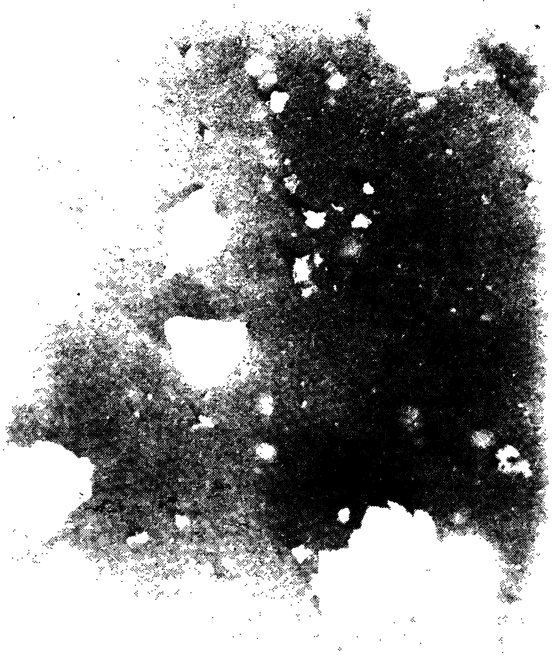

FIG. 3. Fuller's earth (FE). High mortality.

vestigated (*6*). The repetition of these experiments, however, gave in some instances significantly different results from those already published—this in spite of identical materials and conditions. Nevertheless, the trend of the effect of the different diluents was quite distinct, and the results could be used for a first approach.

For further experiments, about 24-hr-old third and fourth instar Mexican bean beetle larvae were used. They were exposed qualitatively to various aluminum silicate dusts and kept in a Petri dish while feeding on bean leaves. In each experiment 10 larvae were used, and mortality counts were made after 24, 48, and 72 hr. Because of inadequate supply of larvae, only those experiments were repeated which gave 25% or higher mortality in 24 hr. The silicates were screened with a 200-mesh sieve and dried in a desiccator. The temperature was 75° F, and the RH 48% in all experiments. Adequate untreated controls were under identical conditions.

Most effective of the diluents used were: Barden clay and Attaclay, fuller's earth and asbestine, Bancroft clay; least effective, EMTCO 23 Talc, Filtrol X-415, and Talc No. 6-J.

It was found that if the $SiO_2:Al_2O_3$ ratio of the above diluents was plotted against the mortality of Mexican bean beetles, in many cases the mortality increased with decreasing ratio of the $SiO_2:Al_2O_3$ (Fig. 1). Since the solubility of these compounds in the fluids and lipids of the insect body is quite negligible, the shape and the structure of the microcrystals had to be investigated. From all the above-mentioned powders x-ray diffraction pictures were taken, and the resulting Debye-diagrams recorded and evaluated by using a microphotometer, but no coherent or convincing explanation of above phenomenon could be achieved by this method.

The pictures of the inert diluents, taken with the electron microscope, have resulted in some information, yet it is contrary to expectation. Those diluents with little or no insecticidal effect show sharp edges and points (Fig. 2), whereas the highly effective members of above series appeared much less "abrasive" (Fig. 3). This could indicate that the dusts probably absorb, more than abrade, the waxy layer of the exocuticle or that the combined action is responsible for the effect of inert diluents on insects.

It is obvious that more research has to be done to elucidate these interesting problems of insect physiology. The use of different kinds of insects and other methods and materials may bring forward the answer. Such experiments are in progress and will be reported when completed.

References

1. ZACHER, F., *et al. Arb. biol. Reichsanstalt Land- u. Forstw., Berlin-Dahlem,* **18**, 201 (1936).
2. RICHARDSON, C. R., *et al. J. Econ. Entomol.,* **25**, 1176 (1932).
3. BRISCOE, H. V. A. *J. Roy. Soc. Arts,* **91**, 593 (1943).
4. BOYCE, A. M. *J. Econ. Entomol.,* **25**, 1053 (1932).
5. WIGGLESWORTH, V. B. *J. Exptl. Biol.,* **21**, 97 (1945).
6. HUNT, C. R. *J. Econ. Entomol.,* **40**, 215 (1947).

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Uranium in the Clay of a Black Radioactive Shale

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The location of uranium in black shales is not well understood, and various reports suggest different loci for the element. McKelvey and Nelson (*1*) summarize the possibilities well as follows: "In fact, it is possible that no distinct uranium-bearing mineral is present in many of the shales, for the uranium may be in an organic compound or the uranium ion may be held by ion exchange, or by adsorption on organic matter or clay minerals, or as impurities in the crystal lattice of common minerals." The results of a brief study of a black radioactive shale from Ste. Genevieve Co., Mo., show that the uranium contained in it is located predominantly in a relatively fixed condition in the fine clay fraction, and not in the black organic matter.

This result is at variance with the suggestion (*1*, p. 40) "that the uranium in the black shales is more likely attached to organic matter than to clay" and does not support Frederickson's suggestions (*2*) that the UO_2^{++} ion may be "adsorbed between the graphite layers of carbonaceous material, forming a strong structure due to the stable UO_2^{++} holding the two layers together." On the other hand, simply because the uranium was not in closest association with the organic matter in the shale, it does not follow that the same relationships hold universally.

A thin black shale layer in the Spergen limestone 5½ miles north of Ste. Genevieve, Mo. (*3*), is radioactive and apparently was the source of the constituents that gave rise to a carnotite film on limestone below. The shale was found by spectrographic analysis to contain uranium and vanadium.

Shale visibly barren of carnotite was disaggregated and separated into size fractions as follows: coarse fraction $> 4\ \mu$ (settling equiv to spheres); medium fraction, 1–4 μ; fine fraction, 1–0.2 μ; and superfine fraction $< 0.2\ \mu$ (*4*). The coarse and medium fractions contained illite, quartz, and calcite, and the finer fractions contained only illite, as shown by x-ray powder diffraction patterns. Carbon was concentrated progressively in the finest fractions as shown by darker colors, and by more pronounced exothermic reaction in differential thermal analysis.

The uranium content of the fractions was tested by fusing .05 g of a 1:1 mixture of shale and a standard kaolinite, with 2 g sodium fluoride, and by comparing the fluorescence of the fusion under the ultraviolet light (Mineralight) with a standard arbitrary scale of shale-kaolinite mixtures. The medium and fine fractions of the shale showed unit fluorescence, the coarse fraction fluoresced equivalent to a one-half shale mixture, and the superfine fraction fluoresced equivalent to a one-tenth shale mixture. Hence, the shale fraction richest in carbon gave the weakest fluorescence, from which it is concluded that the uranium is concentrated in the clay and not in the carbon fractions.

Leaching experiments were conducted to determine the ease of removal of uranium. Two g shale was stirred and allowed to stand in 50 ml solvent for 24 hr. After filtering, the filtrates were evaporated to 15 ml, and 10 drops of each was fused with 2 g sodium fluoride. Hydrochloric, nitric, and sulfuric acids, aqua regia, and dilute sodium carbonate were effective solvents, but hot and cold water, ethyl alcohol, carbon disulfide, and carbon tetrachloride did not extract enough uranium to produce fluorescence. Normal propyl alcohol dissolved a small amount, which fluoresced weakly.

Attempt to exchange the uranium cationically was made by mixing 10 g pulverized shale with 1 liter 0.1 *N* KCl and with 1 liter 0.5 *N* $BaCl_2$. Cations of barium and potassium were chosen for exchange because of their relatively large sizes, which are comparable to the uranium and UO_2 ions. After thorough shaking, the suspensions were allowed to stand for 24 hr and then filtered. The filtrates and the clay residues were tested for uranium by the fluorescence methods described above. The filtrates, however, showed no fluorescence, and the clay residues four fifths the intensity expressed as unity; hence, it is concluded that the uranium is held by the clay minerals in a condition not easily exchangeable.

In the absence of further data on behavior of the uranium in the clay it is perhaps best to forego unsupported speculation as to where the uranium resides. Apparently it is with the clay, not primarily with the carbon, and is not easily exchangeable as a cation.

References

1. McKelvey, V. E., and Nelson, J. M. *Econ. Geol.*, **45**, 39 (1950).
2. Frederickson, A. F. *Science*, **108**, 184 (1948).
3. Muilenberg, G. A., and Keller, W. D. *Am. Mineralogist*, **35**, 323 (1950).
4. Brown, J. H., Jr. Unpublished Master's thesis, Univ. Mo. (1952).

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Chromatography in the Purification of Staphylococcal Enterotoxin

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Several methods have been employed for the purification of staphylococcal enterotoxin (*1*), but none has been entirely satisfactory. In an attempt to purify the enterotoxin chromatographically we have found diatomaceous silica to be a satisfactory adsorbent. Other investigators have used this material successfully for the purification of a variety of substances (*2–5*).

The enterotoxin samples were prepared for chromatographing by precipitation from saturated $(NH_4)_2SO_4$ solutions or by precipitation from solution at pH 3.5 (*1*). When these samples were dissolved in citrate-phosphate buffer solution of pH 6.35 and 0.02 ionic strength and passed through a column

TABLE 1

ENTEROTOXIN ADSORPTION ON HYFLO SUPER CEL

Expt No.	Treatment of crude enterotoxin	Equivalent amount fed* (ml)	Mg fed	Mg N fed	Monkey feeding results† (No. positive/No. fed)
1	$(NH_4)_2SO_4$ precipitation	200	7.4	0.670	5/30
1a	$(NH_4)_2SO_4$ precipitation,	200	0.172	0.009	0/6
	adsorption on Hyflo Super Cel	1000	0.860	0.045	5/6
2	Dried	40	416.8	37.7	1/6
		200	2084.0	188.4	4/6
2a	pH 3.5 precipitation,	200	0.260	0.020	2/6
	adsorption on Hyflo Super Cel	400	0.520	0.040	6/6

* Volume of crude toxin solution used to obtain the amount of material fed.

† Assay for the presence of enterotoxin was made by feeding the samples in solution to young rhesus monkeys by stomach tube. Vomiting within 5 hr was accepted as a positive reaction for enterotoxin.