MINERALOGY OF CLAY FRACTION OF SELECTED SOIL PROFILES IN THE ŽITNÝ OSTROV

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Abstract: Six soil profiles have been selected from the area of Žitný Ostrov for the identification of mineralogy of the clay fraction. The main mineral association obtained was illite, and chlorite with small admixtures of kaolinite. The clay fraction also contains some clastogenic minerals like quartz and feldspars. Carbonates (calcite and dolomite) of clastogenic and authigenic origins represent very important constituents of the clay fraction. This mineralogy has a great influence on the soil properties of the area studied.

Introduction

The area of Žitný Ostrov is situated very close to Bratislava, in the south-western part of Slovakia. It represents a great water and food resource for the country. It is also considered the largest groundwater aquifer in Central Europe, and is notable for its very special geological, hydrogeological, and hydrogeochemical conditions. As a result, a relatively large number of studies have been devoted for solving different problems in the area. Recently interest in this area has grown still more conspicuously, after the dam construction on the Danube at Gabčíkovo.

Clay minerals in soils bear many important features that make their study essential for understanding the different processes in soils and their dynamics. The clay mineralogy of the area is of special interest as these clays have their own effect on soil properties and groundwater composition. It can be said that only few studies have been carried out on the clay mineralogy of this important and extensive isle, like Hraško (1974) and Čurlík (1977). This study aims to bridge the gap in this subject and to compare the results obtained with those of the previous studies, and of the other parts of the Danubian Lowland, and especially with the clay mineralogy of the neighbouring part of the Hungarian Plain.

General nature of the studied area

Žitný Ostrov represents the area restricted between the Danube and the Small Danube. It forms the lower part of the wider Danubian Lowland and geomorphologically represents an independent unit within it (Hromádka 1956). It is virtually a young structural plain originated by the accumulative activity of the Danube during constantly occurring tectonic subsidence.

Geologicaly the isle is built by gravels, which occur in different amounts, but locally reach 300 m thickness, and are covered by Pleistocene and Holocene sediments of different textures.

The groundwater of the Žitný Ostrov is supplied from the Danube river through the zone of infiltration, which is situated according to the geological data (Porubský et al. 1971) between Bratislava and Palkovičovo. The groundwater flows in accordance with the hydrodynamic laws through the permeable water-bearing strata towards the southeast, almost parallel to the Danube. The water of the Danube is Ca^{2+}-HCO_3^-, weakly alkaline, slightly mineralized and almost saturated with respect to calcite. The chemical composition of the groundwater changes due to the interaction in the soil-rock-water system. Here gradually, different hydrogeochemical zones have formed, Ca^{2+}-HCO_3^-, $Ca^{2+}(Mg^{2+})$-HCO_3^- and $Ca^{2+}(Mg^{2+},Na^+)$-HCO_3^-. The groundwater table fluctuates during the year, and its long period average varies between 4 - 7 m in the upper part of the isle, 2 - 4 m in the middle part and 0 - 2 m in the lower part and depressions (Porubský et al. 1971; Kalnová 1976). Consequently, the geochemical effect of groundwater on soils (and vice versa) is very important, and this is not only a simple hydromorphic influence, but also a geochemical influence that is reflected in the chemical composition of the soils. The soils are represented by carbonatic types, but due to different hydromorphic influences, gley phenomena are also present mostly in the southeastern parts of the area. This has led to the evolution of relatively variegated soil cover in the area.

The area of Žitný Ostrov is climatically hot and dry. The average annual temperature is 9.5 °C. Evapotranspiration (potential evaporation) exceeds the amount of precipitation creating a permanently evaporative regime. According to Kalnová (1976), the annual average precipitation during the period between 1931 and 1970 does not exceed 570 mm, while the average potential evaporation of the same period is 832 mm. It can be concluded that climate is the main factor in the system water-sediments-soils-plants that determines the geochemical influence of groundwater (and surface water-precipitation) on soil cover of the studied area.

Materials and methods

Six soil profiles have been selected from the whole area representing the upper, middle and lower parts of the isle (Fig. 1). These profiles have been taken through the project of soil monitoring carried out by the Soil Fertility Research Institute in Bra-
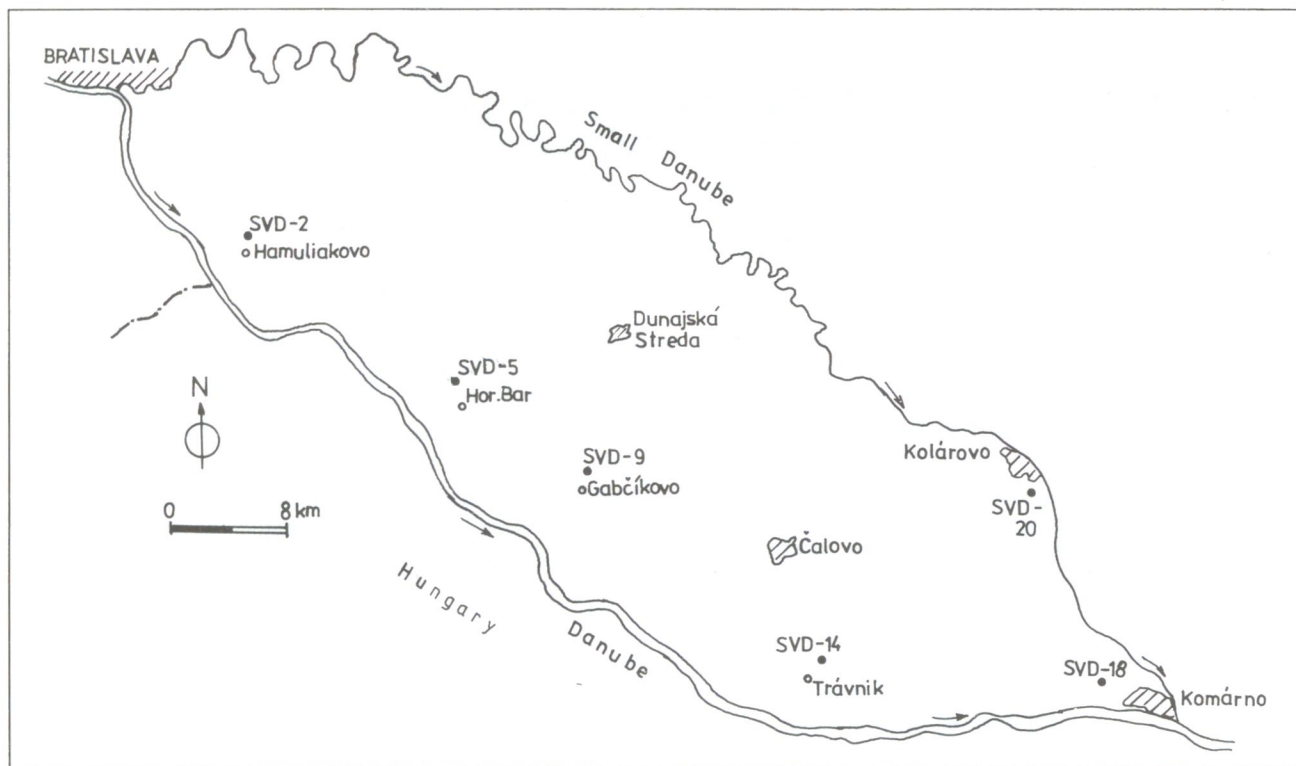
Fig. 1. Žitný ostrov and the locations of the six soil profiles investigated.

tislava. Three samples were selected from each profile, from its upper, middle and lower parts for the study of mineralogy of the clay fraction, as follows:

SVD-2 (Hamuliakovo), 5 - 10 *cm*, 30 - 40 *cm* and 80 - 90 *cm*;
SVD-5 (Horný Bar), 10 - 20 *cm*, 40 - 50 *cm* and 70 - 90 *cm*;
SVD-9 (Gabčíkovo), 10 - 20 *cm*, 40 - 50 *cm* and 80 - 100 *cm*;
SVD-14 (Trávnik), 15 - 25 *cm*, 60 - 70 *cm* and 110 - 120 *cm*;
SVD-18 (Komárno), 10 - 20 *cm*, 50 - 60 *cm* and 90 - 110 *cm*;
SVD-20 (Kolárovo), 10 - 20 *cm*, 20 - 30 *cm* and 50 - 70 *cm*.

The samples were air dried and sieved into different size fractions. The fraction passed through 2 *mm* sieve has been chosen for the clay mineral separation. About 100 *g* of this fraction has been taken, and the clay fraction ($< 2 \mu m$) has been separated by the repeated decantation method according to Sirový (1967). The clay fraction has been obtained from the suspended portion by centrifugation after coagulation with HCl and $MgCl_2$, then the sample was rewashed and dried at 40 °C. Many techniques have been used for the clay mineral identification, mainly X-ray diffraction (XRD). The patterns were obtained using Dron-3 diffractometer with CuK_α radiation. Samples saturation and glycerol solvation have been done according to the method described by Black et al. (1965). Samples were tested after different treatments: **a** - Mg^{2+} saturated, **b** - Mg^{2+} saturated and heated at 550 °C, **c** - Mg^{2+} saturated and glycerol solvated, **d** - Mg^{2+} saturated and heated at 450 °C and **e** - Mg^{2+} saturated and treated with warm dilute HCl (6 *N*), heated at (80 - 90 °C) for 2 hours.

Infrared spectroscopy (IRS) has been carried out using PERKIN-ELMER 598 spectrophotometer for the precise identification of kaolinite. Transmission electron micrographs have been obtained using the transmission electron microscope (TEM) Tesla BS 242 B. JXA-840A Electron Probe Microanalyzer Jeol (EDAX) has been used to look for dolomite in the micrite. Thin sections have been prepared and examined under polarizing microscope.

Results and discussion

All studied samples show almost similar XRD-patterns, especially with regard to the main mineral components (Fig. 2). The main clay mineral is illite showing clear sharp reflections at 9.98, 4.97 and 3.31 Å. The reflections at 14.2, 7.12, 4.75 and 3.56 Å reveal the presence of chlorite or chlorite and kaolinite. In this case, different treatment procedures were very important for the identification of these two components. Diffractograms obtained from samples heated at 550 °C show enhancement of the intensity at 14.2 Å and disappearance of the second, third and fourth orders which ascertain the presence of chlorite (Brindley & Ali 1950). Treatment with warm dilute HCl causes the dissolution of chlorite (Brindley & Brown 1980) which is shown by disappearance of reflections at 14.2 and 4.75 Å, while reflections at 7.12 and 3.56 Å (reflections common for both chlorite and kaolinite) show substantial decrease leaving reflections with very small intensities which indicates the presence of small admixtures of kaolinite. This is also evident from samples heated at 450 °C. Here the 7.12 and 3.56 Å reflections are slightly decreased wich may be expressed by the probable transformation of the kaolinite to the very poorly ordered metakaolin that shows little or no powder diffraction pattern under such treatment, while chlorite survives this treatment (Brindley & Brown 1980). Samples treated with glycerol show no sign of the presence of smectites. However, in a previous study (Čurlík 1977) the presence of smectites was proved in other localities of the area to an extent of about (5 - 18 %). Therefore, the clay mineral association of the area can be estimated to be illite, chlorite in addition to small admixtures of kaolinite and smectite.

The same mineral association has been identified by Hraško (1974), except that he has reported the presence of vermiculite. This mineral association differs from those prevailing in other parts of the Danubian Lowland like that present in the cherno-
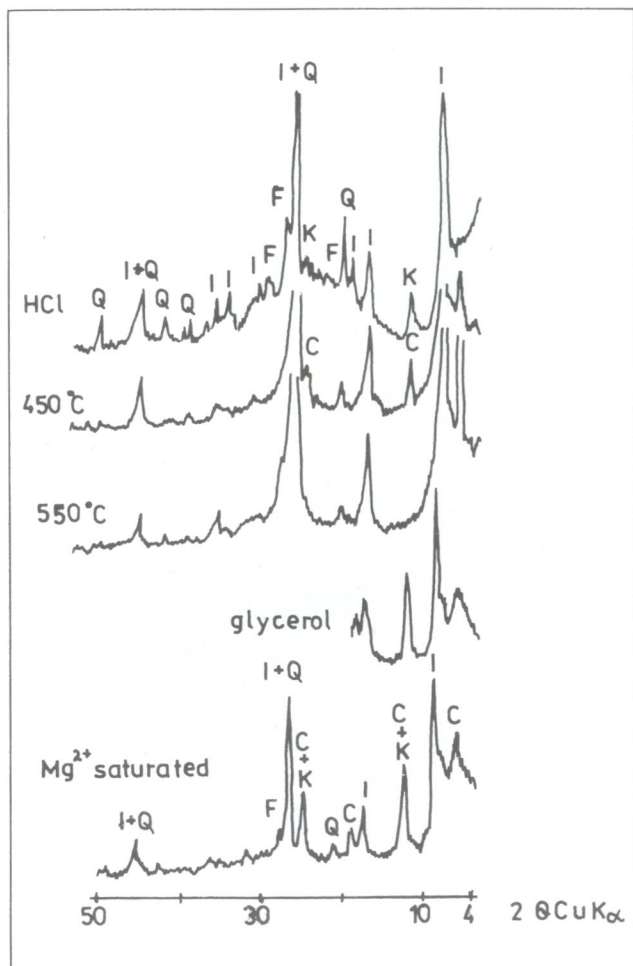
Fig. 2. XRD-patterns of the clay fraction after various treatments. Profile SVD-2 (Hamuliakovo), depth (30 - 40 cm).
I - illite, C - chlorite, K - kaolinite, Q - quartz, F -feldspar, D - dolomite, Ca - calcite.

Fig. 3. XRD-patterns of the clay fraction show presence of calcite and dolomite and dominance of dolomite. Profile SVD-20 (Kolárovo), depth (10 - 20 cm).

zems of the loessy hills which consists of illite, montmorillonite and mixed layer clays (Čurlík 1977). On the other hand, it resembles that which occurs on the right side of the Danube which consists of illite, chlorite and kaolinite, as is revealed by the map of clay mineral associations in the soils of Hungary prepared by Stefanovits & Dombóvári (1985), and this can be attributed to the same type of alluvial Alpine deposits that cover both areas.

The clay fraction also contains other minerals like quartz, carbonates (dolomite and calcite) and feldspars (Figs. 2 and 3).

The XRD-patterns of samples treated with HCl (Fig. 2) are of special interest. In addition to their importance for proving presence of kaolinite, dissolution of chlorite causes enhancement of the reflections of illite, quartz and feldspars, and it is clear that the carbonate components will disappear on these diffractograms.

What has also been observed in this study is that the carbonate components undergo partial or complete disappearance after heating at 550 °C (Fig. 3).

It is also very interesting to record here, that dolomite prevails on calcite in the clay fractions (Fig. 3) and this is contradictory to the fact that calcite prevails on dolomite, which has already been proved by the mineralogical study of the carbonate fraction of the soils studied. This can be attributed to the very fine grain size of dolomite that allows it to remain with the clays during the separation of the clay fraction, or to the relatively higher solu-
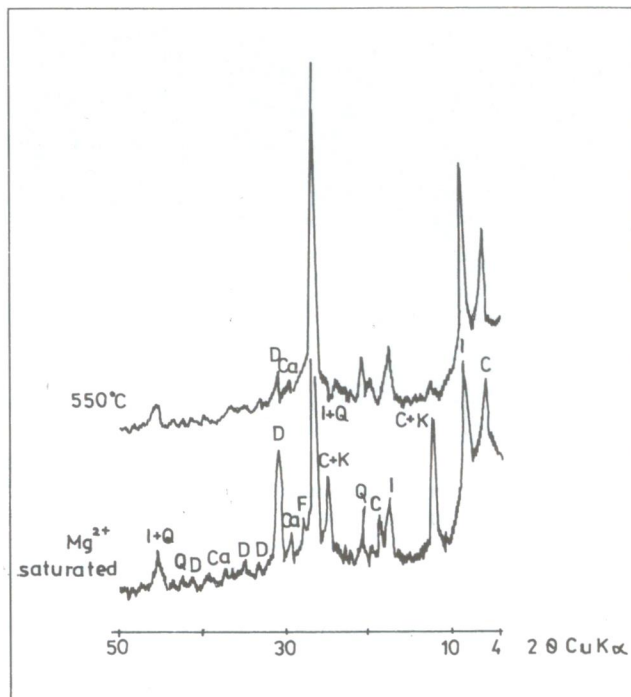
bility of calcite. The very fine grain size of dolomite may elucidate its authigenic origin.

Dolomite can be partially of authigenic origin. This was proved by means of microprobe analysis. Dolomite appears on the scanning X-ray (electron microprobe) images (Fig. 4) as dark irregular patches randomly distributed within the light calcitic micrite. This is very important especially when connected with the problem of dolomitization, because it reveals the formation of dolomite in situ in the soils of Žitný Ostrov.

The IRS patterns (Fig. 5) of the samples studied show a very weak absorption band at 3700 cm^{-1} which indicates the presence of small admixtures of kaolinite (Farmer 1974), and this supports our findings by XRD. This absorption band is absent in the IRS patterns of many other samples, which indicates the absence of kaolinite in these samples.

The results of TEM were not so striking bacause the clay mineral components, did not show their typical morphological characteristics. However, it can be said that these components can be only poorly identified on the TEM micrographs, but with a lot of caution. Kaolinite appears as particles with pseudo-hexagonal borders, illite as platy particles with irregular angular borders and chlorite as platy particles with irregular borders (Fig. 6).

Microscopic study has supported these results, since biotite, muscovite, chlorite, carbonates, quartz, feldspars (orthoclase, microcline and perthitic feldspars) and plagioclase predominate in thin sections.

Conclusions

The main clay mineral association which dominates in the area studied is illite + chlorite in addition to small admixtures of kaolinite and smectite. This association is similar to that identified by Hraško (1974) and Stefanovits & Dombóvári (1985), but differs from that reported by Čurlík (1977), consisted of illite, montmorillonite and mixed layer clays.
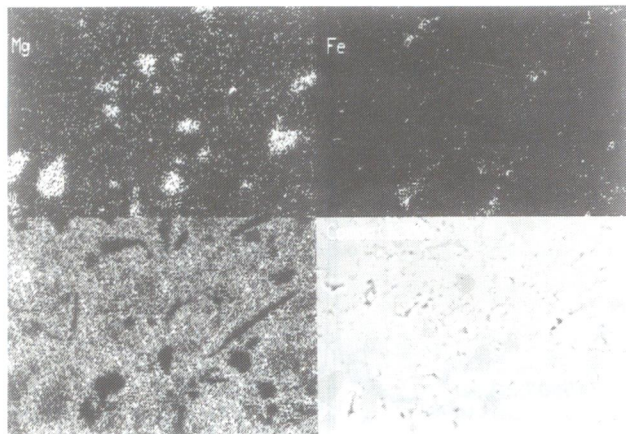
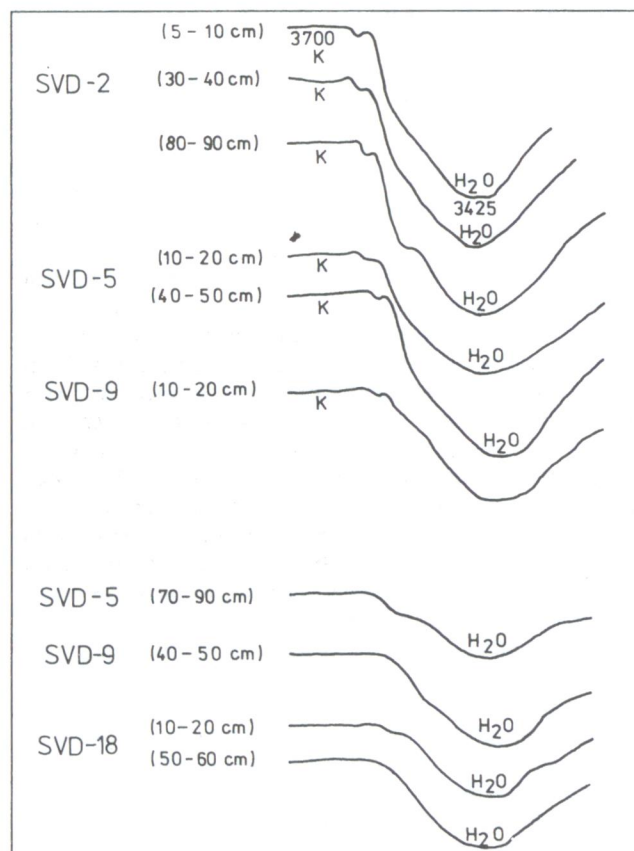**Fig. 4.** Electron microprobe images taken from a polished thin section show dolomite within calcitic micrite.

Fig. 5. IRS (cm^{-1}) patterns of some of the studied profiles.

Carbonates of the clay fraction are partially of authigenic origin. This indicates the formation of dolomite in situ in the soils of Žitný Ostrov.
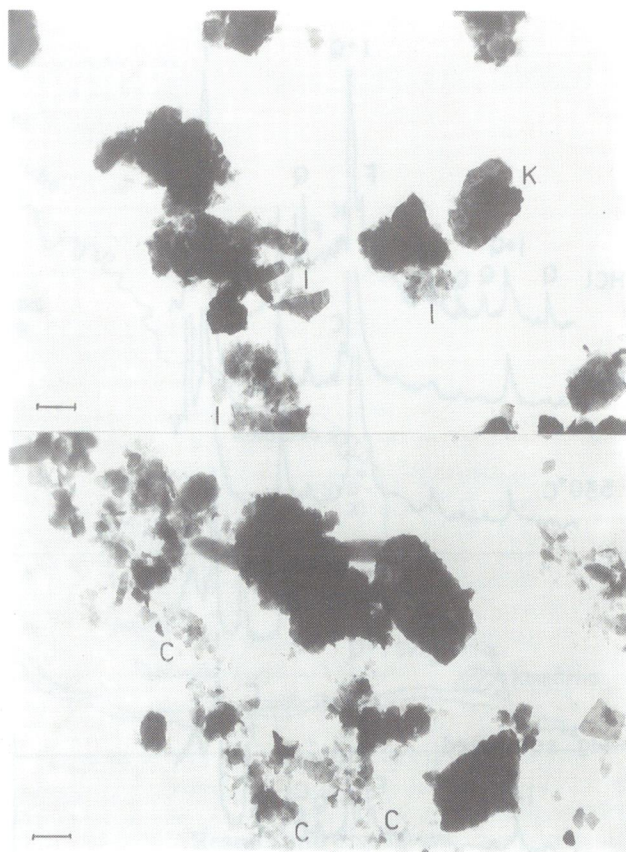
Fig. 6. Transmission electron micrographs show illite (I), chlorite (C) and kaolinite (K). Bar = $1\,\mu m$.

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