

## Soil Gels by Atomic Force Microscopy

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Experimental studies of certain chemical and physical properties of soils and their alteration induced by addition of water to dry soils, as well as scanning electron microscopy, transmission electron microscopy, and small-angle neutron scattering studies, showed that soil colloidal particles are encapsulated in an organic gel matrix at certain distances from one another [1–3]. It was concluded that organomineral gels that coat soil particles consist of the soil humus in a gel state reinforced with organic and inorganic colloidal particles.

Recently, atomic force microscopy (AFM) has come into use in soil science [4–9]. This method has helped to refine the particle sizes existing in soil solutions [4], to estimate the structures generated by particle interactions [5], and to understand the behavior of fulvic and humic acids on mineral surfaces [6–8].

This work was undertaken to assess the utility of AFM for studying soil gel structures and to check the validity of suggested soil gel structures.

Soil samples for this study were taken from high-humus horizons of leached Kuban chernozem, a gray forest soil from Vladimir oblast, and a soddy-podzolic soil from the vicinity of the Yakhroma river floodplain. The properties of these soils determined by routine procedures are found in [3].

Test samples were prepared as follows. Air-dry soil particles 0.1–0.2 mm in sizes were transferred into Petri dishes and capillary moistened; then, the water mirror in Petri dishes was raised. As a result, gel films were separated from soil particles and became buoyant. Next, gel films were transferred onto the atomically smooth surface of a fresh mica cleave as follows: the mica surface was brought in contact with the water surface on which the film floated and was then dried at 40°C [10].

The topography of gel films dried on mica was studied using an NT-MDT N'Tegra Aura atomic force microscope in contact and semicontact modes with NSC 21 and NSC 15 Mikromasch cantilevers, respectively.

For electron microscopic studies, carbon was sputtered onto dried samples in a Leybold Univex 300 thermal evaporator. A Carl Zeiss LEO SUPRA 50 VP scanning electron microscope was used.

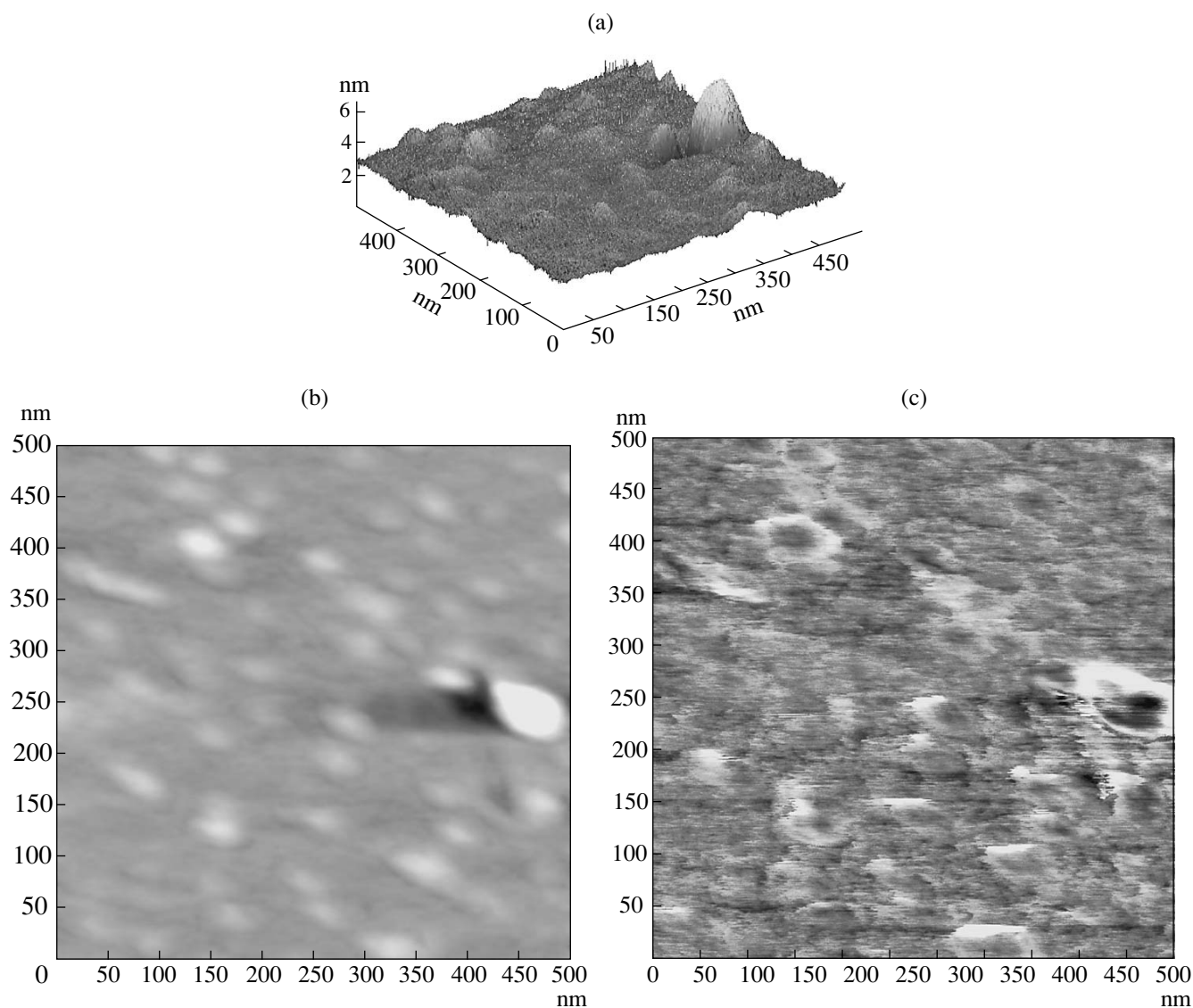
Polymers, biomolecules, and other soft samples are frequently damaged when studied in the contact mode. Our preliminary experiments on gel films isolated from chernozem showed that, in most cases, the interaction of the probe with the soil gel surface leads to unstable scanning and surface damage, which is misleading. In addition, data obtained in the contact mode frequently fail to disclose all topographic features that are observable in the semicontact mode, most likely because of the existence of inhomogeneous adsorbate layers on gel surfaces. Therefore, we used the semicontact mode and simultaneously recorded the topography and phase image. The working vibration amplitude of the cantilever was 10–50% of the free amplitude.

We should mention the fundamental limitations of scanning electron microscopy in topographic studies of organomineral gels. An increase in the accelerating voltage above 5 kV for improving resolution and amplifying SE2 electron signals is offset by an increase in the effective analysis depth and the loss of topographic contrast. A decrease in the accelerating voltage enhances topographic contrast, but the resolution of mineral particles encapsulated in the organic matrix is lost. With a 5-kV accelerating voltage and an InLens electron detector, for example, the resolution of organomineral gel particles is not better than 10 nm. Thus, under 100 000 magnifications, particles encapsulated in gels are observable, but their boundaries are sufficiently blurred. Particle sizes of 40–50 nm are resolved when they are separated by at least 10 nm, but they cannot be distinguished when they are in contact in the gel layer.

Atomic force microscopic data obtained on chernozem in the semicontact mode (Fig. 1) show that this method gives surface topography images for humus

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**Fig. 1.** AFM images of surface topography for a gel film separated from chernozem to mica: (a) 3D image of surface topography obtained in the semicontact mode, (b) surface topography obtained in the semicontact mode, and (c) surface image obtained by phase imaging.

gels with nanometer resolution. It is clear that particles with sizes of 20–100 nm reinforce the chernozem humus gel; the height difference on topographic surface images changes as little as by several nanometers (Fig. 1a). Similar trends regarding the sizes and heights of minerals encapsulated in the humus gel are observed for all test soil samples. This unambiguously signifies that the humus gel is mainly reinforced by lamellar nanoparticles, apparently clay minerals, which are oriented parallel to the gel film surfaces and generate oriented structures.

Comparing AFM images for chernozem, gray forest, and soddy-podzolic soils, we see noticeable morphological distinctions between the soil gel structures on  $500 \times 500$  scales. For the soddy-podzolic soil, there

are many resolved small peaks with heights of 1–1.5 nm. Particle sizes encapsulated in the film are 100–150 nm. In the gray forest soil, small peaks are connected to one another; therefore, a smoother surface topography is observed. Particle sizes in the gel film are on the order of 50 nm. In chernozem, small peaks have subnanometer sizes. This is well seen in areas  $100 \times 100$  nm in size. Particles in the film have sizes of 5–40 nm.

Estimates of the particle sizes in gel films confirm the familiar postulate of soil science that the fraction of fine particles increases in the zonal series from soddy-podzolic soils to chernozems. This trend was established for micron-sized particles; however, it also holds for nanoparticles.

We may suggest that fine peaks arise from the organic matrix. The existence of a great number of resolved peaks in the gel films separated from the soddy-podzolic soil is likely indicative of a weaker connectivity of humus gel blocks and their higher potential mobility. Humus gels in gray forest and, especially, chernozem soils are stabilized by an increasing percentage of humus. These results and their interpretation completely correlate with the properties of the test soils known from soil science.

The high image contrast obtained in a semicontact mode at a fixed amplitude (Fig. 1b) is noteworthy compared to the image built on the basis of phase shift (Fig. 1c). In this case, the boundaries between particles in the films from chernozem (as in the other test samples) are blurred and, in some cases, even undistinguishable. In view of the higher sensitivity of phase imaging to force interactions with the surface, we can assume that the gel film and particles encapsulated in it are coated with a humus gel layer of lower density. As a result, the images obtained by the more sensitive phase imaging show the structure of the upper humus gel layer, whereas the topographic images show the structural features of the lower (denser) layer in which mineral particles are contained.

For a polymer gel, this suggestion is sufficiently substantiated: for an ideal coil, the average unit density [11] decreases from the center to periphery in an inverse proportion to the square root of the number of units in a linear chain. In an ideal solvent or good solvents, the increase in density from zero to one-half maximum calculated for polymers with degrees of polymerization of about 1000 is observed for distances on the order of 10 nm. In concentrated polymer solutions (with  $c > 1\%$ ) and melts, there is mutual penetration of macromolecular segments into coils, and a decrease in segment density must occur only at the fringes of polymeric entities.

Our study substantiates the representation of soil gels as humus gels reinforced with nanoparticles. This

study also proves that AFM is a promising tool for investigating soil gels and gaining more data on their structural organization.

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