Table 2. The N^{15}-content (ΔN^{15}) of various forms of nitrogen in soils.

Form of nitrogen	Soil type*				
	Grundy SiCL	Hayden SiL	Austin C	Clarion SiL	Glencoe SiCL
Total	+16	+7	+5	+3	+2
Hydrolyzable:					
Total	+18	+10	+7	+5	+4
Ammonium	+7	+7	+3	+6	+5
Hexosamine	+25	+8	0	+2	−2
Amino acid	+16	+14	+12	+5	+8
Hydroxyamino acid	+19	+11	+8	+7	+3
Nonhydrolyzable	−3	−2	−1	0	−4
N—mineralized†	+6	+2	+1	+1	+1
Fixed ammonium	+6	+6	+4	+2	0

* SiCL, silty clay loam; SiL, silt loam; C, clay. † Inorganic nitrogen produced by incubation of the soil at 30°C and at 50 percent water-holding capacity for 2 weeks.

jacent cultivated soils and from various depths in the profiles of soils receiving different treatments, and by determining the N^{15} content of various forms of nitrogen in soils. The methods used for determination and isotope-ratio analysis of different forms of soil nitrogen have been described (*3*). Variation in N^{15} content, expressed as ΔN^{15}, was calculated as follows:

$$\Delta N^{15} = \frac{\begin{pmatrix}\text{Atom-}\\ \text{percent } N^{15}\\ \text{in sample}\end{pmatrix} - \begin{pmatrix}\text{Atom-}\\ \text{percent } N^{15}\\ \text{in standard}\end{pmatrix}}{\text{Atom-percent } N^{15} \text{ in standard}} \times 10^3$$

Some of the data obtained are presented in Tables 1 and 2. They show that there is a significant variation in the nitrogen isotope-ratio of soils and of different forms of soil nitrogen. The data indicate that the N^{15} content of the nitrogen in soils ranges from slightly below the generally accepted value for the natural abundance of N^{15} (0.366 atom-percent N^{15}) to appreciably above this value, the average being 0.368 atom-percent N^{15}, or $\Delta N^{15} = +5$. Among the various forms of soil nitrogen, the amino acid and hexosamine fractions tend to have higher N^{15} contents than the other fractions, but the data are not consistent.

In selecting a reference standard for calculation of ΔN^{15}, some have assumed a constant value as natural abundance (*4*), and others have determined the N^{15} abundance separately, using atmospheric nitrogen, compressed nitrogen, or deoxygenated air as standard (*5*). For this work, a reference nitrogen gas sample obtained from the National Bureau of Standards and a sample of reagent grade ammonium sulfate from a commercial source were used. The nitrogen-isotopic abundances in these two materials were determined by the Ames Laboratory of the U.S. Atomic Energy Commission and found to be the same (0.3663 atom-percent N^{15}). The ammonium sulfate was preferred as the reference standard. In a precision study that we made, using the ammonium sulfate standard, 12 samples were analyzed, and the amount of N^{15} in the standard was found to be 0.3663 ± 0.0001 atom-percent.

The precision of the method used to determine the N^{15} content of soils is further illustrated by the data obtained from analysis of a Marshall silty clay loam soil of Iowa. Five samples of this soil were subjected to Kjeldahl digestion (*3*), and two portions of each digest were distilled and titrated to obtain a total of ten ammonium samples for analysis of N^{15}. The abundance of N^{15} in this soil, as determined by mass spectrometer analysis of these samples on four different dates by two independent operators, was 0.3677 ± 0.0004 atom-percent.

The methods used in our work for isotope-ratio analysis of different forms of nitrogen in soils were developed from systematic studies of sources of error in N^{15} analyses (*6*). For the mass spectrometer analysis, we used a Consolidated Electrodynamics Corporation mass spectrometer model 21-620 modified to include an isotope-ratio accessory and a linear d-c electrometer amplifier.

The gas conversion system used was built on the mass spectrometer so that the nitrogen gas produced from the ammonium sample was introduced directly into the instrument. Extensive testing of our methods indicates that they are accurate and precise. Therefore, the variation detected by these methods cannot be attributed to analytical errors.

In conclusion, the variation in the isotopic composition of soil nitrogen appears to be small and, for many investigations of the fate of N^{15}-enriched compounds in soils where N^{15} is used as a tracer, this variation can probably be ignored. However, for studies in which N^{15} added to soils is diluted many times (for example, in investigations of nitrogen transformations resulting from long-term biological and nonbiological reactions in soils), the natural variation in the N^{15} content of soils and of different forms of soil nitrogen must be considered for proper evaluation of the results.

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References and Notes

1. K. Rankama, *Isotope Geology* (McGraw-Hill, New York, 1954); T. Hoering, *Science* **122**, 1233 (1955); A. Parwel, R. Ryhage, F. E. Wickman, *Geochim. Cosmochim. Acta* **11**, 165 (1957); K. I. Mayne, *ibid.* **12**, 185 (1957); T. C. Hoering and H. E. Moore, *ibid.* **13**, 225 (1958); R. S. Scalan, thesis, Univ. of Arkansas (1959).
2. H. H. Cheng, thesis, Univ. of Illinois (1961).
3. J. M. Bremner, in *Methods of Soil Analysis*, C. A. Black, Ed. (American Society of Agronomy Monograph, in press).
4. The generally accepted values for natural abundance of N^{15} are 0.365 ± 0.001 atom-percent N^{15} obtained by A. O. Nier, *Phys. Rev.* **77**, 789 (1950), and 0.3663 ± 0.0004 atom-percent N^{15} obtained by G. Junk and H. J. Svec, *Geochim. Cosmochim. Acta* **14**, 234 (1958).
5. For example, T. Hoering, *Science* **122**, 1233 (1955); L. D. Owens, *Soil Sci. Soc. Am. Proc.* **24**, 372 (1960); A. E. Martin, E. F. Henzell, P. J. Ross, K. P. Haydock, *Australian J. Soil Res.* **1**, 169 (1963).
6. J. M. Bremner, H. H. Cheng, A. P. Edwards, Report of the IAEA-FAO Technical Meeting on the Use of Isotopes in Soil Organic Matter Studies, Braunschweig, Germany, 1963 (International Atomic Energy Agency, Vienna, 1964).
7. This report is Journal Paper No. J-4942 of the Iowa Agricultural and Home Economics Experimental Station, Ames, Project 1070. Supported in part by the Tennessee Valley Authority and by a grant from the Rockefeller Foundation.

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Marshes Prograding in Oregon: Aerial Photographs

Abstract. *When nearly circular clumps of vegetation abound in aerial photographs of mud flats in estuaries in regions of temperate climate the indication is that the marsh is expanding rapidly.*

The most obvious indicators of the expansion of tidal marshes in estuaries on the Oregon coast are numerous, nearly circular, colonies of marsh plants. In a study of seven estuaries

I found proof that such colonies were everywhere associated with recent expansion of the marsh (*1*). The study was provoked by circular patterning that appeared in aerial photographs taken in 1939 of Nehalem Bay. The spots looked like expanding mold platelets in an agar culture, and some biological process of marsh formation was suspected.

The species composition of the vegetation of these clumps and adjacent tidal marsh was investigated. Recent changes in extent of the marsh were determined from aerial photographs taken in 1939 (Fig. 1, left) and 1960 (*2*). Earlier records of the marsh boundaries were compared with the earliest U.S. Coast Survey chart (1875) of Nehalem Bay (*3*). The extent of the marsh in the summer of 1961 was mapped in the field. An aerial photograph taken in May 1963 (Fig. 1, right) illustrates the changes since 1961. Other estuaries in Oregon were similarly analyzed.

Figure 2 illustrates the marked increase in the amount of tidal marsh in Nehalem Bay during the last century. In the lowest habitats, near the deep channels of the river, sea arrow grass (*Triglochin maritima* L.) grows in clumps up to 2.0 meters in diameter. On higher and broader expanses of the mud flats two kinds of large, erect vascular plants form the clumps. Marsh bulrush (*Scirpus robusta* Pursh) forms about 75 percent of these circles, and Lyngbye's sedge (*Carex lyngbyei* Hornem.), the remainder. On sites that are a few centimeters higher, Lyngbye's sedge apparently replaces marsh bulrush, usually after the mud flats become covered by continuous vegetation. Farther inland on the marsh, at elevations 20 to 30 cm higher than the margin, tufted hair grass [*Deschampsia caespitosa* (L) Beauv.] becomes the dominant and tallest marsh plant, although Baltic rush (*Juncus balticus* Willd.) matures earlier and is frequently the most abundant in late April and May.

The circular colonies do not seem to remain in dynamic equilibrium, at least on coasts that are not subsiding. The clumps either increase and coalesce in areas between developing tidal channels or are destroyed by erosion as the streams shift. The clumps, which

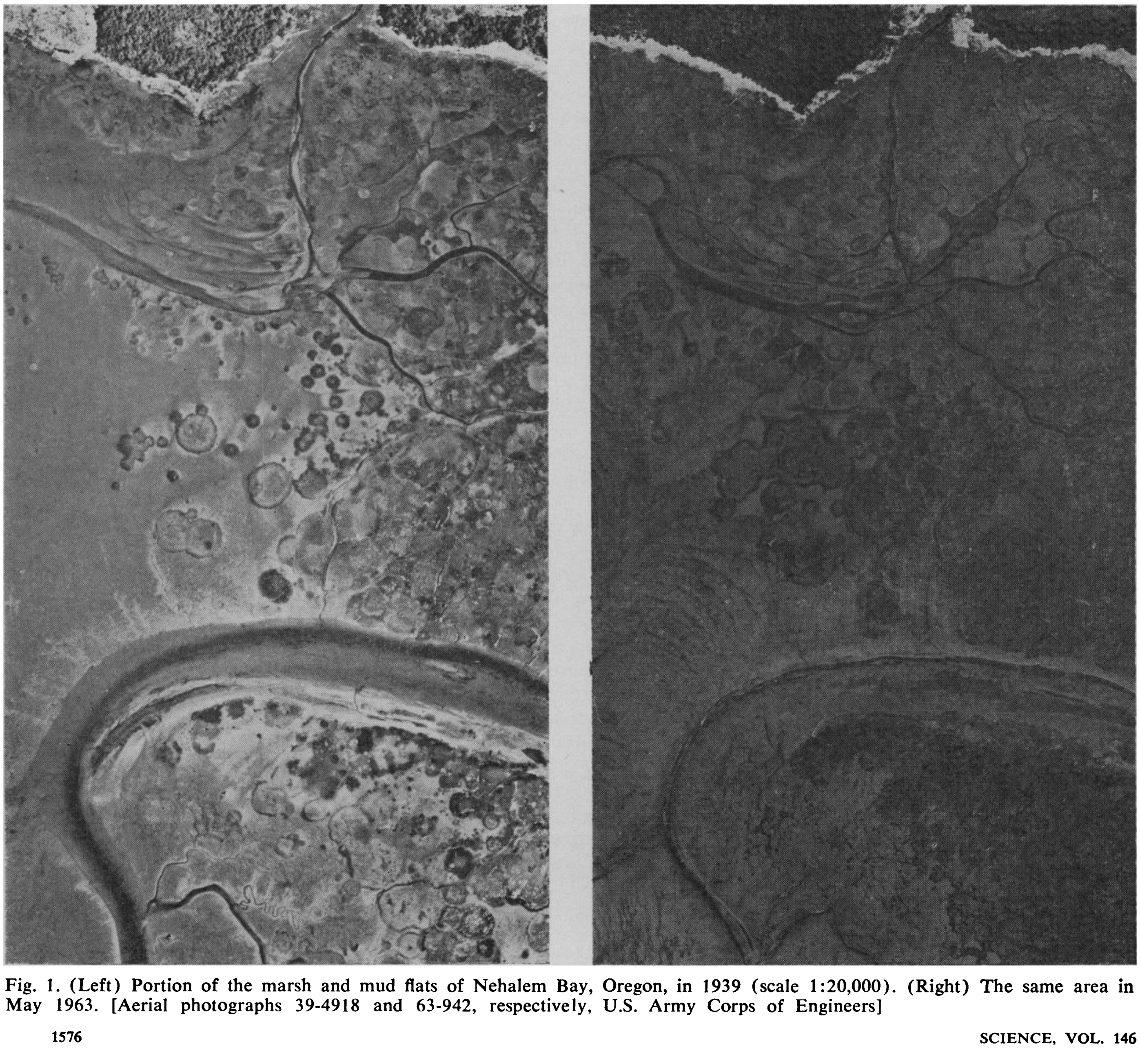

Fig. 1. (Left) Portion of the marsh and mud flats of Nehalem Bay, Oregon, in 1939 (scale 1:20,000). (Right) The same area in May 1963. [Aerial photographs 39-4918 and 63-942, respectively, U.S. Army Corps of Engineers]

usually spread laterally by tillering, trap sediments and slowly increase the ground elevation. Clumps of marsh bulrush sometimes die out in the centers, which are then usually colonized by Lyngbye's sedge. As more sediment is deposited and ecological conditions become drier, other species establish themselves; they also may maintain a roughly circular form in otherwise homogeneous associations.

The U.S. Coast Survey map of 1875 shows two types of marsh in the estuary. The outer margin of this "lower" marsh, dated 1875, is recorded in Fig. 2. Assuming a pre-1875 rate of advance of the marsh comparable with the recent rate, extrapolation indicates that 15 to 25 years before 1875 the margin was probably the edge of the higher and older marsh surface shown in Fig. 2; a line is drawn to indicate the probable extent of the marsh about 1850. From the standpoint of photo-

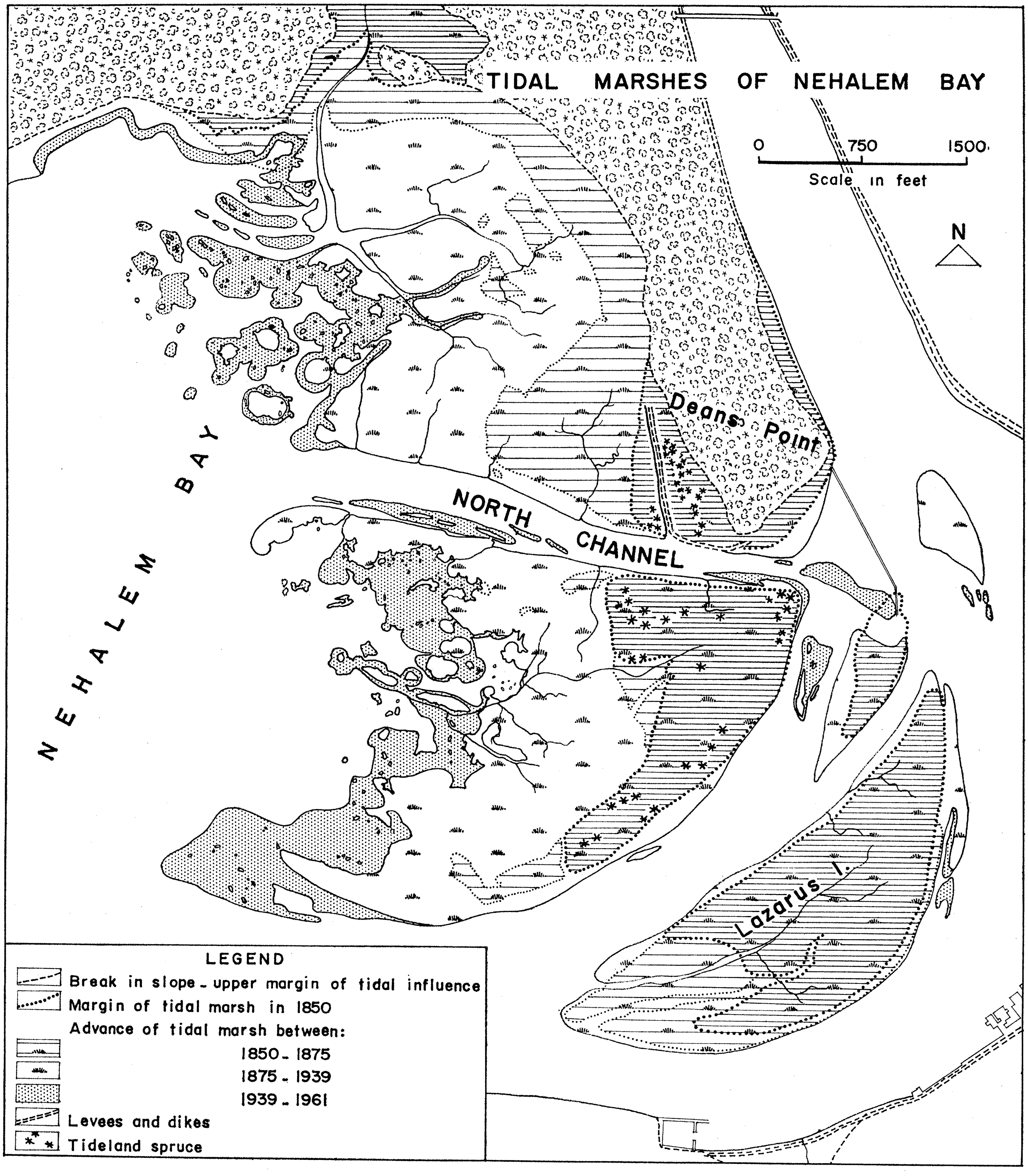

Fig. 2. Recent map of Nehalem Bay marshes.

interpretation, it is interesting to note that the demarcation between the old, high marsh and the lower, more recent marsh (less than 100 years old) is frequently made clearly visible elsewhere in the aerial photographs by the deposition of drift logs at the declivity between the two types of marsh and by the drier nature of the high marsh.

Similar circular colonies of marsh plants are found on expanding marshes in the Tillamook, Umpqua, Coos, and Coquille estuaries. Only in the Alsea estuary, of those investigated, has there been practically no marsh expansion during the last 100 years; with one small exception, no circular colonies exist along the margin of the marsh. This exception is in front of a levee, built in 1958, that effectively blocks a slough and changes the tidal flow in the main channel of the river. Because of the levee, sediments have been deposited recently and marsh plants, especially sea arrow grass, have colonized rapidly.

In summary, the appearance of abundant circular clumps of vegetation, 0.3 to 15 meters in diameter, in aerial photographs of estuarine mud flats in temperate regions predicts that the marshes are expanding rapidly.

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References and Notes

1. C. L. Johannessen, "Shoreline and vegetation changes of the estuaries," in "Some Recent Changes of the Oregon Coast," final rept., project NR 388-062, Department of Geography, University of Oregon (1961), pp. 100–138.
2. Photographs TC 7-68 and TC 7-67, Oregon Tax Commission.
3. U.S. Coast Survey, Sec. XI, "Coast of Oregon between latitudes 45°38′ and 45°45′, including mouth of Nehalem River" (1875).

4. Supported by contract ONR 2771 (04), project NR 388-062, and by the Graduate School, University of Oregon.

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Ancient Copper and Copper-Arsenic Alloy Artifacts: Composition and Metallurgical Implications

Abstract. *Various copper and copper-arsenic alloy artifacts from the Dead Sea area lack the tin and zinc that are normal trace elements. The trace elements found in the artifacts suggest that a copper sulf-arsenate ore was used in making some of them. The metallurgical use of such ore around 3000 B.C. has not been previously reported.*

Unlike our knowledge of early pottery, little is known of the development of metallurgical techniques. Very few early metal artifacts are found sufficiently well preserved. Analyses have been difficult, and systematic analyses of trace elements are not found in the archeological literature on finds made in the Middle East, although much work has been done on artifacts from western Europe. In the Middle East the archeologist has usually been interested only in tin content to determine whether or not he is dealing with bronze artifacts.

It has been assumed that the art of metallurgy developed over a fairly long period and that considerable time elapsed between the first use of copper, smelted from green, easily recognized copper ore [as in Egypt (*1*)] and the later use of copper sulfide ores which needed the double process of roasting and smelting (*2*).

The discovery of a large hoard of excellently preserved copper and copper-alloy objects enables us to reconsider these views. The hoard was found buried, wrapped up in a thin reed mat, in a cave in the extremely arid Dead Sea region. The find is described, with archeological details, in another paper (*3*). Carbon-14 determinations on the mat gave an age of approximately 5000 years. Such a minimum age for the metal objects agrees well with the archeological similarities to other late-Chalcolithic finds.

The metal objects of this unique hoard comprised 240 "mace-heads," 80 "staff-heads" or "wands," 10 crowns, and 20 chisels or axes; they were covered by black organic grime but had no oxide coating (Figs. 1 and 2). Preliminary x-ray fluorescence examination by L. Heller of the Geological Survey of Israel revealed significant amounts of arsenic in some of the mace-heads, amounts that led me to believe that sulfide ores had been the source of the copper. Eleven mace-heads, 11 staff-heads, and 8 tools were investigated, as well as a similar staff-head, badly oxidized, from Beersheba and a mace-head and a chisel found in a cave in Wadi Nahal Tse'elim nearby.

Emission spectrographic methods were then used to determine As, Sb, Ag, Bi, Pb, and Ni, which were present as traces or in greater amounts. Tin and zinc were sought but not found in any of the objects analyzed. The equipment consisted of a quartz-glass spectrograph and a high-voltage condensed spark unit. The very well-preserved objects were rubbed lightly with sand-paper before sparking. A National spectrographic graphite upper electrode was used, and the sample was excited at 0.03 mh and 15 kv, with a 10-second prespark followed by a 60-second exposure; the gap was 2 mm. The spectra were photographed on Kodak 103-0 plates and developed normally. The relative deviation from the mean of duplicate determinations on four standard samples was 12 percent for Pb and less than 10 percent for the other elements determined. Replicate determinations to detect possible variations at the surfaces of three objects and on a freshly sawn face in one object also fell within these limits.

Results of some of the spectrographic analyses are presented in Table 1. The 22 ornaments all contain silver; only one lacks nickel, two lack antimony, three lack bismuth, and five lack measurable amounts of arsenic. This indicates that the ornaments either are the products of one workshop or reflect the use of one rough formula. With one exception, the tools, by contrast, are of impure but unalloyed copper.

Table 1. Minor elements of five artifacts (percentages).

Specimen No.	As	Sb	Ag	Bi	Pb	Ni
			Ornaments			
351	3.50	0.178	0.123	0.0013	0.034	0.170
121	11.90	0.609	0.210	0.0240	0.039	1.22
(Beersheba)	12.00	0.715	0.258	0.0420	Trace	0.048
			Tools			
147	1.92	Trace	.010			
148			.042			1.90