thickness of 10 cm, we calculated output profiles for several different assumed input profiles. Figure 2 shows an example of one of these which fits the observed ^{10}Be profile reasonably well. As can be seen in Fig. 2, the bioturbation has three effects. It attenuates the maximum increase in production rate; it tends to smooth out rapid variations; and it moves the ^{10}Be levels down by approximately the assumed mixing depth.

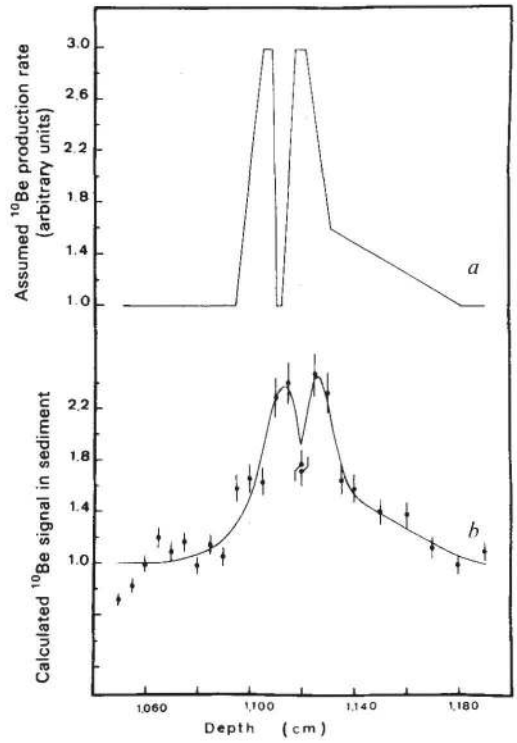

Fig. 2 *a*, Assumed ^{10}Be production rate profile; *b*, solid curve is calculated signal in sediment, using the bioturbation model described in the text, with a mixing depth of 10 cm. Points are experimental data from Fig. 1.

The input profile of Fig. 2 is, of course, not unique, and others which fit the experimental data equally well, or better, could be found. However, we do have some constraints. First, the maximum increase in production during the reversal cannot be significantly larger than the factor of 3 we have chosen, which corresponds essentially to a zero-intensity magnetic field[2]. Second, the total area under the input and observed curves must be the same. Thus, the input function in Fig. 2 should represent at least the major features of the actual production curve. In particular, the mean duration for the production increase (and thus magnetic intensity decrease) should be approximately correct. As can be seen in Fig. 1, the interval of increased ^{10}Be is significantly longer than the time taken for the reversal of inclination. Such a result is consistent with other evidence which suggests that the geomagnetic field intensity is low before and after the change in inclination[1,18]. From Fig. 1, the interval of increased production is ~30–60 cm, depending on what level of increase is chosen. Assuming a sedimentation rate of 2.5 cm kyr^{-1}, this interval corresponds to ~12,000–24,000 yr; this is similar to the time interval for the decreased magnetic field at another reversal, as estimated in ref. 18.

As can be seen in Fig. 2, the minimum at 1,120 cm implies a very significant decrease in production. However, the magnitude and duration of this decrease are obviously very strongly dependent on the parameters of the bioturbation model used. Thus, even if this decrease is due to an increased field intensity, the quantitative nature of the required change remains uncertain. It is interesting, however, that other authors have also found evidence for high intensities midway through reversals[19,20]. More definite conclusions along these lines will necessitate more detailed ^{10}Be and palaeomagnetic profiles, comparison between several cores and more reliable bioturbation modelling. With regard to the latter, although the bioturbation depth used here is fairly typical[16,17], we wonder whether it can be reconciled with the rather abrupt variations seen in ^{10}Be, ^{9}Be and calcium carbonate[7], over intervals as small as 5 cm. Piseas has recently made the same point regarding oxygen-isotope profiles in other cores[21]. Reduced bioturbation would mean that the actual ^{10}Be

production profile would approach more closely the observed ^{10}Be profile.

As we have discussed earlier[6], the location of the ^{10}Be peak compared with the reversal level can also provide information on the depth at which remanent magnetization is acquired in marine cores. In the present case, it can be observed that the midpoint in the ^{10}Be peak is ~10 cm above the change in magnetic inclination (or ~15 cm if we use the input profile of Fig. 2). Neglecting the residence time of ^{10}Be in the ocean[22], and assuming that the ^{10}Be midpoint corresponds to the change in direction, this would indicate that the magnetic remanence was 'locked in' at a depth of ~10–15 cm in the sediment (or slightly more, allowing for later compaction). This is consistent with the idea that the magnetic remanence is acquired at the base of the bioturbation zone.

We have presented the first direct evidence for increased cosmic ray radiation in the Earth's atmosphere during a geomagnetic reversal. Making some reasonable assumptions, the data also allow one to deduce significant information on the magnitude and duration of the magnetic intensity decrease during a reversal, and the depth at which detrital magnetic remanence is acquired in a marine sediment. It will be interesting to pursue this type of study at other reversal boundaries to determine whether there are significant differences in their intensity profiles, and, if so, whether they could be correlated with other features such as the severity of faunal extinctions. This work also demonstrates that ^{10}Be should be a potentially powerful tool for testing the global nature of various geomagnetic 'excursions' that have been observed during the Brunhes epoch[23].

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Re-dating the English art-historical tree-ring chronologies

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Precisely dated oak (*Quercus petraea* Liebl. and *Q. robur* L. and their hybrids) tree-ring chronologies that show consistent cross-dating from Germany to England to Ireland[1,2] have been labelled Type H[3]. In contrast, there have been difficulties in specifying the exact date ranges of some oak chronologies (termed Type A)[3] constructed from art-historical timbers in England[4,5] and the Netherlands[6,7]. It has been asserted that the oak planks and boards used in the English art-historical chronologies derived from England and Flanders[3,8]. The failure of these chronologies to date uniquely against Type H chronologies from the British Isles has led to suggestions that the timbers were imports, probably from the Baltic area[1,9], views supported by historical evidence[10,11]. It has also been suggested that the dating procedure used for these chronologies has an element of circularity which could result in an erroneous placement of the chronologies going undetected[12]. Evidence is presented here which indicates that the art-historical chronologies have been incorrectly dated, that they represent imports into England and Flanders and that failure to take account of exotic origins has led to the use of unsuitable estimates for missing sapwood.

In 1975, information on cold winters in the fifteenth century was derived from a section of art-historical oak tree-ring chronology, MC18, dated[13] to AD 1234–1550. This section of chronology had originally been designated[4] to the years 1230–1546 and subsequently reference chronologies related to MC18 (designated Refs1–4) were returned to this same '1546' dating[3,5,14]. These chronologies, all >270 yr in length, form an internally consistent group covering the period from the early twelfth to the early seventeenth centuries. At other times Refs1–4 have been moved 1-yr-back, equivalent to a '1545' dating[8,15,16] of MC18. The possibility of a circular argument in the dating of these art-historical chronologies has recently been discussed in an article which also gives documentary evidence for importation of oak planks and boards into England and Flanders from the Baltic during the later Middle Ages[12]. Since that publication, three new pieces of evidence relevant to these Type A chronologies have become available.

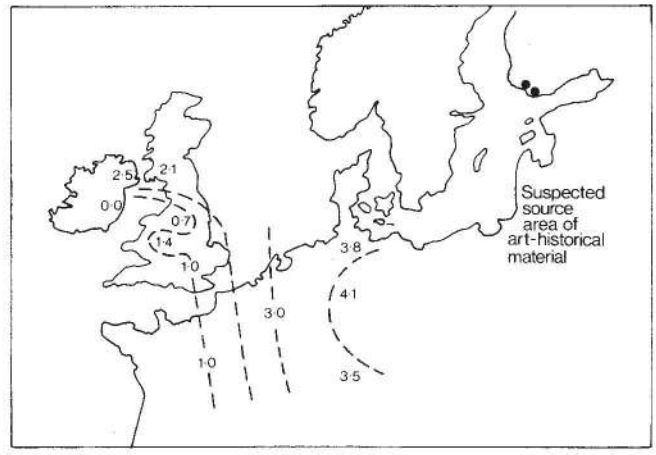

Fig. 1 Mean '*t*' values for the nine art-historical chronologies compared with 11 available Type H chronologies as in Table 1*c*, with the Type A chronologies in the 4-yr-forward or '1550' position. ●, The source of the Finnish oak sapwood values.

First, one of us (J.H.) acquired some medieval timbers from excavations at Ipswich. The mean ring pattern of three timbers was found to span the years AD 1128–1293 by cross-dating against the established, and absolutely dated, German Type H (after Huber[3]) chronologies of Eckstein (personal communication) and Delorme[17]. The correlation values between the Ipswich mean ring-pattern and these two chronologies, obtained using the Belfast CROS program[18], were '*t*' = 7.2 and '*t*' = 4.1 respectively for overlaps of 166 yr (normally '*t*' values >3.5 in association with overlaps of more than 100 yr are regarded as significant indicators of a likely tree-ring match). No significant