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Amorphous Coatings on Mineral Surfaces

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R. C. JONES AND G. UEHARA[2]

ABSTRACT

Amorphous coatings on mineral surfaces too thin to be resolved by most electron microscopes were detected bridging particles suspended over holes in the supporting substrates. The coatings are gel-like in appearance, may flow when wet, shrink and become porous when heated, cement primary particles into large masses, and exhibit a coat-of-paint effect with curved solid-air interfaces. Amorphous gel coatings were found in alumino-silicate systems, in high aluminum soils, and on quartz surfaces.

Additional Index Words: gel-hulls, alumino-silicate system, aluminum system, silica system, electron microscopy, holey substrates.

WHILE THE ROLE played by amorphous materials in influencing soil behavior remains speculative, enough has been learned in the past few years to warrant reexamination of the topic. This paper presents new information which shows how amorphous materials are distributed in the clay fraction of soils. The evidence is illustrated through a series of high resolution electron micrographs.

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METHOD

The electron microscope used for this study was a Hitachi HU-11A, operated at 100 kV with an emission current of less than 20 μA. Two anticontamination devices filled with liquid nitrogen were used at all times. Specimens were never exposed to the electron beam for more than 1 min. As soon as an area of interest was recorded on film, a new grid window was selected for the next exposure, thus preventing accumulation of contaminants of more than 10 Å on any one window of the grid.

A small quantity of soil was placed in a beaker containing distilled water and subjected to mild sonication with a Biosonik probe for 30 sec at a power of 300 W (20 kHz). No chemical dispersant was used to avoid formation of chemical artifacts. This suspension was washed through a 325-mesh screen. The concentration of the suspension was adjusted by visual inspection to provide adequate quantities of solids for sufficient coverage of the substrate. The suspension was sprayed onto the grid with a nebulizer. No attempt was made to separate clay from silt.

The carbon substrates were prepared in the following manner: A 7:1 mixture by volume of 2% formvar in ethylene dichloride solution to water was prepared. The mixture was emulsified with a probe-type sonicator. Immediately after sonication, one drop of the emulsion was placed on a clean water surface to form a film of Formvar containing numerous entrapped water droplets. A 400-mesh grid was inserted below the water surface and gently raised through the film. The grid, now coated with this film, was soaked twice for 30 sec in acetone to dissolve the thin Formvar film surrounding each water droplet. This operation produced a holey film. A carbon substrate was deposited on this film and the underlying Formvar film was dissolved with ethylene dichloride. The end result was a holey carbon substrate. (The method of preparing the holey carbon substrate was perfected by Georgianna Honea, a Junior Science Apprentice participating in a 10-week Student Scientist Training Program at the Univ. of Hawaii supported by the National Science Foundation.)

This type of substrate enabled us to observe amorphous materials stretched over the holes.

RESULTS

Figures 1*A*, *B*, and *C* illustrate the advantage of using holey substrates. Figure 1*A* shows a conventional electron micrograph of clay particles (kaolin) from an Aridisol. The same sample when viewed over a hole (Fig. 1*B*) shows a gel-like material bridging the particles. The light, fine-grained areas in Fig. 1*B* are free of substrate (the hole). Figure 1*C* shows clay-sized particles suspended over a hole and supported by a thin gel-like film which stretches from the particles to the substrate.

Some soils developed from volcanic ash (Andepts) contain a very high percentage of noncrystalline materials. Figures 2*A* and 2*B* are electron micrographs of a Hydrandept (Akaka series) and a Eutrandept (Waimea series), respectively. Figure 2*A* shows gel-like material covering or partially covering holes in the substrate. A high magnification micrograph of a gel-like material from the Eutrandept, stretched over a hole is shown in Fig. 2*B*.

Figure 3 is an electron micrograph of the clay fraction of a Gibbsihumox (Halii series). The individual crystals of gibbsite and geothite range in size between 50 and 200 Å in diameter. In most instances, these particles occur in clusters which are encased in gel-like masses. The light outlines which are Fresnel fringes (arrow A) surrounding many of the particles were caused by dehydration of the gel. This effect is typical of highly hydrated gel coatings. Where there has been no separation of the gel from the particles, the light outlines are absent, for example at arrow B, Fig. 3. In some cases, the gels become porous and resemble sponge-like masses as a result of exposure to the vacuum and beam heat of the electron microscope. The Halii soil is highly aggregated and possesses excellent physical properties in the field.

To illustrate that gel-like coatings are not solely confined to soil materials, a single quartz crystal (from Hot Springs, Ark., Wards Natural Science Establishment) was finely ground in a tungsten carbide ball mill. The coarse fraction was removed by settling in distilled water.

Freshly crushed quartz particles revealed little in the way of gel coatings except for their tendency to aggregate. However, standing in water for long periods produced the gel coatings shown in Fig. 4*A* and *B*. Figure 4*A* shows a micrograph of clay size quartz particles which stood in water for 3 months. Note that the particles appear agglutinated and some enveloped in a gel. Some gel-like material can be seen smeared onto the substrate. After standing in water for 6 months, the gel coated quartz particles have coalesced to form a coat-of-paint effect (Fig. 4*B*).

DISCUSSION

Approximately 50 soil samples and geologic materials have been examined by high resolution electron microscopy. About half of them contained some gel-like material. In some Andepts, the major portion of the soil consisted of noncrystalline material. In other soils, which consisted predominantly of crystalline minerals, the gel-like materials occurred as coatings on the crystalline particles and not as discrete amorphous bodies.

As early as 1952, the existance of a surface coating on freshly ground quartz was surmised by a number of workers who studied the silicosis problem in the British coal mining industry. The first of a series of papers dealt with a "high-solubility layer" on siliceous dusts. Clelland, Cumming, and Ritchie (1952) reported chemical evidence for a "high-solubility layer" on the surfaces of dust particles from "rock crystal," silica sand, fused amorphous silica, olivine, and orthoclase feldspar. Clelland and Ritchie (1952) and Dempster and Ritchie (1952) asserted that the "high-solubility layer" was not a hydrated silica but rather a vitreous layer of the Beilby type (to be described later) that developed as a result of mechanical crushing and grinding. Estimates of the mean thickness of the "high-solubility layer" vary from 0.03 to 0.15μ (Gibb, Ritchie, and Sharp, 1953; Dempster and Ritchie, 1952; Nagelschmidt, Gordon, and Griffin, 1952). Gordon and Harris (1955) concluded that the amorphous layer on quartz was not of a definite thickness but consisted of a gradual transition from a non-crystalline exterior to a crystalline core. This conclusion was based on X-ray diffraction analysis which showed that particles smaller than 0.5μ seemed to display an X-ray amorphous character with virtually no crystalline core. Recently, Rieck and Koopmans (1964) used peak intensities of Debye-Scherrer lines of finely-ground quartz to conclude that the thickness of a

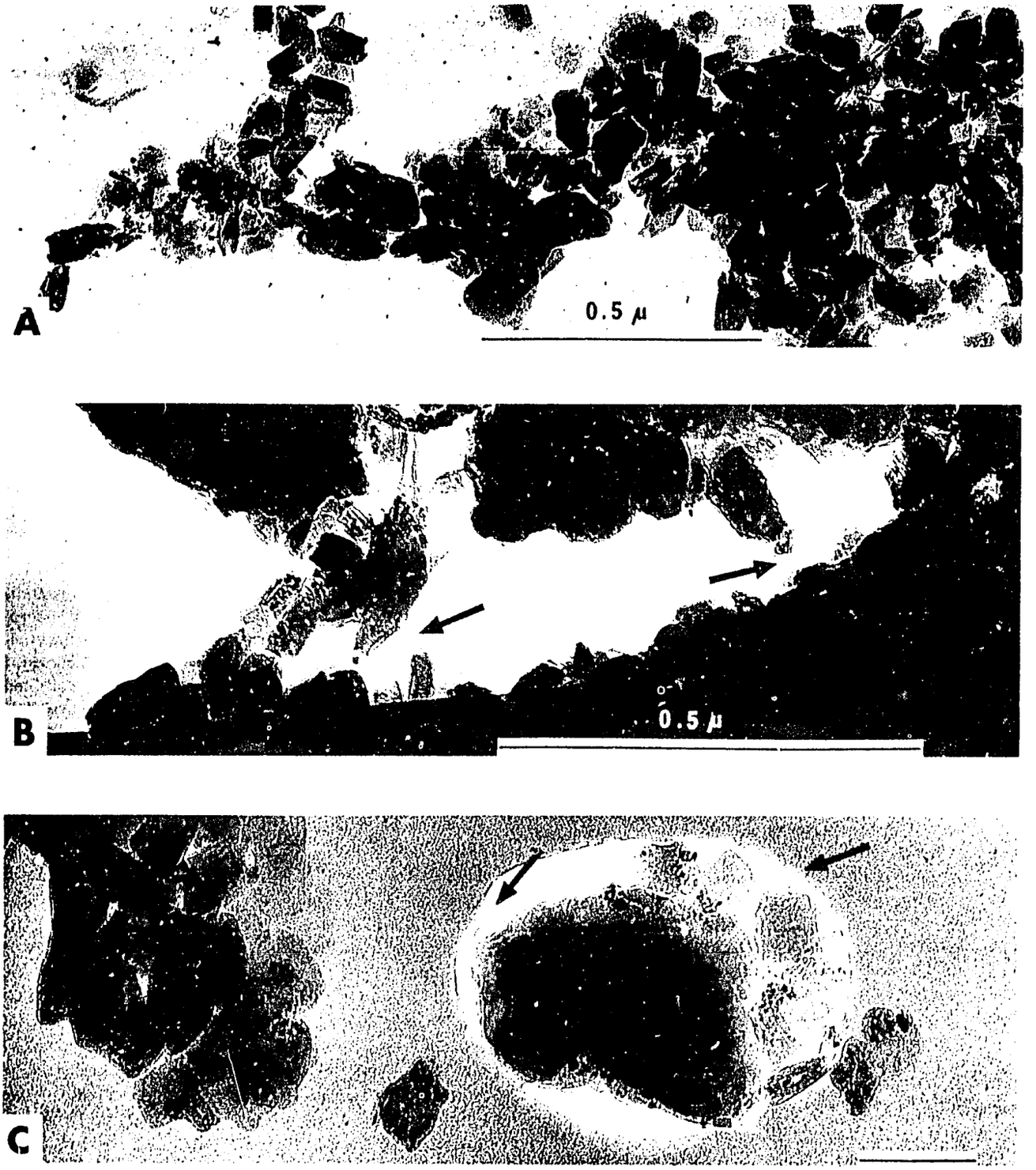

Fig. 1—Transmission electron micrographs of Kaolin particles from a Hawaiian Aridisol: *A*. Particles mounted on conventional carbon substrate. Prepared in this manner, this specimen fails to show gel-hulls; *B*. Same material as in Fig. 1*A*, mounted on holey substrate. Light, fine-grained area represents the hole. All materials in upper portion of this figure are suspended over the hole. Gel coattings (arrows) hold particles in place; and *C*. Even at higher magnification (210,000X), the gel coatings, clearly visible along perimeter of hole (arrows), is not discernible on substrate surrounding the hole.

"disturbed layer" was at least 0.4μ. The existence of such a layer on quartz is confirmed by Fig. 4*A* and 4*B*.

X-ray diffraction techniques were extended to the study of kaolinite by Engelhardt (1955) who estimated the thickness of the amorphous coatings to be 1 to 10 A. Van der Marel (1966) stated that amorphous coatings on clay minerals may be formed by hydrolysis as a result of weathering and not necessarily as a result of grinding as had been

Fig. 2—Gelatinous material from Andepts stretched over holes in the substrate: *A*. Thin, gelatinous material from a Hydrandept covering holes in carbon substrate. The appearance of the material in the upper left hole suggests that in going from a wet, gel-like state to a dry elastic state, the membrane ruptured; and *B*. Noncrystalline material from a Eutrandept stretched over a hole. Soil materials from Hydrandepts (Fig. 2*A*) dry irreversibly, whereas material from Eutrandepts do not.

previously asserted in the literature. However, he referred to all surface coatings as Beilby layers regardless of their origin or composition. We prefer to call the naturally occurring surface coatings gel-hulls and to use the term Beilby layer for features associated with polished surfaces.

Beilby (1921, p. 129) studied polished metal surfaces by means of a microscope and noticed that these surfaces had a glossy film that seemed to flow into minute scratches and obscure all signs of metal's structure. French (1933) repeated Beilby's work and confirmed that there was indeed the appearance of a "super-cooled liquid" layer on the surface of highly polished metal which he called the Beilby layer. In "A Dictionary of Mining, Mineral, and Related Terms" (Thrush, 1968), the Beilby layer is defined

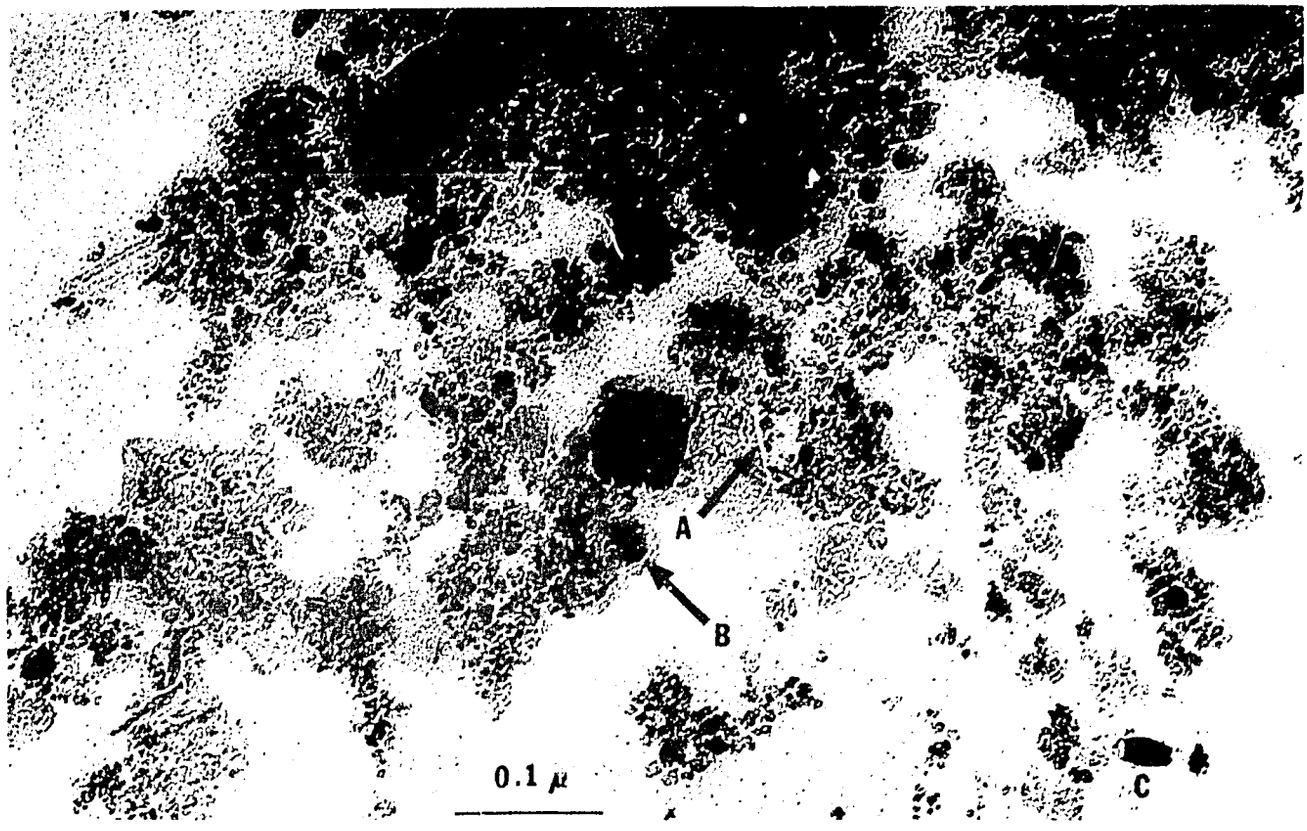

Fig. 3—The fine fraction of a Gibbsihumox mounted on a standard carbon substrate. Most of the black appearing particles contain a high percentage of iron. The lighter particles are mostly gibbsite and the barrel-shaped particle at C (lower right) is anatase. Since the particles absorb more heat from the electron beam than the gel or the substrate, gel dehydration and shrinkage occurs most frequently at the particle-gel-hull interface. Shrinking and cracking are typical when highly hydrated gels are dehydrated.

as, a "Flow layer resulting from incipient fusion during polishing mineral surfaces, and therefore, not characteristic of true lattice structure" and "The mirror-like surface layer, on all well-polished stones. . ." There is no mention of Beilby layers resulting from a chemical reaction.

There are several reasons why particle surface coatings have not previously been observed and measured on electron micrographs. The first and most likely reason was the limited capabilities of earlier electron microscopes. The absence of clear-cut evidence in support of surface coatings can be attributed to the low resolving power of electron microscopes available commercially as late as 10 years ago. Owing to the relatively high costs, most research organizations have been reluctant to replace these earlier prototypes with improved models which now permit routine resolution of 10 Å, and in more sophisticated instruments, 3Å or better. For example, Fieldes and Williamson (1955) suggested that positively charged noncrystalline aluminosilicate might exist as surface coatings. They, however, postulated that these coatings would exist as ultrafine particles beyond the resolving power of their electron microscope. An electron micrograph of finely particulate allophane occurring as a coating on an illite crystal has been published by Mitchell, Farmer, and McHardy (1964). Here again, because of limited resolution, the actual nature of the coating was not discernible.

Another and less obvious reason for difficulties with direct observation of surface coatings is the problem of specimen contamination and damage due to the electron beam. Particle growth in the electron microscope was observed by Cosslett (1947) to occur on zinc-oxide particles. Watson (1947) observed that carbon black particles grew in size with exposure to the electron beam and attributed the phenomenon to the accumulation of carbonaceous material from organic vapors in the microscope column. However, Cosslett (1947) disagreed with Watson (1947) and explained the particle growth as an "ejection" of adsorbed material and perhaps the metal itself (in the case of metallic oxides) and from the carbon black (in the case of Watson's observations). Burton, Sennett, and Ellis (1947) bombarded various salt samples with an intense electron beam and noted that the specimens became more electron transparent while "fine opaque particles" were being deposited around the specimen. They suggested that the interaction of the electron beam with the specimen induced ion migration. Evidence presented by Ennos (1953 and 1954) supported the carbon accumulation theory proposed by Watson (1947). Drawing on Ennos' findings, Noake, Hiroto, and Mizushima (1956) noted that intense electron irradiation for periods of 40 to 75 min on MgO smoke crystals produced an "interlayer" between the particle and the contaminant. They found that by dissolving away the specimen the interlayers were vacant. Although Noake et al. (1956) had no ready expla-

nation for the gaps, they advanced the idea that there may be an electron beam reaction with the crystal as well as a buildup of contamination. Chute and Armitage (1968) also found this to be true for clay minerals. They showed that besides carbon buildup which grows linearly with time, there is an additional deposit which grows with the square root of time and apparently at the expense of the clay mineral. Since this type of rim growth was found to be particularly true in the case of kaolinite, Chute and Armitage postulated that hydroxyls diffused from the edges of the crystal and reacted with hydrocarbon vapors.

The materials shown in the electron micrographs presented in this paper reflect a minimum of electron beam damage and contamination. We can be sure of this on two counts. First, the emission current was held low and fine apertures were used in the condenser system so that the specimen current was never higher than absolutely necessary for focusing. A 100 kV beam potential was used for good penetration and minimum specimen heating. A large number of exposures were rapidly made and our interpretations of results is based on examination of micrographs rather than on observation of specimen in the microscope.

Secondly, the most convincing evidence for the authenticity of gel-hulls can be found in the micrographs themselves. In Fig. 2*A* and *B*, the noncrystalline material is stretched across holes in the substrate. This material must have been present on the grid prior to exposure to the electron beam. In Fig. 1*B*, particles of halloysite are suspended over holes in the substrate by gel-coatings. Here again the gel-coatings must have been present before the specimen was exposed to the electron beam. Soil particles possessing very thin gel-hulls fall through the holes in the substrate thus leaving the holes clear of particles.

Finally in Fig. 5, soil iron oxide particles cast shadows which originate some distance from the particle indicating the presence of a low density material. Close inspections of the interface between particle and shadow reveals the electron transparent material. Since the sample was shadowgraphed before placement in the electron microscope, we can conclude that this coating cannot be an electron beam contaminant (For the technique of shadowgraphing see Chapter 47, Electron Microscopic Techniques by J. A. Kittrick in C. A. Black (ed.) Methods of Soil Analysis Agronomy 9, Part 1, 1965.)

The occurrence of amorphous gel-like material as coatings on crystalline particles is particularly important. One can speculate that the chemical and physical behavior of porous bodies will depend heavily on amorphous materials if the amorphous fraction occurred as coatings on crystalline particles. The capacity of amorphous coating to act as viscous bodies when moist and elastic bodies when dry can have a pronounced effect on the porous body as a whole. Some amorphous materials, as in the case of the gel-like substance in Fig. 2*A*, irreversibly lose their viscous property upon drying. They are the high oxide systems. On the other hand, the high silicon system (Fig. 4*A* and 4*B*) appears to be able to alter reversible between the viscous and elastic states. These features may have strong implication in irreversible crusting of laterites, reversible crusting in irrigated soils of the arid regions and soil aggregation in general.

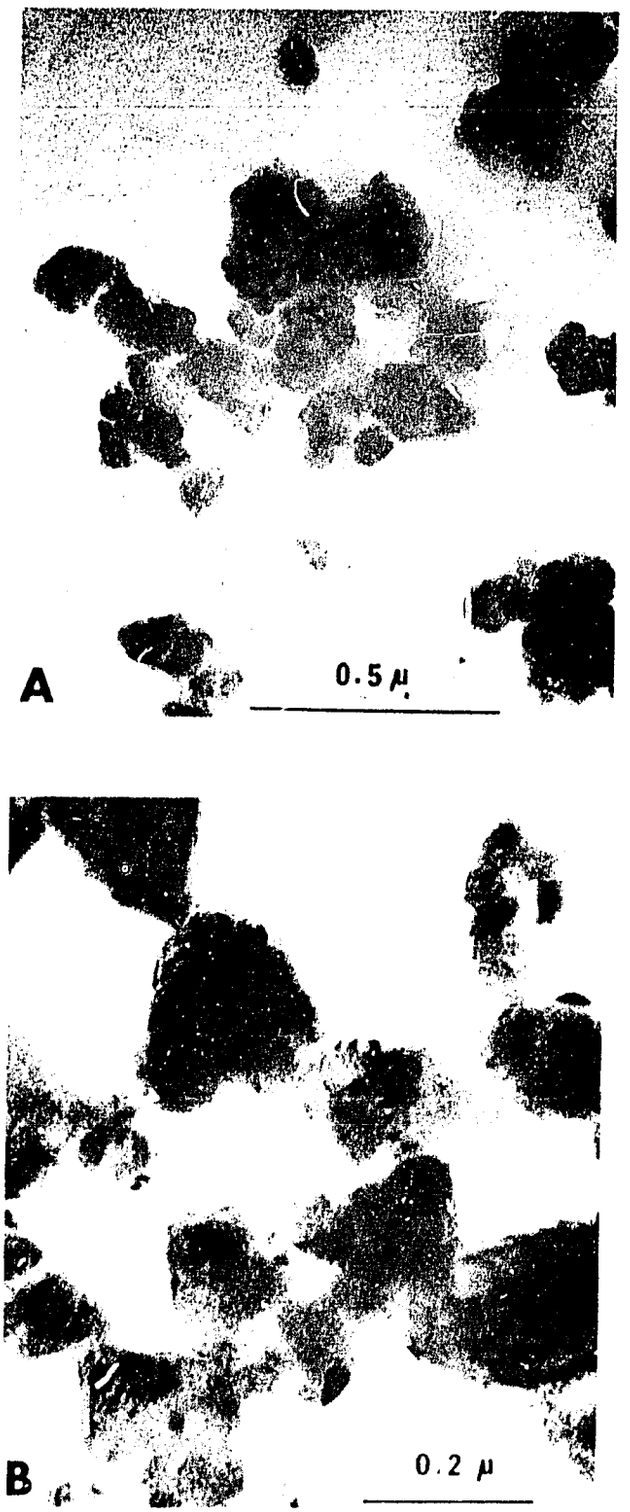

Fig. 4—Silica gel on the surfaces of finely-ground quartz. Freshly-ground quartz appeared relatively free of gel coating. After standing in water for 3 months in the dark, the quartz particles became encased in a gel which can be seen smeared over the particles and substrate (*A*). After standing for 6 months gel hulls coalesce to form a "coat of paint" effect (*B*).

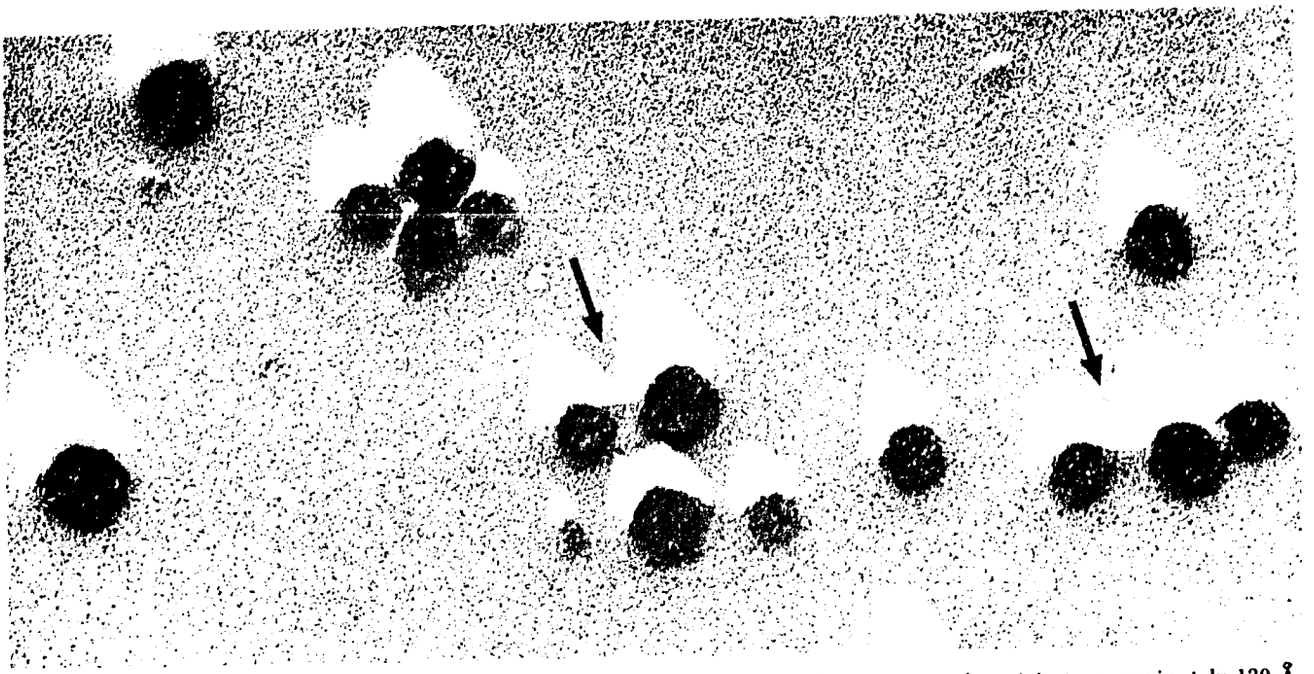

Fig. 5—Soil iron oxide particles shadowgraphed with platinum. The shadows cast from the particles originate approximately 130 Å from the surfaces of the particles, indicating the presence of an electron transparent coating. Particles slightly separated from one another cast shadows which over-lap because their gel coatings are in contact (arrows).

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