kinds of crabs. Observations similar to these were not made for the other species. More precise studies are indicated.

Much physiological data pertaining to the concentrations of inorganic ions in the blood and body fluids of Crustacea have been established from pooled samples from two or more individuals. If there is a correlation between the ionic composition and protein content of the blood (2), and if the latter varies as much, under uniform conditions of environment, as is indicated in Table 1, then errors may result from the practice of pooling the bloods before making determinations. It is entirely possible, also, that no relationship exists between the proteins and ionic concentrations of the blood. Further studies on this subject are needed.

References

- 1. FLORKIN, M., and BLUM, H. F. Arch. intern. physiol., 38, 353 (1934).
- PROSSER, C. L. (Ed.). Comparative Animal Physiology. Philadelphia: Saunders, 104 (1950).
 PRYOR, C. W., and LEONE, C. A. Biol. Bull., 103, 433
- 3. PRYOR, C. W., and LEONE, C. A. Biol. Bull., 103, 433 (1952).
- 4. DRILHON-COUTOIS, A. Ann. J. Physiol., 10, 377 (1934). 5. WERD, D. A. DECE, Soc. (London), 7100, 107 (1944).
- WEBB, D. A. Proc. Roy. Soc. (London), B129, 107 (1940).
 ALLISON, J. B., and COLE, W. H. J. Biol. Chem., 135, 259 (1940).
- (1940).
 CLARK, E., and BURNET, F. M. Australian J. Exptl. Biol. Med. Soi., 20, 89 (1942).
- TYLER, A., and SCHEER, B. T. Biol. Bull., 89, 193 (1945).
 BECK, A. B., and SHEARD, K. Australian J. Exptl. Biol. Med. Sci., 27, 308 (1949).

Manuscript received May 8, 1953.

Occlusion of Copper and Zinc by Some Soil Materials of Lower Mississippi River Area¹

V. P. Sokoloff

The Johns Hopkins University, Baltimore, Maryland

This preliminary note reporting a selective occlusion of small amounts of copper and zinc by some Mississippi River materials and by some soils derived from them is a part of a detailed report now in preparation. Observations on the occlusion of copper and zinc are parts of a general study of geochemistry of archaeological sites. The study itself was undertaken as a search for the means, the methodology, whereby the knowledge of weathering phenomena could be brought to bear on archaeological-anthropological problems, specifically, on the physical-chemical history of archaeological terrains.

Field indications and experimental evidence suggest existence of mechanisms in soil materials, soils, and parts of some soil profiles that are capable of occluding rather than exchanging very small amounts of copper and zinc, singly or in the presence of each other, under certain conditions. Such mechanisms exist in some but not in all of the materials examined. Their presence or absence may be correlated with origin and extent of weathering of the materials or horizons. The number of comparisons made so far is only 75 and, obviously, far more work is needed to ascertain the correlations and to identify the occluding mechanisms. The results obtained to date are so consistent, however, and the test employed is so simple and clearcut, that a preliminary note here presented appears to be permissible and, indeed, desirable.

A soil material shaken with a solution containing as much as 20 ppm Cu or Zn, singly or in the presence of each other, at the terminal pH from 5 to 8, responds generally in one of the following three ways: (a) both Cu and Zn are withdrawn from the aqueous phase quantitatively, (b) Cu is withdrawn but Zn is not, or (c) neither Cu nor Zn is withdrawn.

Reactions (a) and (b) take place at ordinary temperatures, seem to be instantaneous, and are reversible on the acid side of pH 2. They are not influenced by Ca⁺⁺, Mg⁺⁺, Na⁺, Fe⁺⁺⁺, Cl⁻, SO₄⁻⁻, HCO₃⁻, CO₃⁻⁻, or NO₃⁻, but are inhibited by citrate and, to a lesser extent, by tartrate and acetate. They are not affected by enriched bacterial or yeast growth on added sucrose or by the enrichment of denitrifying microorganisms. The occluding mechanisms are not impaired by prolonged heating of the soils in question at 300–400° and appear to be associated with the mineral rather than with the organic fraction of soils. The organic chelators or fixers of Cu and Zn were encountered only in some humous topsoil horizons but their study is outside the scope of this note.

The occlusion of Cu and Zn, in the amounts studied, is independent of their calcium carbonate content, or of the proportions of acid-soluble iron and possibly the entire iron group.²

Cu is occluded on the alkaline side of pH 4, and Zn on the alkaline side of pH 5.5 or so. The occlusion does not take place on the acid side of these ranges. On the alkaline side of about pH 8, the occlusion is obscured by other phenomena. Occluded Cu and Zn can be recovered quantitatively at pH 2, as a rule, and in still more acid solutions.

Soil materials that do not occlude Cu or Zn appear to be more kaolinized, on the whole, than the occluders of both Cu and Zn. However, a detailed study of the occluding factors still remains to be carried out, and it is not clear yet whether the factors or the surfaces in question are associated with certain series or species of the clay minerals. They may prove to be associated with simpler substances of colloidal dimensions, judging by the responses of some sands. The author regrets the unavailability of laboratory facilities for further work in this connection.

The only seemingly positive correlation between the occlusion response and the kind of occluding material

² Freshly precipitated $Fe(OH)_3$ occludes both Cu and Zn on the alkaline side of pH 4. Amounts of occluded or coprecipitated Cu and Zn increase at pH 5, 6, 7, and 8, under comparable conditions. Zn is occluded by $Fe(OH)_3$ more readily than Cu. CaCO₃ added to lime-free nonoccluding materials seems to have no effect on the occlusion.

¹The studies here reported were made possible by two grants-in-aid from the Wenner Gren Foundation for Anthropological Research. This generous aid is most gratefully acknowledged.

TABLE 1

Occlusion Response and Extractable Copper and Zinc in Louisiana-Mississippi Soil Materials*

Occlusion response	Per cent of Ma- terials Ex- amined	Extractable Cu, ppm		Extractable Zn, ppm	
		Range	Aver- age	Range	Aver- age
a. Both Cu and Zn occluded in presence of each other	15 1	0-150	19	11–150	59
b. Cu occluded in presence of Zn; Zn not occluded in presence or in absence of Co	n	0-7	1	1-63	13
c. Neither Cu no Zn occluded singly or in presence of each other	r 45	0-1	0.2	024	4

* The occlusion test consists of the following operations: (a) 50 g of air-d₁y soil shaken in a 200-u-stoppered bottle with 100 ml of a solution containing 20 ppm Cu⁺⁺ and 20 ppm Zu⁺⁺ in 0.01 N HCl and allowed to settle; (b) supernatant liquid is withdrawn, filtered, if necessary, and tested for Cu⁺⁺ and Zn⁺⁺ by the dithizone method. pH of the system is maintained between 5 and 7.5 by HCl or NH₄OH. The appropriate blanks are run concurrently. With soils occluding both Cu⁺⁺ and Zn⁺⁺, the blanks are scarcely required. Such soils, in fact, can be used to remove traces of the two metals from distilled water and reagents, including ammonia.

 \dagger One-fifth of these materials showed a small or a doubtful capacity to occlude Zn.

is shown in Table 1, and is as follows. The greater the amounts of HCl-extractable Cu and Zn in the soil, the more likely is the soil to occlude additional small amounts of Cu and Zn. This crude generalization suggests merely presence or absence of certain mechanisms responsible for the reaction. Quantitative studies of a "Cu-Zn capacity" or some such possible characterization of our materials are deferred. Empirically, however, the test has already shown some value in the field, as may be illustrated by a summary of Table 1.

In this table, materials believed to be representative of the area studied are grouped in three categories: (a) Occluders of both Cu and Zn, singly and in the presence of each other. These materials include freshly deposited Mississippi River sediments, some midden soils near Sicily Island, Louisiana, buried middens in the delta south of New Orleans, deeper horizons of natural levees at Mauvais Bois, Point au Chien, and Carlysle, La. Their texture ranges from silty sand to clay and their calcium carbonate content is highly variable. (b) Occluders of Cu but not of Zn. This prominent group contains mature loess profiles. to 100 in. depth or so, near Natchez, Miss., leached and unleached loess near Doloroso, Miss., some artificial levee horizons (in place for 75 years or so), and some topsoil horizons from Poverty Mound, in the Arkansas River area. Their texture and $CaCO_3$ range are like those in the preceding group. (c) Occluders of neither Cu nor Zn. This most numerous group includes soil profiles on Red River deposits, degraded loess, "brown loam" soils on the older Pleistocene Mississippi River terrace, mature soils on the Prairie terrace (late Pleistocene), the lower Atchafayalla backswamp clay, materials from Teche I channel, most of the Poverty Mound Traverse, leached clays near Sicily Island, La., profiles near Marksville, La., both on made ground and natural buried soil, and senile soils on early Pleistocene and pre-Pleistocene materials throughout the area.

It may be possible to make use of the occlusion test in the identification of sediments in areas where geomorphologic-geologic data alone are insufficient for the purpose, especially in the Recent geologic areas in the delta. This possibility, if sustained, may be realized right in the field. All equipment and reagents for the test are easily portable and the test itself requires only a few minutes. It is my hope to ascertain further validity of the test in the coming season, all other things being favorable.

A tentative view of the significance of the observations here stated may be as follows. The Cu-Zn occluding mechanisms are very common in Recent materials of Mississippi River origin but not in the Red River sediments and, perhaps, not in the Arkansas River sediments. These mechanisms may deteriorate when the sediments containing them are exposed to subaerial pedogenesis. The zinc-occluding mechanisms tend to deteriorate and disappear, in the Recent, far more rapidly than the copper-occluding mechanisms. Loessification of sediments tends either to conserve or to produce the copper-occluding mechanisms.

Manuscript received May 6, 1953.

Some Observations on the Pathogenicity of Isoniazid-Resistant Variants of Tubercle Bacilli¹

Gardner Middlebrook and Maurice L. Cohn Department of Research and Laboratories, National Jewish Hospital at Denver and the University of Colorado School of Medicine, Denver

It has been demonstrated (1) that the incidence of variants of tubercle bacilli resistant to isoniazid (INH) is even higher than is the case with streptomycin—a most disappointing observation in terms of what one could predict at that time concerning its usefulness in the treatment of tuberculosis. Since then we have had the opportunity of investigating more intensively the properties of these INH-resistant mutants both in the experimental laboratory and in the clinic.

The Vallée strain (bovine) and the H37Rv strain (human) were exposed to isoniazid on the oleic acid

¹Presented before the Colorado Trudeau Society April 18, 1953.