Reports

Early Thai Bronze: Analysis and New Dates

Abstract. Electron probe analysis of the earliest metal found at the northeastern Thailand site of Non Nok Tha indicates that it is a bronze containing 4 to 6 percent tin. Recent thermoluminescence dates substantiate the presence of a welldeveloped bronze technology prior to 2300 B.C. and suggest a date of about 2700 to 2500 B.C. for the first appearance of bronze at the site.

The site of Non Nok Tha in northeastern Thailand was the subject of two fairly large excavations (150 and 190 m²) in 1965–1966 (1) and 1968 (2). Subsequent dating of the site and analysis of materials have indicated a surprising antiquity for several economic developments previously thought to have entered Southeast Asia from elsewhere at a late date. These include the following: the presence of rice prior to 3500 B.C. (3); the presence of bovines very similar to domestic Bos indicus (4), and possibly domesticated pigs (2), at the same date; and a well-developed bronze-casting technology prior to 2300 B.C. (5, p. 899; 6-8). A distinctly different type of socketed tool, apparently of copper rather than bronze, was also recovered from a burial indirectly dated 3590 ± 320 B.C. (sample GaK-1034) (9). Two very small fragments of metal featuring the same brilliant green patina as the socketed tool were recovered from another burial pit cut from this early level. These were the only other finds of metal from this level, which is the third (Early Period 3) of 17 levels conveniently grouped into three periods (Fig. 1).

Qualitative analysis of the tool indicated that it apparently contained neither tin nor lead (8); both of these elements occur in the bronze tools of Middle Period levels 1 through 8 (10). All impurities were thought to be present in quantities small enough for the metal to be considered copper; the presence of phosphorus and a trace of arsenic suggests that the metal is smelted rather than native.

To further investigate the nature of the first metal at the site, the larger of the only other two pieces of metal recovered from Early Period 3 was analyzed at the University of Otago (11). Because the maximum area of metal 30 JUNE 1972 exposed after the fragment had been polished was considerably less than the minimum required for analysis by x-ray fluorescence (12), the electron probe was used. However, the finer discriminatory power of the electron probe method (13) allowed sampling of both metallic and nonmetallic areas exposed on the polished surface. Spot analyses revealed that the metal consisted of 94 to 96 percent copper and 4 to 6 percent tin; it would thus appear that the material is a deliberately made tin bronze (14). In contrast to the case for the copper tool, arsenic, phosphorus, iron, and lead were not detected in either the metallic or the nonmetallic portions of the fragment, a finding that would also suggest that the alloy was deliberately made. Certain tin-rich portions of the nonmetallic areas contained a minimum of 44 percent tin, with 25 to 53 percent copper. Sulfur was also present in the nonmetallic regions, reaching a maximum concentration of about 33 percent in one spot probed and ranging between 0.01 and 0.2 percent in the tin-rich portions; however, the overall proportion of sulfur in the material was extremely low.

The dating of this first appearance of metal at Non Nok Tha remains somewhat problematical; however, the absolute chronology of the overall se-



Fig. 1. Radiocarbon and thermoluminescence (TL) dates from Non Nok Tha. A standard deviation of 1- σ range is shown. Circled dates are those for samples suspected of having modern contamination.

quence at the site is considerably more secure than it was when the first ten radiocarbon dates were published in 1968 (6). We now have 26 radiocarbon dates and 4 recent thermoluminescence dates (15) from 1965-1966 and 1968 excavations, and the general outlines of the chronology seem apparent (Fig. 1). Particularly secure is the middle portion of the bronze period (Middle Period levels 3 through 6), which extends from 2300 to 900 B.C. For Early Period 3, however, the three dates are in conflict; a collagen date on skeletal material from the burial containing the copper tool $(720 \pm 95 \text{ B.C.})$ sample I-5324) is in sharp disagreement with a thermoluminescence date on pottery from the same burial $(2420 \pm 200 \text{ B.C.}, \text{ sample PT-276}), \text{ as}$ well as with the 3600 B.C. date mentioned above (from a burial typologically very similar to the one in question). In view of the secure relative chronology afforded by the stratigraphy, the intersections of burials (203 from both excavations), and the distinctive styles of burial of each of the levels, I am unable to explain the collagen date. It can be combined with four other dates (two of them from a series of samples we suspect to have been contaminated) to form a "late sequence" (Fig. 1), but the "early sequence" of 12 dates appears much more reliable at present. In addition, these earlier dates are supported by several recent ones from other bronzeperiod sites in mainland Southeast Asia (15, 16). I know of no recent dates from the area which support the late sequence. I have discussed the problems involved in the chronology of the area in detail elsewhere (2, 8); at present, I believe that it is possible to say with a high degree of confidence that a welldeveloped bronze technology was present in mainland Southeast Asia prior to 2000 B.C. Moreover, this technology is very likely an indigenous one; no clear relationships link this technology with the Near East or the presumably later technologies of northern China and the Indus (8).

Given the evidence of numerous burial intersections, present between all pairs of adjacent levels except Early Period 3 and Middle Period 1, and the very rapid degree of change taking place in metal and ceramic technology during Middle Periods 1 and 2, I would conclude that the thermoluminescence date on Early Period 3 pottery is closer to the actual age of the burial than the indirect date of 3600 B.C. In view of the thermoluminescence dates of 2535 ± 200 B.C. (sample PT-278) and 2350 ± 150 B.C. (sample PT-279) on pottery from a Middle Period 1 burial, I would assume an estimate of about 2700 to 2500 B.C. for Early Period 3 and the first introduction of metal to the site. Hopefully the chronological problems will be solved in the near future, and this solution will allow investigators to pay closer attention to the more important questions of how and why the pervasive changes evident in the early Middle Period took place (2,p. 40).

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- 17. I thank Dr. Y. Nakamura (Geology Departthe electron probe analysis and interpreting the raw data; R. H. Parker and C. F. W. Univer-Higham (Anthropology Department, sity of Otago) for their comments on this report during its preparation; and the offi-cials of the Fine Arts Department, Ministry of Education, Bangkok, for making my field-work in Thailand possible. Research sup-ported by NSF grant GS 1877.
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Potential Energy Surface Including Electron Correlation

for $F + H_2 \rightarrow FH + H$: Refined Linear Surface

Abstract. A priori quantum mechanical calculations have been carried out at about 150 linear geometries for the fluorine plus hydrogen molecule system. An extended basis set of Gaussian functions was used, and electron correlation was treated explicitly by configuration interaction. Comparison with the experimental activation energy and exothermicity suggests that the theoretical potential surface is quite realistic.

We have reported (1) an a priori quantum mechanical potential energy surface for the chemical reaction F + $H_2 \rightarrow FH + H$. About 350 individual calculations (each referring to a par-



Fig. 1. Traditional contour map of the linear FH2 potential energy surface.

ticular FH₂ geometry) were carried out, yielding a wealth of qualitative information about both the surface itself and the usefulness of various theoretical approaches to the calculation of potential surfaces. For example, the minimum energy path or reaction coordinate was found for a linear F-H-H arrangement, with the perpendicular approach of F to H₂ lying 12 kcal/mole higher. The calculations showed that a single configuration or Hartree-Fock wave function inevitably yields a barrier height or activation energy much greater than experiment. However, the explicit inclusion of electron correlation by way of configuration interaction (CI) results in a small barrier height, in qualitative agreement with experiment.

Nevertheless, our preliminary $F + H_2$ surface (1) was not of "chemical ac-