Reports

range of the dendrochronological corrections (*4*).

In Tito Bustillo, the Magdalenian people executed a large panel of horses, deer, and other animals on a sloping section of the cave roof near the end of a passage, several hundred meters from the entrance in which they camped. Evidence of this activity is preserved in a single level 50 cm below the present floor in the form of intrusive artifacts in the otherwise sterile strata of layered fine quartz sands. This setting affords an unambiguous stratigraphic association with the paintings.

This association was investigated by obtaininng 17 25-mm cylindrical specimens of sediment representing a complete coverage of the exposed 54-cm section down to the level utilized by the artists. Remanent magnetic declination, inclination, and intensity for each sample were then obtained by using a Digico spinner magnetometer (*2*). The natural remanent magnetization was "cleaned" in an alternating field of 150 oersteds, and the cleaned data were plotted as shown in Fig. 1. Certain features of the three plots of the field vector record at Tito Bustillo can be recognized in the corresponding Windermere curves, Fig. 2.

We first discuss the inclination record. In Fig. 1 it can be seen that the measured values exhibit a cyclic pattern roughly symmetrical about the ordinate, which is drawn at the value expected at the site of the cave for an axial dipole field. The mean of the measured inclinations corresponds to a paleomagnetic latitude of 46.5°N, which is sufficiently close to the actual site latitude of 44.5°N for us to accept, with some confidence, that the sediment accurately records the ancient inclination. This being so, we may attempt a correlation of the three maxima in inclination, labeled A, B, and C in Fig. 1, with features recognized in the inclination record for Lake Windermere (*2*) (Fig. 2), where several oscillations of similar amplitude (10°) are, in fact, observed. When we consider the intensity and declination data as well (below), we find that the most reasonable correlation is with the features labeled A, B, and C in Fig. 2, all within the stratigraphic unit b.

We now examine the intensity records, bearing in mind that this parameter depends on the mineralogical composition of the sediment (different at the two sites) as well as the strength of the ancient geomagnetic field. This

Paleomagnetic Dating of Cave Paintings in Tito Bustillo Cave, Asturias, Spain

Abstract. *Geomagnetic variations recorded in sediments deposited in Tito Bustillo Cave, Asturias, Spain, have been correlated with part of the geomagnetic record established for Lake Windermere, England. An age of between 11,200 and 11,600 years is suggested for a frieze of animals discovered in the cave, so that these polychrome paintings may be attributed to late Ice Age hunters (Magdalenian V–VI).*

We have used paleomagnetic data to supply archeologists with the first dates for Upper Paleolithic cave paintings determined independently of stylistic comparisons or the radiocarbon method. A frieze of animals in the recently discovered (1969) cave of Tito Bustillo, Ribadesella, Asturias, Spain, has been dated at between 11,200 and 11,600 years before present by comparing the magnetic declination, inclination, and intensity curves from this site with reference data from Lake Windermere, England (*1, 2*). These polychrome paintings are thus attributed to late Ice Age hunters (Magdalenian V–VI) of the final phase of the last glaciation, an interval that accords well with Leroi-Gourhan's (*3*) chronology for the "classical period" of Upper Paleolithic parietal art.

Firm dating of Upper Paleolithic cave paintings has long been a problem for prehistorians. A large proportion of the sites—heavily concentrated in contiguous karst areas of Spain and France but also occurring in Portugal, Italy, Turkey, and southern Russia—were well known and excavated before the discovery of the radiocarbon technique. Even with the availability of the ^{14}C method much parietal art could not be dated because it is usually located in remote areas of the caves, in perpetual darkness, where contemporary human visits were rare enough to result in the deposit of little charcoal or other datable organic material. Further, stratigraphic evidence, even when it could be unequivocally connected with the paintings overhead, offered no absolute chronology. Therefore, dating of cave art has relied on stylistic comparisons and on relatively few radiocarbon dates. These radiocarbon dates are themselves insecure because of uncertain accuracy beyond the

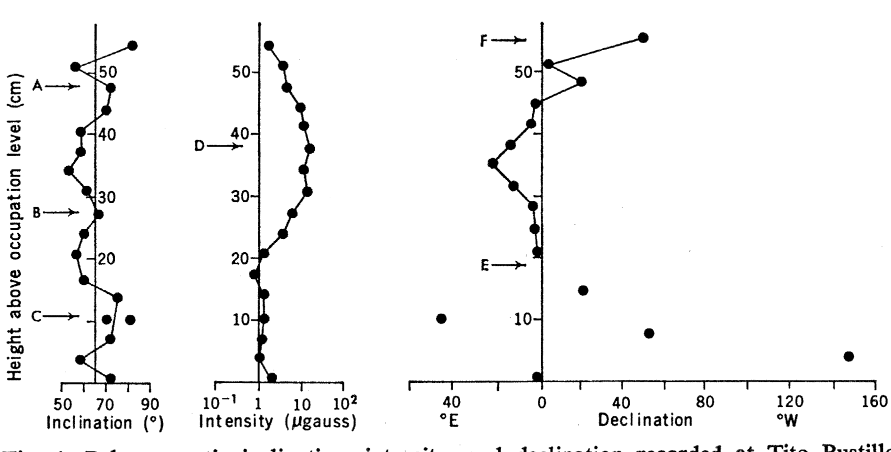

Fig. 1. Paleomagnetic inclination, intensity, and declination recorded at Tito Bustillo Cave, Asturias, Spain, after cleaning in an alternating magnetic field with a peak value of 150 oersteds.

difficulty is not as restrictive as might be imagined because at both sites we are concerned with a homogeneous layer of sediment within which we do not expect to find notable changes of concentration of the magnetic mineral content. Hence, the intensity log at both sites can be used as a rough guide to variations in the strength of the ancient geomagnetic field which induced the remanent magnetism. The Tito Bustillo samples reveal an intensity maximum labeled D in Fig. 1, and this maximum is correlated with the intensity peak also labeled D in the Windermere record in Fig. 2.

Turning to the variations in declination, we now refer to perhaps the most striking feature of all, the wide scatter recorded within the climatic amelioration horizon at Windermere (unit c in Fig. 2) above which, in units b and a, the sinusoidal pattern of declination variations is developed. In Fig. 1 we note that the declination at Tito Bustillo also shows considerable scatter in the lower 20 cm. The horizon at which the declination ceases to exhibit large scatter at Tito Bustillo Cave and at Windermere is labeled E in Figs. 1 and 2 and is used as a point of correlation between the two curves. Another useful feature exhibited by the declination curve at Windermere is an easterly declination swing which also occurs within the finely laminated clay, unit b. It attains a maximum at the point labeled F in Fig. 2. In Tito Bustillo the declination is observed to become increasingly easterly between levels of 40 and 54 cm (top) above the occupation level, but the peak of this easterly swing is not observed in the section of sediment sampled. However, assuming that the topmost sample records the maximum easterly declination, it can be correlated with the level labeled F in Fig. 2.

We now estimate the ages of features A through F which we have used to correlate the records from Tito Bustillo with those from Windermere. Mackereth and co-workers (*1*) showed that the swings in declination recorded by the finely laminated clay and postglacial organic units had a regular period, which could be determined from the suite of radiocarbon ages summarized in the column at the right of Fig. 2. Thompson (*2*) estimated the period to be 2800 years by Fourier and spectral analysis of the variations, and with this value "magnetic" ages can be assigned to the core. The age of swing F is thus determined to be 10,500 years, and if

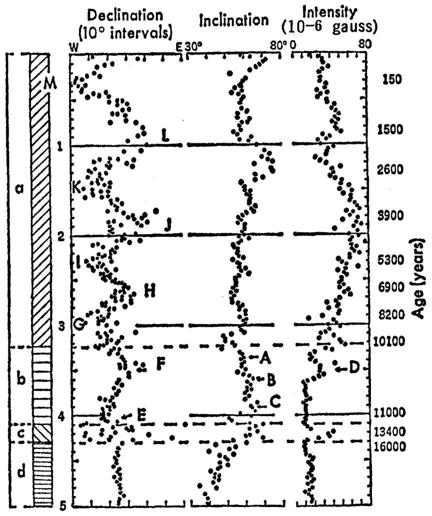

Fig. 2. Paleomagnetic declination, inclination, and intensity record from Lake Windermere, England. [Modified from Thompson (*2*)]

E is taken as the peak of the previous westerly swing in declination, its age should be 11,200 years. Features B, C, and D are next dated by assuming a uniform rate of deposition between the depths of features F and E. The top of the finely laminated clay occurs midway between swings F and G and can therefore be dated at 9800 years ago. Feature A is then dated by assuming a fixed deposition rate in the top part of the finely laminated clay unit. The assumption of fixed deposition rates is an approximation, and we have accepted a faster rate of deposition (0.8 mm/year) in the lower parts of this unit, between features E and F, than in the upper parts above F (0.3 mm/year), the justification being the distorted shape of the "sine" curve, which

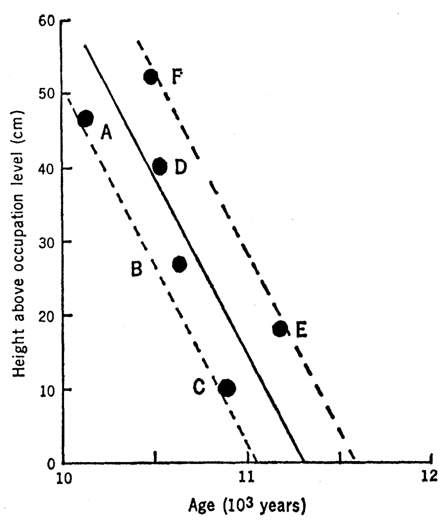

Fig. 3. Summary of magnetically determined ages of Tito Bustillo Cave samples.

appears stretched between features E and F.

Our estimates of the age of the sediment at Tito Bustillo Cave are summarized in Fig. 3, where we plot height above occupation level against the magnetic age estimated by using the six points of correlation with the Windermere record. A straight line has been fitted to the points by eye and taken as indicative of a uniform sedimentation rate in this cave, which we find to be 0.5 mm/year. The scatter of the data points is to be expected because, judging from the geographical pattern of the contours of the present nondipole field, we would not expect to find that the geomagnetic field variations with periods or characteristic times of about 300 years observed at Windermere would be reflected exactly at Asturias in northern Spain, some 1300 km distant. Furthermore, a quasi-periodic disturbance such as that observed in inclination might vary over a geographic distance of several hundred to a thousand kilometers, but this would not upset our correlation by more than one period, or about 300 years in this case.

Bearing uncertainties such as this in mind, we have obtained an estimate of the age of the occupation level of 11,300 years. The dashed lines bounding the data points in Fig. 3 cross the time axis at 11,100 and 11,600 years and define upper and lower limits to our estimate.

Paleomagnetic determinations of any kind demand stability of the remanent magnetism of the samples. The cave sediments proved adequate in this respect in that cleaning in an alternating field of peak value 150 oersteds produced no significant change in the pattern of the direction and intensity logs. To learn more about the source of this stable magnetism and to better understand sedimentation processes in the cave, David Krinsley studied one sample (No. 14) by scanning electron microscopy (SEM). The Lake Windermere work (*1, 2*) dealt with lacustrine sediments, in which the magnetic mineral constituent consisted of hematite derived as detrital grains and magnetite probably produced as the result of organic activity. Sedimentation processes in caves are not well understood, and the sources of remanent magnetism are open to conjecture.

Krinsley's unpublished study shows that incomplete rounding and other features of the individual grains indicate their original deposition under eolian conditions, probably as periglacial dune sands in this area, which flanks the once glaciated Cantabrian Mountains. Transport into the cave was unquestionably by water action, and it is significant for correlation that deposition ceased abruptly around 10,200 ± ∽250 years ago (according to Fig. 3), at the close of the Pleistocene. Subsequently, no further sediments were deposited in this area of the cave, and the sands underwent a lengthy period overgrowth under the aegis of a long-term *p*H change. These factors imply that the sands were relatively undisturbed in the postdepositional period and could, therefore, be expected to preserve the original orientation of magnetic particles. Sources of remanent magnetization could not be positively identified, but by correlation with other SEM data (*5*) blebs on Tito Bustillo sand grains appear to be goethite and indicate that some detrital iron minerals appear as coatings on such grains. Because of the restricted bacterial action in deep caves with rapidly accumulating deposits, it is thought that limited chemical diagenesis occurred and that remanent magnetism, therefore, reflects the secular field at the time of deposit.

Additional paleomagnetic dating of cave sediments (*6*) appears to verify the suitability of such materials for this technique. As more reference curves become available, the technique can be extended to cover increasingly greater time periods, periods that are not now adequately covered in the archeological record. This dating method has several advantages over other chronological techniques: paleomagnetic determinations can be made rapidly, and they require no intrusive elements—organic or otherwise—in the strata being investigated.

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Water Salination: A Source of Energy

Abstract. *The thermodynamically reversible mixing of freshwater and seawater at constant temperature releases free energy. Salination power as a resource is comparable with hydroelectric power in magnitude; U.S. freshwater runoff could yield over 10^{10} watts. The energy flux available for natural salination is equivalent to each river in the world ending at its mouth in a waterfall 225 meters high. An osmotic salination converter could possibly operate at 25 percent efficiency. This energy source is renewable and nonpolluting. Although its full utilization would destroy estuarine environments, it might be practical for specialized purposes.*

The quest for new energy sources has heightened recently with world political and economic developments. Along with a growing realization of the need for more energy has come a simultaneous realization that the energy sources must be clean and renewable. These requirements suggest that naturally occurring geophysical energy fluxes be tapped. Direct solar energy conversion, the utilization of tidal, geothermal, wind, and hydroelectric energy fluxes (*1*), and even the energy available from the nonequilibrium state of the oceans (*2*) have been proposed as energy sources. Yet there is one large natural energy flux which, though readily available, I have not seen mentioned as a resource, namely, salination of water or the energy released from the mixing of freshwater with seawater.

That energy in fact can be extracted from the mixing of freshwater and seawater is best illustrated by considering the reverse process—energy is required to extract freshwater from seawater. The reversal of any desalination process should, in theory, release energy. Rather than present a full thermodynamic argument, I derive the amounts of energy involved through a heuristic approach (*3*). Let a volume V_1 of pure water mix irreversibly at constant temperature T with a volume V_2 of solution with an osmotic concentration of C_2, resulting in a solution of volume $(V_1 + V_2)$ and concentration $C_2V_2/(V_1 + V_2)$. Consider the osmotically active particles of solute as a "gas," initially with $N = C_2V_2$ moles of particles confined in volume V_2. After mixing, the "gas" has expanded isothermally to a volume $(V_1 + V_2)$ with an entropy increase $\Delta S = NR \ln (1 + V_1/V_2)$, where R is the gas constant. If the expansion were to proceed, instead, reversibly at constant temperature T, it would release energy $\Delta W = T \Delta S$. Normally, V_2 is much larger than V_1; the oceans act as an infinite reservoir of constant concentration. Hence,

$$\Delta W = NRT(V_1/V_2) = (RTC_2)V_1$$

Since seawater has an osmotic concentration of approximately 1 osmole/liter, each liter of freshwater added to the ocean would release 22.4 liter-atm of energy. In more practical units, a freshwater flow of 1 m^3/sec could provide 2.24 megawatts of salination power.

Substantial amounts of power are available from this source. The total surface runoff of water in streams and rivers into the oceans from the coterminous United States corresponds to a flow rate of 5.3×10^4 m^3/sec, which could release 120×10^9 watts, several times the present U.S. water power consumption, and almost equal to the total U.S. hydroelectric potential (*4*). The Mississippi River alone accounts for about one-third of the total runoff. A salination power plant using only 10 percent of the flow at an overall efficiency of 25 percent would deliver 1000 megawatts.

The salination energy is readily converted to mechanical or electrical energy. The proportionality constant, $P_0 = RTC_2$, between the energy released and the volume of water used has units of pressure, being in fact the osmotic pressure of seawater. An osmotic converter is illustrated in Fig. 1; other thermodynamic conversion schemes would work equally well. In the apparatus shown, freshwater is separated from seawater by a semipermeable membrane under a pressure head, P, which need not actually be a water column. If P is infinitesimally smaller than P_0, an infinitesimal volume of water, dV, will flow into the pressure chamber, spill off the top of the column, and release $P\,dV = (RTC_2)dV$ energy in the resultant waterfall. A conventional waterwheel and generator can then be used to produce electricity at an efficiency of nearly 100 percent (*5*). The tremendous energy flux available in the natural salination of freshwater is graphically illustrated if one imagines that every stream and river in the world is terminated at its mouth by a waterfall 225 m high, the height of a