

Application of various methodological approaches for assessment of soil micromorphology due to VESTA program applicable to prediction of the soil structures formation

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This work introduces concepts of methodological approach (theoretical investigation) in terms of soil structure analysis. The aim of this work is using VESTA program application as appropriate alternative to quantification of micromorphological analysis as complementary method. This evaluation mainly with regard to effects for soils structure at the interactions/predictions with many aspects of aggregate destruction-stability-reactivity in soil system. This work elucidates different kind of methodological approaches such as implementation 2D micromorphological model, X-ray analysis and their extrapolation in VESTA program. There is some evidence that construct data and parameters gained from this program are suitable for other pedological features and their more detailed survey and interpretations. For these points is possible to assign of reaction kinetic, established minerals phase and genetic relationships in soil system, detect of potential transformation, mobilization and immobilization activity, distribution of elements species even by general and specific properties of aggregate forms. Detailed characterization (modeled design) of rocks and minerals inorganic particles of soil aggregate forms on the atomic level has significant importance due to detailed data examinations input. In the case of operation module could eliminate of influence various undetected (non-identify) factors and in additionally refine on standardize appropriate fitted the more realistic model.

Keywords: methodological approach, micromorphology, X-ray analysis, VESTA design

1 General overview on the micromorphological analysis

The natural systems consist with mutual interactions at the different hierarchical levels which continuously take place (Gadd, 2007). In aerobic and anaerobic sub-systems reactions between litho-, atmo-, hydro-, and antroposphere generate agronomical important sphere – pedosphere (Juma, 1999). Influence of every natural entity (bio-, chemo-, physic-) from the sub-system should play a key role to form organic matters even by led to bio-geochemical processes such as weathering. Mutual relationship accelerated the mechanical, chemical and biological destruction of primary rocks, minerals and support formation of secondary soil minerals (Čurlík and Kolesár, 2014; Kolenčík et al., 2011). Generally, soil contains from 95 to 99% of inorganic compounds (particles) and from 1 to 5% of organic matters (Juma, 1999; Lal and Shukla, 2004). Soil system poses characteristic ubiquitous interactions and for this reason is obvious to quantify their material composition from atomic background through micro-, and macro- aggregate forms up to extrapolation larger

geomorphological complexes – landscape systems. On the other side, the microscopic observations could underline the basic and specific chemical and physical properties. One of the most fundamental features of soils is the soil structure (Roger-Estrada et al., 2010).

Soil structure refers to the size, shape and arrangement of solids and voids, continuity of pores and voids, their capacity to retain and transmit fluids and organic and inorganic substances, and ability to support root growth and development. Soil structure is an important aspect of agricultural soil quality and soil ecology (Kay, 1998; Šimanský, 2012). Soil structure is dynamic complex which is not very well understood despite numerous advances in clay mineralogy, colloidal chemistry and other scientific area which have since led to better understanding of genesis, characterization, and management of soil structure (Carter and Stewart, 1996). Formation of aggregates in soils is one of the most important problems of soil science. Formation of soil aggregates as basic unit of pedal soil structure is a function of physical forming forces (such as: inter and intramolecular forces, electrostatic, and gravitational

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forces) between soil particles (Grosbellet et al., 2011; Li and Fan, 2014; Hu et al., 2015) however, its stabilization is influenced by internal and external factors, and their interactions (Chenu and Cosentino, 2011; Paradelo et al., 2013; Šimanský et al., 2013; Jozefaciuk and Czachor, 2014; Šimanský and Bajčan, 2014). There are several mechanisms of aggregation. Aggregates are formed in stages, with different bonding mechanisms dominating at each stage (Tisdall and Oades, 1982). Hierarchical theory of aggregation proposes that microaggregates join together to form macroaggregates and the bonds within microaggregates are stronger than the bonds between microaggregates (Edwards and Bremner, 1967). Microaggregates are formed from organic molecules (OM) attached to clay (Cl) and polyvalent cations (P) to form compound particles (Cl-P-OM), which are joined with other particles (Cl-P-OM) to form macroaggregates $[(Cl-P-OM)_x]_y$. In addition, the concentric theory of aggregation suggests that external layers are concentrically built upon the external surface of the aggregate, with younger carbon in outer layers of aggregates than in aggregate interiors (Santos et al., 1997). The precipitation of hydroxides, oxides, phosphates and carbonates enhances aggregation. Cations such as Si^{4+} , Fe^{3+} , Al^{3+} and Ca^{2+} stimulate the precipitation of compounds that act as bonding agents for primary particles. Cations also form bridges between clay and soil organic matter particles resulting in aggregation. If we can define and quantify these impacts, so we can predict changes in soil structure. One of the most effective tools for assessment of soil structure may be its modeling, which is based on relevant data, which have been described between the phases of soil environment. Basic attribute of model formation is defined elementary relations and interactions as individual mineral phases, and their chemical attractions. Nature of chemico-physical bonds is accordingly examined on the inter-atomic, inter-layer, coordinated, and polyhedral background. Interestingly, the progressive evaluation with long-term effect has had detailed study with phases interface, liner and the vector space coordination which settled mineral reaction stability, their subsistent facets, and overall bond-structural integrity. The possibility of using several methodological approaches for example as: microscopic study or X-ray diffraction analysis could be very useful because they can substantially streamline modeling and predicting of the structural state in soils differing in their genesis and texture under different soil management. During a short time, created a model after substituting variables should know to provide relevant information on the structural state of the soil, which is essential not only from the view point of agronomy (forestry, construction, industry, and etc.).

Due to this reason our work was concentrated on the detailed survey of micromorphological analysis from various methodological points of view. In order to complete concept of theoretical investigation the 2D cross section of soil, modeled X-ray analysis with extrapolated visualization to make 3D design structure and morphology particles in modeled VESTA program was evaluated. Firstly, this work (theoretical concept investigation) introduces as basic background for further study of soil aggregate formation in different soil types. The next section was evaluated the methodological approach examinations, which are mainly attributes for prediction behavior of individual mineralogical phases. In this context it concludes examined structure-spatial relationship and interactions localized in aggregates.

2 Methods for mutual relationship assessment of inorganic particles in soil system

2.1 Microstructure analysis in polarization microscopy

Microscopic observation carried out in polarization microscope belongs to basic soil analysis. The 2D cross section soil sample (micromorphological analysis) determines different aspect of interactions and relationships. These details involve particle size distributions, aggregate forms, particles morphology (isomorphic, anhedral, allotriomorphic grains, dominant crystal planes vs. destruction structures, and etc.), homogeneity-heterogeneity of grains, their genetic associations with surrounding grains distribution, for instance, in sand samples it usually examined zircon-rutile-tourmaline index (also called ZRT index).

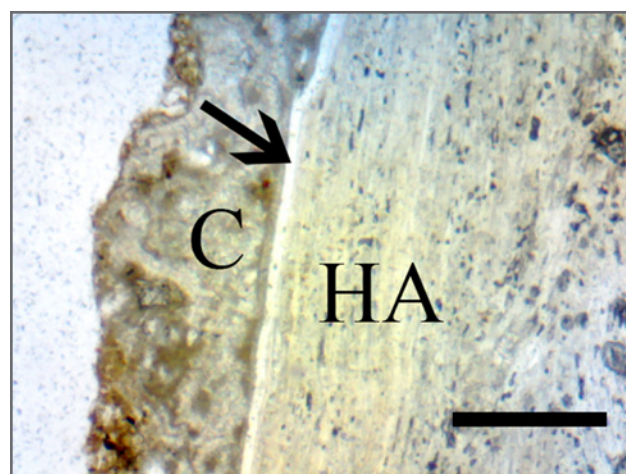


Figure 1 Examples of 2D micromorphology of soil cross section are shown mineralogical association of stable phases of hydroxyapatite (HA), and calcite (C). The reaction rim (C) contains insignificant content of quartz, Fe-hydroxides and clay minerals. Visualized arrow has pointed interface between two dominant phases, inserted line have 0.2 mm, and visualization was performed in unpolarized light

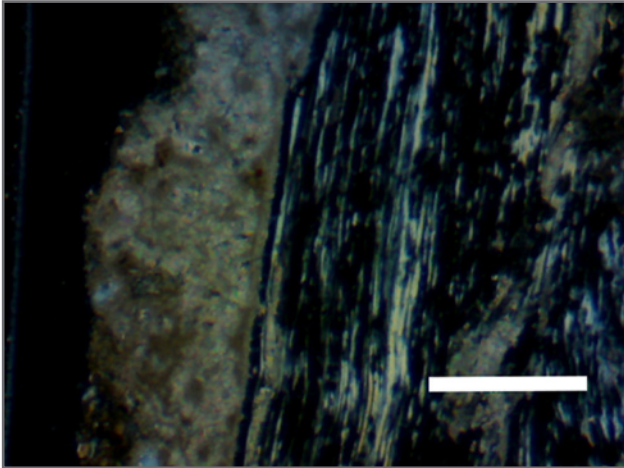


Figure 2 The same sample visualized from figure 1 using by polarized light regime where we could detect hydroxyapatite (HA) with relicts biogenic origin with re-crystalized lamellar bone fibers and relative homogenous calcite (C) as dominant reaction rim

From the texture characteristic, it elucidated primary and secondary minerals development, linear grain organizations, homogeneity vs. polygenetical intergrain materials – matrix, weathering haloclasty and their dispersion intimal interlinked with individual grain and further genetic features (Čurlík and Kolesár, 2014; Čurlík, 2011). Micromorphological cross section analysis of soil is shown in figure 1. and the most dominant minerals was detected hydroxyapatite (HA) ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and calcite (C) (CaCO_3). HA presents re-crystallization form with

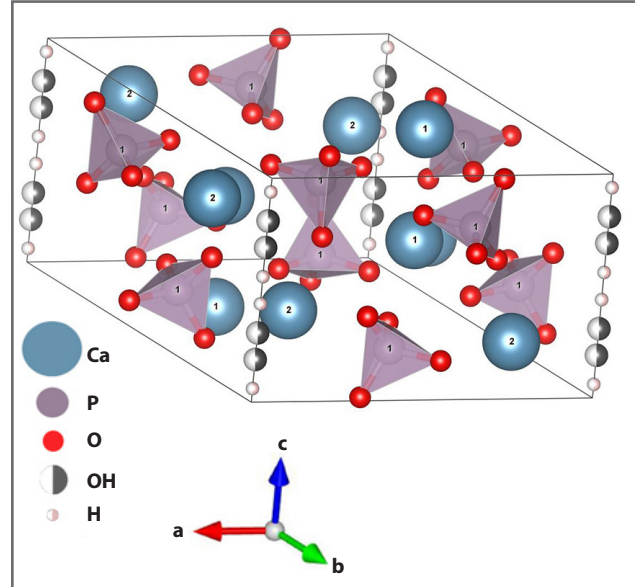


Figure 4 Fabrication of structure model of hydroxyapatite (HA) in VESTA program, visualization is carried out in polyhedral regime according to methodology Momma and Izumi (2014). Direction of a -, b -, c - axis determine spatial configuration of apatite structure. For designed this model was applied X-ray diffraction analysis which come from Wilson et al. 1999e

parent biogenic material (lamellar bone fibers) (Figure 2). The reaction rim contained calcite associated with insignificant content of quartz (SiO_2), and Fe oxides and hydroxides and clay minerals (Figure 1 and 2). Reaction surfaces were detected between two dominant phases and separated each other.

Idealized crystal structure of apatite and calcite modeled in VESTA program is shown in figure 3, and figure 4. There is some evidence that significant substitution may occurred between CO_3^{2-} (trigonal planar polyhedron) and PO_4^{3-} (tetragonal polyhedron) due to their geochemical speciation, structural configuration and equilibrium relationship between hydroxyapatite and calcite (Samasundaran et al., 1985, Kuo, et al., 2009).

Evaluation of dissolution rate (aggregate stability) could be affected by soil pH, concentration of P and Ca, moisture content and particle size distribution (Kuo et al., 2009). The effect of particle size range come from its inverse relation to particular surface area associated with dissolution being interfacial (surface) controlled process.

Presented samples from figure 1 and figure 2 were gained from calcite saturated horizon localized on the loess. Generally, from these observations it can be deduced type and degree of weathering processes even by possible impact on the mode of mineral (structural) disintegration accompanied with elements mobilization (Barker et al., 1998; Čurlík, 2011). Both mentioned phases

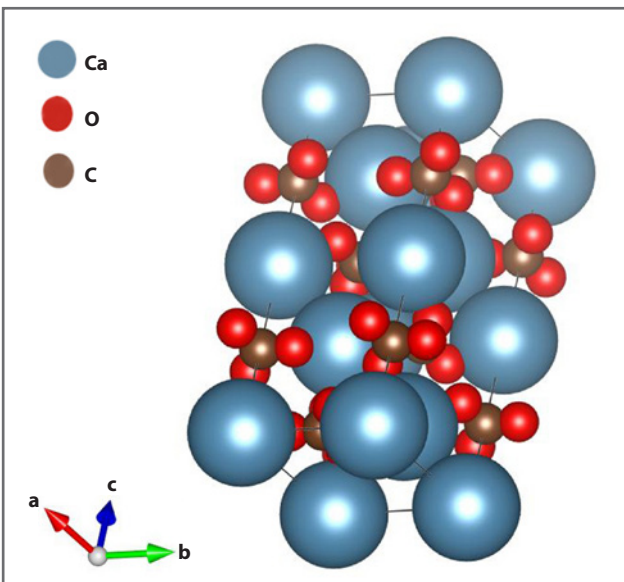


Figure 3 Fabrication of structure model of calcite in VESTA program, visualization is carried out in space-filling regime according to methodology Momma and Izumi (2014). Direction of a -, b -, c - axis determine spatial configuration of calcite structure

hydroxyapatite and calcite have insignificant deteriorate and degradable impact.

2.2 Physico-chemical analysis of soil, separation technique for X-ray analysis particle evaluation

Overall assessment of average soil sample in individual soil types (in the Slovak Republic - Morphogenetic system of soils in Slovakia, 2014; in the World - classification of WRB, 2006), we have to do multiple types of chemical and physical analysis. We have to start from the previously known information on external and internal factors and their interactions that fundamentally affect soil structure (Bronick and Lal, 2005). The most important factors include: soil organic matter (Šimanský et al., 2013) polyvalent cations (Paradelo et al., 2013), particle-size distribution and clay minerals (Kögel-Knabner et al., 2008), and etc. Determination of chemical and physical properties of the individual part of systems provides an explanation for the general behavior (prediction) and assessments of further function properties. Generally, every modeled program is based on the principle to achieve the less part of the system. In our case this point represent unit cell dimension of minerals. Accordingly,

we can evaluate information about atomic spatial configuration, crystal structure determination, and their connections in aggregate. For operation model is suitable either specification of above-mentioned physic-chemical properties (soil organic matter, polyvalent cations, etc.) or precise determination of individual mineralogical phase. X-ray analysis allows us to quantifying inorganic soil particles at structure level and identification of amorphous and crystalline substances. These information take advantage of define the thermodynamic state of substance; create the steady-state equilibrium model, suppose chemical distribution, and elements speciation. The quantitative and qualitative assessment of soil for X-ray analysis is profitable to choose the most dominant soil minerals. Firstly, according to methodology González et al. (2007) soils separate on different particles size distribution, content of organic matter (humus substances), etc. Depending of soil sample type, e.g. determination of clay minerals which was associated with carbonates minerals we use following procedures. The clay fraction in air-dried samples after saturation mode with magnesium was calcinated at 550 °C for two hours and after an ethylene

Table 1 "Modelled" diffraction analysis of calcite with different kind of parameter such as cell parameters, space group, X-ray wavelengths, intensity, *d*-space, etc. (Markgraf and Reeder, 1985). These parameters were used to design of structure in VESTA program

2-theta	Intensity	D-spacing	H	K	L	Multiplicity
23.01	8.05	3.8655	0	1	2	6
29.11	100.00	3.0675	1	0	4	6
30.72	1.62	2.9103	0	0	6	2
36.09	14.45	2.4890	1	1	0	6
39.37	12.96	2.2885	1	1	3	12
43.23	11.11	2.0927	2	0	2	6
46.64	16.31	1.9474	0	1	8	6
47.01	5.72	1.9328	0	2	4	6
48.10	14.36	1.8916	1	1	6	12
56.74	1.67	1.6224	2	1	1	12
57.54	5.91	1.6018	1	2	2	12
60.35	2.03	1.5337	2	0	8	6
60.50	1.20	1.5302	1	1	9	12
60.66	4.03	1.5266	2	1	4	12
63.98	2.11	1.4552	0	0	12	2
64.89	3.41	1.4370	3	0	0	6
69.25	1.14	1.3568	0	2	10	6
72.37	1.82	1.3057	1	2	8	12
75.71	1.45	1.2562	1	1	12	12

*parameters gain from X-ray analysis which was employed to VESTA design, cell parameters $a = 4.9780$, $b = 4.9780$, $c = 17.4620$, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 120.00$, space group R-3c, X-ray wavelength: 1.541838, max. abs. intensity/ volume **2: 23.23709141

glycol solvation (González et al., 2007). Šucha et al. (1993) as the first step samples have to be pulverized in agate mortar under 0.2 mm followed by ultrasonic probe disintegration. Subsequently, treated sodium acetate buffer and sodium dithionite conducted with minimize organic content recommend using by H_2O_2 . For better interpretive form of clay mineral due to expandable layers performed on the X-ray analysis saturation by the ethylene-glycol accompanied with vapour for 8 h at 60 °C is profitable procedure.

2.3 X-ray diffraction analysis

X-ray diffraction analysis is the most common technique for identification and characterization minerals (clay minerals, carbonates, etc.) from various type of matrices (Čurlík, 2011; Čurlík and Kolesár, 2014; Markgraf and Reeder, 1985; González et al., 2007). The X-ray analysis (beam of rays) belongs to part of electromagnetic spectra which be generated by the swift movement braking with fast flux electrons on the physical barrier. By means of goniometer with detector is scanned to the X-ray diffraction measurement. Interactions between X-ray with crystal structure one another atom become sources of X-ray scattering with the same wavelength. Produced beams has interfered each other and generate many characteristic diffraction maximums. Export X-ray diffraction analyses are data directly interlinked with from X-ray beams where diffraction maximums shows different kind length and width displayed in digital record (Prince et al., 1999). In case of generated data we further can use it for soil system with various modeling/ calculating and visualization evaluations.

2.4 Application of VESTA program for inorganic substances in soil system and their specific assessment

Acquirement of completely diffraction data could serve as numerical calculates to the crystalline parameters, for instance define crystal structure, linear and space groups, unit cell dimension, fraction coordinates, and lattice angle α , β , γ , and a -, b -, c - distance, etc. (Table 1).

In natural system, atoms, ions, ligands etc. attempt to stabilize (coordinated) with minimum energy and maximal efficiency. Due to this reason minerals with precise physical parameters and stoichiometric pure forms have tendency coordinated with symmetrically repeated equivalent identity (unit cell) in 3D space of crystal lattice. There is some evidence that X-ray analysis provides highly applicable background for detail physico-chemical specification of soil inorganic substances. It may be the case that the primary and secondary minerals (inorganic minerals) with different value of crystallinity contained dominant components. The extrapolation gained diffraction data either X-ray or densities of

coherent-scattering lengths (nuclear densities) to model from VESTA program (Momma and Izumi, 2011), we acquire further appropriate functions. VESTA program also provides another supported VICS – Visualization of Crystal structure, VEND – Visualization of Electron/ Nuclear Densities, PRIMA – Practice Iterative MEM Analysis, ALBA – After Le Bail Analysis for the maximum-entropy Patterson method, and Alchemy which converted structure factor and determine standard uncertainty. VESTA program based on algorithms is able to convert from X-ray diffraction analysis of minerals to their 3D visualization design (Fig. 2). Progress was achieved also structure-redefined techniques and methods maximum entropy (MEM). Additionally, program has capacity to find more precise information about fractional coordinates direct in crystal structure (retain up system), define spatial vectors (reactive less stable direction in the individual crystal integrity), volumetric parameters including electron and nuclear density. Morphology visualization (habitus), combine with multiple structural models, crystal facets, designed is surface within different grades is also practical. The interatomic bonds and define algorithm present “sophisticate” complex molecules, for instance the simulation of sorption a few organic substances (molecules) on the mineral surface, calculate of electron and nuclear density, Paterson function, integration electron and nuclear density by Voronoi tessellation are also possible to calculate and display. The supported information for other statistical program e.g. anisotropic atomic substitution (displacement) determines symmetric operations are including in program.

3 Conclusions

Observation of interrelations in 2D micromorphological cross section analysis could define their chemical equilibrium, local thermodynamically details, potential reactivity, spatial configuration on the atomic level. Based on the clear define (discrete vector parameters), predicted the mode of chemical and mechanical disintegration and decomposition accompanied with formation of new thermodynamically stable secondary minerals. Assessment sequence and successive models for mobilization, distribution, and bioavailability based on observed soil reactive products. Form “ideal” soil samples are profitable to use dominant minerals for X-ray analysis deal with modeled in VESTA program. This is applicable from the view point of detailed specification for determine several interactions e.g. water medium (dispersive system – hydrophobic interaction) for soil solution, natural bio-geochemical cycles and prediction mechanisms inorganic substances in soil system. Apparently, this topic underlines theoretical introduce investigation of methodological approach and is desirable to apply this model in the real condition at the near future.

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