Time and Trace Metals in Archaeological Sites[1, 2]

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A MIDDEN IN THE WEATHERING ZONE is a geochemical anomaly undergoing dissipation. The anomaly here means a departure from the norm characteristic of the given climate and terrain. The departure has the following geochemical expressions:

1) *The amounts* of certain chemical elements are greater in the midden at zero time than in the corresponding nonmidden profiles and horizons.

2) *The distribution* of certain chemical elements in midden profiles is generally different from their distribution in nonmidden profiles, or ''blanks,'' all other things being comparable.

3) *The initial form* in which certain chemical elements exist in the middens may be different from the form of their occurrence in the corresponding blanks.

The cause of the anomaly in question is man's refuse introduced in the weathering zone in the form of garbage and excreta. Depending on his diet and occupation, his refuse may be enriched with respect to copper, zinc, tin, lead, gold, manganese, and of course phosphorus, nitrogen, etc.

The anomalous amounts, distribution, and forms of some chemical elements in middens within the weathering zone tend to disappear in the course of time. The weathering and the soil-forming processes responsible for the normal or zonal distribution of the chemical elements in the blank profiles tend ultimately to produce similar levels and patterns in the midden, in the absence of catastrophic events. An orderly dissipation of the anomaly here visualized is necessarily a function of time. The rate of this dissipation is variable, tending to be relatively slow but depending on a large number of factors, such as the original character of the anomaly, parent materials of the soil, topography, climate, geological-geochemical history of the site, and others. If the dissipation rates of the anomaly can be established for the given climate and terrain, and if the existing levels and distribution patterns of certain critical elements in the midden profile can be ascertained, the extent of the departure of the existing anomaly from the blank may be an indication of the approximate age of the midden, under certain favorable conditions.

The working hypothesis here stated is an outcome of an earlier study in geochemical exploration[3] and of a number of observations related to our current studies of the rates of soil formation.[4] This hypothesis is designed chiefly for middens outside the suitability and the time range of the carbon 14 method. It is evident a priori that the hypothesis needs to be verified empirically, that it has potentially only a local usefulness, and that it will not yield any quantitative results even under nearly ideal conditions. Our aim, however, is not quantitative. We aim at an attainment of certain criteria that would help differentiate, for example, a midden 1000 years old from a midden 10,000 or 100,000 years old. The data here presented show that a difference of only 1000 years may be recognized in some datable midden profiles under certain conditions.

THE TEST AREAS

Florida. A qualitative test of our supposition that the intensity of the midden anomaly, in the geochemical sense, tends to decrease with the midden's age was carried out as follows: Two middens differing only in age were located on a sandspit in the Melbourne Beach Area, Florida.[5] Both are situated on the sand ridge forming the present shore. Their geologic age, parent material, altitude (*ca.* 20′–25′ above sea level), vegetation, relief, and the microclimate are nearly identical. They were, and are, exposed to about the same kind of weathering solutions in post-Pleistocene time. Their original character was very nearly the same, judging by their area and the development of the midden layers. One of these middens, here designated as 1000–2000 B. P., is datable by the fragments of pottery it contains as belonging to the "Malabar Period."[6] The other midden, designated as 2000–3000 B. P., is dated by the potsherds as belonging to the "Fiber-Tempered or Orange Period."[7] The approximate reliability of such typological dating is here assumed and appears to be sustained by the geochemical data herein to be reported. To complete the set, a "blank" site ridge was located on the same ridge, comparable in every respect to the two middens, but showing no signs of human occupancy.

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[1] We are indebted to the Wenner-Gren Foundation for Anthropological Research for the support of these studies and especially to Paul Fejos, director of research of the foundation, for his interest and encouragement of our work. We are also indebted to the Office of Naval Research for its interest in these studies.

[2] Based on an address presented at the Section E meetings of the AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, December 27, 1951, in Philadelphia.

[3] V. P. Sokoloff. *Geochemical Prospecting for Ore.* Denver: Colorado Mining Assoc. (1948) ; *Geochimica et Cosmochimica Acta,* 1, 284 (1951).

[4] G. F. Carter, and V. P. Sokoloff. The Humisol (in preparation).

[5] We are greatly indebted to W. Edwards, Florida Geological Survey, for his interest and active cooperation in the project.

[6] Mr. Edwards identified the sherds and suggested the age and culture correlations.

[7] Culture and age for these periods are given also in Irving Rouse's "A Survey of Indian River Archaeology." *Anthropology,* (44–54), (1951).

Pedogenesis at all three sites was ascertained to be of one and the same kind—namely, a leaching with weathering solutions at a pH approaching 7.0,[8] in the nearly complete absence of the neutral salts. The net effect of such pedogenesis, including local and seasonal reversals in the movement of the weathering solutions, is to cause a noticeable downward migration of alumina, ferrous iron, and other metals of the iron group (Ni, Co, Cu, Zn, Mn, Cr).[9] A degree of sorting of the metals of the iron group accompanies pedogenesis. According to our view, based on the previously cited studies in geochemistry, the sorting of copper and zinc during this process is particularly diagnostic.

Although pedogenesis on the blank site is sufficiently advanced to have produced a humisol profile exceeding 20 inches in thickness, the presence of human refuse in both midden sites was sufficient to retard, if not to modify, the pedogenesis. The soil sections of the three profiles follow:

Blank site: 0 to 2″. Buff-white sand; fairly well sorted; some organic matter and many small fragments of shells.

2″ to 6″. Grayish-white sand; considerable amounts of humus and humus-bound iron; some undecomposed organic matter.

6″ to 13″. Pale yellow sand; relatively poorly sorted.

13″ to 20″. Yellow sand; poorly sorted; uniformly stained with iron rust.

1000–2000 B. P. midden site: 0 to 2″. Gray sand; loamy feel, caused by the high organic matter content; fairly well sorted; high content of humus-bound iron; small fragments of shells.

2″ to 6″. Dark-gray sand, as above; shell fragments less conspicuous; very high humus-bound iron.

6″ to 20″. Yellow sand; poorly sorted; uniformly stained with iron rust.

2000–3000 B. P. midden site: 0 to 2″. Gray, loamy sand; poorly sorted (well graded); some shell fragments; some humus-bound iron.

2″ to 6″. Gray sand; well graded; little humus-bound iron; a few shell fragments.

6″ to 20″. Yellow-white sand; poorly sorted; some shell fragments; no humus-bound iron.

The lower boundary of the two middens, shown above at 6 inches, is variable and may exceed 12 inches. Duplicate midden profiles, however, show the same sequence of the horizons and essentially the same trace metal distribution as the ones to be reported here.

Georgia, Kinchifoonie site.[10] This ancient midden is apparently preceramic (at least *ca.* 3000–4000 B. P.). The midden occupies an old land surface, possibly of Pliocene age. The exposed profiles contain a great thickness of a senile soil at their base, chiefly goethite-cemented quartz sand. The Kinchifoonie soil section is as follows:

0 to 6″; agricultural soil: Light reddish-brown sandy loam showing evidence of cultivation and of crop growth, probably also of repeated fertilization. Vestigial bleaching noticeable—characteristic of the forest-crop successions. A typical man-made horizon imposed on the humisol pedogenesis. Present vegetation: mixed grass.

6″ to 12″; bleached midden: Light reddish-brown, sandy loam; amorphous silica present. Weak crumbly structure, probably senile. Severely altered crude artifacts of flint present (resembling the European paleolithic), as well as a very few unaltered artifacts of a superior workmanship. The artifacts are apparently in place and are neither extrusive nor intrusive.

12″ to 28″; midden material: Less severely bleached than the overlying horizon. Reddish-brown, crumbly, sandy loam. The lower few inches of this horizon are cemented apparently by silica. Some charcoal present. Abundant severely altered primitive flint artifacts.

28″ to 100″; senile soil: Apparently a part of the "B" horizon of an ancient humisol. Compact red sand (quartz cemented by goethite), resembling the red sandstone of Macon Plateau, Ga. Numerous most severely altered primitive flint artifacts. Some filled rodent holes.

100″ to 106″; senile soil: Loose red goethite-sand mixture.

At base; yellow sand: Limonite, amorphous silica present; some secondary quartz may be present; locally iron-manganese concretions, gravel-sized.

The blank for the Kinchifoonie site was located within less than 0.5 mile of the midden, in the terrace of the same age cut by the same stream. The soil section in the blank was analogous to the previously described exposure, except that no midden materials were present and there were no other signs of human occupancy. The pedologic age of the blank may be more advanced in comparison with the midden profiles, judging by the intensity of the red colors in the weathered mass, a greater abundance of iron concretions, and other indications of the sorting of iron. The topsoil of the blank was an agricultural soil of the same kind as in the midden profile; it was underlain by a senile soil apparently identical with the 28-inch to 100-inch horizon of the midden profile, minus the intrusive and the extrusive materials; the base of the blank was the same as that of the midden.

SAMPLE AND TESTING

Samples of approximately one pound each were taken from every horizon of the profiles described. The samples were grab composites in the vertical sequence of the soil section. They were stored in paraffin-coated cartons, screened through a 2mm pure iron sieve (Zn-free, Cu-free), mixed, and air-dried in the basement of Rogers House, The Johns Hopkins University, where the temperature is about 75° F

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[8] Due apparently to the shell fragments in the weathering mass; pH of the atmospheric waters in this area is probably on the acid side of 7, perhaps 6 to 5.

[9] The nearly universal dispersion of iron and the iron group in nature is overlooked only too often. Even "pure" quartz sand, free from the heavy minerals, contains more than 10–20 ppm Fe by analysis and, as a rule, determinable traces of other metals.

[10] On Georgia Highway 19, about 2 miles northeast of Albany, Ga. Discovered in August 1951 by G. F. Carter. Described in Sokoloff's letter of Sept. 4, 1951, to Paul Fejos, director of anthropological research, Wenner-Gren Foundation.

and the relative humidity rarely exceeds 25 per cent in the winter.

Copper and zinc were determined by the dithizone procedures previously described.[11] Chloride and bicarbonate[12] were determined volumetrically, by titration of the aqueous extracts with $0.05N$ $AgNO_3$ and $0.05N$ H_2SO_4, respectively. The pH was gauged approximately, with "Hydrion" paper, in pastes, suspensions, and extracts of the soils.

The test results for copper and zinc are accurate probably to one significant figure only. A greater degree of accuracy is not required in the present search for differences in orders of magnitude, although the dithizone methods in general are capable of yielding two significant figures, or even three, provided one is willing to expend the time and energy necessary for such attainment.[13]

Copper, zinc, and many other metals occur in soils and soil materials in several different forms, both mineral and organic. They may be present in the crystal structures of some clay minerals, in combination with organic substances of different kinds, and, moreover, in various states of accessibility to the extracting solvents. In senile soils, especially, chiefly zinc but also copper may be present in states of occlusion by materials and surfaces still remaining to be ascertained. Finally, there may be extremely small amounts of ionic copper and zinc present locally or periodically in the soil solution.

A qualitative recognition of these different forms is relatively easy in the laboratory. Their separate quantitative estimation is generally so difficult as to be almost impossible. For example, a separate estimation of the organic forms requires an isolation of the organic fraction of the soil. There can be no assurance during any isolation procedure that the trace metal content of the organic fraction will remain as it was before the isolation. There seems to be no definite boundary between the soluble, the occluded, and the exchangeable forms. Nor is it possible to isolate the clay minerals from the soils without the risk of their becoming modified in the course of the isolation.

For these and many other reasons, it became necessary to employ rather arbitrary means of recognition of the different forms of copper and zinc in our materials. These means were as follows:

Extractable forms.[14] Zinc was extracted at pH 6.0 with $0.5N$ ammonium acetate at 70° C; copper was extracted at pH 1.0 with about $0.1N$ hydrochloric acid. A certain small fraction of the organic forms was probably extracted, alongside the occluded and the reagent-soluble forms.

Organic forms. The extracted and washed residues from the preceding treatment were digested repeatedly with small amounts of 30 per cent hydrogen peroxide and a few drops of strong hydrochloric acid. They were heated over an open flame, in silica dishes, so as to aid the oxidation, in the hope of avoiding losses caused by the volatile carbonyls of Zn and Cu, assuring good aeration of the samples. The residue was extracted as above, using acetate for zinc, and hydrochloric acid for copper. The metals were determined in the extract and designated as organic forms. These determinations are subject chiefly to negative errors (losses of the carbonyls, imperfect oxidation, incomplete extraction), and the results reported here, high as they may seem, are probably too low rather than too high.

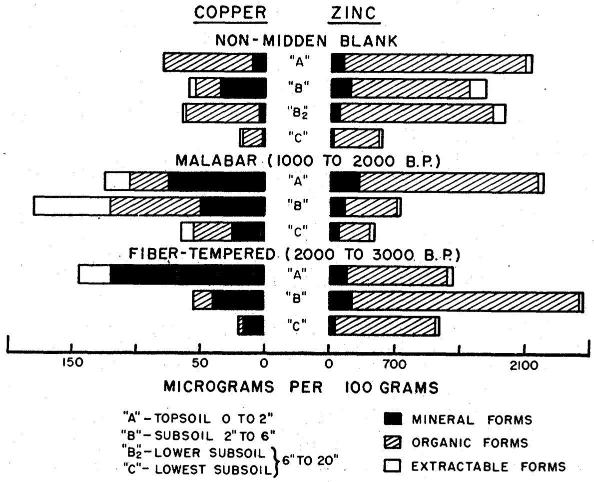

FIG. 1. Distribution of copper and zinc in two midden soil profiles of different age and in a nonmidden blank.

Mineral-bound forms. Following the removal of the organic forms, the residue was fused with potassium bisulphate in Vykor glass tubes, and the acid melt then examined for copper at pH 1 and for zinc at pH 6.0. The positive tests, which were ascribed to the mineral forms of these metals, as here reported, are probably too low, despite the possibility of some compensating errors. The tendency toward low results is due to the presence of unfused particles of quartz and, in some samples, of some dark mineral substance. The slight compensation may be due to some nonmineral forms carried through from the previous treatments. The sum of the extractable, organic, and mineral forms is shown as the total in Figs. 1 and 2. The orders of magnitude of these different forms are so different, however, as to justify a qualitative and perhaps a semiquantitative appreciation of the results.

Thus, the organic forms of zinc are preponderant over the others, indicating magnitudes often exceeding 1000 μg/100 g dry substance, as against 20–300 for the mineral forms, and 10–180 for the extractable. The organic forms of copper, however, range from 0 to 70 μg/100 g dry substance, as against 0–120 for the mineral and 0–60 for the extractable.

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[11] V. P. Sokoloff. *Mining Mag.* (Colorado School of Mines), 15 (Nov. 1950).

[12] The data are not included in this report.

[13] Even with these limitations, the dithizone methods are superior to the spectrographic procedures in their rapidity, sensitivity, and reliability. See V. P. Sokoloff. Project Notes on Dispersion of Lead and Zinc in Kokomo Mining District, Colorado. U. S. Geological Survey File Report (1948).

[14] No water-soluble forms of Cu and Zn could be detected in any of the materials. Under conditions of the tests, this means the water-soluble trace metal content was less than 0.5 μg/200 g (i.e., less than 0.0025 ppm).

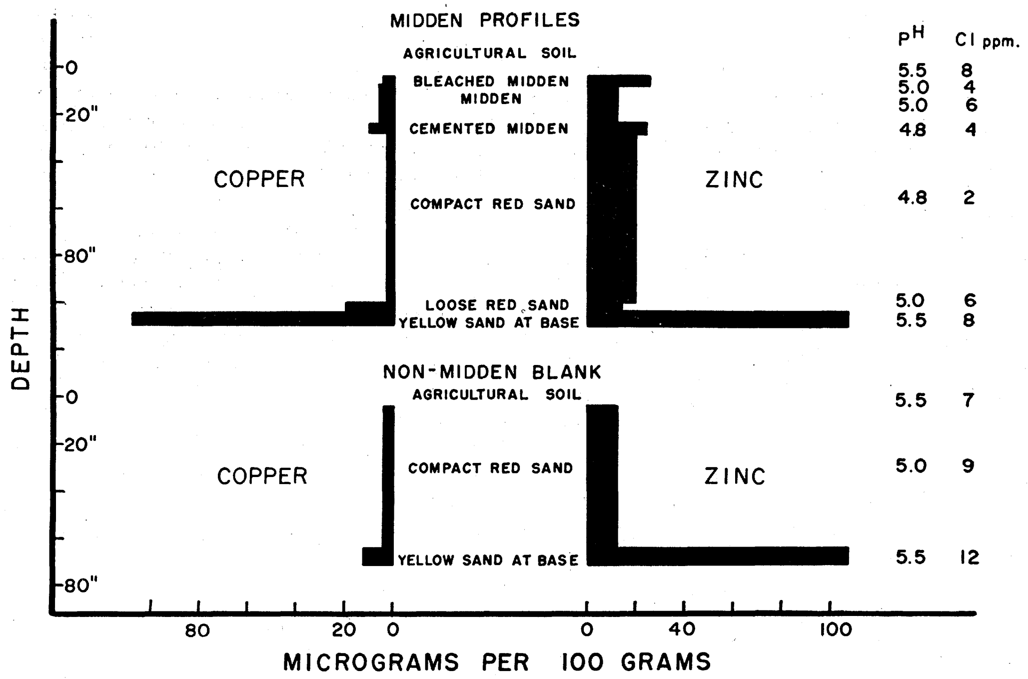

FIG. 2. Distribution of extractable copper and zinc in Kinchifoonie (preceramic) midden soil profiles and in nonmidden blank.

The fractionation of metals was not carried out in the Kinchifoonie profiles. It became evident early in the latter study that the extractable forms of copper and zinc are sufficient for the establishment of the geochemical expression of the midden. In contrast with the Indian River profiles, the organic forms of these metals were inconsequential here, except in the agricultural soil, and the mineral forms were nearly absent. If so, a most severe weathering and a very old age are indicated for the Kinchifoonie site, sufficient to have caused an almost complete decomposition of the clay minerals other than goethite, as well as an analogous decomposition or degradation of the metal-organic complexes.

These considerations made the geochemical investigations relatively easy at the Kinchifoonie. The collected materials were examined on the same day by the dithizone methods previously described,[15] and a preliminary report on the site was completed the same day.[16]

RESULTS

The analytical data on Melbourne Beach and Kinchifoonie midden profiles presented in Figs. 1 and 2 are largely self-explanatory. The following supplementary observations are not included in the diagrams:

1) The pH of the Indian River profiles is 7.4 to 7.5 in the topsoil, 6.0 to 7.0 in the lowest horizons, and 6.5 to 7.0 in the intermediate horizons.

2) Chloride in the Indian River profiles was remarkably uniform—11–30 ppm in the topsoil and 4–11 ppm in all other horizons.

3) Triplicate midden profiles at the Kinchifoonie site are so similar, with respect to their trace metal distribution and other constituents, that only average values for all are shown in Fig. 2. The greatest variation exists only in the upper few inches of the agricultural soil.

A measure of exaggeration of details was not avoided in the diagrams. Thus the few micrograms indicated for certain forms in certain horizons are mere traces, detectable but too small to be shown on the scale.

The analytical data shown in Figs. 1 and 2 may be interpreted as follows:

1) Both blank and midden profiles are in the process of *rather severe leaching,* judging by the levels and the distribution of the extractable chloride. The chloride present in all these profiles is probably cyclic[17] and is introduced there by the atmospheric waters. The pH of the Kinchifoonie profiles is at the

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[15] We are indebted to Mr. Cordell, superintendent of schools, Albany, Ga., for the use of the laboratory space at the local high school. Reagents, glassware, and equipment are generally carried on all exploration trips. We are also indebted to A. B. Kelley, professor of archaeology at the University of Georgia, for his interest and cooperation in this study, for his cultural placement of the site, and for his generous aid in our preliminary work in Albany. We hope that Dr. Kelley will report the Kinchifoonie site in greater detail.

[16] There is no reason for delays, transportation, and storage of samples, and elaborately slow chemical procedures in the geochemical-archaeological reconnaissance here exemplified. As the Australian prospecting experience has shown, the entire laboratory gear for the purpose can be carried in a properly packed jeep, as well as the sampling tools, drafting instruments, typewriter and a filing case, camping equipment, etc.

[17] G. F. Carter and V. P. Sokoloff. Studies in Rates of Soil Formation in Chesapeake Bay Area. ONR Report (mimeo.).

common humisol levels, further characteristic of rather advanced leaching and weathering. The pH of the Melbourne Beach profiles is on the alkaline side of the humisol levels, probably on account of the still undecomposed shell fragments.

2) Both copper and zinc are noticeably concentrated in the topsoil materials, chiefly in their organic forms. Their high levels in the topsoil may be due, in the Kinchifoonie profiles, to man's agriculture, as well as to their chelation by the organic complexes. Geochemically the topsoil has little or no bearing on our problem.

3) Extractable copper in the subsoil midden materials, in relation to the corresponding blanks, is significantly higher but tends to approach the blank as the age of the midden profile is increased. Thus, the following comparison is possible:

Midden profile	Malabar	Fiber-tempered	Pre-ceramic
Extractable copper in subsoil	10–60	0–8	0–8
Extractable copper in corresponding blank	0–3	0–3	ca. 5

The trends of extractable zinc in this connection are obscure. It is evident that a certain sorting of copper from zinc takes place, with time, in the course of the humisol pedogenesis. The Kinchifoonie profiles are nearly identical with the blank, as respects the extractable copper and, to a lesser degree, as respects the extractable zinc, if we disregard the local cementation in midden B horizon. It is evident also that the 1000–2000 B. P. (Malabar) Melbourne Beach midden profile is still anomalous with respect to its extractable copper, and that the 2000–3000 B. P. (fiber-tempered) and the preceramic midden profiles tend to resemble the blanks.

4) The organic and the mineral forms of both zinc and copper may be considered as showing trends not dissimilar from those of the extractable forms, but their significance needs to be ascertained by further work.

It is entirely possible, for example, that the mineral forms are chiefly clay-bound. If so, they tend to attain their maximum levels in the mature stage of the pedogenesis, whereupon they decline and tend to disappear in the senile stage. If so, the low mineral form-content is characteristic of both juvenile and senile stages of the pedogenesis.

It is possible also that the trace metals chelated by the organic fraction of the soil complex may serve as a reservoir, so to speak, for the clay-bound trace metals; it is possible that, as the age of the soil increases, the ratio of the organic to the mineral forms tends to decrease, from the juvenile to the mature stage of the humisol.

There are numerous other implications in this preliminary study. Further empirical and fundamental evidence is forthcoming. In the meantime, it appears that we have made a beginning in a relatively new method in archaeology.

A functional relationship is proposed between time and the establishment of normal trace metal dispersion patterns in midden soil profiles, under favorable conditions. It is shown conclusively that, in Florida, a period of 1000 or 2000 years is not enough to bring the distribution of trace minerals in a midden around to that in a comparable undisturbed site.

Certain forms of copper, in particular, appear to be well suited to serve as criteria of the pedologic age of midden soil profiles. The pedologic age may be a direct indicator of the chronologic age, all other things being comparable. These possibilities, however, are suggested rather than proved in the present study. The basis of the proposed correlation is empirical; namely, a study of three midden profiles datable archaeologically within one or two thousand years of each other but comparable with respect to their geomorphology, lithology, and pedogenesis. The comparisons are made also by reference to nonmidden profiles in the same environments and terrains. It may be stated even now that the establishment of the normal dispersion patterns for copper and, with less clarity, for zinc is probably a matter of several millennia, in the humisol terrains.

The problem is posed rather than solved in this preliminary investigation. Further detailed work is needed seriously to test our hypothesis. The geochemical approach to the approximate chronology of archaeological sites illustrated here may prove to be useful, especially for profiles outside the time range of the other methods of dating. Our endeavor is to arrive at the orders of magnitude of time rather than to aim at an "exact" dating, steering clear of any such archaeological delusion as the latter. At its best the geochemical method may enable us to tell the difference between a midden 1000 years old and another 10,000 (or 100,000) years old, but it certainly cannot distinguish the difference between 999 and 1001 years, all other things being favorable.