part of the masseter probably equivalent to the superficial masseter of modern mammals.

Dinnetherium documents an intermediate stage in the evolution of mammalian jaw musculature and movement, but in the development of an angular region it is clearly more advanced than previously known mammals of the time. The finding that Sinoconodon is a mammal (5), and the clear differences that distinguish Dinnetherium from contemporaneous taxa strengthen the view that Rhaeto-Liassic mammals were more diverse than previously thought (17). A simple dichotomy between morganucodontids (nontherians) and kuehneotheriids (therians) no longer appears to be an accurate representation of the complex, early evolution of mammals (18).

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  A recently discovered skull of *Sinoconodon* arguidas definitive evidence that this form is a 4.
- provides definitive evidence that this form is a mammal, but the relation of the genus remains unclear (Sun Ai-lin and A. W. Crompton, personal communication). The site (Gold Spring Quarry 1), in the middle of
- 6 The site (Goid Spring Quarry 1), in the induce of the Kayenta section, is located 35°45'47'N, 111:5'21'W, and approximately 1 mile west-southwest from Gold Spring (U.S. Geological Survey 7.5-minute topographic series, Gold Spring Quadrangle) on land of the Navajo Nation
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- 13. Dinnetherium nezorum might be classified as an amphilestid on the basis of the familial diagnosis

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("Premolars symmetrical and submolariform, molars more than four in number, with anterior and posterior cusps small relative to the main cusp"). But we believe that these primitive features do not adequately define the group, and the therian or nontherian affinities of amphiles tids remain unclear

- 14 Combined medial translation and rotation would have been necessary to effect the facets seen in the Jurassic triconodontid Trioracodon, and have been documented in a cineradiographic and electromyographic study (U. Oron and A. W. Crompton, unpublished data) of *Tenrec* ecaudatus
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- 16. In an undescribed Chinese specimen of Morgan*ucodon*, the reflected lamina of the angular abuts the posterior margin of the pseudangular process (Sun Ai-lin and A. W. Crompton, unublished data).
- W. A. Clemens (2) expressed the opinion, based on studies of European material, "that Rhaeto-17.

Liassic mammals can no longer be easily classi-

- The second secon 18. E. Jenkins III for neig assistance, m. m. Amaral and C. R. Schaff for laboratory prepara-tion; E. Selig for scanning electron microscopy; A. H. Coleman for photography; L. L. W. Maloney for technical assistance; and W. A. Clemens for a review of the manuscript. The discovery of the first mammal specimens in 1980 (by W.R.D. and J. Kirkland) was facilitated by L. L. Jacobs and E. Hoyt, and financed by R. Downs. We thank the Navajo Tribal Council and the Coal Mine Mesa Chapter (T. T. Nez, president) for permission to conduct paleonto-logical exploration on Navajo land, and the National Geographic Society for generous support of this research. Present address: Department of Geology,
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## **Determination of Thermal Histories of Archeological Cereal** Grains with Electron Spin Resonance Spectroscopy

Abstract. The thermal histories of archeological cereal grains were examined by electron spin resonance spectroscopy. Studies with modern samples of heated cereal grain showed that the parameters of the electron spin resonance signal characterize the maximum temperature to which the sample had previously been heated. This technique has applicability in archeology and other disciplines.

Although traces of the heating of an artifact or of fire in an archeological site can be important indicators of technological or cultural achievement, identification of such traces is often based on a subjective assessment of appearance. Errors in interpretations of ancient cultures and technologies will occur unless a sound basis can be established for ascertaining ancient thermal histories.

We have described how the effects of ancient heating of chert (1), bone (2), and ivory (3) can be identified by the detection of radical carbon with electron spin



Fig. 1. Dependence of radical carbon g value on maximum temperature of previous heating for modern Emmer grains; the error of each gvalue measurement is  $\pm 0.0002$ .

resonance (ESR) spectroscopy. Radical carbon is indefinitely stable (1) and gives rise to a readily observed ESR signal, which we have proposed as an indicator of previous heating. We have also noted that heating modifies transition metal (4) and organic (5) ESR spectra in chert, which points to other potential heat markers.

We now report a study of cereal grains, which are widely encountered in archeological sites. The particular grain chosen was Emmer wheat (Triticum dicoccum) since it is found throughout Europe and southwestern Asia in sites ranging from the earliest Neolithic to late Classical times. Emmer grain was collected in northeast Turkey, where it is still under cultivation. Three archeological samples were studied: two of Emmer wheat and one of six-row barley. One Emmer sample, although slightly darkened, is in a state of nearly complete preservation through desiccation and comes from King Zoser's pyramid (Egypt,  $\sim$  3000 B.C.). The other consists of blackened and brittle grains and comes from the immolation of the Mycenae granary (Greece,  $\sim 1100$  B.C.). The six-row barley sample is from Wadi Kubbaniya, Egypt, and is of unknown date. It is blackened in appearance but retains its morphological characteristics.

Our experiments involved the measurement of values for the g factor, line widths ( $\Delta H$ ), and spin concentrations (c) of radical carbon ESR signals generated

in modern samples of Emmer wheat that had been subjected to a variety of temperatures and heating regimes in the laboratory. The manner of heating was found not to be important provided that the sample was exposed to a particular temperature for at least 4 hours. The dependence of the g value on the maximum temperature of previous heating (MTPH) for whole grains of modern Emmer wheat is shown in Fig. 1. Experiments on other modern whole cereal grains and on isolated grain fractions indicate that this curve applies universally to cereal grains. Accordingly, we propose that the MTPH of ancient cereal grains can be estimated by measuring the g value of the ESR signal and reading off the requisite temperature with an accuracy of about  $\pm 30^{\circ}$ C. Attempts to use the line widths and spin concentrations in a similar manner were not successful. However, all three parameters  $(g, \Delta H,$ and c) were found to vary in a consistent manner when the sample was heated in the cavity of the ESR spectrometer. There was no appreciable change until the MTPH was reached, after which g and  $\Delta H$  decreased and c increased significantly. If, however, the sample had been exposed to its MTPH for periods appreciably shorter than 4 hours, c and  $\Delta H$  (but not g) started to change at lower temperatures than the MTPH. Thus any discrepancy between the temperature indicated by the g value and the changes in the other parameters for ancient samples might well point to an upper limit for the time that a particular sample had been exposed to its MTPH, thus providing further information on overall thermal history.

It was clear both from the morphology and from historical accounts of Early Dynastic burial practices that the grain from Zoser's pyramid had not been charred. The g value (2.0039) for these grains indicates an MTPH of about 100°C. In contrast, the morphology of the Mycenae grain exhibited all the signs of charring at fairly high temperatures, an observation supported by information on the source context (the Mycenae Citadel was destroyed in a conflagration). The g value obtained for these grains (2.0031) fully supports such a history: the MTPH is estimated to be 250°C (Fig. 1). The temperature estimates for these two archeological samples are confirmed by the results of the heating experiments: the g values and spin concentrations (Fig. 2) begin to change rapidly only for temperatures above the MTPH. The changes in line width for archeological samples differ from those for modern grains, the initial values and the changes



з

2

(arbitrary units)

υ

Log

0

100

200

т (°С)

heating of a sample, since one heated in

ancient times would show little variation

300

in line width. A basic question concerning archeological grains is their antiquity. Farreaching cultural implications depend on whether a hoard of grain is genuinely ancient or merely a modern intrusion. A recent case occurred at the Nile Valley site of Wadi Kubbaniya (6), where a find of domestic barley in deposits dated by associated wood charcoals to  $\sim 18,000$ years old appeared to overturn all existing ideas on the origins of agriculture and Near Eastern civilization. An accelerator radiocarbon date of the Wadi Kubbaniya grain has not yet been published (7), but close microscopic analysis of the grains indicated that, although black in color and seemingly charred, they were in fact probably uncharred and therefore very unlikely to have survived for any length of time in the Wadi Kubbaniya deposits which, at the time of occupation, were subject to seasonal flooding. Our determination of the thermal history of the Wadi Kubbaniya grains clearly indicates that they have not been exposed to the temperatures necessary for charring. The g value of 2.0036 indicates an MTPH of 150°C, which is confirmed by the rapid increase in spin concentration at temperatures higher than this (Fig. 2). The results for the Wadi Kubbaniya grain show a much closer resemblance to those for the uncharred grain from King Zoser's pyramid than to those for the charred grain from Mycenae. Therefore, they are probably modern intrusions.

The difference between the results for the Zoser and Wadi Kubbaniya grains

may well reflect the difference between the temperature reached by the grain heaped in the Pharaonic threshing yards in the particular year the Zoser grain was harvested (before its emplacement in the cool burial chamber) and the higher temperature at the surface of the desert sands on which the Wadi Kubbaniya grain must have lain before its probable intrusion into the archeological deposits below.

We have now correlated g values with previous heat treatment, considered changes in the ESR parameters on further heating of the sample, and extended these ideas quantitatively to an investigation of archeological samples. It appears that the radical carbon ESR in burnt organic materials has provided information on thermal history that is not accessible by other means. Applied in archeological contexts in which adequate structural or archeobotanical evidence is lacking, this technique may be useful in identifying the functions of archeological artifacts that served originally as open hearths, bread ovens, parching kilns, or furnaces as well as in characterizing the nature of large-scale destruction of the sort that befell the Mycenae granary. The technique should also prove useful in other disciplines where heat treatment is of importance.

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