

Binding of Organic Matter into an Oxidation-Resistant Form during the Interaction of Clay Minerals with Plant Residues

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Abstract—The binding of organic matter by clay minerals was studied in experiments simulating the transformation of clay rock with a high content of dioctahedral 2 : 1 phases in the soil during its interaction with decomposing plant residues. Using modern methods (X-ray phase analysis, thermal analysis and Fourier-transform IR spectroscopy, and adsorption–luminescence analysis), it was shown that the binding of organic matter into a form resistant to treatment with 30% H₂O₂ entailed changes in the actual structure of the clay aggregates. Peculiar organic–silicate compositions with their structure disordered along the *c** axis were formed, in which organic matter was localized both on the surface of the particles and in the interlayer spaces.

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INTRODUCTION

Soils form one of the major reservoirs of organic carbon in the biosphere. Because of changes in the planet's climate and the increasing CO₂ emission, the capacity of soils to accumulate organic matter in forms kinetically resistant to biological decomposition began to be considered as a promising basis for the development of technologies capable of decreasing the concentration of CO₂ in the atmosphere [26, 31]. In physicochemical terms, the interactions between the organic matter and the highly heterogeneous layered 2 : 1 aluminosilicates are of key importance for the kinetic stabilization of the organic matter in forest-steppe soils [9]. A special role is assigned to the interactions of the organic matter with different products of the negative transformation of structurally disordered micas in the form of interstratified illite–smectite or (and) illite–dioctahedral vermiculite phases. In the systems of this level of complexity, the interactions between the organic matter and finely dispersed minerals cannot be explained by the simple sum of the surface adsorption or adhesion reactions not affecting the internal structure of the reagents. Therefore, the mechanisms of the organic–mineral interactions in the soils are still insufficiently understood, and this is especially true for the formation of the organic carbon pool defined in some turnover models as inert organic matter resistant to biological attack [16, 22].

No universal methods have been developed for the preparative separation of this organic matter pool from the less stable fractions of organic components. Promising chemical procedures include the treatment of

soils with oxidants [27], e.g., H₂O₂ [15]. Some authors [32, 35] think that this treatment removes organic components from the surface of the clay minerals without affecting the interlayer space. The treatment with H₂O₂ can be considered as the simulation of the biochemical destruction of organic matter, which is also an oxidation process. It was shown, e.g., that phenanthrene bound in the interlayer space of artificial organic–montmorillonite complexes (composites) becomes inaccessible for bacteria using free phenanthrene as a carbon and energy source [37]. Experimental evidence has been recently obtained concerning the important role of poorly crystallized and amorphous Fe and Al oxides and hydroxides in the protection of organic matter from chemical oxidation [15, 23, 28].

The fulfillment of an adequate set of sorption experiments is a common approach to determine the mechanism of the binding of organic matter by mineral surfaces and the effect of the possible variable factors. A large number of works on the sorption of different organic compounds by dispersed minerals deal with the formation of stable clay–organic structures. However, the results of most experiments cannot be extended to soils, because the interaction of the organic and mineral substances in nature always involves living organisms performing bio-abiotic interactions (Vernadsky), including the decomposition of crystal phases with extremely low solubility. The biogenic destruction of minerals strongly differs from the abiogenic one in the rate, mechanisms, and final and intermediate products [5].