the sun to the Crab Nebula. Since it is thought that other weaker sources observed are clustered around the galactic center (*3*), which lies at a distance of about 8 parsec, the Scorpius source would then be an object of comparable absolute intensity.

The measured spectrum from the Crab Nebula agrees with that of Peterson *et al.* (*6*) for photon energies greater than 20 kev. The shape of this spectrum is different from that of Sco XR-1. Our data are reasonably fitted by a straight line drawn on Fig. 6. Thus, the spectral intensity is of the form $I(h\nu) \propto (h\nu)^{-1.3\pm0.2}$ between 1 and 20 kev. Peterson finds that, between 20 and 100 kev, $I(h\nu) \propto (h\nu)^{-0.9\pm0.1}$. X-rays from the Crab Nebula are expected to be synchrotron radiation because optical and radio emission of this form has been observed. This is the expected spectral shape for such synchrotron radiation if the differential spectrum (*10*) of the high-energy electrons producing x-rays is of the form $N(E) \propto E^{-m}$, where $N(E)$ is the number of electrons of energy E, and m is a constant. For the data of Fig. 6, $m \approx 3.5$. Our counting errors were too large to allow reliable spectral information below 1 kev of x-ray energy.

Because of the apparent weakness of the Cygnus source there are large uncertainties in the measured spectral data caused by statistics and background subtraction. It is clear, however, that the x-radiation from this source is harder than that from the others. The Cygnus source was close to the horizon when this measurement was made.

From the position given by Bowyer *et al.* (Fig. 3), calculated atmospheric thickness between source and detector at apogee is approximately 10^{-4} g/cm^2, and atmospheric absorption should be negligible down to 1.5-kev energy. The source position would have to be in error by about 6° for atmospheric attenuation to account for the observed spectral hardness. The source intensity is much weaker than that given by Bowyer *et al.* who measured Cyg XR-1 in the region of 1.5- to 4-kev photon energy to be 1.3 times as strong as Tau XR-1. If the source position is correct, this source has changed considerably since the time of the measurement (June 1964). Our measurement agrees with that of Fisher *et al.* (*4*), who found that Cyg XR-1 is about 5 times weaker than the measurement of Bowyer *et al.* and also that the radiation is harder than that from Sco XR-1. The data of Fig. 7 may be fitted with a straight line such that $I(h\nu) \propto (h\nu)^{-0.5\pm0.2}$.

Our measured source intensities between 1 and 20 kev are: Sco XR-1 is equal to 5.5×10^{-7} erg/(cm^{-2} sec^{-1}); Tau XR-1 is equal to 8×10^{-8} erg/(cm^{-2} sec^{-1}); Cyg XR-1 is approximately 2×10^{-8} erg/(cm^{-2} sec^{-1}). The spectra of these three sources are obviously different. This study does not eliminate synchrotron radiation as a possible source mechanism for Sco XR-1. Since the spectrum expected from a synchrotron radiation source is dependent on the electron-energy spectrum and magnetic field strength, the measured spectrum from the Scorpius source can be attributed to synchrotron radiation if one assumes an electron energy spectrum different from that assumed for the Crab Nebula.

Note added in proof. A recent measurement (*11*) has also shown that the intensity of Cyg XR-1 has greatly decreased. This experiment also resolved several sources in the Cygnus region. Accordingly, the spectrum given in Fig. 7 probably contains x-rays from both Cyg XR-1 and the radio galaxy Cyg-A.

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Copper Artifacts: Correlation with Source Types of Copper Ores

Abstract. *Six out of eight minor chemical elements, determined by spectroscopic and neutron-activation techniques, were found to be critical in computing a probability that a given copper artifact was derived from one of three types of copper ore: native metal, oxidized ore, reduced ore. Two elements, gold and tin, were apparently alloyed deliberately in many artifacts from both the Old World and the New World.*

Copper, one of the earliest known metals, has played a very important role in the history of man. One of the intriguing problems associated with it has been the identification of the types of ores and the location of the mining areas used by ancient civilizations. If the relationship between artifacts and copper source could be established, a clearer picture of trade and travel between different areas could be obtained. Several studies along this line have been undertaken in the past (*1*). The earlier investigators surveyed impurities present in various ores and sought to associate them with impurities present in artifacts on the assumption that they would alloy in significant amounts in the copper formed. This is, of course, not necessarily the case. Most of the analyses were based on conventional chemical or spectrographic techniques. In the work we now describe various ore types and artifacts were analyzed by optical spectrographic methods of high sensitivity and by neutron activation. The latter method was employed for those metallic impurities which were below the limits of spectrographic detection. Activation techniques are very useful in the study of impurities in native copper since the metal, as it occurs naturally, is essentially spectroscopically pure.

In addition to analyzing ore minerals, metallic copper was produced from them by chemical reduction in what was considered to be the simplest, most primitive method possible. Each ore was ground with charcoal and the mixture was heated in a crucible to about 1300°C; the metal formed a button on the bottom. The resulting metal and, in some cases, the slag generated by this process were analyzed to obtain a better insight into the behavior of the metallic impurities and their distribution between slag and metal. This type of approach revealed which impurities were the best indicators of the original ore type and were most likely to be reliable tracers for relating an artifact to its original source.

Approximately 130 ore samples from localities throughout Europe, Africa, Asia Minor, and the Americas and about 40 artifacts from the Middle East and the Western Hemisphere have been analyzed.

Copper ores can be divided into three groups corresponding to the ease of chemical reduction to the metallic state. The groups are naturally occurring metallic copper, "oxidized type" ore, and "reduced type" ore.

Occurrences of native copper metal are known from numerous New and Old World localities. In general it is safe to assume that the metal was utilized directly by primitive peoples. It may have been heat-treated to improve on the natural properties, but very probably no melting and alloying was undertaken. Samples for this work were obtained from the large deposits in the Lake Superior region; a small number were obtained from scattered areas throughout the Western Hemisphere and the Middle East. Variations in the amounts of impurities in samples from the same area seemed almost as large as the variations between samples from different areas. However, all native copper samples analyzed so far exhibit extremely low impurity levels, except for the element silver.

Ores of the "oxidized type" consist of oxygen-bearing compounds of copper, such as oxides (for example, cuprite), carbonates (malachite), and mixtures of these types. These ores were grouped together because they could all be reduced to copper metal by simply heating with charcoal. They are, generally, brightly colored ores (green and blue) and hence eye-catching; they are readily identified as copper ores. Members of this group were probably the first ores to be made into copper metal by primitive metal workers.

Ores of the "reduced type" are the sulfides and sulfosalts of copper (for example, chalcocite, chalcopyrite, tetrahedrite). These ores require a two-stage process to produce metal—namely, roasting to convert them to oxides and then reduction of the oxides to copper by the charcoal method. This two-step process represents a higher level of metallurgical sophistication. Furthermore, these minerals are not readily identified in outcrops as ores of copper. Hence, it is felt that this type of ore was utilized at a later period in the development of a given civilization.

"Oxidized type" and "reduced type" ores were obtained from deposits scattered through Africa, Europe, and the Americas.

From our studies on the metal produced by reducing many different ores it was found that silver, arsenic, bismuth, iron, antimony, and lead were the most important metallic impurities in relating the metal back to the original type of ore. In describing the range of impurities it was found convenient to use the following logarithmic-type of scale.

Unit	Range of concentration (%)
1	< 0.004
2	0.004 to 0.01
3	0.01 to 0.04
4	0.04 to 0.1
5	0.1 to 0.4
6	0.4 to 1.0
7	1.0 to 4.0
8	4.0 to 10
9	> 10

Table 1 lists the distribution of impurities for the three different ore types in terms of the concentration scale described above. If no samples of given concentration range were found, the probability was arbitrarily set at <.005 for this range. In addition to the previously mentioned metallic impurities, it was found that tin and gold were much more abundant in many of the artifacts than in any of the ores stud-

Table 1. Relative probabilities of occurrence of impurities in the three types of ores (I, native copper; II, "oxidized type" ore; III, "reduced type" ore).

Unit concentration range	Silver			Arsenic			Iron		
	I	II	III	I	II	III	I	II	III
1	0.1	0.62	0.27	0.84	0.62	0.43	0.42	0.35	0.10
2	.05	.08	.03	.05	.04	.03	.26	.04	.07
3	.26	.12	.13	.05	.08	.03	.10	.15	.03
4	.58	.04	.27	.05	.19	.23	.05	.08	.03
5	<.005	.15	.13	.05	.04	.07	.05	.08	.20
6	<.005	.04	.17	<.005	.08	.13	.05	.19	.13
7	<.005	<.005	.03	<.005	<.005	.03	<.005	.04	.03
8	<.005	<.005	.03	<.005	<.005	.10	<.005	.08	.10
9	<.005	<.005	<.005	<.005	<.005	<.005	<.005	.08	.30

Unit concentration range	Bismuth			Lead			Antimony		
	I	II	III	I	II	III	I	II	III
1	1.00	0.73	0.60	1.00	0.46	0.40	1.00	0.85	0.50
2	<0.005	.04	.03	<0.005	.04	.03	<0.005	.04	.03
3	< .005	.19	.23	< .005	.12	.30	< .005	.04	.17
4	< .005	.08	.03	< .005	.27	.07	< .005	.08	.03
5	< .005	<.005	.03	< .005	.04	.13	< .005	.04	.17
6	< .005	<.005	.10	< .005	.04	.03	< .005	<.005	.07
7	< .005	<.005	<.005	< .005	.04	.03	< .005	<.005	.03
8	< .005	<.005	<.005	< .005	.04	.03	< .005	<.005	.07
9	< .005	<.005	<.005	< .005	.08	.03	< .005	<.005	<.005

Table 2. Relative probability of occurrence, in a nail from Palestine, of copper from each of three types of ore.

Probability of occurrence						Product of probabilities	Normalized probability (%)
Ag	As	Fe	Bi	Pb	Sb		
			Native metallic copper				
0.26	<0.005	0.05	1.0	<0.005	<0.006	$<1.625 \times 10^{-11}$	<0.0078
			"Oxidized type" ore				
.12	.08	.20	0.73	.12	.08	1.35×10^{-4}	65
			"Reduced type" ore				
.13	.13	.08	.60	.30	.03	7.30×10^{-5}	35

ied. In general the concentration of gold in the ores was as follows (in parts per million where 1 ppm = .0001 percent):

Type	Gold concentration (ppm)
Native metal	0.0052 ± .003
"Oxidized"	0.028 ± .007
"Reduced"	0.009 ± .003

Much larger amounts, over ten times more, were found in many artifacts; it is presumed that gold must have been added either deliberately or was a contaminant from some source other than the copper ore. Tin was detected in almost none of the ores—that is, its concentration was generally less than 0.001 percent. The exceptions were some ores from tin-producing areas such as Cornwall (England), Bolivia, and Peru. In these cases the tin content in the copper ores varied from 0.02 to as much as 1 percent. There were a few rare ores such as enargite and tetrahedrite that contained larger amounts of tin; however, these ores are not readily reduced to copper metal and because of their rarity were not included in the list of ores.

Table 3. Classification of artifacts. Type I, native copper; type II, "oxidized type" ore; type III, "reduced type" ore.

Artifact number	Comments	Date (A.D.)	Concentration range		Relative probability (%)		
			Gold	Tin	I	II	III
A16440	Battle axe, Palestine		1	8	<0.1	1.4	98.5
A22605	Battle axe, Palestine		1	6	1.5	14.6	83.9
A18360	Axe, Palestine		4	6	0.4	1.0	98.6
Z48001	Mexico, Mixtec	1400	1	8	<0.4	71.3	28.3
Z95222	Mexico, Mixtec	1400	1	6	<5.1	55.0	39.9
Z1936	Club, Peru	1200-1500	ND*	1	<0.2	28.5	71.4
Z2175	Axe, Peru	1400-1500	ND*	6	78.5	9.4	12.1
Z2177	Axe, Peru	1400-1500	ND*	6	75.4	23.8	0.8
Z2181	Chisel, Peru	1400-1500	ND*	9	<0.1	33.4	66.5
Z1954	Chisel, Mexico	1000-1200	ND*	4	27.6	52.6	19.8
Z95934	Chisel, Mexico	1200-1400	1	8	<0.1	14.1	85.9
Z962821	Bell, Mexico	1000-1500	ND*	6	78.5	9.4	12.1
Z962826	Bell, Mexico	1000-1500	ND*	5	87.9	2.0	10.0
Z96345	Celt, Mexico	1200-1500	1	1	<0.4	6.6	93.0
Z13	Eskimo, copper		ND*	ND*	98.1	1.2	0.7
Z8	Dumaw creek†		ND*	ND*	91.9	7.4	0.7
Z9	Oceana chest†		ND*	ND*	97.0	2.1	0.8
Z11	Oceana head†		ND*	ND*	97.0	2.1	0.8
Z12	Oconto†		ND*	ND*	98.1	1.2	0.7

* Below the limits of detection. † American Indian.

Using the distributions of impurities shown in Table 1, the relative probability that a given artifact came from one of the three different types of ores can be calculated. For example, a small nail from Palestine has the following concentrations of impurities:

Impurity concentration (%)	Unit range
Ag 0.03	3
As 0.5	6
Au 0.001	1
Bi not detected	1
Fe 0.2	5
Pb 0.3	3
Sb 0.06	4
Sn 5.0	8

For each impurity the corresponding probability of occurrence for each ore type can be found in Table 1. For example, for silver in range 3 the probability is 0.26, 0.12, and 0.13 for the three ore types, respectively. Similarly, for arsenic in range 6, the probabilities are < 0.005, 0.08, and 0.13. For this particular nail the relative probabilities so found are listed in Table 2.

The relative probability that these concentrations will occur in a given ore type is related to the product of the individual probabilities for each impurity for that ore type. These products are listed in Table 2. Since we are assuming that the nail had to come from one of these three types of ores, the total probability should be normalized to 100 percent. Therefore the individual products are divided by the sum of the three products and multiplied by 100. These are listed as the normalized probabilities which are then the relative probabilities that the nail originated from each of the three types of ores (*2*).

If an artifact had an impurity at a concentration far beyond the normal range for the three ore types then it was concluded that this particular chemical element was deliberately added. Such is the case for all those artifacts having more than 0.1 percent tin and clearly not related to the three localities where tin is mined (Cornwall, Bolivia and Peru). The tin content strongly suggests deliberate alloying.

Table 3 lists the relative probabilities calculated in the fashion described for 20 artifacts from various locations. In the calculations we have, of course, assumed that there was no mixing of ores or copper produced from different ores. In the majority of cases this is a safe assumption, but in some cases mixtures may have been used.

One other possible error in the technique is that the impurity concentrations could vary with the type of metallurgical process used to produce the copper from the ore. Experiments have shown that 80 to 100 percent of the impurities selected here as reliable tracers are transferred from the ore to the metallic copper during the reduction process.

The ability to determine the type of ore used to produce a given artifact is one major step in the determination of the location of the ore. When more experiments and analyses have been completed it may be possible to extend the same statistical treatment to the geographical origin of a given artifact.

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2. A computer program is currently under development to do these calculations for artifacts whose impurity concentrations for these six elements are known. Copies of the computer program can be made available to interested authors who have access to an IBM-1620 or comparable machine.
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