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AUI
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Soil mineralogy in two apple-orchards, Fălticeni and Sârca (Moldavian Platform)

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Abstract

The present paper is focused on the mineralogical analysis of soils from two apple orchards (Fălticeni and Sârca) from the North-Eastern region of Romania, geologically located on the Moldavian Platform. 20 samples have been analysed from both areas (11 from Fălticeni and 9 from Sârca), through SEM-EDS and XRD (powder method). The main minerals which were identified are quartz, feldspar, illite and partially calcite. As secondary minerals and trace minerals, chlorite, smectite, glauconite, kaolinite, pyrite, apatite and oligoclase were also identified. Generally, the most abundant mineral is quartz and while for the Sârca area illite is present in notable quantities, in the samples taken from Fălticeni, calcite was identified as a main mineral alongside quartz.

The main factor which controls the distribution of minerals within the soils from the two orchards is the geological substratum. The results, correlated with the geochemistry of the soils reveal differences between the soils from the two areas, in matters of their ability to bond certain microelements, especially those with a notable toxic potential, as a function of their mineralogical composition. The principal components' analysis suggests that the distribution of microelements is controlled by the presence of clay minerals, oxides and amorphous material, while Cu points towards an anthropic origin due to agricultural practices.

Keywords: soil mineralogy, SEM-EDS, XRD, apple-orchard, Fălticeni, Sârca.

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1. Introduction

The genesis of the soil has two stages, which happen almost simultaneously. The first stage is the weathering of the pre-existing material through physical and chemical processes, while the second is the forming of the soil profile

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itself (Kabata-Pendias, 2011).

The inorganic components of the soil encompass primary minerals (e.g. feldspar and quartz) as well as secondary ones (normally clay minerals e.g. illite, kaolinite etc., oxides and amorphous material), both of which can become weathered through chemical processes (Sparks, 2003).

The soils' mineral phases bring significant contributions in controlling the mobility of microelements. For soils within orchards, this aspect ought to be given even more consideration as the soil mineralogy can influence and reflect on the quality of the fruits themselves through the retention and accumulation of some potentially toxic elements. For example, Bradl (2004), Sipos et al. (2008 and 2009) and Reis et al. (2011) have shown the adsorption and retention of some potentially toxic microelements such as Pb, Cu, Ni, Cr and V by clay minerals and $CaCO_3$ from soils.

Furthermore, the mineralogy and geochemistry of soils is influenced by the mineralogical composition of the geological substratum. In a study by Bonifacio et al. (2010), the authors explain the high Ni and Cr contents in soils through the mineralogy of the geological substratum.

The present paper is focused on exploring and revealing some of the relationships between the mineralogical composition of soils from two different areas (Fig. 1) and their microelements contents.

The distribution of microelements within soils from the two areas has been investigated before, by Prundeanu and Buzgar (2011), Huzum et al. (2012), Prundeanu et al. (2012 and 2013) and the contents for the analysed samples are summarized in Table 1.

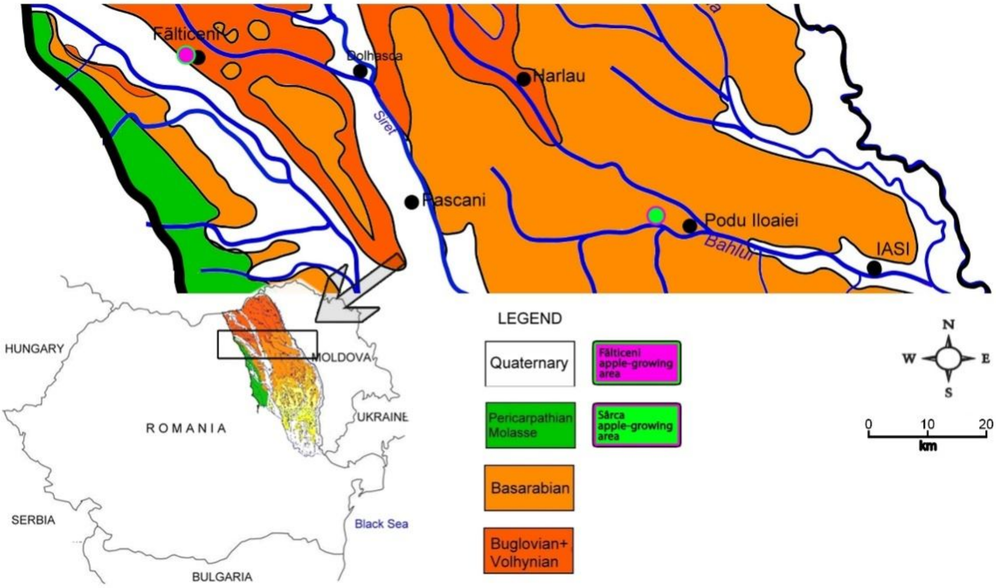

Fig. 1 Location of the two studied areas within the Moldavian Platform map (modified after Ionesi et al., 2005).

2. Location and geology of the source areas

The Fălticeni orchard belongs to the Fruit Production Research Station on the Fălticeni Plateau. The predominant type of soil is haplic phaeozem and rendzina phaeozem (Costan and Botez, 1962). Geologically, the area is on the Moldavian Platform and the deposits described based on the outcrops and boreholes are Volhynian. Lithologically, these deposits are comprised from layers of clay, sandy clay and sand, having a thickness of up to 500 m. Also, up to 8 levels of calcareous sandstones and oolitic limestone were identified and separated by Mutihac and Ionesi (1974).

Tab. 1 Contents of microelements in soil samples from the Fălticeni and Sârca orchards (determined by ED-XRF)

Orchard	Sample	Fe	Mn	Ni	Pb	Zn	Cd	Co	Cr	Cu	As
					(mg/kg)						
Fălticeni	FRI1	33432.16	851.90	45.80	22.10	81.42	0.031	23.15	82.44	50.94	11.54
	FRI2	36789.37	1161.69	46.61	21.30	74.10	0.089	22.85	89.61	41.21	20.61
	FRI4	27137.40	402.72	26.28	15.04	61.65	0.067	15.52	68.02	53.19	11.24
	FRI6	30774.38	952.58	44.91	21.72	67.83	0.04	20.08	78.33	59.74	11.04
	FRI7	24409.67	681.52	29.77	15.76	59.46	0.047	14.36	80.67	58.21	10.64
	FRI9	33362.22	882.88	43.55	24.30	91.34	0.056	20.95	71.28	60.64	11.37
	FRI22	33362.22	898.37	46.35	24.63	75.93	0.08	21.69	80.51	53.49	11.14
	FVD1	32662.80	867.39	48.15	21.11	74.53	0.049	21.75	83.88	44.45	12.07
	FVD11	30914.26	1215.90	33.76	20.01	68.75	0.063	19.47	69.69	41.98	13.28
	FVD14	27487.11	906.11	38.54	23.11	72.30	0.073	17.13	77.82	65.86	10.80
	FVD19	37348.90	1634.10	36.50	22.23	69.23	0.038	24.50	97.24	37.95	15.53
	Mean	**31607.32**	**950.47**	**40.02**	**21.03**	**72.41**	**0.06**	**20.13**	**79.95**	**51.60**	**12.66**
	Max	**37348.90**	**1634.10**	**48.15**	**24.63**	**91.34**	**0.09**	**24.50**	**97.24**	**65.86**	**20.61**
Sârca	SIC3	33991.70	844.16	47.85	27.58	83.99	0.097	22.22	71.36	36.07	11.47
	SIC11	34621.17	867.39	49.47	23.44	82.72	0.054	23.56	73.10	34.47	11.43
	SIC14	36299.77	890.63	50.91	23.71	82.55	0.09	24.66	81.28	34.76	12.25
	SIC23	36859.31	929.35	51.22	24.13	85.64	0.1	24.49	78.35	40.69	12.60
	SIC26	34621.17	859.65	50.07	23.00	81.84	0.056	22.93	66.40	39.27	11.93
	SIC29	34691.11	867.39	48.89	21.70	80.10	0.108	23.23	73.25	38.23	11.91
	SVD1	35530.42	882.88	50.75	23.50	85.42	0.089	22.79	68.54	39.60	11.72
	SVD17	36929.25	882.88	54.48	22.78	82.66	0.083	25.53	73.09	41.58	12.32
	SVD19	32872.63	813.18	46.91	24.90	81.88	0.062	21.90	71.60	38.19	11.48
	Mean	**35157.39**	**870.83**	**50.06**	**23.86**	**82.98**	**0.08**	**23.48**	**73.00**	**38.10**	**11.90**
	Max	**36929.25**	**929.35**	**54.48**	**27.58**	**85.64**	**0.11**	**25.53**	**81.28**	**41.58**	**12.60**

The second orchard belongs to Farm no. 6 from the Sârca Orchard complex, on the South-Western high-plains of the Jijia River. Pedologically, the predominant type of soil is cambic and calcaric chernozem (Boronia, 2010). The geological substratum is represented by the Sarmatian deposits of the Moldavian Platform (Bessarabian), together with some quaternary accumulations.

The lithology is dominated by pelitic accumulations (*Cryptomactra*-rich clays) extending up to 320–350 m (Ionesi and Barbu, 1996) and subsequently sands, clay-rich sands, calcareous sandstones and oolitic limestones (Mutihac and Ionesi, 1974). The mineralogical study of the Bessarabian deposits of the Moldavian Platform has been performed by Dill et al. (2012). The authors highlighted the great variety of sources for the sedimentary material accumulated in this stratigraphic interval which was based on the mineralogical and geochemical composition.

3. Methods and materials

3.1. Samples collection and preparation

To determine the soil mineralogy, 20 samples were analysed (11 from Fălticeni – Fig. 2 and 9 from Sârca – Fig. 3). The selection of these samples was made through assessing the macroscopic aspect and its' variations out of a total of 152 samples. The samples were taken from the superior horizons with a manual drill, each sample weighing between 1.5 and 2 kg.

Afterwards, the samples were dried at room temperature for 30 days, then manually grinded and subsequently split into granulometric fractions.

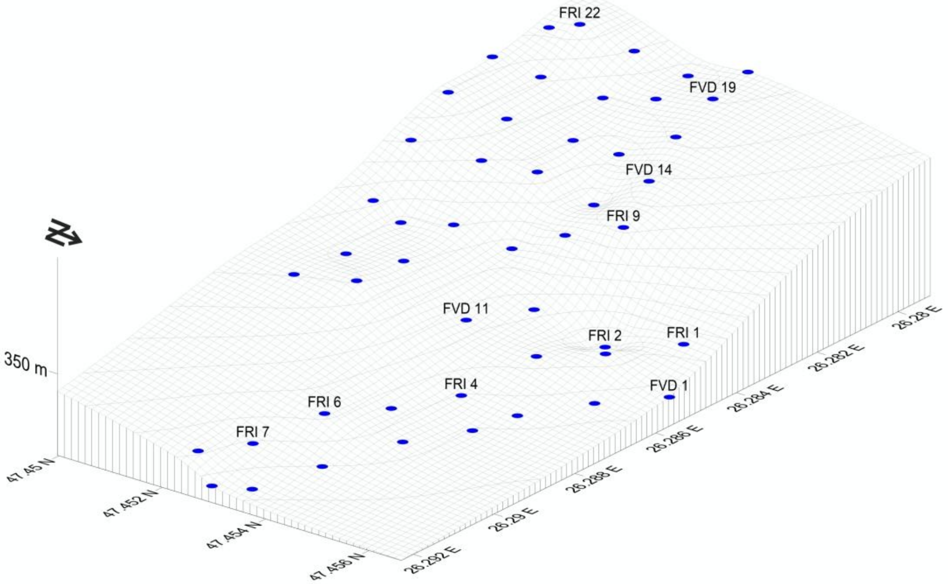

Fig. 2 Sampling points from Fălticeni orchard (labels show samples with mineralogical analysis).

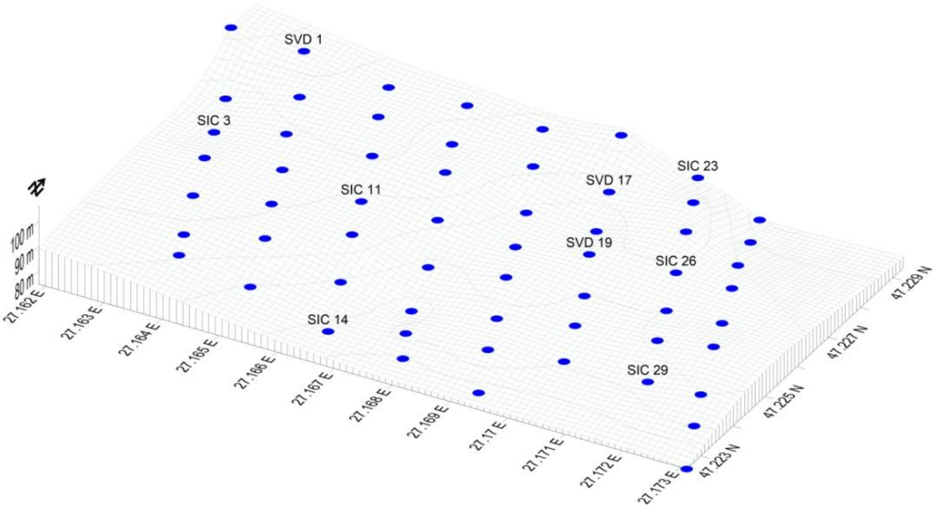

Fig. 3 Sampling points from Sârca orchard (labels show samples with mineralogical analysis).

For the SEM-EDS, from the < 1mm fraction, 4.5 g of dry sample was weighed, to which 7.5 g of Araldite epoxydic resin was added. This mixed was centrifuged for 3 minutes at 2000 rpm with a Planetary Centrifugal Mixer "Thinky Mixer", after which it was left to cool. The cast was then cut with a Struers Accutom-50 device. After drying it, a 30-micron thick layer of Carbon was applied (Quorum Q150T).

3.2 Determination of the mineralogical composition

To analyse the mineralogy of the soil, a semi-quantitative method (SEM-EDS) and a qualitative method (XRD-powder method) were used.

The SEM-EDS analyses were performed by a scanning electronic microscope Qemscan FEI. The calibration was done with 3 standards – gold, copper and quartz. Quality control was constantly maintained by activating the detector's autocalibration function for each 6 samples.

Although the SEM-EDS images are in grayscale, the software can automatically attribute colours to images (Fig. 4).

For the mineralogical analysis through XRD, a diffractometer Philips X'Pert PW3710 was used (Cu-Kα radiation at 40 kV and 40mA), with a 1° slot, secondary monochromator, a detector and sample feeder. The diameter of each sample was of 28 mm. The samples were investigated between 2° and 80° 2Θ, at a step of 0.02° 2Θ and a measuring time of 3 second/step.

3.3 Statistical factorial analysis

The use of factorial analysis in case of microelements contents and mineralogy seeks to identify the processes/sources which influence the distribution and control mechanisms for the studied elements. Many authors (Yalcin, 2009; Cai et al., 2012; Lu et al., 2012; Huzum et al., 2015; Apostoae, 2016) have made use of such analysis to reveal

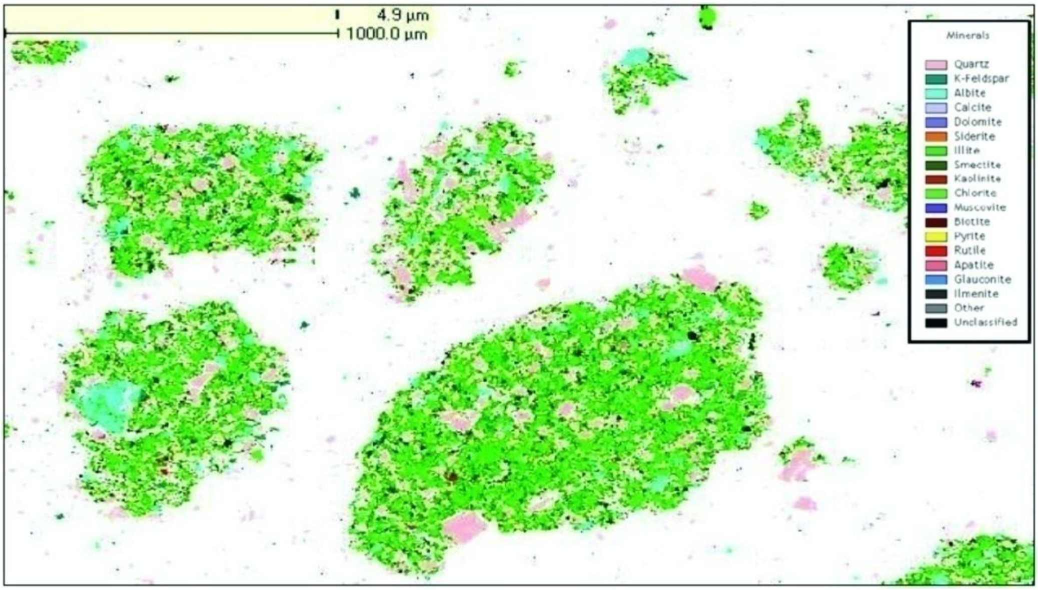

Fig. 4 Colour attribution for differentiating the various minerals (SEM-EDS–sample SIC 3).

the distribution of heavy metals in agricultural soils, as well as urban ones or in sediments.

There is a series of recommendations presented in different papers (e.g. Osborne and Costello, 2004; Shaukat et al., 2016) on the minimum number of samples necessary for carrying out a factorial analysis of the Principal Component Analysis. A comprehensive analysis of the existing models in literature was made by Zhao (2009) who discusses issues such as the number of samples, the number of variables and the ratio of the variables' number to the factors' number.

In this study, the Principal Component Analysis was used with a Varimax normalized rotation in SPSS software. Variables were grouped into five factors. The mineral contents determined in this study were taken into consideration together with the microelement contents given by Prundeanu et al. (2013) for soil samples from both orchards.

4. Results and discussion

The SEM-EDS results are given in Figure 5. The comparison between the results shows that quartz is the dominant mineral for both orchards, with proportions ranging from 39.53 % to 92.28 %. It is worth noting that the higher end of this interval is almost entirely related to the Fălticeni area, while the soils from Sârca are characterized by a rather high content of clay minerals, especially illite (on average 31.73 %, whereas Fălticeni only had 13.28 %) and chlorite.

Two samples from Fălticeni (FRI1 and FRI4) have a high calcite content and a lower quartz content, which may be due to the geological substratum. K-feldspar and albite have a relatively uniform distri-

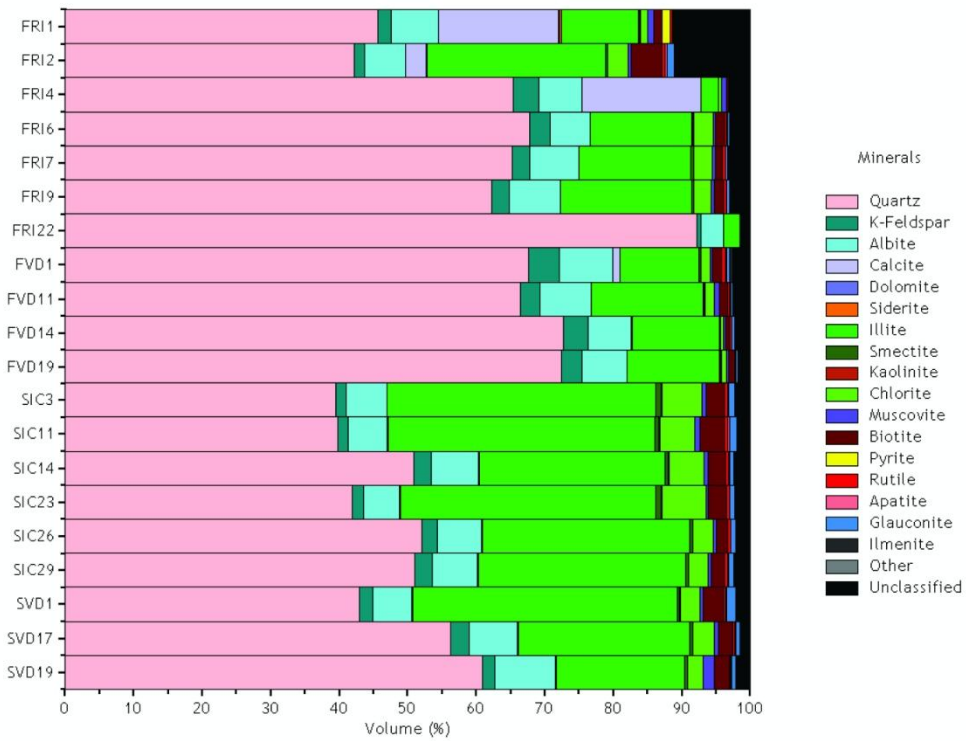

Fig. 5 Mineralogical composition of soils for the two areas (SEM-EDS) *Others – pyrite, siderite, rutile, dolomite, glauconite, kaolinite, smectite, apatite, ilmenite, oligoclase and not classified.

bution within the soil of the two orchards, while the quantity of biotite is higher in the Sârca soils.

Alongside illite and chlorite, other phyllosilicates were also identified, such as biotite and muscovite, but not in significant quantities. Other constituents were pyrite, siderite, rutile, glauconite, kaolinite, smectite, dolomite, ilmenite, apatite (Fig. 6) in roughly the same quantities for both areas.

The minerals identified through XRD are summarised in Table 2. The mineralogical composition given by this method widely confirms the SEM-EDS results, even though SEM-EDS is a semi-quantitative method and XRD is a qualitative one. For example, sample FRI4 is comprised, per quantitative analysis, of 65.42 % and calcite (17.36 %), K-feldspar 3.7 %, albite 6.28 %, clay minerals (illite, muscovite and chlorite) 3.61 % and this distribution pattern has been confirmed by the XRD analysis.

XRD generally shows a mineralogy dominated by quartz. Feldspar, clay minerals and calcite (for 2 samples) are the main and secondary minerals for both studied areas (Fig. 7). Traces of chlorite, calcite or smectite have also been identified.

Quartz does not weather under pedogenetic conditions and accumulates in large quantities (Lăcătușu, 2000). For

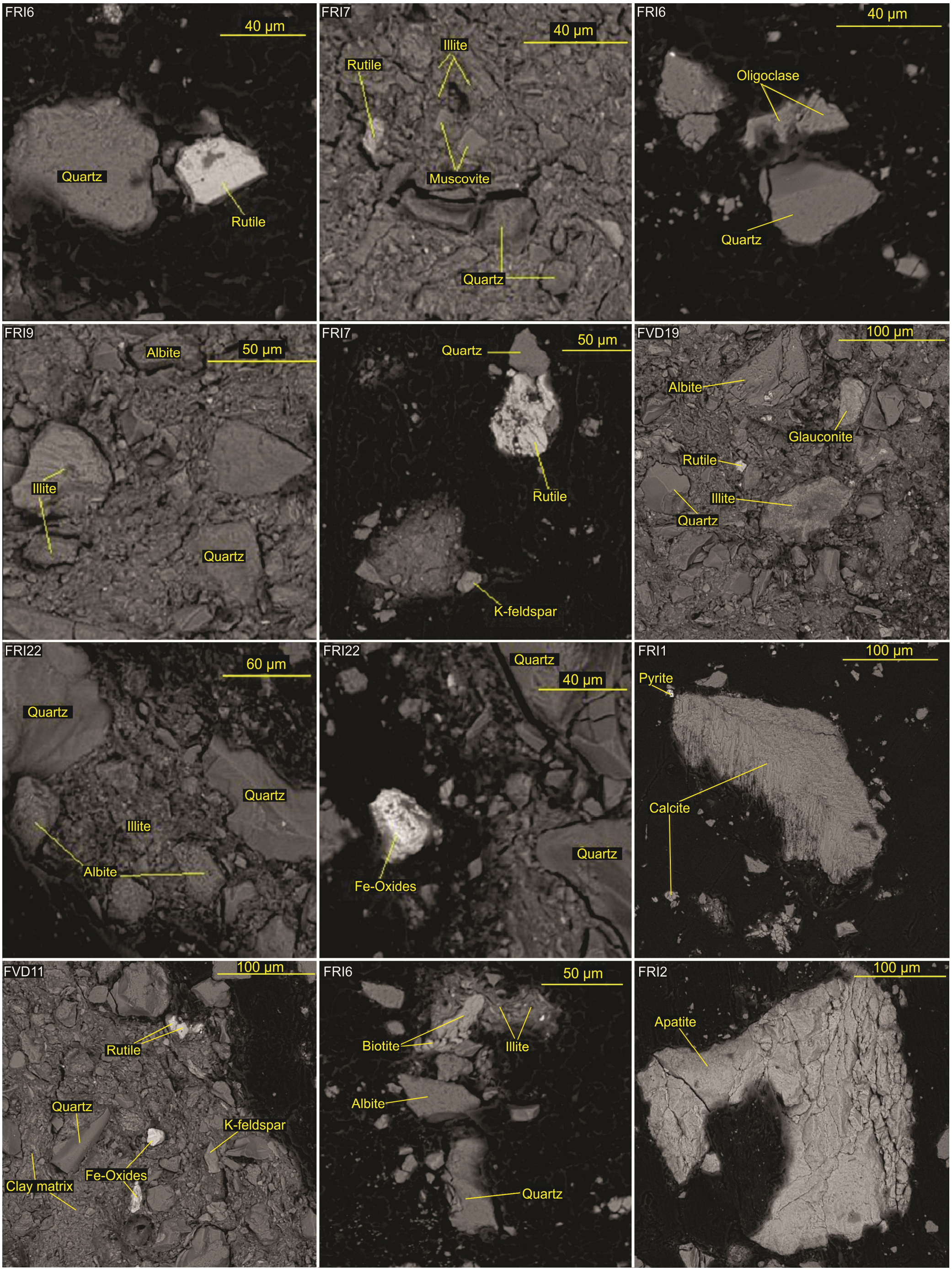

Fig. 6 Main and secondary mineralogical constituents identified through SEM-EDS.

Tab. 2 Main, secondary and trace minerals identified through XRD for both areas

		Mineralogical content (XRD analysis)	
Orchard	**Sample**	**Primary minerals**	**Secondary/Trace minerals**
Fălticeni	FRI1	Quartz, Calcite	Feldspar, Muscovite-Illite, Chlorite
	FRI2	Quartz	Feldspar, Muscovite-Illite, Calcite, Chlorite
	FRI4	Quartz, Calcite	Feldspar, Muscovite-Illite, Chlorite, ±Smectite
	FRI6	Quartz	Feldspar, Muscovite-Illite, Chlorite, Smectite
	FRI7	Quartz, Feldspar	Muscovite-Illite, Chlorite, Smectite
	FRI9	Quartz, Feldspar	Muscovite-Illite, Chlorite, ±Smectite
	FRI22	Quartz, Feldspar	Muscovite-Illite, Chlorite
	FVD1	Quartz	Feldspar, Muscovite-Illite, Chlorite, ±Calcite, ±Smectite
	FVD11	Quartz	Feldspar, Muscovite-Illite, Chlorite
	FVD14	Quartz	Feldspar, Muscovite-Illite, Chlorite
	FVD19	Quartz, Feldspar	Muscovite-Illite, Chlorite, ±Smectite
Sârca	SIC3	Quartz	Feldspar, Muscovite-Illite, Chlorite
	SIC11	Quartz	Feldspar, Muscovite-Illite, Chlorite
	SIC14	Quartz, Feldspar	Muscovite-Illite, Chlorite, ±Smectite
	SIC23	Quartz, Feldspar	Muscovite-Illite, Chlorite, ±Smectite
	SIC26	Quartz, Feldspar	Muscovite-Illite, Chlorite
	SIC29	Quartz, Feldspar	Muscovite-Illite, Chlorite
	SVD1	Quartz	Feldspar, Muscovite-Illite, Chlorite
	SVD17	Quartz	Feldspar, Muscovite-Illite, Calcite, Chlorite, ±Smectite
	SVD19	Quartz	Feldspar, Calcite, Muscovite-Illite, Chlorite

the two studied areas, the percentage of quartz is given by the nature of the rocks forming the geological substratum. The quartz content for the Fălticeni samples is much higher due to the dominating presence of arenites within the geological substratum. Other oxides which were detected by the SEM are rutile, ilmenite, as well as iron and Mn oxides.

Feldspars are the most abundant minerals in rocks forming Earth's crust and their weathering processes and conditions have been intensely studied (Murray, 1994). In soils from the two studied areas, the most notable feldspars are albite, K-feldspar and oligoclase. Apart from K-feldspar, which are present in higher quantities in Fălticeni study area, the feldspar minerals have a similar distribution throughout both areas.

Calcite is sometimes encountered as a main mineral, whereas in some cases it is a secondary one. The occurrence of calcite as a main mineral in the Fălticeni orchard can be explained by the fact that in this area soils have developed on a carbonate geological substratum, with marl and calcareous claystone. Apart from

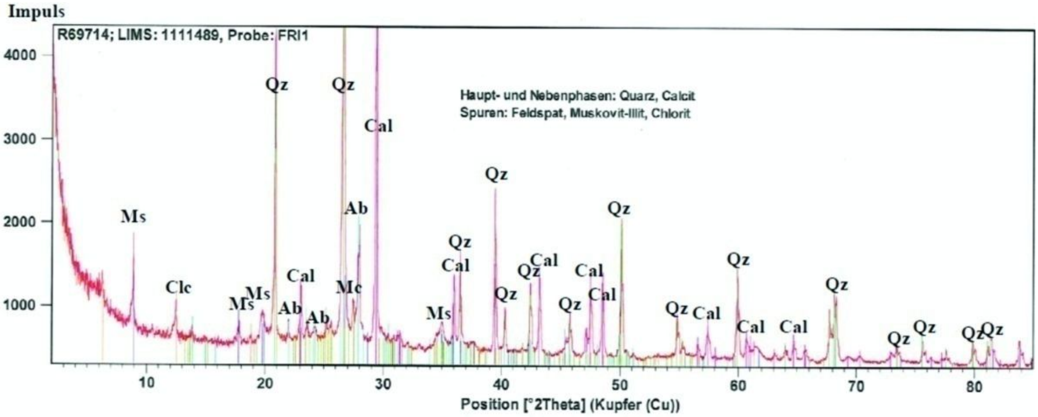

Fig. 7 XRD spectrum for sample ref. FRI1 showing the main identified mineral.

that, calcite appears through precipitation from bi-carbonated supersaturated solutions. Other carbonates, which have been identified for both areas are dolomite and siderite.

Illite is a clay mineral which may result from weathered muscovite (di-octahedral illite) or weathered biotite (trioctahedral illite) (Lăcătușu, 2000) and which was also identified in analysed samples.

The results of the SEM-EDS analysis show higher illite contents for the samples originating from Sârca area compared to those from Fălticeni area, due to the pre-existing material of an argillaceous nature (*Cryptomactra*-rich clay).

Through PCA analysis, the 5 factors which were considered have revealed some of the aspects related with the distribution and correlations between the microelements and the soil's mineralogy for the two studied areas. Considering the low number of available samples (11 for Fălticeni parcel and 9 for Sârca) and the high number of variables (29 variables), the analysis was performed in order to present an overview of the combination of minerals and microelements in the studied soils. For this reason, the interpretation should be treated with caution and for results with a high degree of confidence, a larger data set is required.

For the dataset from the Fălticeni soils we will comment on the first 5 factors that control 84.76 % of the total varimax rotated loadings.

The first two factors, summing 41.88 % of the data variability, represent the main mineralogical composition of the soil, controlled by quartz, carbonates and clay minerals (fig. 8a).

Factor F4, accounting for 14.39 %, is characteristic to oxides (as rutile and ilmenite) and feldspars (albite and K-feldspar); a possible common source of these minerals in the geological sub-stratum can be argued.

Regarding the F3 and F5, these factors sum up approximately 28.49 % of the variability, and the main components that control these two factors are the elemental data resulted from the XRF analysis.

The only two elements that do not show major influence in these factors, F3

Fig. 8 Principal Components Analysis (PCA) for the mineralogical and geochemical composition of the Fălticeni (a and b) and Sârca orchards (c and d).

and F5, are Cu and Cd. Cd shows a completely different distribution compared to the one exhibited by the variables that dominate F4. While Cu presents a unique distribution of the compositional data, which cannot be complied with any of the other variables used in the PCA analysis. Cu cannot be associated with any of the main minerals, nor to any other elements (fig. 8b) as its distribution is controlled by human activity, namely the use of pesticides (e.g. Wenqing et al., 2005; Zhou et al., 2011).

The only elements which has shown an important affinity to some of the main minerals determined in Fălticeni study area (i.e., illite and biotite) is As. To a shorter extent, in terms of linear correlation, the elements distribution seems to be influenced by illite, biotite and glauconite, from the clay minerals group. Siderite and pyrite are other two minerals that have an impact on the elemental distribution.

No major links between mineralogy and elemental data distribution have been identified. They seem to linearly correlate inside each group, respectively mineralogical data and elemental data, adding them up in completely different factors while using PCA data analysis. This behavior makes it difficult to spot comprehensive information about the main bulk of the data.

In the other study area, Sârca, we approached the first three factors, accounting for 64 % of the variability.

From the F1 and F2 diagram (fig. 8c) it can be easily observed that the behavior of microelements in relationship to the soil mineralogy is different than the one from the other study area.

Most microelements are distributed similarly with the oxydes (Fe, Mn, Cd, Ni, Co, Cr and As), and to a second degree they are influenced by the clay minerals and pyrite (especially Zn).

Very interesting is the association of apatite and Pb in F1, as it is well known that the Pb toxicity in soils can be controlled by the use of P amendments (Hettiarachchi and Pierzynski, 2004; Cui et al., 2016; Katoh et al., 2016; Valipour et al., 2016). At Sârca, the Pb occurrence in soil seems to be directly linked to the apatite abundances.

The contents of Cu are again related to the human activity, while quartz, K-feldspar and muscovite originate from the geological substratum (fig. 8d).

5. Conclusions

The mineralogical composition of soils from the two orchards is clearly influenced by the Sarmatian-age geological substratum on which they have developed.

The main and secondary components which were identified through SEM-EDS and confirmed through XRF are quartz, feldspar, illite, calcite, chlorite and smectite, with traces of glauconite, kaolinite, pyrite, apatite and oligoclase.

The main mineral in both cases is quartz, which originates from the arenitic substratum and did not suffer significant weathering during paedogenesis.

The higher quantity of the illitic fraction at Sârca is closely linked to the pelitic deposits, which have accumulated in this area during Bessarabian, to which the weathering of muscovite and biotite in soil may also be added.

The presence of calcite as a main mineral in two of the Fălticeni samples is correlated with the type of soil from which the samples were taken (rendzina), a soil developed on marl and calcareous clay.

The other minerals which were analysed show a similar distribution for both studied areas.

The results of the PCA analysis gives a series of information about the source of microelements in the soil, as well as on the correlations between minerals and the geochemical composition. The distribution of some trace elements in the soils of the two orchards is controlled by the clay minerals (particularly As at Fălticeni and Zn at Sârca). Also, the source of Cu is anthropic for both parcels, due to the pesticides use. The association between Pb and apatite for Sârca parcel may be a hint for the use of P amendments and their capacity to control the toxicity of Pb.

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