# The Exodus enigma

SIR — We have obtained six high-precision radiocarbon dates of cereal grains from Tell es-Sultan (Jericho), stratigraphically related to the end of the Middle Bronze Age (MB-IIC). The cereal samples belong to stratigraphic phase HAF.XII–XIII.lii.liii, the time of the final destruction and conflagration of Middle Bronze Jericho[1].

Data from six cereal samples

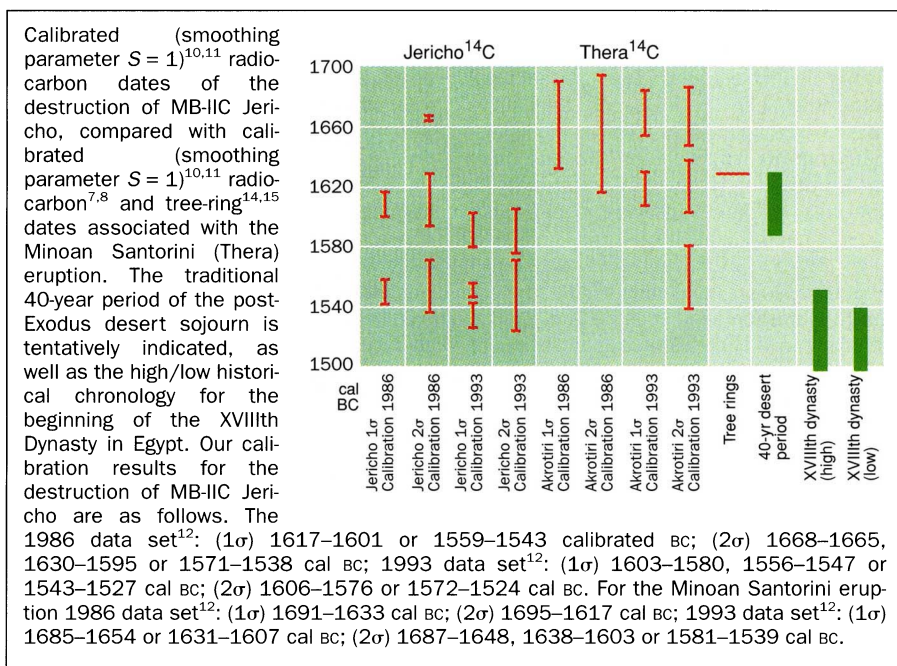| Lab. no. | 14C date (yr BP) | δ13C (‰) | Sample no. | Material |
|---|---|---|---|---|
| GrN-18539 | 3,312 ± 14 | −23.09 | Jp.H.14.3;  Hopf largest box | Grains, *Hordeum vulgare* |
| GrN-18542 | 3,288 ± 20 | −23.54 | Jp.H.10.1b; Hopf #89 | Grains, *Triticum* sp. |
| GrN-18543 | 3,331 ± 18 | −23.31 | Jp.H.10.1; Hopf #87 | Grains, *Triticum* sp. |
| GrN-18544 | 3,312 ± 15 | −23.28 | SA-143 Jp.H.10.1 Hopf #87 | Grains, cereal, fragmented |
| GrN-19063 | 3,240 ± 18 | −23.72 | SA-58 Jp.H.14.3g Hopf #92 | Grains, *Hordeum vulgare* |
| GrN-19064 | 3,375 ± 25 | −21.86 | SA-36 Jp.H.14.3b Hopf #91 | Grains, cereal, fragmented |

The samples come from squares H-II,-III and -VI at Tell es-Sultan (Jericho), belonging to stage/phase HAF.XII-XIII.lii.liii, (the end of the Middle Bronze Age). Sample numbers from the excavations reported in refs 1,2 are also included.

These cereal samples, excavated in the 1950s[1], were kindly provided by M. Hopf, who has investigated their palaeobotany[2]. Conventional radiocarbon dating of these and other Jericho samples from the period was performed at Groningen University[3]. The table shows the six high-precision 14C dates. GrN-18539, -18542, -18543 and -18544 cluster outstandingly, averaging at 3,311 ± 8 years before present (BP). Inclusion of the oxalic acid standard σ in the last result gives a 14C date for Jericho's destruction of 3,311±13 yr BP.

We note that the Minoan eruption at Santorini produced the largest volcanic dust cloud over the eastern Mediterranean in the second millennium BC. A possible relationship between this eruption and the Exodus plague of "darkness that can be felt" (Exodus 10:21), was suggested by geologists, who found Minoan ash in sediments of the eastern Mediterranean Sea[4–6] and Nile delta[6].

Two averaged 14C data sets on short-lived materials from Akrotiri, measured at Oxford (3,357±21 yr BP)[7] and Copenhagen (3,355±32 yr BP)[8], exist for the Minoan Santorini eruption. These averages, taken together, yield 3,356±18 yr BP, 45 radiocarbon years older than our 14C destruction date for MB-IIC Jericho. This time difference is rather striking, as it could fit the desert period of 40 years separating the Exodus from the destruction of Jericho, mentioned in ancient Hebrew texts.

Taking the geologically based Santorini–Exodus link as a serious option may be anathema for archaeologists who ascribe the widespread destruction of MB-IIC sites in Canaan, including Jericho, to Egyptian armies of the XVIIIth Dynasty. However, the latter association is unsatisfactory in social terms, considering the radical change in Canaan at the transition between the Middle and Late Bronze Ages, as expressed by Gonen: "The causes of destruction of the Middle Bronze sites have not been adequately clarified... In any case, hardly a single site escaped massive destruction"[9].

We calibrated[10] the radiocarbon dates of Jericho and Akrotiri, using a smoothed function (smoothing parameter $S$ =1)[10,11] through a decadal dendrochronologically obtained data set (see figure). We included both the original (1986) and revised (1993) version[12] in our calculations[10,11] because it is uncertain which one is preferable[13].

The calibrated date for the destruction of MB-IIC Jericho is admittedly ambiguous, due to a mid-sixteenth century 'wiggle' in the calibration curves. However, the low-chronology option requires unsatisfactory stretching of the 45-year difference between the Santorini and Jericho 14C dates in relation to the 1628 BC dendro-event[15]. We prefer the (medium) high chronology, which is older than the XVIIIth Dynasty (see figure). A high-precision wiggle-matched 1,503-year dendrochronology from Turkey[14] provides major new evidence for the tree-ring signal of 1628 BC as the date of the Minoan Santorini eruption[15]. If the latter eruption is associated with the Exodus plague of darkness[4–6], then the 40-year desert period (see figure) fits the high chronology of our calibrated 14C date for Jericho's destruction, calibrated[10,11] with the 1993[12] calibration curve, which suits the 1628 BC dendro-signal. If we consider only the Akrotiri radiocarbon results, the 40-year desert period fits the Jericho (medium) high-chronology 14C dates, calibrated with either curve.

Various theories and dates, ranging



Calibrated (smoothing parameter $S$ = 1)[10,11] radiocarbon dates of the destruction of MB-IIC Jericho, compared with calibrated (smoothing parameter $S$ = 1)[10,11] radiocarbon[7,8] and tree-ring[14,15] dates associated with the Minoan Santorini (Thera) eruption. The traditional 40-year period of the post-Exodus desert sojourn is tentatively indicated, as well as the high/low historical chronology for the beginning of the XVIIIth Dynasty in Egypt. Our calibration results for the destruction of MB-IIC Jericho are as follows. The 1986 data set[12]: (1σ) 1617–1601 or 1559–1543 calibrated BC; (2σ) 1668–1665, 1630–1595 or 1571–1538 cal BC; 1993 data set[12]: (1σ) 1603–1580, 1556–1547 or 1543–1527 cal BC; (2σ) 1606–1576 or 1572–1524 cal BC. For the Minoan Santorini eruption 1986 data set[12]: (1σ) 1691–1633 cal BC; (2σ) 1695–1617 cal BC; 1993 data set[12]: (1σ) 1685–1654 or 1631–1607 cal BC; (2σ) 1687–1648, 1638–1603 or 1581–1539 cal BC.

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from around 2200 to 1200 BC, have been proposed for the Exodus tradition and emergence of Israel in Canaan, based on different interpretations of the archaeological dataset (ref. 16). Nevertheless, although they are powerful tools, archaeology and pottery are not the sole avenues that can be used to unravel the human past. Environmental events, high-precision radiocarbon dating and precise regional dendrochronologies may provide information unobtainable through archaeological associations[17]. New, high-precision ^{14}C data series of XVIIIth Dynasty Egypt and Levantine Middle Bronze Age

sites are required. Wiggle-matching linkages with the Aegean dendrochronology[14] may lead to truly absolute dating.

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# Marine gamete-release pheromones

SIR — In contrast to the large body of experimental evidence for the existence of sex pheromones in marine invertebrates, only a few chemical structures of these compounds have been elucidated[1,2]. Here we report the isolation and identification of two gamete-release pheromones of marine invertebrates. By bioassay-guided fractionation and purification, we identified uric acid as the sperm-release pheromone of *Platynereis dumerilii* and inosine as the main component of the egg-release pheromone complex of *Nereis succinea* (Annelida, Polychaeta). These compounds contain the purine ring system, which has not as yet been identified in sex pheromones of any species.

Within the marine invertebrates, the Nereidae are well suited for chemical investigation of sex pheromones because of their distinctive breeding behaviour. In both species, reproduction strictly depends on an exact spatial and temporal synchronization. High population densities within restricted areas and the synchronization in time are responsible for the formation of swarms.

The reproduction process occurs as follows: (1) in these swarms mate recognition is achieved by chemical signals[3]. (2) At the moment of recognition the male discharges the egg-release pheromone (ERP)[4,5]. (3) The female is stimulated to swim with high velocity in narrow circles surrounded by swarming males. After an

induction period of 10–40 seconds the female spawns. The discharged egg cloud contains the sperm-release pheromone (SRP). (4) Males achieve immediate fertilization by circling around the eggs and emitting sperm clouds.

It is known that the coelomic fluid of the oppposite sex is the source of the gamete-release pheromones[6,7]. With reference to the well-examined volatile sperm attractants in marine brown algae[8], we first investigated volatile compounds of the coelomic fluid. These studies led to the elucidation of substances responsible for mate recognition in both species[2,3,9,10]. However, none of these compounds elicited the gamete release, in contrast to the natural pheromone-containing coelomic fluid. Hence, in the present study we analysed the non-volatile, water-soluble compounds of the coelomic fluid for pheromonal activity.

To follow the target substances during isolation and purification, we developed a reliable behavioural bioassay. We injected samples with a microlitre syringe just in front of a mature specimen swarming in a glass dish. The release of a visible sperm cloud or loss of the total amount of eggs represented a positive pheromone response. We tested chromatographic fractions of the coelomic fluid both singly and in combination. (Details of methods are obtainable directly from the authors.)

In the case of *P. dumerilii* , we identified the bioactive single peak fraction finally obtained as uric acid. This SRP is effective at a threshold concentration of 0.6 μM (solubility of uric acid in sea water, 32%, pH 8.2, 23 °C: 180 μM). We measured the total amount of uric acid in the coelomic fluid of one female as $1.0 \pm 0.1$ μg. When we dissolved this quantity of uric acid in 2 cm$^3$ sea water (egg cloud volume) we found an actual pheromone concentration of $3.0 \pm 0.3$ μM. This fivefold excess is essential to ensure successful fertilization taking into account natural conditions such as the effects of dilution by turbulence and currents in

sea water.

In the case of *N. succinea,* we identified inosin as the main component of the ERP-complex. (We are investigating the complete composition of the ERP complex separetely.) We are now trying to identify the SRP of *N. succinea* and the ERP of *P. dumerilii,* so that we can compare males and females in the same species. Our preliminary results suggest that both uric acid and inosin are species- and sex-specific. They represent the first identified gamete-release pheromones in marine invertebrates. Remarkably, the purine ring system has not as yet been reported to be a feature in sex pheromones.

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# A silicon sensor for SO$_2$

SIR — Initially synthesized about 30 years ago, porous silicon is now attracting considerable attention because it both photoluminesces[1] and electroluminesces[2] in the visible portion of the optical spectrum. Although much of the recent interest in porous silicon is related to the possibility of generating an electroluminescent device having applications in the areas of display technology and information storage, we here suggest that the photoluminescent properties of this material make it attractive as a highly sensitive sensor for sulphur dioxide. Our suggestion is based on our recent observation that the photoluminescence of oxide-coated porous silicon is rapidly and reversibly quenched on a selective basis by gas-phase SO$_2$.

It is well documented that exposing freshly etched porous silicon to various organic reagents results in non-selective quenching of the observed photoluminescence[3]. We have also previously reported selective quenching by gas-phase and aqueous Brönsted bases when a thin surface oxide is present[4]. The observed quenching is reversible; subsequent exposure to a Brönsted acid restores the photoluminescence to its initial intensity. Partial quenching of the photosensitive luminescence by Brönsted bases results in a blueshifting of approximately 40 nm in the emission maximum. As with the photoluminescence intensity, exposure to acid returned the emission maximum to its initial position. The base-quenching/acid-restoration cycle can be repeated many times.

We now report that SO$_2$ gas is another effective quencher of oxidized porous sili-

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