*Acta Mineralogica-Petrographica, Szeged 2006–2007, Vol. **47**, pp. 25-46*

ACTA
Mineralogica
Petrographica

MINERALOGY OF PLIOCENE TO MIDDLE PLEISTOCENE RED CLAYS IN SE TRANSDANUBIA (HUNGARY). REVIEW OF THE QUANTITATIVE DATA

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ABSTRACT

Red silty clays filling fissures in limestone, karstic depressions and recent caves in the Villány Mts. (SE Transdanubia, Hungary), and Pliocene to Quaternary red clays of the surrounding hilly areas were studied. For comparison also yellow clays and Pannonian basin sediments were investigated. The quantitative mineral composition was determined by X-ray diffraction for the bulk sample and for the <2 µm fraction. For a statistical evaluation in triangular diagrams the data of 181 quantitative analyses of the bulk composition and 129 analyses of the <2 µm fraction were collected. Minerals in the *whole rock* were sorted into 3 groups according to their genetic significance: (1) carbonates, (2) detrital and slightly weathered minerals and (3) products of strong weathering. The 3 groups for clay minerals in the *<2 µm fraction* were: (1) illite and chlorite, (2) smectite and vermiculite and (3) kaolinite and gibbsite. Two main associations of minerals could be distinguished. A *highly weathered association* consisting of the minerals of disordered kaolinite, kaolinite/smectite mixed-layer mineral, smectite and occasionally gibbsite was selected which normally contains Ti-oxides and more hematite than goethite. Quartz contents are low, feldspars are absent. Calcite is high only when secondary cementation or admixture of wall rock fragments occurs. The association represents a weathering crust formed on the karstified surface during a warm and humid climatic period of the Middle Pliocene. The other, more widespread, *less weathered association* contains well crystallised clay minerals, dominantly illite accompanied by smectite, illite/smectite, chlorite or kaolinite, relatively much quartz and feldspars but little calcite. The typical iron mineral is here goethite. This association represents weakly or moderately weathered terrestrial or shallow basin sediments of Pliocene to Middle Pleistocene age. The genetic conclusions obtained agree well with results obtained by the study of Vertebrate fossils.

Key words: red clays, karst, kaolinite, kaolinite/smectite, SE Transdanubia, Tengelic Fm., Pliocene, Quaternary

INTRODUCTION

The range of the Villány Mts. consists mainly of carbonate rocks of Mesozoic age. In the cavities of the karstified limestone, such as fissures, sinkholes and recent caves various fine grained sediments have been accumulated. The most widespread karstic sediments are red clays which are considered to belong to the stratigraphic unit Tengelic Red Clay Formation which is widespread in a large area around the Villány Mts. The formation is part of the young terrestrial sequence of the area. Another type of red clay occurs in basal palaeosol layers underlying the Middle Pleistocene Paks Loess Formation. In the immediate vicinity of the Villány Mts. shallow local basins are filled with lacustrine to terrestrial Upper Pannonian to Quaternary sediments, in which, however, red clays do not occur. These grey and yellow fine grained sediments were studied for comparison with the red clays. The area of study and local names are shown in Fig. 1.

Stratigraphic relations of the terrestrial sediments are described in the classical studies of the Vertebrate fauna by Kretzoi (1956, 1969) and Jánossy (1986) and in the more recent summaries by Kaiser (1999), Kordos (1991, 2001), Koloszár and Marsi (2002), Koloszár (2004) and Császár, Kordos (2004). Schweitzer (1993) collected field observations, geomorphological data such as position of terraces, formation of travertine etc., mineralogical and palaeontological evidence and radioactive age determinations. In conclusion he distinguished and characterised the subsequent periods set up by the former authors called *Ruscinium-Csarnótanum* (4.5-3.0 million years), *Villányium* (3.0-1.8 million years) and *Biharium* (younger than 1.8 million years).

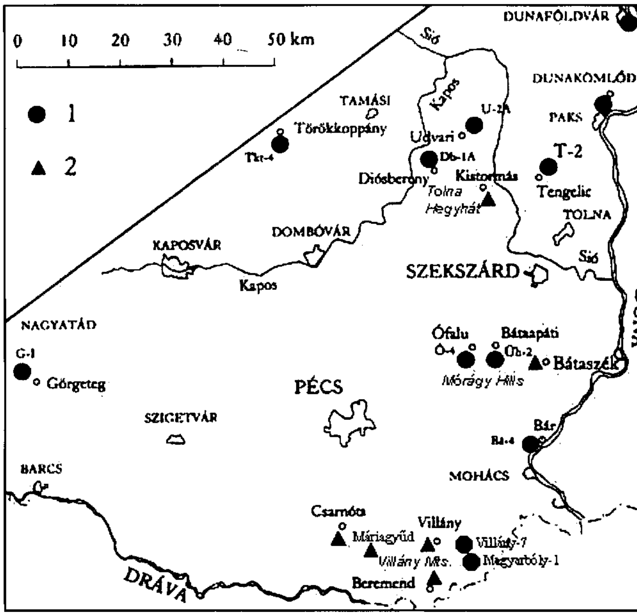

Fig. 1. Map showing SE Transdanubia and localities mentioned in the paper according to Koloszár (2004), modified. Legend: 1: borehole, 2: outcrop.

Mineralogical data related to the Pliocene to Quaternary sediments of the area were collected and evaluated as well as history of the former mineralogical investigations was given by Viczián (2002a). Karstic sediments of the Villány Mts. were recently investigated in detail by Marsi and Koloszár (2004) and by Dezső et al. (2007). Specimens of special bauxitic composition were investigated by Császár and Farkas (1984). The mineralogy of red clays in the wider surrounding territory was investigated by Földvári and Kovács-Pálffy (2002). They compared three stratigraphic units, (1) loess, (2) palaeosols in the loess, and (3) the Tengelic Red Clay Formation in the Tolna Hegyhát and Mórágy Hills areas. Diagnostic values were set up by which these units can be distinguished.

The core material of some of the boreholes penetrating the Pannonian basin sediments was analysed in the Geological Institute of Hungary and the data are available as unpublished reports. Most published reports contain quantitative data on the mineralogical composition. The aim of the present study is to collect and evaluate these quantitative data and to compare the results with those obtained from geomorphologic and palaeontologic studies.

METHODS

Quantitative data related the mineralogy of the samples have been obtained first of all by the X-ray diffraction analysis. In most cases data were corrected by comparison with the results of thermal analysis of Mária Földvári.

The majority of the measurements were carried out in the X-ray laboratory of the Geological Institute of Hungary. The instrumental parameters are the following: Philips PW 1710 type X-ray diffractometer, CuKα radiation, 40 kV, 30 mA, graphite monochromator, goniometer speed: 2 °/min. The X-ray diffraction analysis for the samples considered in the paper by Dezső et al. (2007) was carried out in the laboratory of the Department of Earth and Environmental Sciences, University of Pannonia, Veszprém, by Béla Raucsik. Here the instrumental parameters were very similar: Philips PW 1710 type X-ray diffractometer, CuKα radiation, 40 mA, 50 kV, slits: 1°-1°, proportional counter, graphite monochromator. The X-ray diffraction patterns obtained in Veszprém were evaluated quantitatively in the same way as the patterns obtained in the Geological Institute of Hungary.

Normally in each sample the bulk rock and the <2 μm fraction were investigated. The <2 μm fraction was obtained by sedimentation. The following preparations were used: for bulk samples: random powder preparations and for the <2 μm fraction: oriented samples on a glass plate made by pipette method and dried at laboratory temperature. The oriented specimens were investigated in untreated form and after saturation with ethylene glycol. Only the basal reflections of clay minerals were compared in the <2 μm fraction samples, in order to avoid orientation problems. For the bulk samples the total composition was considered.

The quantitative method used is the standard method of the Geological Institute of Hungary which is based on the works of Náray-Szabó and Péter (1967), Viczián (1967), Rischák and Viczián (1974) and Szemerey-Szemethy (1976). The basic idea of the method is the direct comparison the intensities of selected reflections of minerals. The intensities are multiplied by experimentally determined or estimated factors which enable the direct comparison of the intensities obtained from minerals of different composition and different structural order. Slight differences may occur in the factors applied, depending on the person carrying out the analysis. Considering these circumstances the results obtained cannot be considered as strictly quantitative and have to be considered with some precaution, however, the data obtained are sufficiently uniform to enable comparison of the composition of samples and to reveal basic tendencies in the variation of the composition.

RESULTS

Table 1 contains the source of quantitative data considered in the present review. The data of 180 quantitative analyses of the bulk composition and 129 analyses of the <2 μm fraction were collected. In the table the formations studied are listed according to their relative stratigraphic age.

Results relating the quantitative composition of the various sediment types were summarised in form of triangular diagrams constructed for the bulk composition and for the <2 μm fraction, respectively. In the triangles the 3 vertices represent the percentages of groups of mineral species. The minerals were grouped according to their presumed genetic significance.

In the diagrams relating the composition of the *bulk rock*, these groups are the following:

Carbonate minerals: calcite, aragonite, magnesian calcite, dolomite, siderite. Among these minerals only calcite is abundant, the others are very rare. The calcite contents of the samples are very variable, in most cases however, it does not bear much significance in respect of the provenance of the silicate phase. In the fissure fillings calcite is either secondary precipitation from the karstic water or is the material of limestone blocks that were broken down from the wall of the fissure. It has more significance in the lacustrine basin sediments. In the reduced basin sediments pyrite occurs which was included into this group.

Detrital minerals and products of moderate weathering: The minerals quartz, plagioclase, potassium feldspar, the clay minerals illite and chlorite were considered as detrital phases not affected by weathering. In most cases it can be demonstrated that illite is the well crystallised 2M modification. The clay minerals smectite, mixed-layer illite/smectite and vermiculite however, may be the product of moderate weathering of the former detrital phases under relatively dry climatic conditions. They are here considered together with the unchanged detrital phases, but in diagrams of the <2 μm fraction they will be treated separately.

Products of intense weathering: The phases listed here are considered to be formed during strong weathering under warm and humid circumstances. The most abundant mineral is kaolinite which is typically very disordered and forms mixed-layer structures with smectite. Several oxides and hydroxides are formed during intense weathering, such as the iron minerals goethite, hematite, (lepidocrocite) and amorphous iron hydroxides and the Ti-minerals anatase and rutile. An important member of this group is the bauxite mineral gibbsite.

In the diagrams representing the composition of the *<2 μm fraction* only the relative amounts of the clay minerals and gibbsite were considered. The 3 groups shown on the 3 poles of the triangles are the following:

Table 1. Sources of quantitative mineralogical data on Pliocene to Lower Pleistocene sediments in SE-Transdanubia.

Type of sediment	Locality	Stratigraphic position	Number of analyses Bulk rock	<2 μm	X-ray analyst	References
Grey clay, fissure filling	Magyarbóly-1 borehole	Miocene?	-	2 (<0.06mm)	G. Rischák, revised by I. Viczián	Rischák (1987): unpublished report
Lacustrine and terrestrial sed.	Magyarbóly-1 borehole	Szák Fm., Upper Pannonian, Quaternary	18	11	I. Viczián	Viczián (1988): unpubl. rept., Ta-nács, Viczián (1995)
Lacustrine and terrestrial sed.	Villány-7 borehole	Upper Pannonian, Quaternary	15	-	I. Viczián	Viczián, Földvári (1988): unpubl. rept.
Red bauxitic clays, fissure filling	Beremend	Upper Cretaceous? - Tengelic Fm.?	4	-	L. Farkas	Császár, Farkas (1984)
Red clays, filling of a broad hole	Beremend, locality No. 26	Tengelic Fm., Beremend Member	48	40	P. Kovács-Pálffy	Marsi et al. 2001: unpubl. rept., Marsi, Koloszár (2004)
Yellow silts, fissure filling	Villány, Somssich Hill, locality No. 2	Lower Pliocene	14	-	A. Szemethy, revised by I. Viczián	Szemethy, Földvári (1978): unpublished report
Red clays, terrestrial sed., eluvial-deluvial and residual facies	Bár-5, Tengelic-2 boreholes, Mórágy Hills, Tolna Hegyhát	Tengelic Fm., Tengelic Member	34	32	I. Viczián, P. Kovács-Pálffy	Viczián (1971, 1979): unpubl. rept., Halmai et al. (1982), Földvári, Kovács-Pálffy (2002)
Red clays, palaeosols	Mórágy Hills, Tolna Hegyhát	Basal layers of Paks Loess Fm. (PD, Pv_1-v_5)	27	27	P. Kovács-Pálffy	Földvári, Kovács-Pálffy (2002)
Various karst-related sediments	Villány Mts.	U. Pannonian, Tengelic Fm., basal layers of Paks Loess Fm. (PD)	21	17	B. Raucsik, revised by I. Viczián	Dezső et al. (2007)

Detrital minerals: Illite and mixed-layer illite/smectite, *if* the composition is close to the pure illite.

Products of moderate weathering: As it was discussed in the case of the bulk rock, the minerals smectite and vermiculite are considered here. Mixed-layer illite/smectites belong to this group when their composition varies in wide ranges or is close to pure smectite. Also mixed-layer kaolinite/smectite was listed here, first of all because of methodological reasons, because it cannot be separated safely from pure smectite. However, it is already transition to the intense weathering.

Products of intense weathering: Kaolinite, which is in high amounts, is always very disordered and randomly oriented. The product of the strongest leaching is gibbsite.

In the following the SE-Transdanubian red clay and related formations will be briefly described according to their approximately decreasing geological age. Mineral composition will be characterised using the two triangular compositional diagrams.

Grey clay fissure filling in the Magyarbóly-1 borehole (older than Upper Pannonian)

In the Magyarbóly-1 borehole, a few kilometres away in SE direction of the Villány Mts. Jurassic limestone was cut under the covering Pannonian sediments. There are numerous fissures in the limestone filled with grey or

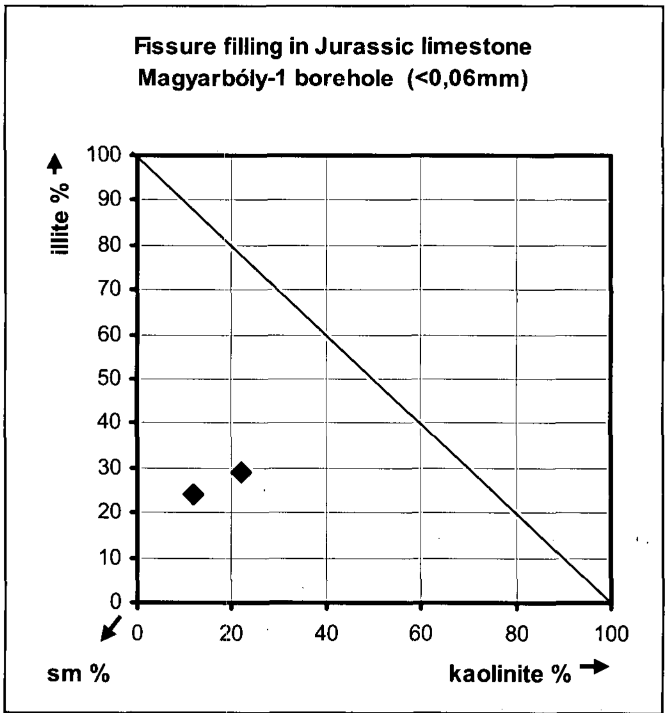

Fig. 2. Clay mineral composition of fissure filling clays in Jurassic limestone, Magyarbóly-1 borehole (<0,06mm).

greenish grey clay. The <0.06 mm fraction of two grey clay samples were analysed (Fig. 2). The clay mineral assemblage is rich in smectite, there is relatively much kaolinite while chlorite is absent. This indicates moderately weathered sedimentary material. The age of the emplacement in the fissure must be older than the oldest covering formation on the top of the limestone, i.e. the Lower Pannonian Szák Fm., and is probably contemporaneous with a tectonic phase which produced the fault system (presumably old Cainozoic, according to Koloszár, 2004). The age of the formation of the corresponding weathering crust on the ancient surface is even more uncertain but may be partly much older than the age of the filling of fissures.

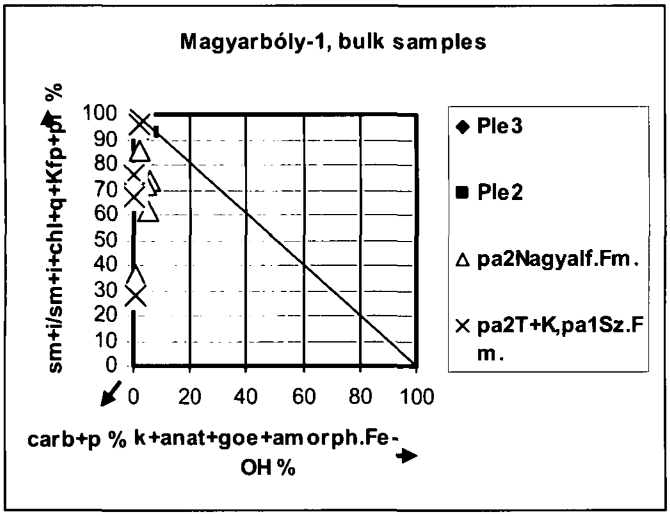

Fig. 3. Mineral composition of bulk samples of fine-grained sediments in Magyarbóly-1 borehole. Legend: Ple2: Middle Pleistocene, Ple3: Upper Pleistocene, pa2Nagyalf.Fm.: Upper Pannonian Nagyalföld Formation, pa2T+K,pa1Sz.Fm.: Upper Pannonian Tihany and Kálla Formations and Lower Pannonian Szák Formation.

Lacustrine and terrestrial sediments in basins adjacent to the Villány Mts. (Pannonian)

There are mineralogical analyses available on the core material from the boreholes Magyarbóly-1 and Villány-7, which are in the immediate vicinity of the eastern end of the Villány Mts. In these boreholes the Lower Pannonian Szák, the Upper Pannonian Kálla, Somló, Tihany and Nagyalföld Formations and Quaternary sediments occur (according to unpublished core descriptions by Jámbor, 1986). In the diagrams representing the whole rocks of the boreholes (Fig. 3 and Fig. 4, respectively) the high variation in the carbonate contents is conspicuous. In the Pannonian there may be high carbonate contents which are not only calcite but also dolomite, sometimes in very high amounts, and magnesian calcite in the Szák Formation. On the other hand, Quaternary sediments in these boreholes are almost carbonate-free. The non-carbonate components are clearly not weathered or moderately weathered. The clay fraction was investigated only in the Magyarbóly-1 borehole. In the diagram (Fig. 5) there is a wide scatter in the low-kaolinite domain, the dominant clay minerals are illite, smectite and mixed-layer illite/smectite. Chlorite and kaolinite are less abundant, they occur in nearly equal amounts, kaolinite however, seems to increase up to almost 20 % with increasing smectite contents. The latter composition corresponds to slightly more weathered material. The variation in the illite to smectite ratio seems to be independent from the stratigraphic position. The scatter is as high in the Pannonian formations as in the Quaternary sediments.

All these features are in accord with the usual composition of the Pannonian and Quaternary basin sediments as found elsewhere in the Pannonian Basin (see e.g. Viczián, 1984, 2002a,b, Tanács and Viczián, 1995) and

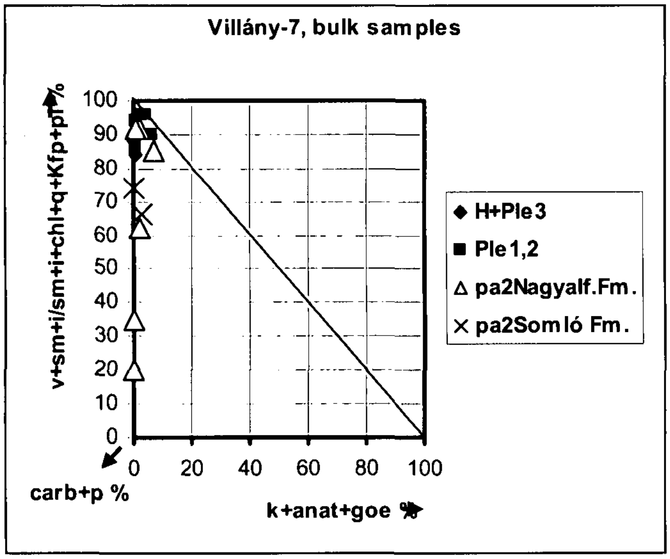

Fig. 4. Mineral composition of bulk samples of fine-grained sediments in Villány-7 borehole. Legend: H+Ple3: Holocene and Upper Pleistocene, Ple1,2: Lower and Middle Pleistocene, pa2Nagyalf.Fm.: Upper Pannonian Nagyalföld Formation, pa2SomlóFm.: Upper Pannonian Somló Formation.

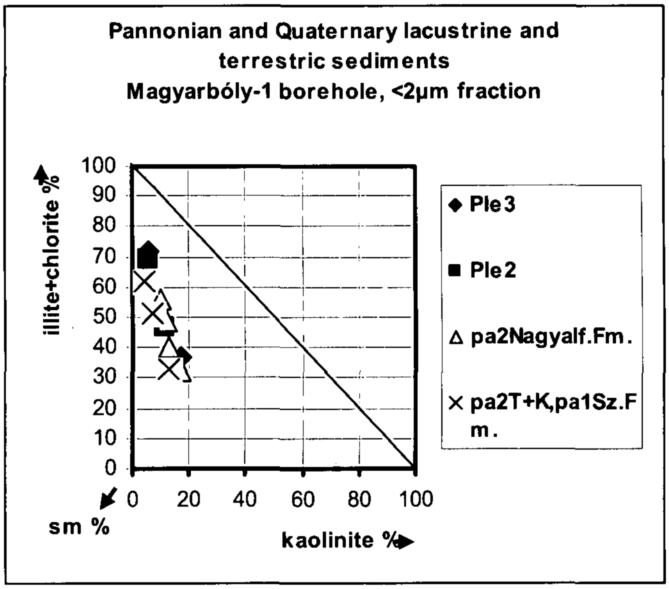

Fig. 5. Clay mineral composition of Pannonian and Quaternary fine-grained sediments, Magyarbóly-1 borehole, <2μm fraction. Legend: see Fig. 3.

are quite different from the composition of the more or less weathered terrestrial sediments preserved in fissures and karstic depressions of the Villány Mts.

Red clays of the Tengelic Formation. Overview of the startigraphic relations and regional distribution

The red clays are widespread in the hilly and mountainous areas of SE Transdanubian area underlying the Pleistocene Paks Loess Formation. Their mineralogy was studied very early by Földvári Vogl by the DTA method (Vadász 1968). Later Szöőr studied these clays by derivatographic thermal and IR methods (Schweitzer, Szöőr 1997, Schweitzer 1993). They recognised that among the red clays two compositional groups can be subdivided: one rich in kaolinite and one rich in illite and smectite.

The kaolinite-rich variety is restricted to the karstic surfaces of the Villány Mts. and it seems to be the older variety (*"Beremend Member"* of the *Tengelic Fm.*, Koloszár 2004). Examples are the localities Siklós, Vokány, Villány, Beremend and Csarnóta which were studied by X-ray diffraction and thermal methods by Bidló (1980, 1983b, 1985). He was the first to recognise the extremely disordered character of the kaolinite in these clays. Red clays occurring at Beremend were investigated recently by Dezső et al. (2007).

The illite-smectite-rich variety is more widespread. It occurs in the hilly areas and is generally younger (*"Tengelic Member"*of the *Tengelic Fm.*, Koloszár 2004). The red clay is the uppermost bed of a 25-60 m thick sequence consisting from the bottom upward of alluvial sand, occasional bentonite derived from basalt tuff, eluvial-deluvial variegated clay and clayey silt and finally the red clay which is of eluvial-deluvial and residual facies. The whole sequence itself deposited with considerable hiatus on the eroded surface of Upper Pannonian sediments. Its age is supposed to be Lower Pleistocene. The thickness of the red clay is varying between a few metres up to nearly 20 m. The red clay beds are overlain by another red clay beds which are the starting members of the Paks Loess Fm. The colour is actually less deep red and has been called "reddish" by Schweitzer and Szöőr (1997).

Red bauxitic clays in the Beremend quarry (Upper Cretaceous?, Beremend Member of Tengelic Fm.)

In the limestone quarry at Beremend red bauxitic clays filling fissures and karstic depressions were described by Császár and Farkas (1984). They published 4 mineralogical analyses, the data of which are shown in the diagram of Fig. 6. The samples differ in carbonate contents. The carbonate-free composition is essentially the same, kaolinite varies between 50-60 %, the bauxite mineral is gibbsite which varies between 2 and 21 %. Typical bauxitic features are the absence of quartz and the presence of anatase, hematite and goethite, but clay minerals like montmorillonite and illite and the very strongly disordered nature of kaolinite are not typical for bauxites. The sample most interesting from the point of view of bauxites is that with 21 % gibbsite and with somewhat better ordering of kaolinite, because of the low gibbsite contents however, even this sample may be called only bauxitic clay according to the classification of Bárdossy (1982, Fig. 66). The authors stressed the difference from the known Lower Cretaceous Harsányhegy Bauxite Fm. because it is surely older than the Nagyharsány Limestone Fm., and because there is no gibbsite in the Harsányhegy Bauxite Fm., where the aluminium minerals are boehmite and diaspore (Dudich, Mindszenty 1984) or diaspore alone (Császár 2002, Table 6 and Table 7, analyses by J. Bognár and M. Földvári).

The age of the bauxitic clay is uncertain. In contrast to the Harsányhegy Bauxite, Császár and Farkas (1984) considered the bauxitic clays of Beremend to represent an "upper" or "second bauxitic horizon". They pointed out that it must be younger than the Lower Cretaceous Nagyharsány Limestone Fm. which is the host rock, but the upper limit is not known because of the lack of covering formation. They tentatively suggested Upper Cretaceous age, either older that the Bisse Marl Fm., or most probably younger than the post-Senonian general uplift and denudation. The same opinion was repeated in the monograph of Császár (2002) and in the field guide by Kordos, Császár (2004). They remarked however that in this case there is not much chance for preservation of a deposit of economic value because the territory remained uncovered until the Miocene. The question of the age of the gibbsite-bearing samples will be discussed later in a separate chapter.

Red clays, filling a broad hole in the Beremend quarry (locality No. 26, Beremend Member of the Tengelic Fm.)

In the Beremend quarry a huge pile of red clay of 24 m height and of diameter of several tens of m was left over by the mining which is the remnant of the filling of a broad karstic depression. The locality listed as No. 26 was subject of detailed study by Marsi and Koloszár (2004). The column was subdivided into 5 horizons and mineralogical analysis was made from samples taken from each half meter. Quantitative X-ray data made by P. Kovács-Pálffy are

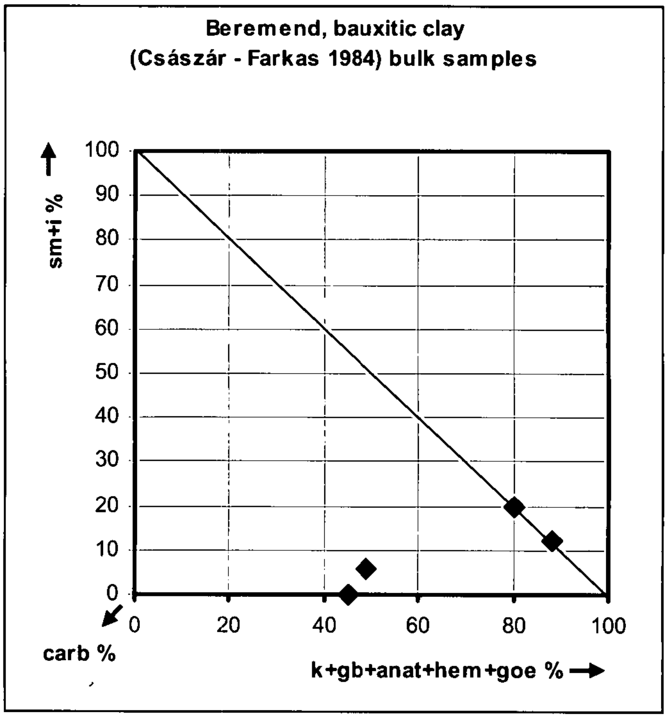

Fig. 6. Mineral composition of bauxitic clays, Beremend quarry, bulk samples (Császár, Farkas 1984).

included into the unpublished report by Marsi et al. (2001). In the diagram of the bulk rock composition (Fig. 7) and of the <2 μm fraction (Fig. 8) the data of each horizon are shown separately. The whole set of data is remarkably uniform: the ranges of scattering of the points in each horizon overlap each other, but the average values for each horizon are nearly the same. Some variation is due only to the carbonate contents in the bulk composition, higher carbonate contents arise from blocks of the host rock which is indifferent from the point of view of genesis of the red clay. This uniformity is in accord with the results of the palaeontological determination which has shown relatively short time interval, about 2 hundred thousand years for the emplacement of the sequence. The age of the deposition of the material in the depression is 3.1 to 3.3 million years according to the Vertebrate fossil studies by Kordos (2001). The locality is the stratotype of the Beremend Member of the Tengelic Formation as proposed by Koloszár (2004).

The mineralogy of the bulk rock (Fig. 7) shows almost carbonate-free, moderately weathered, smectite dominated material. In the composition however, disordered kaolinite is the second abundant clay mineral and also hematite and Ti-oxides are present. Quartz is moderately frequent (10-20 %), illite is low (less than 10 %). In the <2 μm fraction (Fig. 8) the dominance of kaolinite is more striking (60-80 %), smectite is low (<10 %), the second clay mineral is illite+illite/smectite (20-40 %). Kaolinite is very disordered with transitional phases to smectite. No gibbsite was found in this locality (only traces in two samples). The authors consider that the source material of this red clay filling was mainly a locally developed weathering crust on the top of the isolated elevation of the limestone block at Beremend.

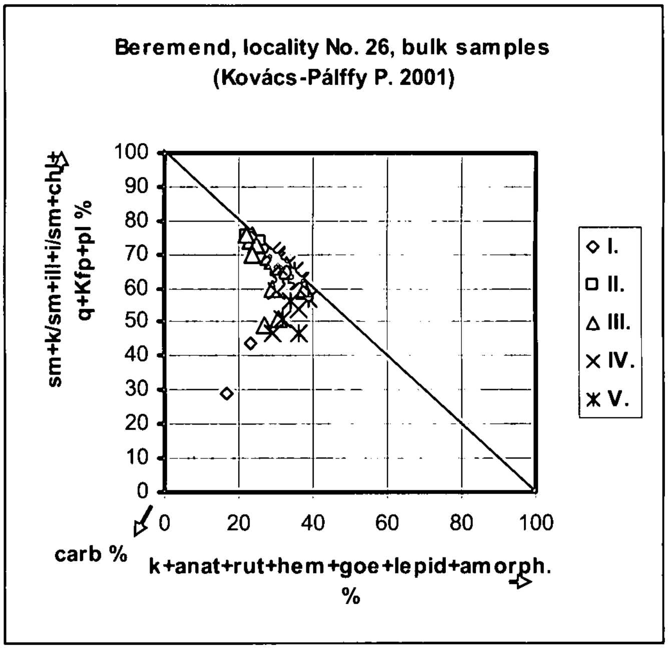

Fig. 7. Mineral composition of red clays, Beremend quarry, locality No. 26, bulk samples (Kovács-Pálffy P. 2001, see Table 1). Legend: I., II., III., IV., V.: horizons from top to bottom.

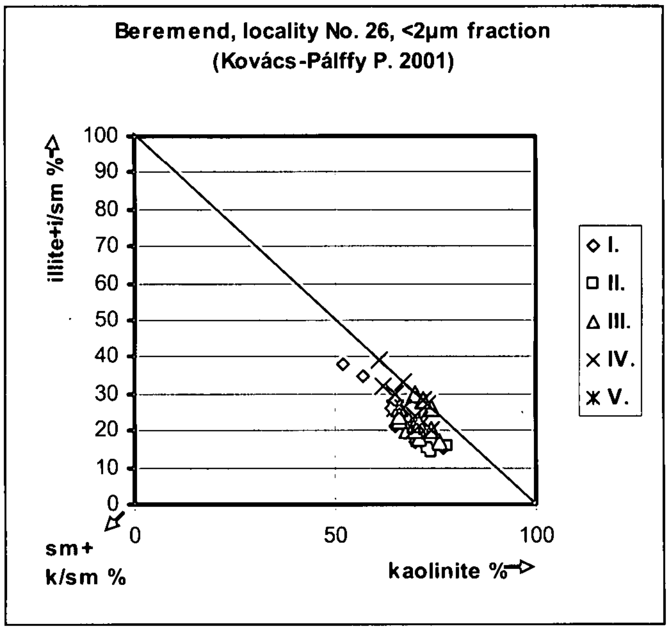

Fig. 8. Clay mineral composition of red clays, Beremend quarry, locality No. 26, <2μm fraction (Kovács-Pálffy P. 2001, see Table 1). Legend: see Fig. 7.

Yellow, fissure filling silts at Villány, Somssich Hill, site No. 2 (Lower Pleistocene)

Somssich Hill is an important locality of Vertebrate fossils on the eastern end of the Villány Mts., near the town Villány. At site No. 2 the fissure developed in Upper Jurassic Szársomlyó Limestone and is filled with yellow silty material. The age of the fossils found here is *Templomhegy* stage in Vertebrate stratigraphy, Lower Pleistocene (Jánossy 1986) which corresponds to 0.9 million years. According to the Mollusc studies of Krolopp (2000) the fauna indicates the Lower Pleistocene cooling period.

The composition of the rocks is different from the red clays previously discussed. As it can be seen on the diagram of Fig. 9, the samples contain about 20-40 % carbonate which is exclusively calcite. The silicate phase contains medium quartz (15-30 %), little feldspar. Kaolinite is very low, together with some iron minerals such as goethite and amorphous iron hydroxide, their amount is less than 10 %. The dominant clay mineral is detrital illite, in the diagram the whole compositional range is close to the non-weathered pole of the triangle. The general character of the composition is transitional to that of true loess (Kordos, 1978, unpublished report).

There seems to be some vertical zoning: kaolinite occurs in the lower part of the sequence while in the upper part little chlorite appears instead of kaolinite. In a similar manner, the ecological character of the Vertebrate fossils shifts toward the top of the outcrop what was interpreted by Jánossy (1986) as an episode in the general trend of cooling of the climate in the Early Pleistocene. The shift in the mineralogy is in good agreement with his conclusion.

Red or reddish clays of Tengelic Formation in the wider surrounding of Villány Mts. (Tengelic Member of the Tengelic Fm.)

In the hilly areas, at Tétel-halom (SE of Solt) and at Dunaföldvár mixed-layer illite/smectites were identified as the main clay minerals in red clays, accompanied by little kaolinite at Dunaföldvár (Borsy and Szöőr 1981). It was again Bidló (1983a) who analysed first red clays in this area by X-rays and found dominantly disordered kaolinite in a sample from Dunaújváros (this exceptional composition in the hilly areas indicates probably an occurrence of the *"Beremend Member"*).

The first quantitative X-ray diffraction analyses from the hilly areas were made on a sample of red clay underlying the basalt lava flow at Bár (Viczián 1971). The eruption of the basaltic volcano at Bár (Viczián 1965) occurred before 2.17 Ma, during the period of accumulation of the Tengelic Red Clay Fm. and produced lavas of a potassium rich basaltic rock (Hőnig 1971 in Szederkényi 1980, Balogh et al. 1986). In the borehole Bár-4 loess-containing clay covers and brick red and bright red clay of 12 m thickness underlies the basalt flow. In borehole Bár-5 loess and brick red clay of 14.5 m thickness alternating with loess intercalations covers and 2.6 m brick red clay underlies the basalt flow. In borehole Bár-6 loess with intercalations of red clay overlies basalt. The borehole stopped within the basalt. There are vertical fissures in the central part and vesicles in the upper margin of the basalt flow filled with red clay. The sample studied was taken from the borehole Bár-5, 53.3-53.7 m. This is near to the lower margin of basalt. The composition does not show strong contact effect because it contains much smectite. In addition to smectite it is a typical "detrital" assemblage, much quartz, muscovite, illite, feldspars. There is almost no carbonate, the iron mineral is hematite. The sample can be considered to be an older deposit of the *Tengelic Member* of the *Tengelic Formation.* Its composition fits well into the group of samples of the same unit (Fig. 10).

Later two brownish red clay samples were studied from the Tengelic-2 borehole (Viczián 1979, see Halmai et al. 1982). This borehole gave the name of the *Tengelic Formation* and the sequence found here is now proposed to be the stratotype of the *Tengelic Member* of the formation (Koloszár 2004).

The mineralogy of these "reddish" clays of the has been extensively studied in the last years in connection with the prospecting for disposal of radioactive waste materials. Detailed geological and palaeopedological studies were carried out on occurrences of the Tengelic Fm., such as in the Tolna Hegyhát area by Jámbor (1997), for borehole Udvari-2A: Koloszár (1997), for borehole Diósberény-1A: Marsi (1997) and in the Mórágy Hills area. For the Mórágy Hills see papers by Koloszár and Marsi (1999), Koloszár et al. (2000), Marsi (2000, 2002) and Marsi et al. (2004).

In the present chapter only the relations of the quantitative mineralogical composition of the younger, illite-smectite-rich type are considered. The partly unpublished X-ray diffraction data were collected and made available for our statistical study by M. Földvári. The data comprise samples from the Udvari-2A and Diósberény-1A boreholes from the Tolna Hegyhát area and from the Üveghuta boreholes from the Mórágy Hills area.

In the diagram showing the bulk composition (Fig. 10) data points are concentrated around the non-weathered to moderately weathered pole of the triangle. No significant differences can be recognised between the Mórágy Hills and Tolna Hegyhát areas. Carbonate is usually very low, there is, however, not solely calcite, but a little dolomite, too.

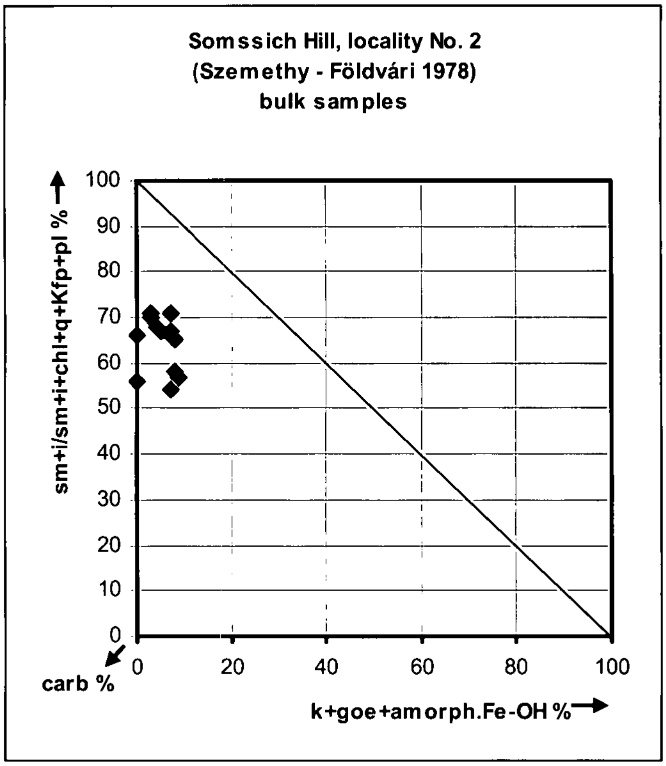

Fig. 9. Mineral composition of yellow clays, Somssich Hill, locality No. 2, bulk samples (Szemethy, Földvári 1978, see Table 1).

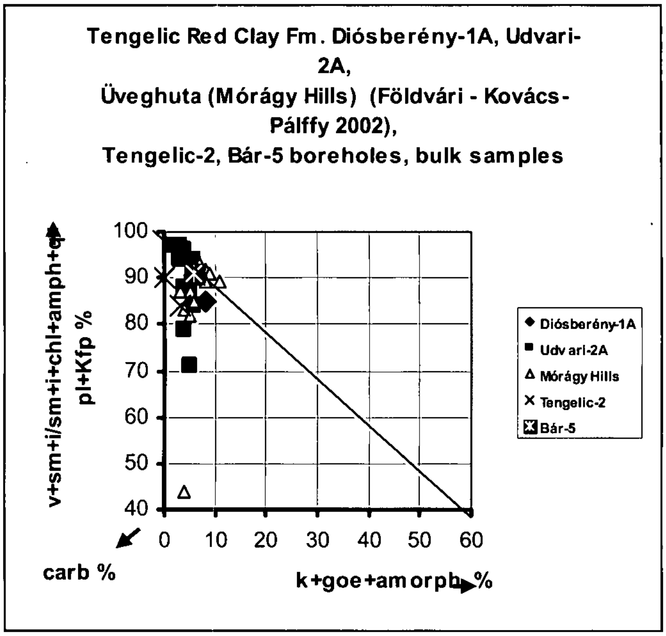

Fig. 10. Mineral composition of Tengelic Red Clay Formation, Diósberény-1A, Udvari-2A, Üveghuta (Mórágy Hills) (Földvári, Kovács-Pálffy 2002), Bár-5, Tengelic-2 boreholes, bulk samples.

Kaolinite is absent or less than 3 %, a few per cents of crystalline or amorphous iron hydroxides are responsible for the red or "reddish" colour of the samples. Among the not weathered silicate minerals quartz is sometimes very abundant ranging from about 35 to 60 %. Marsi (2000) recognised enrichment of resistant minerals such as quartz in the samples of Tengelic Fm. He thinks that it indicates "long-lasting semi-arid weathering". The feldspars plagioclase and potassium feldspar are well represented in every sample which again indicates absence of strong weathering. Among the clay minerals smectite is the most widespread (15-30 %). Smectite is in some samples replaced by vermiculite. Other clay minerals are in decreasing order illite and chlorite, both are well crystallised.

Comparing these data with the average values for the Tengelic red clays published by Földvári and Kovács-Pálffy (2002) we can find good agreement. In general, they have found that these clays are poor in carbonates (calcite and a little dolomite), plagioclase, illite and chlorite and contain predominantly smectites among the clay minerals. They also stressed the very low kaolinite contents (less than 2 %) and recognised that smectite can be replaced by vermiculite. They have found Mórágy Hills (Üveghuta boreholes) to be somewhat more weathered than the Tolna Hegyhát area. This is more evident in our study from the <2 μm fraction.

Among the clay minerals of the <2 μm fraction (Fig. 11) either illite, or the 14 Å minerals (smectite or vermiculite) are the main clay minerals. Kaolinite is generally low. There is large scatter in the illite to (smectite+vermiculite) ratio. A high variety of mixed-layer structures between vermiculite, smectite, chlorite and illite was identified. Vermiculitic minerals seem to be preferably associated with high illite contents and chlorite, while samples with lower illite contents tend to contain rather smectite and somewhat more kaolinite. This variation can be interpreted by two types of assemblages. There is a very weakly weathered assemblage with dominant illite + chlorite and vermiculite and a moderately weathered assemblage with dominant smectite + illite and kaolinite. As for the regional differences, according to the composition of the <2 μm fraction the red clays of the Mórágy Hills area tend to be somewhat more weathered than those of the Tolna Hegyhát area.

In conclusion, red clay samples in the wide hilly surrounding of the Villány Mts. belonging to the Tengelic Member of the Tengelic Formation reveal little or moderate weathering and oxidation of the terrestrial sedimentary material.

Red palaeosol beds at the base of the Paks Loess Formation in the wider surrounding of Villány Mts.

During the studies connected with the radioactive waste disposal a group of red clays was separated from the Tengelic Fm. and was considered as an independent stratigraphic unit. These are red clays on the basis of the Middle Pleistocene Paks Loess Fm., their stratigraphic position is Lower Pleistocene to lowermost Middle Pleistocene (0.8 to ~1.2 million years). The stratigraphic position is given by the scheme of Koloszár and Marsi (2002). Geology and mineralogy of the palaeosol is treated in the same papers which were cited in the former chapter on the Tengelic Red Clay. In particular, Marsi and Koloszár (2004) identified the red palaeosol layer in the Beremend quarry with the *"Paks Double" soil complex* (PD, 0.8 my). Red palaeosols found in the Diósberény-1A and Udvari-2A boreholes were correlated with the soil beds Pv_I-v_5 and PA (Jámbor, 1997). In the Mórágy Hills area red palaeosols belong to the PD horizon (Koloszár, Marsi 2002).

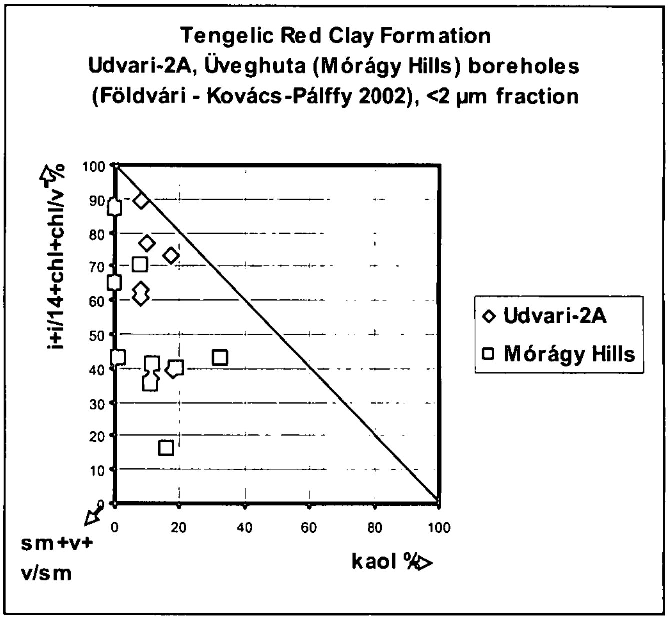

Fig. 11. Clay mineral composition of Tengelic Red Clay Formation, Udvari-2A, Üveghuta (Mórágy Hills) boreholes (Földvári - Kovács-Pálffy 2002), <2 μm fraction.

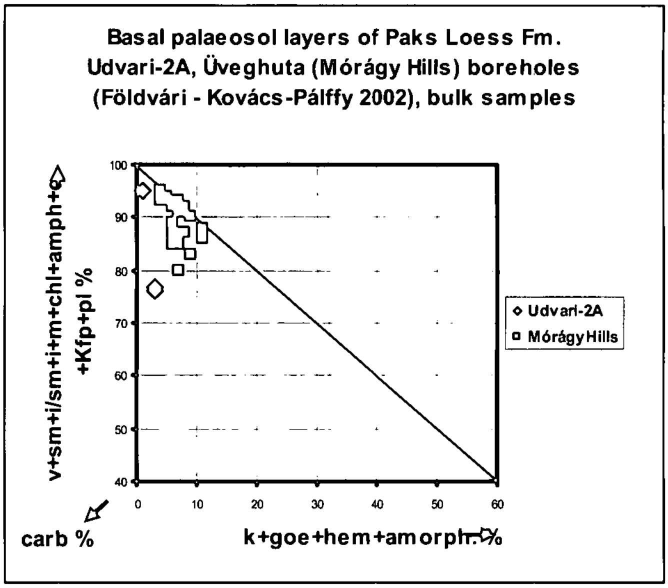

Fig. 12. Mineral composition of Basal Palaeosol layers of Paks Loess Fm., Udvari-2A, Üveghuta (Mórágy Hills) boreholes (Földvári - Kovács-Pálffy 2002), bulk samples.

Similarly to the Tengelic Fm., quantitative mineralogical data were obtained by the courtesy of M. Földvári.

Considering the diagrams for the bulk composition (Fig. 12) and for the <2 μm fraction (Fig. 13) the similarity with the corresponding diagrams of the Tengelic Fm. is conspicuous. General quantitative relations of the minerals in the bulk composition of the Tengelic samples can be applied also for the red palaeosol layers. This fact indicates similar genetic relations for both stratigraphic units. In the <2 μm fraction the differences are more visible. Smectite contents seem to be generally higher and illite and chlorite are lower in the Tengelic clays than in the palaeosol. This observation agrees with the results of Földvári and Kovács-Pálffy (2002) who demonstrated in more detail that there are significant differences between the Tengelic red clays and the palaeosols in several parameters. They have found higher smectite, total clay mineral, H_2O and (H_2O+OH) contents and lesser illite, chlorite and plagioclase carbonate contents. In general, they have shown higher degree of weathering in the Tengelic Formation than in the palaeosol.

Various karst-related sediments in the Villány Mts. area (Upper Pannonian, Tengelic Fm. and Paks Loess Fm.)

In a comprehensive study completed recently (Dezső et al. 2007) the filling sediments of fissures and caves of various origin were investigated in the central and SE part of the Villány Mts. The sites studied are often closely related to famous localities of fossil Vertebrate fauna. The filling sediments represent various red clays, redeposited loess and in some cases sandy siltstones and products of their disintegration.

The mineralogical composition was determined in the bulk samples (Fig. 14) and in the <2 μm fraction (Fig. 15) by X-ray diffraction. Two types of the mineral associations can be distinguished.

In the *weakly or moderately weathered type* the clay minerals are represented by variable amounts of illite and smectite, less kaolinite or chlorite, fairly much quartz and feldspars. Kaolinite is medium ordered. The iron mineral is dominantly goethite. Weakly or moderately weathered associations can be found

- in Nagyharsány quarry in the debris of the overlying Pannonian siltstone and in redeposited loess,
- in Beremend quarry in the red palaeosol that covers the limestone and underlies the loess and in a few red clay fissure fillings in the limestone and
- at the town Villány in clays deposited in the caves Borpince and Templomhegy-zsomboly (shaft cave).

In the *intensely weathered type* the main clay mineral is strongly disordered kaolinite accompanied by smectite and mixed-layer kaolinite/smectite. There are anatase and rutile and gibbsite appears in lesser or medium amounts. Usually

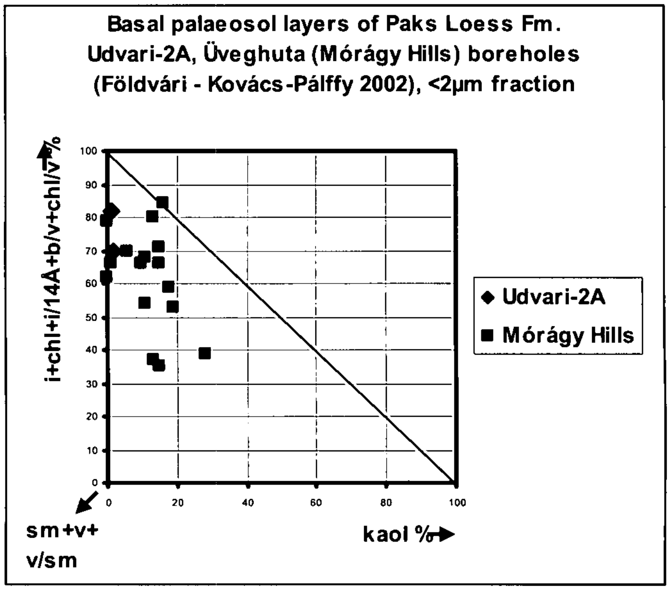

Fig. 13. Clay mineral composition of Basal Palaeosol layers of Paks Loess Fm., Udvari-2A, Üveghuta (Mórágy Hills) boreholes (Földvári - Kovács-Pálffy 2002), <2μm fraction.

quartz is very low or missing. Normally hematite is more abundant than goethite. Such sediments were found

- in several fissure fillings of the Beremend quarry,
- in fine grained clays in the Macskalyuk cave at Máriagyűd.

There are two *transitional* samples between the two types well visible in Fig. 15: the lowermost filling in the Borpince cave at the town Villány, and a concretion from the Nagyharsány quarry.

Considering the age and stratigraphic position, the oldest formations studied in this particular set of samples from the Villány Mts. area are the remnants of the overlying Pannonian sandy siltstone which is normal lacustrine basin sediment. Highly weathered red clays belong to the starting period of terrestrial accumulation of the *Tengelic Red Clay Formation* (*Beremend Member*). For the sample that was taken from the locality No. 26 in the Beremend quarry (see

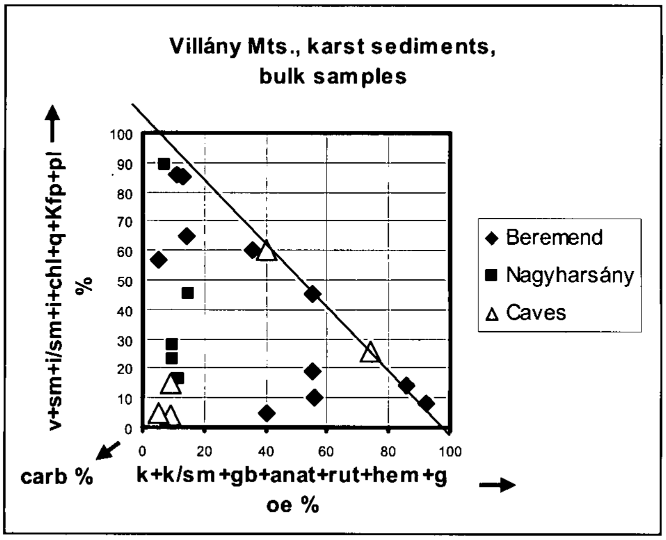

Fig. 14. Mineral composition of karst sediments, Villány Mts., bulk samples.

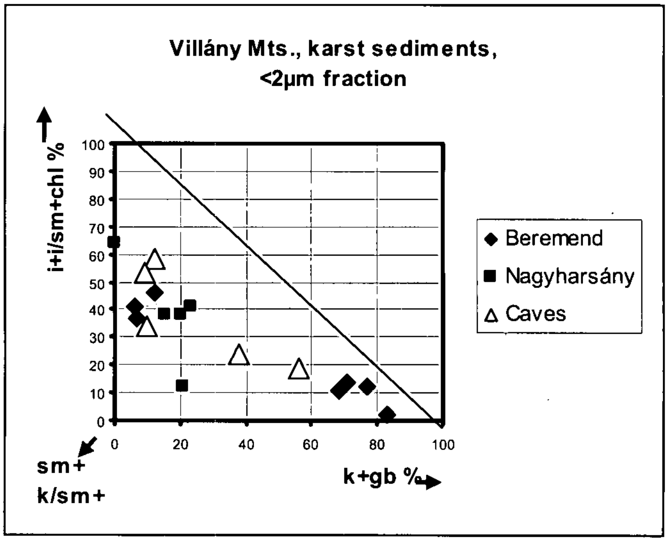

Fig. 15. Clay mineral composition of karst sediments, Villány Mts., <2μm fraction.

the corresponding chapter) this period can be dated to about 3.1 to 3.3 million years in the Pliocene but other red clays may have been deposited earlier or somewhat later. During the further, longer period of the accumulation of *Tengelic Red Clay Fm.* (*Tengelic Member*) as well as during the formation of the red palaeosol and of the loess the weakly or moderately weathered types were formed. Both highly and weakly weathered types may be found among the cave sediments depending on the time of transport and accumulation in the cave.

Discussion

The possible mechanical effect of the transport into the karstic cavities

The granulometry of the karstic sediments of the Villány Mts. was studied by the laser method by J. Dezső (see Dezső et al. 2007). Various environmental factors could be recognised by the statistical evaluation of the grain size distribution curves of fissure fillings and cave sediments, like the effects of aeolian transport, type of the parent rock, the weathering process and ways of underground sediment transport. Most cave sediments and concretions have distribution curves with a single maximum in the clay size domain. Distribution curves with a single maximum in the silt size domain are typical for the debris of the overlying siltstone, for the redeposited loess and for the red palaeosol underlying the loess. Red clay fissure fillings and some cave sediments display bimodal distribution curves with maxima both in the clay and silt domain.

The products of the surface weathering were transported into the karstic cavities by running or slowly infiltrating water. Slow infiltration with intermediate sediment traps may have produced separation of the grain size fractions, and accordingly, further enrichment of the fine-grained weathering products. This may be the case for the cave sediments, especially for the extremely fine-grained clays of the Macskalyuk cave at Mariagyűd. This clay bears only highly weathered mineral assemblage in the bulk composition because coarser, less weathered grains were sorted out during the infiltration (Fig. 14). On the other hand, highly weathered red clays in the karstic cavities of the Beremend limestone quarry are not extremely fine-grained. It was shown by Dezső et al. (2007) that all samples bearing gibbsite and kaolinite and some samples without gibbsite but with high contents of disordered kaolinite have equally bimodal grain size distribution and may be classified as silty clays. The amount of silt-size fraction is in no correlation with the gibbsite or kaolinite contents and the silt/clay ratio is near to 1.

A special way of displacement of the covering sedimentary material is the collapse of the overlying beds. In the Nagyharsány quarry a broad fault is filled with the debris of the overlying Pannonian siltstone. In this case the filling sediment is completely unsorted containing blocks of several 10 cm size embedded in a silt size matrix. The matrix has practically the same mineral composition as the blocks showing that there was no additional chemical alteration in the silt size debris.

All these considerations may concern only the bulk composition. Compositional differences in the <2 μm fraction should not be influenced by the amount of the coarser fraction in the sample and by the way of transport into the underground cavities.

Chemical action of the karst water

Most probably the water which transported the sediments from the surface into the fissures and caves did not modify their chemical composition. The loosely accumulated clay was later saturated by karst water. Under these conditions the possible formation of gibbsite from kaolinite and the possible transformation of other clay minerals into kaolinite are of special interest. Recent measurements have shown that the pH of the karst water below the Beremend quarry is near to neutrality (J. Dezső, pers. comm.). According to experimental data (see Bárdossy 1982, Fig. 157 and Fig. 158) both kaolinite and gibbsite are stable at pH = 7. The decisive factor for the formation of gibbsite from kaolinite is the silica content of the ground water. At concentrations H_4SiO_4 < 2 ppm kaolinite dissolves incongruently and gibbsite remains. When this would be the case, "intense percolation by ground water and a positive Eh made even a kaolinitic primary material yield gibbsite, a situation observed in numerous laterite profiles" (Bárdossy 1982, p. 322). The limiting concentration of silica may be even higher than 2 ppm. According to Lippmann (1981) the metastable equilibrium between kaolinite and gibbsite lies approximately at the activity value $[H_4SiO_4] \approx 8$ ppm.

We have analytical data of the silica concentrations from the water found in a shaft in the Beremend quarry. Here in dominantly Ca-Na hydrocarbonate waters the H_2SiO_3 concentration is 17.80 mg/l, water temperature: 26 °C. The water of the subthermal spring coming from the same limestone contains 2.60 mg/l H_2SiO_3 (20-21 °C) about 5 km away, at Kistapolca (analyses by S. Rapp-Sík, see Fülöp 1966, p. 42 and p. 40). H_2SiO_3 concentrations are in the range of 10-20 mg/l in cool, subthermal waters of similar composition in the Buda Mts. (see Schulhof 1957). We can estimate activity values of $[H_4SiO_4]$ in the range 2 to 20 ppm and this means that water composition is in the metastable stability field of kaolinite but close to the boundary toward gibbsite. Considering the concentration relations of silica gibbsite might have been formed occasionally in the subsurface conditions provided that there were fluctuations in the silica concentration and the water flow was sufficiently strong. On the other hand, montmorillonite (smectite) is surely to be transformed into kaolinite at these concentration values. It is persistent at much higher H_4SiO_4 concentrations than kaolinite (higher than about 0.01-0.1 % H_4SiO_4, Lippmann 1981). Transitional phases like mixed-layer kaolinite/smectite indicate intermediate steps in this transformation. One has to remark that the reaction in the reverse direction is excluded even because of the lack of sufficient silica.

The progress of chemical reactions would be supported by intense movement of water and high permeability. In most cases however, calcitic cement and void-filling druses precipitated from the karst water were observed. We can suppose that cementation prevented further water flow and completion of the progress of the reactions.

Gibbsite formation would require oxidising conditions. The recent descending water in the quarry has positive Eh but the ascending subthermal karst water is in reduced state (J. Dezső, pers. comm.). Therefore gibbsite from kaolinite and kaolinite from smectite have been formed more probably in the well drained and oxidised soil profiles on the surface than in the karstic fissures.

From the point of view of chemical action of the ground water the alteration of a basaltic dyke intruded into the limestone complex of the Beremend quarry may be of interest (Molnár, Szederkényi 1996, Nédli, M. Tóth 2003). The dyke is 1-3 m thick, highly altered. Its age is Upper Cretaceous. The alteration products were identified by XRD as calcite and nontronite. Another two basaltic dykes were described by (Fülöp 1966, the alteration by Viczián). Fülöp considered them to belong to the Lower Cretaceous magmatism but Nédli and M. Tóth (2003) suppose Upper Cretaceous age based on recent measurements and analogies. One dyke occurs in a quarry on the western end of the mountain range at Babarcszőlős. The dyke intruded into Upper Anisian dolomite is 10 to 190 cm thick, and is again highly altered on the rims. The altered rim may be 40-50 cm thick. Its colour is violet and red. The main alteration products are "limonite", calcite and montmorillonite but there is a few kaolinite too. A third dyke occurs in the borehole Turony-1, at 209-213 m. Its colour is grey but the groundmass and most feldspar are altered to nontronite. Nontronite was identified in microscope and by the 060 reflection in the XRD pattern. Additional clay minerals are little illite and mixed-layer illite/nontronite. The dykes never have been exposed to subaerial weathering until the recent mining works they still have highly altered rims. Their alteration must be the effect of the subterranean groundwater flow through the carbonate host rocks. Those being close to the recent surface are highly oxidised. In each case the main alteration product is a smectite mineral (nontronite) which can be accompanied by little illite in the lower levels and by kaolinite close to the recent surface. High amounts of kaolinite and gibbsite do not occur. All that shows that ground water or karst water may cause the transformation of silicatic material into a smectite group mineral.

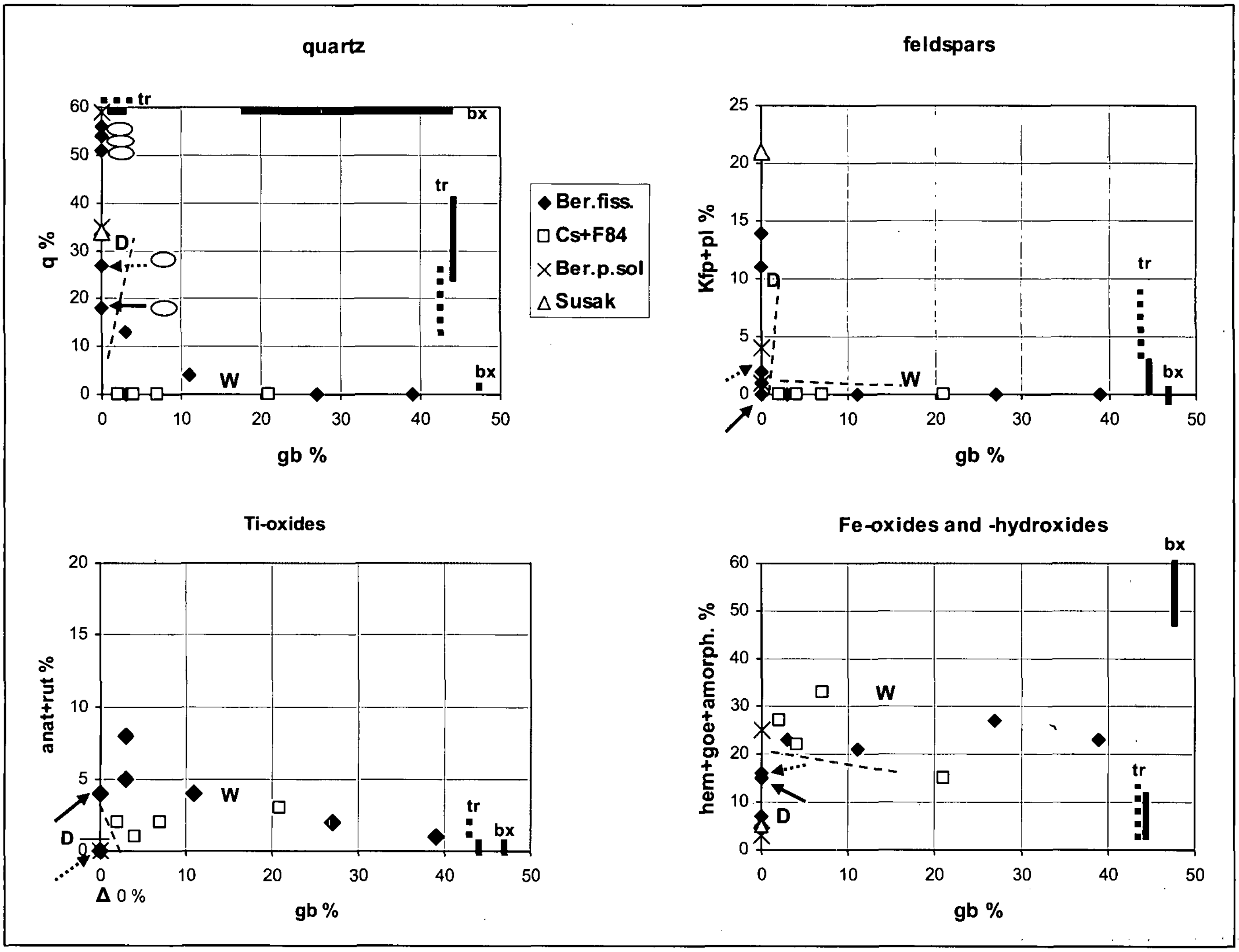

Fig. 16. Variation of minerals in function of the gibbsite contents in the bulk composition of red clays in the Beremend quarry. The percentages are converted to carbonate-free material. Legend: D: "detrital" type, W: "weathered" type. Dotted lines are tentative boundaries of the types. Arrows indicate the point representing locality No. 26. Source of data: *Ber.fiss.*: fissure filling clays (Kovács-Pálffy: average of 40 samples, solid arrow, Dezső et al. 2007: dotted arrow), *Cs+F84*: bauxitic clays (Császár, Farkas 1984), *Ber.p.sol*: palaeosol (Dezső et al. 2007). Ellipses in the quartz diagram indicate fossil bone rests in the sample. Continuous thick lines on the upper and right side of the diagrams indicate ranges of values measured in Aggtelek-Jósvafő area (N Hungary), tr: *terra rossa*, bx: bauxite pebbles in *terra rossa,* dotted thick lines represent *terra rossa* analyses from the Dinaric range (Bárdossy 1982, Tables 48 and 47). Data points for Susak Island: from Bognar et al. (2003).

In conclusion, in most cases, differences in the mineral composition of the fine fraction of the fissure-filling clays should reflect real differences in the intensity of weathering on the ancient surface. In the subsurface conditions weathering processes might have continued until the formation of smectites but only occasionally further, until the formation of kaolinite or gibbsite.

Mineralogical and petrographical aspects of the origin of gibbsite in red clays of the Beremend quarry

From the point of view of prospecting for bauxite deposits the gibbsite-bearing sediments are of special interest. As it was mentioned before, red clays containing gibbsite were found first by Császár and Farkas (1984) in the Beremend quarry. Similar and even higher gibbsite contents were detected also by us from other points in the same quarry. In two now existing caves the lowermost accessible sediments also contain a few per cent gibbsite in the <2 μm fraction (Dezső et al. 2007). The question arises, what is the relation of these gibbsitic or bauxitic clays to other red clays that occur in the quarry. Whether they form two separate compositional groups or are they connected by several transitions. In order to answer these questions diagrams were constructed, in which the variation of the amounts of minerals in function of the gibbsite contents are shown (Fig. 16, Fig. 17 and Fig. to 18). Because the carbonates are supposed to be secondary, not influencing this relationship, the percentages were recalculated into carbonate-free material.

The diagrams of most minerals in the bulk composition (Fig. 16 and Fig. 17) show clearly the difference between the samples without gibbsite and samples containing gibbsite even in low amounts (from 1 % on in the carbonate-free material). The gibbsitic composition can be called here for the simplicity as intensely "weathered" and the gibbsite-free type as "detrital" because it is probably not or only slightly weathered. The gibbsite-containing samples contain no or very little quartz, no feldspar and chlorite. On the other hand, the group with zero gibbsite always contains quartz, usually high quantities, up to almost 60 %, and systematically a few per cent of feldspar and chlorite. As for illite, there is a tendency that illite contents are higher in the no-gibbsite group and lower or zero in the gibbsitic type. In addition, the

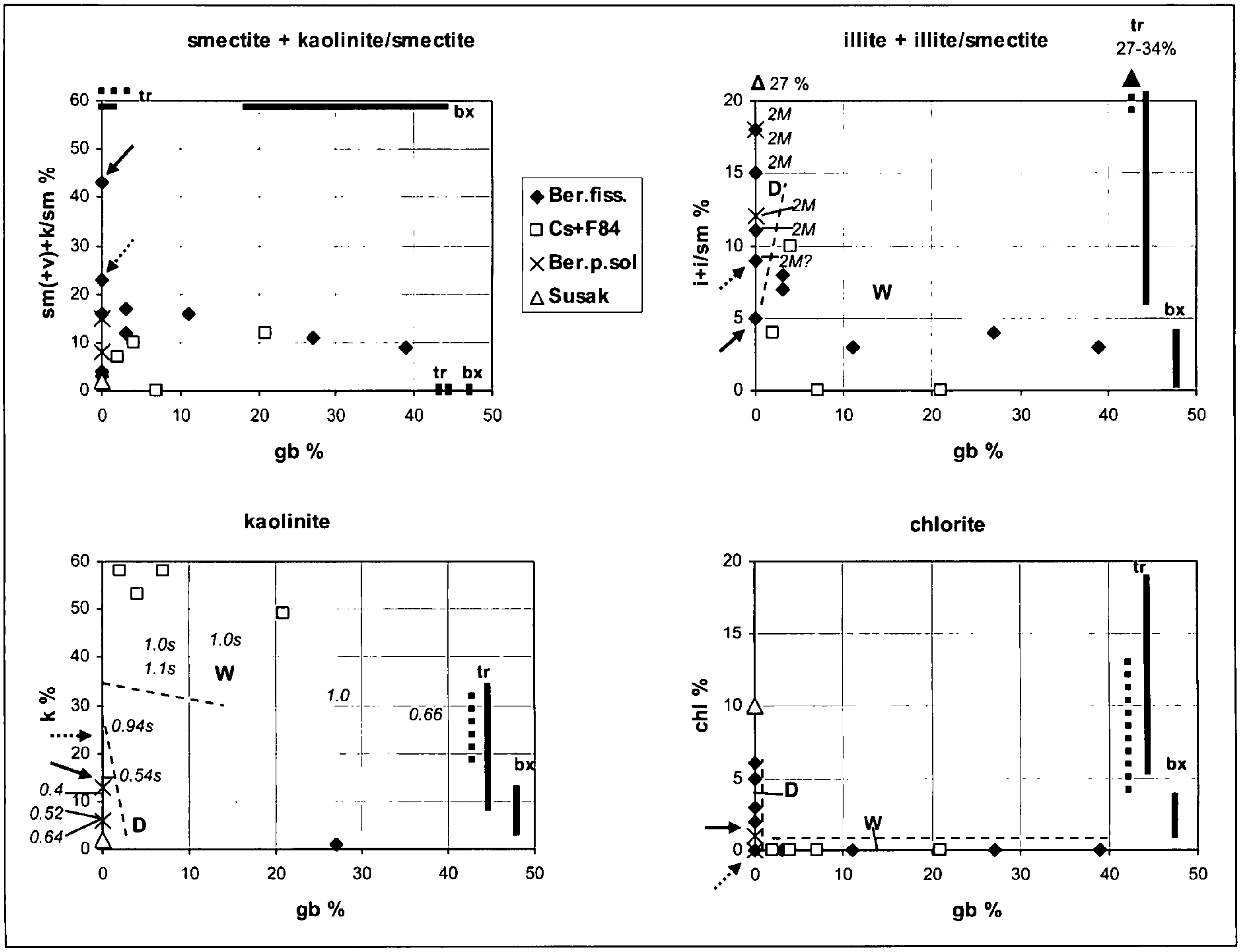

Fig. 17. Variation of clay minerals in function of the gibbsite contents in the bulk composition of red clays in the Beremend quarry. The percentages are converted to carbonate-free material. Legend: In the illite diagram: *2M*: illite-2M can be identified. In the kaolinite diagram: *numbers* refer to width of the 001 basal reflection in 2Θ° units, *s*: k/sm>5 %. For other signs and abbreviations see Fig. 16.

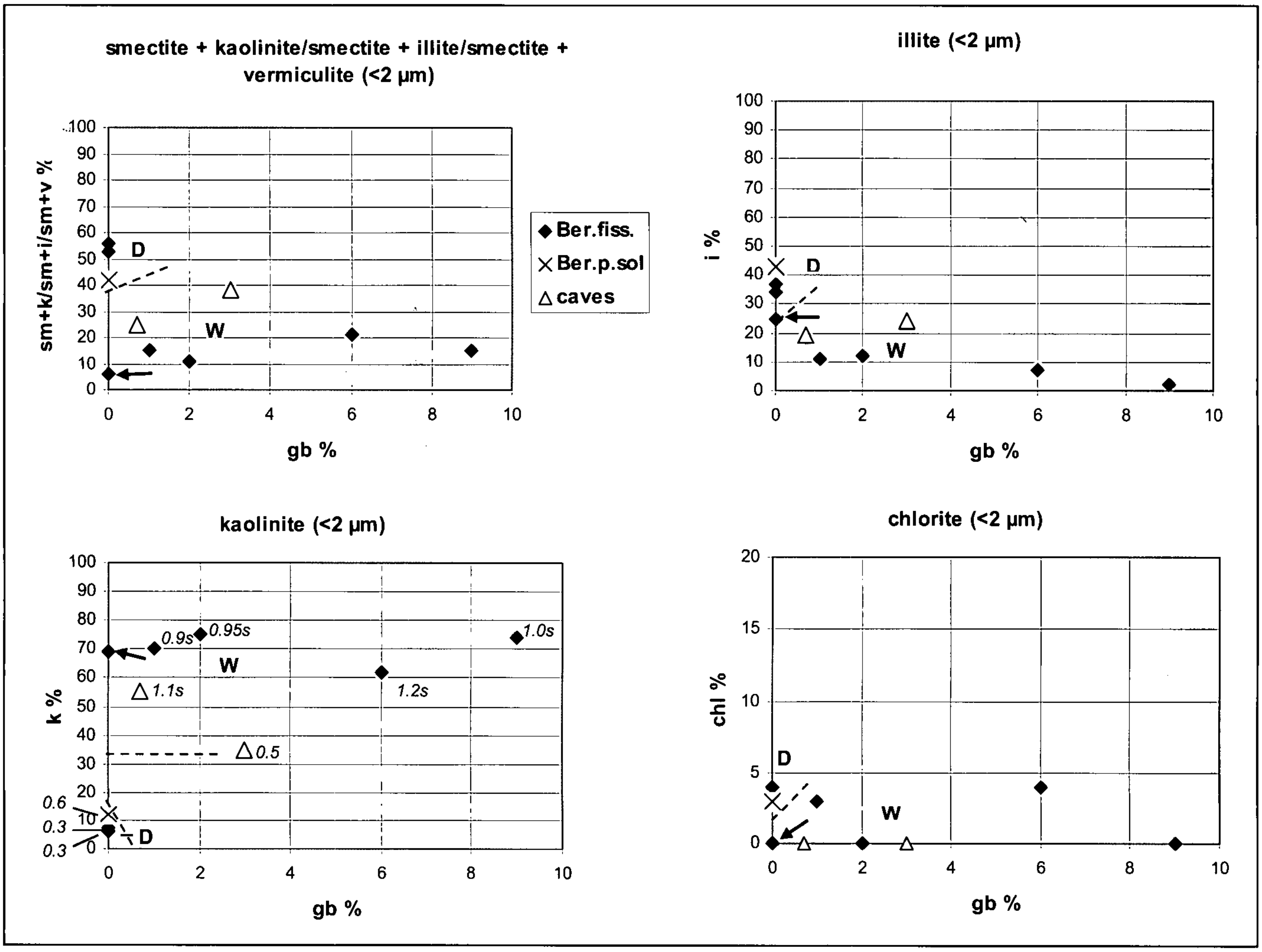

Fig. 18. Variation of clay minerals in function of the gibbsite contents in the <2μm fraction of red clays in the Beremend quarry and in cave sediments of Villány Mts. The percentages are converted to carbonate-free material. For signs and abbreviations see Figs 16 and 17.

well-crystallised 2M modification could be identified exclusively in the no-gibbsite group. The boundary is, however, much less sharp than in the previous cases.

In the gibbsite-free, "detrital" group kaolinite contents are by 10-20 % lower than in the gibbsite-containing group. On the contrary, the most striking feature of the "weathered" group is the high kaolinite content. Kaolinite is about 50-60 % when gibbsite percentages are low. It decreases again to about 25 % when gibbsite contents grow higher than about 25 % (in the bulk composition). It shows probably that kaolinite has been converted to gibbsite during the progress of weathering or alteration. There are clear differences in the degree of order between the kaolinites of the two groups as measured by the width of the first basal reflection at half height in 2Θ° units. In the "detrital" type these values are in the range 0.4-0.6°, kaolinites have sharp basal reflections, they are well or medium ordered. The "weathered" type kaolinites are highly disordered. The width values are between 0.9 and 1.1° when gibbsite is less than about 30 %. Again, in the sample with the maximum gibbsite content the ordering increases, accordingly the width of the basal reflection decreases to 0.66° 2Θ. Similar observation was already made by Császár and Farkas (1984). This shows probably that bauxitisation runs parallel with ordering of the kaolinite structure. The same rule holds when the kaolinite/smectite mixed-layers are considered, the highest amounts are in the low gibbsite range of the "weathered" group (indicated by "*s*" in Fig. 17).

The repartition of the iron oxides and hydroxides (hematite+goethite) is similar to that of kaolinite. In samples where there is no gibbsite, iron minerals are generally low (less than 10 %) and in the gibbsite-containing samples there are high iron mineral contents (20-30 %). There seems to be a compositional gap between the two groups however, the scattering of the data is rather high. As a rule, the gibbsitic samples contain more hematite while the gibbsite-free, less weathered samples more goethite. The gibbsitic clays always contain Ti-oxide minerals, anatase or rutile, or both, while members of the "detrital" group never.

Contrary to the minerals discussed so far, contents of smectites and mixed-layer kaolinite/smectites do not display clear differences between the two groups. Their amounts scatter between 0 and 20 % irrespective of the gibbsite contents throughout the whole range of increasing bauxitisation. This is an indication that the weathering affected a dominantly smectitic material which has gradually transformed into kaolinite, but the process did not went to completion.

The clay minerals in the <2 μm fraction (Fig. 18) display the same regularities as the clay minerals in the bulk composition but the variation of the gibbsite contents is much lower than in the bulk composition. The highest gibbsite percentage is lower than 10 %. The "detrital" and "weathered" types in the smectite-like minerals are more clearly separated here than in the bulk composition. In addition to the Beremend samples two cave sediments are shown here for comparison. The clay sediment from the Macskalyuk cave at Máriagyűd (gibbsite = 1 %) fits more into the "weathered" group than that from the Borpince cave at the town Villány (gibbsite = 3 %), which is somewhat transitional to the "detrital" type.

Although most minerals show two compositional groups, in the case of almost every mineral there are transitional samples between the two groups. This is true also for gibbsite which gradually grows from 0 % to 1 % and so on, higher and higher. It is interesting to mention that the samples taken of the widest karstic depression, locality No. 26 occupy in most cases transitional position between the two groups. The corresponding points are specially noted by arrows in the diagrams. For most minerals, this sample belongs more to the "detrital" group, but its kaolinite is disordered, there is much kaolinite/smectite, and the width of the 001 reflection is 0.9° 2Θ, like in the "weathered" group. In the diagrams the values for the bulk composition from the data set of Dezső et al. (2007) differ from the average values of the quantitative data determined by Péter Kovács-Pálffy (like in Fig. 7). The reason is that the method of the determination was somewhat different and the two data sets cannot be directly compared. Smectites seem to be overestimated at the expense of other clay minerals, kaolinite and illite as compared to the data of Dezső et al. (2007). All other minerals give similar values, transitional between the two compositional groups. Unfortunately, the <2 μm fraction of this sample was not analysed by us. In the diagrams for the <2 μm fraction we have only the average values of the data of Kovács-Pálffy for the locality No. 26 (Fig. 18, signed by arrows). Like for the bulk samples, they occupy transitional position between the two groups, but closer to the "weathered" group. The difference between the bulk composition and the clay fraction indicates the dependence of the mineralogy from the grain size. In the bulk composition there is a considerable proportion of silt size material which is less weathered than the fine fraction. As it was mentioned in the Chapter of the Results, there is practically no gibbsite in the locality No. 26 therefore there is no need to argue for the derivation of a portion of the sedimentary material from the bauxites of Harsány-hegy, as it was done by Marsi and Koloszár (2004) and Koloszár (2004).

The two palaeosol samples are specially noted. It can be seen in the diagrams for the bulk samples (Fig. 16 and Fig. 17) that they are typically in the "detrital" group and fit well into its compositional range with three other red clay samples which were taken from fissures. Also in the <2 μm fraction (Fig. 18) the palaeosol sample is similar to the red clays "detrital" group.

All these considerations show that among the red clays in the Beremend quarry we have to deal with the products of different intensity of weathering:

(1) *Strong weathering* dissolved most silicate minerals and produced much disordered kaolinite, various but mostly low amounts of gibbsite, much hematite, goethite and Ti-oxides. The low gibbsite contents, the disordered nature of kaolinite and the existence of little smectite and of transitional mixed-layer phases show that the most intense phase of weathering approximated but did not reach the true lateritisation or bauxitisation.

One could suppose true bauxitisation only in the case of the occasional high (20-40 %) gibbsite contents. This is restricted to 3 samples coming from 2 occurrences close to each other (or more probably from the same single fissure) in the SE corner of the 100 m working level of the Beremend quarry. In this case derivation from a locally preserved old bauxite or bauxitic clay cannot be completely excluded. The idea of an older generation of fissure filling could be supported by the morphology of this particular fissure. Unlike the others, this fissure is very thin (about 10 cm thick), closed, it does not show the dissolution features of the wall rock limestone. On the other hand, as it was mentioned before, the known pre-Pannonian fissure system in the Magyarbóly-1 borehole is not filled with red or weathered clay material which would be something similar to bauxite. Therefore it seems to be more probable that these samples indicate material coming from the same Pliocene soil sequence as the others, but from its most intensely weathered part.

(2) The other type of weathering, producing the *"detrital"* assemblage was weak, quartz and most silicates remained unchanged. Even in this assemblage there are small amounts of kaolinite, but this is relatively well crystallised and may be detrital. Only iron hydroxides and probably smectite were formed.

The existence of samples with transitional composition, the similar macroscopic appearance and colour in both groups indicate that there were two stages of different weathering intensity following each other rather than two completely different events of mineral formation. The similar secondary calcitic cementation from the karst water with several calcite-filled voids in both groups shows that most red clays were in a loose, soft state during the Pliocene karstification. This and the incomplete lateritisation make less probable that the time of the formation of the gibbsitic composition was as early as Late Cretaceous.

Another argument in favour of the relatively young formation of gibbsite is its thermodynamic nature. Gibbsite is the more metastable, i.e. the least stable phase among the aluminium oxi-hydroxide minerals gibbsite, boehmite and diaspore. Gibbsite relatively easily transforms into boehmite and then boehmite further into diaspore (Lippmann 1981). This statement is supported by the geological evidence collected by Bárdossy (1982). The overwhelming majority of pure gibbsitic bauxites were formed during the Quaternary and the Miocene-Pliocene period (Table 16). Upper Cretaceous to Eocene bauxites, like in the Transdanubian Central range contain rarely gibbsite alone, normally boehmite in addition to gibbsite. Older bauxites, like the Harsányhegy and Pădurea Craiului occurrences have boehmitic-diasporic character and do not contain gibbsite. Gibbsite cannot survive redeposition. According to the observations of the textural elements of bauxites gibbsite "soon worn in the course of transport, ... is fairly rare as an independent clastic mineral" (p. 238).

All this makes improbable that redeposition of gibbsitic bauxite took place from previously existing Upper Cretaceous – Palaeogene bauxites into the fissures during the Pliocene.

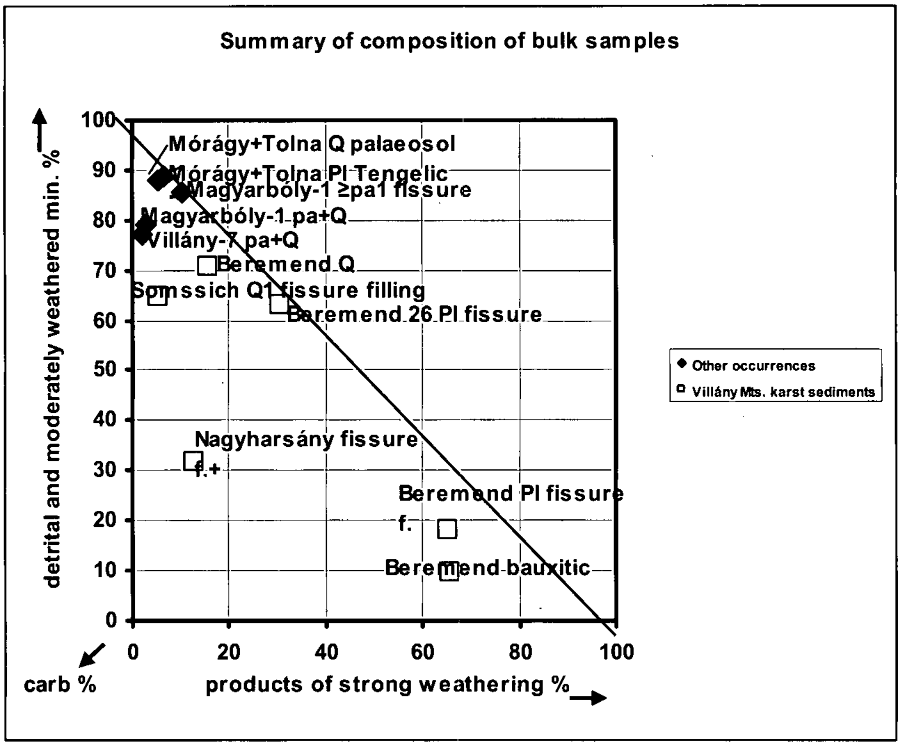

Fig. 19. Summary of mineral composition of bulk samples. Legend: ≥pa1: Lower Pannonian or older, pa: Pannonian, Pl: Pliocene, Q1: Lower Quaternary, Q: Quaternary.

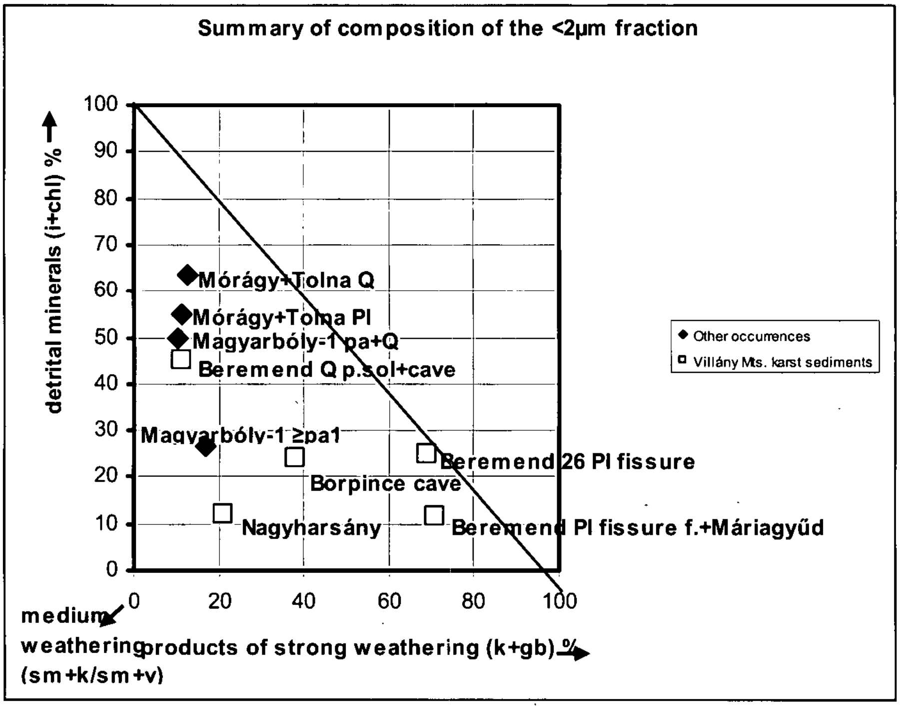

Fig. 20. Summary of clay mineral composition of the <2μm fraction. Legend: see Fig. 16.

Summary of the quantitative results for SE Transdanubia

The existence of two compositional groups of the red clays which were found in the Beremend quarry considering the quantities of minerals in relation to the gibbsite contents can be extended to the whole SE Transdanubian area studied. In order to compare the quantitative mineral compositions found in the localities discussed above the average values were determined and put on similar triangular diagrams as for the particular occurrences. The bulk composition is shown in Fig. 19 and the composition of the <2 μm fraction in Fig. 20. Karst sediments of Villány Mts. studied by Dezső et al. (2007) and other occurrences are shown separately in the diagrams.

Considering the *bulk composition* (Fig. 19), the points obtained by averaging do not express the variation in the carbonate contents which may be high in some groups such as in the Pannonian basin sediments and in the highly weathered red clays and bauxitic clays of Beremend quarry. There is however much less variation in the relation of weakly to highly weathered minerals what is favourable in the genetic evaluation.

Most red fissure filling clays of the Beremend quarry and the red clay sediment of a cave (Macskalyuk cave) belong to the highly weathered type. The average composition of the bauxitic clays formerly studied by Császár and Farkas (1984) is close to these red clays.

Almost all other formations are concentrated in the detrital, slightly or moderately weathered, carbonate-poor corner of the diagram. The less weathered ones are the Pannonian basin sediments, the pre-Pannonian fissure filling in the Magyarbóly-1 borehole, the red clays of the Tengelic Fm. and the Quaternary palaeosol in the Mórágy and Tolna Hegyhát areas. The Lower Pleistocene fissure filling silts of Somssich Hill belong to the same type only the carbonate contents are higher. The palaeosol found at Beremend is close to the other palaeosols, however, contains clearly more kaolinite.

The remnants of the former Pannonian covering sandy siltstone found in the fissure filling of the Nagyharsány quarry clearly differ from the Pannonian basin sediments in their higher kaolinite contents which can be due to a higher proportion of local source material. As it was discussed above, the red clays of the locality No. 26 of Beremend quarry studied by Marsi and Koloszár (2004) occupy transitional position when the bulk composition is considered, however, they move much closer to the highly weathered red clays in the diagram of the <2 µm fraction.

In the diagram summarising the *composition of the <2 µm fraction* (Fig. 20) the localities follow the same arrangement as in the case of the bulk composition. Red clay fissure fillings of the Beremend quarry, including those of the locality No. 26 and the red clay found in the Máriagyűd cave are close to the kaolinite+gibbsite pole of the diagram.

The data points of other localities are in the low-kaolinite range, below about 20 % kaolinite contents. According to the growing smectite contents they are arranged in the following sequence: Quaternary palaeosols of Mórágy Hills and Tolna Hegyhát area seem to be the least weathered, they are followed by the Tengelic Fm. of the Mórágy Hills and Tolna Hegyhát area, the Pannonian basin sediments of Magyarbóly-1 borehole in the surrounding of Villány Mts. The scatter of each data set of these localities is equally high along the same line in the low-kaolinite region, what is not expressed by the average values. Quaternary palaeosol samples of the Beremend quarry, cave sediments of the Borpince cave and those found as collapsed debris in a fissure of the Nagyharsány quarry are shown here by a single point. Their composition is close to each other, it fits well into this series showing the genetic relationship. Unlike the bulk composition, the average kaolinite content in the <2 µm fraction of Beremend palaeosol is not higher than in the analogous occurrences but the higher smectite content indicates somewhat higher degree of weathering than in other Quaternary palaeosols of the surrounding area. The most smectite contents among the low-kaolinite localities are found in the pre-Pannonian fissure fillings of the Magyarbóly-1 borehole indicating either medium strong weathering or admixture of volcanic material. The clay material of two carbonate-cemented concretions is shown here separately because their composition is transitional to the highly weathered type.

The parent material of red clays. The question of the insoluble residue of limestones

In the *mountainous facies*, distinguished as the *Beremend Member* of the Tengelic Formation red clays are deposited immediately on karstified limestone. Therefore the question arises whether they are derived from the insoluble residue the limestone, a question which is frequently discussed in other areas covered by *terra rossa* (see e.g. Bárdossy 1982 and Durn et al. 2006). Concerning the clay mineralogy of the insoluble residue of the carbonate rocks of Villány Mts. we have quantitative data on the composition of formations occurring in the eastern part of the mountain range, namely the Ladinian *Templomhegy Dolomite Member* of the *Csukma Formation* and the Lower Cretaceous *Nagyharsány Limestone*.

In the <2 µm fraction of 2 samples of *Templomhegy Dolomite* taken from the Templom-hegy, lower quarry (see Rálisch-Felgenhauer 1987) the clay mineral is only illite with some mixed-layer illite/smectite of less than about 15 % smectite proportion (unpulished XRD analyses by I. Viczián). This is similar to the composition of the underlying Middle Triassic formations studied in detail in the borehole Nagykozár-2, about 15 km north of the Villány Mts. Here the Anisian *Lapis Limestone Fm.* and *Zuhánya Limestone Fm.* which are analogous with the German Muschelkalk, contain dominantly illite-1Md with some illite/smectite and smectite (Viczián 2000). Such association practically consisting of illite alone does not occur among the red clays. Therefore the insoluble residue of Triassic carbonates in its unaltered form cannot form the red clays. Perhaps they could contribute to the illite content of the red clays to a minor extent.

Concerning the Lower Cretaceous *Nagyharsány Limestone*, we have only one old XRD analysis from the Beremend quarry itself. In the insoluble residue of the limestone there is much illite, medium montmorillonite, little chlorite and goethite and very little kaolinite and quartz (Fülöp 1966, p. 42). In samples taken from the Harsány-hegy quarry 80-90 % of the clay minerals in the insoluble residue is illite + illite/smectite but there is a permanent other component, 10-20 % kaolinite (Császár 2002, Table 6, XRD analyses by G. Rischák). This is again a composition which differs considerably from that of the extremely kaolinite-rich red clays. There is however another mineralogical analysis of *Nagyharsány Limestone* published by Fülöp (1966, p. 29) where the composition is similar to the red clays: At Kistapolca, between the Beremend and Nagyharsány quarry localities medium "metahalloysite" (=disordered kaolinite), montmorillonite, illite and little chlorite and quartz were found in the insoluble residue. It is remarkable that the sample was taken from the immediate vicinity of a subthermal (20-21 °C) karst spring.

In conclusion the insoluble residue of the carbonate rocks of the Villány Mts. cannot be the parent material of the red clays, at least not in its unaltered form. Koloszár (2004) thinks that the main parent material of red clays of the *Beremend Member* was the weathered residue of the Upper Pannonian sedimentary cover of the mountain range which was transported by areal erosion over a pediment surface between the isolated block of the Beremend occurrence and the main body of the mountain range. On the other hand, Dezső et al. (2007) deny the existence of the pediment because in the clastic components on the surface of the Beremend block only local material can be found. According to this opinion, the source material was the weathered soil cover on the top of this local elevation in which the aeolian contribution may have played important role. It is difficult to explain the absence of quartz in the intensely weathered type of red clays. Crystalline quartz is resistant mineral which does not dissolve even during lateritisation (Fekete 1988). One has to suppose that there was little or no quartz in the sedimentary material which underwent weathering. In this respect we can think on very fine-grained sediments, intermediate (andesite) tuffs or vitric tuffs of acid composition. The admixture of basalt tuff is less probable because the eruption of the Bár volcano was by nearly 1 million years later. Unfortunately, micromineralogy was not studied so far.

In the *hilly areas* of SE Transdanubia the question of the parent material is relatively easy to be solved because the red clays in the *Tengelic Member* of the Tengelic Formation are the uppermost members of a generally detrital siliciclastic sedimentary sequence. The immediate parent materials of the red clays are most probably the underlying clay, silty clay and sand beds and locally basalt tuff occurring in the same

Tengelic Member and Upper Pannonian sediments of the surrounding territories. In the particular case of the isolated elevation of the Mórágy Hills the parent material is the granitic rubble underlain by the weathered granite.

As for the *basal palaeosol beds* of the Paks Loess Formation, the red clays occurring here are underlain by a shorter interruption by the red clays of the Tengelic Fm. The parent materials of these red clays are the underlying Tengelic red clays, there may be however already an aeolian contribution (Koloszár 2004). The remarkable similarity of the composition of the two red clay group as was found by us can be explained by the redeposition from the older one into the younger one. On the other hand, the less weathered nature of the *basal palaeosols* of the Paks Loess may be explained by a stronger aeolian contribution as it was found by Földvári and Kovács-Pálffy (2002).

Age and palaeo-environmental relations

It is advantageous that many fissures filled with clays in the Villány Mts. contain Vertebrate fossils. Their study enables us to determine the age and the environmental conditions prevailing during the accumulation of the sediment. The age of the Vertebrate fauna is nearly identical or may be somewhat younger than the age of the soil which the animals were living on. The difference in the age cannot be too large because with the changing environmental conditions the composition of the soil is evolving as well. Unfortunately, mineralogical investigations started much later than palaeontological studies and therefore they were not carried out on the same material except very few cases (e.g. locality No. 26 at Beremend). When determining the age of our samples, in most cases we can rely on analogous occurrences only.

Results of this study are summarised in Fig. 21. We can arrange the age and environmental information concerning the localities studied in this paper in the Vertebrate stratigraphic scheme constructed by Jánossy (1986). For the Pannonian formations occurring in boreholes of the broader surrounding the data of Jámbor were used (1997 and unpublished reports). In the stratigraphic scheme of Fig. 21 the occurrences and formations studied are shown. In each case the name of the locality, the rock, the age, the name of the formation and finally the typical clay mineral association in the <2 µm fraction is given. When considering the palaeo-

P L I O C E N E **L O W E R P L E I S T O C E N E**
„V I L L A F R A N C H I A N" **(„G Ü N Z – M I N D E L")**
ESTRAMONTIAN **V I L L Á N Y I A N** **B I H A R I A N I.**
+RUSCINIAN CSARNÓTA BEREMEND KISLÁNG BETFIA TEMPLOMHEGY
K-Ar years +(estimates, My) ~3.0 ?2.5 2.0 1.0 ~0.7

Udvari-2A, red clay
←? Tengelic Fm. ?→
I v c, V i c

Udvari-2A, red palaeosol
~1.1 my Paks Fm. Pv_3?
I c k

Mórágy Hills, red clay
←? Tengelic Fm. ?→
I v c, I s k

Mórágy Hills, red palaeosol
0.8 my Paks Fm. PD1
I v c, I s k

Csarnóta (1),2,3 red fissure filling
3.5 my
K_d

Somssich Hill 2, yellow fissure filling
0,9 my
I s c, I s k

Beremend, red fissure filing
3.3-3.0 my Tengelic Fm.
K_d s i (gb)

Beremend, red palaeosol
0.8 my Paks Fm. PD1
S I k

Nagyharsány, yellow+reddish violet fissure filling
$\geq M_3 (pa_1)$ ←
I s c, I s k

Magyarbóly-1 ~light green fiss. f. + lacustrine and fluviatile sed. fluviatile and terrestric sediments
$\geq M_3 (pa_1) + pa_1$ Szák Fm. to pa_2 Nagyalföld Fm. ← *(unconformity)* → Q_{2-3}
S i k I s c I s k I s k

VERTEBRATE ECOLOGY (Pazonyi 2006):

My: 3.2 2.15 0.95 → 0.3

warm, humid (Kretzoi 1969) | **dry, open veg. to forest** | **dry, open vegetation to forest** | **steppe to forest steppe, forest, bush**

Fig. 21. Typical clay mineral associations of the formations studied. Locality, stratigraphic position, age in million years and ecological condition derived from Vertebrate palaeontology are given. Legend: s: smectite + kaolinite/smectite + illite/smectite, v: vermiculite + vermiculite/smectite, i: illite, k: kaolinite, k_d: disordered kaolinite, c: chlorite, gb: gibbsite. Capital letters: the most frequent clay mineral, small letters: other typical clay minerals; my: million years, $\geq M_3(pa_1)$: Upper Miocene (Lower Pannoniapppn) or older.

environmental relations in the given time period we relied on the comprehensive characterisation of the stratigraphic units made by Schweitzer (1993) and on the systematic summary of the environmental significance of the faunas made recently by Pazonyi (2006).

According to the diagram, the *highly weathered association* with dominant disordered kaolinite and occasionally gibbsite is restricted to the oldest terrestrial sediments, the accumulation of which started about 3.5 million years ago (*Csarnótan* stage of Vertebrate stratigraphy). As it was shown in the previous chapters, the intensity of weathering did not reach the level of true *lateritisation* of the tropical regions however it may have proceeded under warm and humid climate which lasted for a few hundred thousand years in the Middle Pliocene. This association is most common in the Villány Mts. however former mineralogical analyses have shown that the repartition of the highly weathered association is not restricted to the area of the Villány Mts. It may occur far away in the hilly areas of SE Transdanubia and even east of the Danube.

According to the palaeontological study of the site Csarnóta No. 2, it reflects a time interval when gradual transition started "from forest animal community to a grassland – steppe faunal assemblage" (Jánossy 1986, p. 22). Faunas indicating forest and also aquatic (swamp) environment were reported from the Beremend quarry in the review of Pazonyi (2006), which are somewhat younger than those of the Csarnóta locality, corresponding to the beginning of the *Villányian* stage of Vertebrate stratigraphy. Closed forest developed when the climate was warm and humid. Schweitzer (1993) characterised the climate as subtropical to tropical and emphasized the immigration of SE Asian faunal elements. Koloszár (2004) supposes monsoon climate. A good approximation of the climatic parameters is given by the observations made in various climatic zones of California. Here is precipitation in the winter season and the mean annual temperatures are between 15-21 °C. The distribution of clay minerals and gibbsite in residual soils depends on the amount of rainfall. When the mean annual precipitation is more than about 500 mm, the most frequent clay minerals are kaolinite and halloysite. When annual precipitation is higher than 1000-1500 mm gibbsite begins to form while montmorillonite and somewhat later illite disappear. Vermiculite can coexist with kaolinite and gibbsite (Barshad 1966, cited by Singer 1980). This combination of climatic parameters seems to be the most probable during the formation of the "weathered" type mineral assemblage in the Villány Mts. however, there were no high mountains and the rain season was not necessarily in winter.

Stefanovits and Fekete considered that Hungarian red clays are "genetically diverse" but at least part of them is "similar to the tropical and sub-tropical ferrolite soils regarding to their formation and mineral characteristics" (Fekete et al. 2005). This is in accordance with our conclusions regarding the "weathered" red clays in the Villány Mts. We can conclude that the soil types from which these clays are derived belong to the group of *ferrallitic soils* according to the classification of Fekete (1988). Within this group highly kaolinitic red clays with little illite and smectite and much iron-oxi-hydroxide but without gibbsite correspond to *ferruginous soils.* Such soils are formed in savannah environment with much rain but dry winters. Red clays bearing little gibbsite may have been either *weathered ferrallitic soils* which are common on the top of elevated, well drained plateaus of savannahs or *weakly ferrallitic soils* which occur around the border between the rain forests and the summer rain zone of the savannahs. Today such soil types occur around the central areas of Amazonas and Kongo Basins, Eastern India, Indo-China and in Indonesia (called *alferrites* and *reddish brown savannah soils* by Keveiné Bárány 1998).

The highest stage of lateritisation however, the *leached ferrallitic soils* with dominant gibbsite and kaolinite contents were not achieved. They would need permanently wet rain forest and mean annual precipitation higher than 1250-1750 mm. According to Bárdossy (1982) for the intense *lateritisation* somewhat warmer and more humid climate would be needed, when the mean annual temperature is 20-26 °C and the mean annual precipitation is 2000-6000 mm. For bauxitisation is necessary to have the same conditions but also a dry period during the year.

The *weakly weathered assemblage* is present in the Villány Mts. itself however it is more common in the surrounding hilly areas. In almost all cases, *in red clays belonging to the Tengelic Fm. and to the basal layers of the Paks Loess Fm. and in yellow Lower Pleistocene clays* the dominant clay mineral is illite and the associations are similar in composition. In each case tentatively two types can be distinguished according to the second frequent minerals: one characterised by more smectite and kaolinite and a little less weathered one with more chlorite and vermiculite. It may indicate slight variations in climate, probably more and less humidity. According to the conclusions of Pazonyi (2006) the warm and humid climate ended about 3.0 million years ago. From this date on, she subdivided the time span into three main periods, the limiting dates of which are 2.15, 0.95 and 0.3 million years, respectively. In each stage the dominant vegetation was dry, open savannah or later steppe which became more humid and forested toward the end of each period. The temperature was moderately warm, in the last stage cooler. (We did not study the really cold stages of the Pleistocene.) From the mineralogy follows moderate, slightly variable intensity of weathering. It is in good agreement with the conclusions drawn from the palaeontological studies.

An important process of this type of alteration is called *rubefication* because it produces red or reddish oxidised iron compounds (Kubiena 1956, cited by Fekete et al. 2005). In the Transdanubian area the iron compound is preferentially goethite and much less frequently hematite.

It should be remarked that the presence of Pliocene faunas is not restricted to a special type of mineral paragenesis in the enclosing red clay. From a simply granulometric point of view fossil bone rests belong to the coarse grain fraction, therefore their occurrence is shown in the diagram for quartz variation in the Beremend quarry (Fig. 16). Here they can be found most frequently but not exclusively in the samples which contain dominantly "detrital" minerals but also in the transitional assemblage of locality No. 26. Former studies indicate that the rich Vertebrate fauna at Csarnóta is found in enclosing red clays which consist of highly weathered mineral assemblage (Jánossy 1986, Bidló 1980). It looks like that there is no direct connection between the mere presence of fossil rests and the mineral composition of the enclosing clay in a given occurrence. On the other hand, of course, the specific nature of the fossils and mineralogy are in correlation, as it has been discussed before.

Neither the highly weathered nor the weakly weathered terrestrial composition is reflected in the *basin sediments* which are generally older but partly contemporaneous with the formation of the red clays. According to the core material of Magyarbóly-1 borehole the clay mineral association in the fine fraction is the normal terrigeneous, detrital composition of basin sediments like elsewhere in the Pannonian Basin. The composition of the Upper Pannonian Nagyalföld Fm. which may be contemporaneous with the older Pliocene terrestrial red clays highly differs from their composition but does not differ from the overlying Quaternary basin sediments which in turn are partly contemporaneous with the younger terrestrial red clays. Basin sediments in both cases contain typically much illite and as second frequent minerals smectite and kaolinite. Nagyalföld Fm. is in average somewhat more weathered than Quaternary. The iron mineral is here pyrite, in accord with the reduced state of the sediments.

Analogous occurrences in the Carpathian Basin, Dinaric range and on the Adriatic Carbonate Platform (Istria)

The mineralogy of Pliocene to Pleistocene red clays occurring in mountainous and hilly areas of Hungary was reviewed by Viczián (2002a). Generally similar relations were reported in other more recent publications on various red clay formations of Hungary, from the Aggtelek-Esztramos area (Fekete 2002, Fekete et al. 2005) and from the Northern Bükk Mts. (Vincze et al. 2005). In both areas an older, kaolinite-rich and a younger, less weathered association could be distinguished. The closest correlation can be found with the Mt. Esztramos occurrence and with the Poltár Formation in Southern Slovakia.

On *Mt. Esztramos* red clays occur in a very similar facies as in the Villány Mts. They fill karstic fissures and caves in the limestone. There are numerous fossil Vertebrate finds which make an age determination possible. The mineralogy and the stratigraphic classification of the localities were carried out by Viczián (2002a, see Fig. 4). There are red clays with dominantly strongly disordered kaolinite in accordance with the former results of Bidló. Additional phases are mixed-layer kaolinite/smectite and disordered illite. Calcite and hematite contents are relatively high, quartz is low. The age of the oldest red clay deposits is Middle Pliocene, *Estramontian* in the Vertebrate stratigraphy, which is the same as for the Csarnóta site in the Villány Mts. and only slightly older than the oldest Beremend localities. There are red clays of similar composition with younger faunas of Pliocene to Middle Pleistocene age. There are also red clays with composition corresponding to the less weathered material in the Villány Mts.

No free Al-hydroxides were reported from Mt. Osztramos. Gibbsite was found rarely together with hematite and goethite in rounded bauxite pebbles as allochtonous material in red clays of the *Aggtelek Mts.* (Bárdossy 1982, Table 48).

The "weathered" group of the Villány Mts. red clays can be compared to the bauxite pebbles which were prepared by Bárdossy from the red clays in the Aggtelek – Jósvafő area (N Hungary). He supposed that they were redeposited from older bauxite deposits. From the Beremend samples only the 3 samples having more than 20 % gibbsite contents are comparable with these pebbles. Other samples differ not only in their low gibbsite contents but also in their much higher kaolinite, smectite and mixed-layered kaolinite/smectite contents, in the typical disordered nature of kaolinite and in the occasional appearance of quartz.

The other rock type of similar composition and age is the *Poltár Formation in the Lučenec Basin* in Southern Slovakia (Kraus 1989). This is a fine-grained sedimentary formation overlying sedimentary kaolin deposits. Its age is Pontian, i.e. Pliocene. Kaolinite in this basal sedimentary kaolin is relatively well ordered. On the other hand the main clay mineral of the Poltár Formation is typically disordered kaolinite which is accompanied by smectite of non-volcanic origin and occasionally by small amounts of free Al-oxi-hydroxides, gibbsite and diaspore. Diaspore is more abundant. Diaspore was considered first by Kraus to be product of further weathering of kaolinite. Later he accepted diagenetic genesis of diaspore in the surrounding of coalified plant rests. In any case, there are small amounts of free Al-hydroxides. Very disordered kaolinite is supposed to be the product of intense weathering of metamorphic and granitoid rocks in the broader surrounding. With the exception of the formation of diaspore and the absence of iron minerals, the clay mineralogy, its genesis and the age of the Poltár Formation are very similar to the strongly weathered type of red clays in the Villány Mts. (Viczián 2006).

All these examples show that there was a period during the Pliocene in the Carpathian Basin when conditions were favourable for the formation of intensely weathered soils. All these formations contain typically highly disordered kaolinite and occasionally also free aluminium oxi-hydroxides.

The less weathered assemblage can be compared to red clays which were classified by the former authors as *terra rossa.* In the compositional diagrams of Fig. 16 and Fig. 17 the ranges of composition of various occurrences of *terra rossa* in N Hungary and in the Dinaric range are shown for comparison (data of Bárdossy 1982, Table 47 and Table 48). The "detrital" assemblage formed on the limestone surfaces of the Villány Mts. fits fairly well with the composition of *terra rossa* of these areas. There are only less important differences, e.g. there are more smectite and quartz and less chlorite contents in the Villány Mts. than in the two other areas. This may indicate differences in the parent material and intensity of weathering. Some *terra rossas*, e.g. those occurring on the Istrian peninsula may even lack chlorite and contain dominantly disordered kaolinite (Durn et al. 2006). Even low gibbsite contents are compatible with the notion of *terra rossa.* Bárdossy (1982, p. 336) states that "one of its principal features is that it contains a few percent of gibbsite and nordstrandite as a rule".

Good correlation was found between the red clay deposits on the island of Susak, the westernmost member of the Dalmatian archipelago and the Hungarian occurrences by Bognar et al. (2003). Like in the Villány Mts. in Hungary, two types could be distinguished based on the thermal and geochemical analysis of Gy. Szőőr. There are typical *red* clays filling the karstic cavities of the underlying limestone. They contain kaolinite and diagenetic spherules indicating warm and humid climate similar to the Hungarian *Csarnótan* (4.0 to 3.0 million years BP according to these authors). The immediately overlying *reddish* clays on the basis of the Susak loess complex (labelled as SAV) were correlated with the Hungarian PD soil complex on the basis of the Paks Loess Fm. The *reddish* clays were considered to be *terra rossa*. They were found to contain predominantly montmorillonite and illite and various horizons of $CaCO_3$ accumulation. Quantitative data of a red clay sample were published in the monograph (Fig. 28) and are included into the diagrams on Fig. 16 and Fig. 17 of the present paper. The composition fits well into the field of other *terra rossas* except kaolinite which is lower and the detrital minerals muscovite (illite) and chlorite which are higher than in other Dinaric *terra rossas*. The composition of the analysed sample shows only weakly weathered material and indicates grassy steppe ecotype according to the authors. They were correlated with the Hungarian *Villányian* stage (3.0 to 1.7 million years according to these authors). In the correlation no distinction was made between the Hungarian "reddish" soils belonging to the Tengelic Fm. and to the basal palaeosol of the Paks Loess Fm.

CONCLUSIONS

On the basis of quantitative XRD analyses made on 181 samples correlation was found between the mineralogical composition and environmental relations of Pliocene and Quaternary terrestrial red clays in SE Transdanubia.

1. Little is known about the weathering crust on the top of the Mesozoic sequence of Villány Mts. in the time period *between the post-Senonian uplift and erosion and the Pannonian transgression*. The existence of pre-Pannonian fissure system filled by moderately altered smectite-rich grey clay material under the Upper Pannonian cover can be proved in the borehole Magyarbóly-1. Its age is uncertain, perhaps *Old Cainozoic (?)*.

2. The *Upper Pannonian cover* has been mostly eroded during the Early Pliocene. A few blocks were preserved in collapsed breccias accumulated in a wide fissure in Nagyharsány quarry. Pannonian sediments occur in the surrounding shallow basins adjacent to the Villány Mts. The basin sediments are composed of fine siltstones containing normal detrital polymineralic assemblage. Similar compositions are found in other areas of the Pannonian Basin. Remained blocks of the covering sandy siltstones and their debris are of similar composition but contain clearly more relatively well-crystallised kaolinite.

3. The terrestrial red clay formation of Middle Pliocene to Lower Pleistocene age is called *Tengelic Red Clay Formation*. Red clays filling fissures and recently existing caves in limestone of the Villány Mts. can be divided into two types.

4. The older type corresponding to the *Beremend Member of the Tengelic Fm.* and to the *Csarnótan* biostratigraphic stage is red kaolinitic clay. It contains typically disordered kaolinite, mixed-layer smectite/kaolinite, smectite and little gibbsite. It was formed in the local subaerial weathering crust in warm, humid, subtropical or monsoon climate. Products of similar weathering, mineralogy and age can be found on Mt. Esztramos, N. Hungary and in the Poltár Fm., S. Slovakia.

5. Gibbsite in low amounts has been formed most probably during the *Csarnótan* period together with kaolinite in the weathering crust on the surface. In exceptional cases the preservation of high-gibbsitic clays in an older generation of fissures cannot be completely excluded. Transformation in the ground waters may have produced smectites but did not go so far to produce kaolinite or gibbsite.

6. The younger member of the *Tengelic Fm.* called *Tengelic Member* contains red (or "reddish") clay beds. It is found in the Villány Mts. and in wide hilly areas of SE Transdanubia. It contains relatively fresh material in which the weathering products are predominantly smectite and goethite formed under generally warm and dry climate in environmental conditions of savannah and steppe or forest steppe.

7. Yellow fissure filling clays in the Villány Mts. (e.g. at Somssich Hill, site No. 2) correspond to the cooling period of *Lower Pleistocene* period. They are even less altered and less oxidised than the relatively fresh material of the reddish clays of the *Tengelic Member*.

8. The *basal red clay layers of the Middle Pleistocene Paks Loess Fm.* contain remarkably similar material as the former red clays belonging to the *Tengelic Member*. Like in the *Tengelic Member*, they contain relatively much quartz and other detrital minerals. In both formations typical clay minerals are well crystallised detrital illite and mixed layer illite/smectite. Less frequent clay minerals are smectite+kaolinite or vermiculite+chlorite, depending probably on slight climatic fluctuations during this period. The somewhat lesser degree of weathering in the palaeosols as compared to the Tengelic red clays indicates the cooling of the temperature. It is expressed in minor but clearly defined differences in the quantity of minerals.

9. On the top of the limestone surface of the Villány Mts. red clays in both stratigraphic units can be regarded as *terra rossa* in the same sense as similar red clay deposits in N Hungary and in the Dinaric range. The red clays cannot be derived from the insoluble residue of the underlying limestone.

ACKNOWLEDGEMENTS

József Dezső (University of Pécs) helped in numerous ways in the field work, in collection and granulometric analysis of samples and in the observation of the speleological and geomorphological conditions. Part of the samples was separated and analysed by XRD by Béla Raucsik (University of Pannonia, Veszprém). Thank are due to Mária Földvári and Péter Kovács-Pálffy (Geological Institute of Hungary, Budapest) for submission of their unpublished analytical results and for valuable discussions.

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Received: March 12, 2007; accepted: August 10, 2007