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RUBIFICATION OF *TERRAE ROSSAE* IN SLOVAKIA: A MÖSSBAUER EFFECT STUDY

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Abstract—Mineralogical and ^{57}Fe Mössbauer spectroscopic analyses were made on seven *terrae rossae* and two *terrae fuscae* samples of Pliocene to Early Pleistocene age from Slovakia and limestone residues from their parent materials. In most of the samples, no mineral weathering or clay mineral formation could be detected by optical or X-ray powder diffraction investigation, compared with their parent limestone residues; only one *terra rossa* showed a strong weathering of primary feldspar and phyllosilicates and a high rate of clay formation, especially kaolinite. Mössbauer measurements between 5° and 300°K showed that hematite and goethite are the dominant color pigments in the rubified *terrae rossae* and their corresponding limestone residues. The mean particle size of hematite and goethite was estimated from Mössbauer effects and X-ray powder diffraction data to be 95 and 250 Å, respectively. Reduced values of the hyperfine fields at 5°K of the soil iron oxides, as compared with those of the pure oxides, indicate a partial substitution of Fe(III) by Al. The hematite content correlates with the Munsell color notation of 5 of the 7 *terrae rossae* samples and their corresponding limestone residues. All *terrae rossae* samples showed higher hematite contents than their corresponding limestone residues, indicating that the rubification of such materials is independent of the degree of weathering.

Key Words—Goethite, Hematite, Mössbauer spectroscopy, *Terrae rossae*, Weathering.

INTRODUCTION

Red clayey soils on limestone (*terrae rossae*) are often interpreted as products of intense mineral weathering and clay formation in subtropical and tropical climates. The red color of such soils is the result of rubification, a process defined by Kubiena (1970, pp. 109, 240) as the ". . . peptization of amorphous iron hydroxide and the formation of tiny crystals of goethite and hematite . . . freely suspended in the dense groundmass of a braunlehm[1] and (which) give it a bright red color." Rubification is therefore described micromorphologically; it is not the same as laterization which also produces reddening of the soil (Kubiena, 1970). The formation of hematite in soils of this type is generally believed to take place only in warm climates with seasonal alteration of precipitation and drought because high temperatures and dry conditions favor the development of this mineral. Fossil or relict *terrae rossae* in central Europe are therefore often considered as evidence of a corresponding paleoclimate (see references in Bronger, 1976b). On the other hand, many authors have considered *terrae rossae* as insoluble residues of limestones which contain material from pre-existing rubified soils. In this so-called "residual" theory, the significance of climate in the formation of *terrae rossae* is less important. Such soils are therefore lithomorphic soils, i.e., their genesis is greatly dependent on the parent material.

These contradictory hypotheses (cf. Ćirić and Aleexandrović, 1959; Bronger, 1976b) are due to insufficient knowledge of soil development processes, especially of the type and degree of mineral weathering and clay formation that takes place during rubification. In addition, the effect of the initial rock or parent material has not been considered sufficiently; generally, only bulk analyses have been made, and mineralogical balances have only rarely been made. The association and amount of iron oxides and oxyhydroxides, especially hematite and goethite, have not been evaluated in terms of the rubification process.

In the present study iron oxides and oxyhydroxides in *terrae rossae* and *terrae fuscae* (brown clayey soils on limestones) and residues from their parent limestones from Slovakia have been investigated by ^{57}Fe Mössbauer spectroscopy with regard to their relation to rubification. More conventional means of characterizing iron minerals generally have yielded less satisfactory results; e.g., using transmission and scanning electron microscopy, Bresson (1974) identified only goethite among the iron oxides he thought were responsible for

[1] An intensely weathered alfisol with a dense, clayey fabric containing a few skeleton grains, almost completely quartz, and very few voids (Kubiena, 1970).

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the red color in rubified "Holocene soils" (Munsell color 5 YR 5/4-5/8), "red fossil soils" (2.5 YR 5/8) from France, and "red Mediterranean soils" (2.5 YR 3/5-10 R 3/5). A few selected samples were also studied by X-ray powder diffraction and evaluated by using the subtraction method developed by Schulze (1981). Mineralogical balances (see Bronger *et al.*, 1976) were also made to clarify the relationship between rubification and the intensity of mineral weathering.

EXPERIMENTAL

Sample preparation and mineralogical analysis

Nineteen samples of *terrae rossae* and *terrae fuscae* and their parent limestones from Slovakia were examined. The Slovakian samples were selected for study because of the very young age of the parent material (travertines) or the well-established ages of the *terrae rossae* themselves (Pliocene-Pleistocene) (Smolíková and Ložek, 1962). In other parts of central Europe the limestone parents of *terrae rossae* are mostly of Jurassic or Devonian age, and the age of the *terrae rossae* developed on them is generally unknown. The *terrae rossae* deposits listed in Table 1 were described in detail by Smolíková (1963). Optical investigations of the >63-μm, 20–6-μm, and 6–2-μm size fractions and X-ray powder diffraction studies were carried out on seven *terrae rossae* and their corresponding limestone residues (LR). The limestone residues were obtained by treating the parent rocks with 0.1 N HCl at pH 4–5. The carbonate content of the limestones and travertines is very high (93–99%); only one travertine has a lower carbonate content (84.2%).

Because of the high carbonate content of the parent materials a micromorphological description of the rubification process was practically impossible; hence, Munsell colors of the different size fractions of the LR and the soils were determined. Those of the <0.2-μm fractions are given in Table 1.

Preparation of Al-substituted goethite

As a means of estimating the Al content of goethites in the *terrae rossae*, goethite samples with Al contents between 5.2 and 31.6 mole percent were prepared according to the method described by Thiel (1963). The Al content of the products was determined by chemical analysis.

Mössbauer effect measurements

Mössbauer spectra of the <0.2-μm fractions of the soils and limestone residues were obtained using a 25 mCi ^{57}Co(Rh) source and a constant acceleration Mössbauer spectrometer. Approximately 150 mg of sample (0.05 to 0.1 mg ^{57}Fe/cm^2) was placed in a Plexiglas holder. Spectra were obtained as a function of temperature between 5°K and ambient temperature in a liquid helium cryostat. The Mössbauer parameters were obtained from least squares fits to the data points using Lorentzian line shapes. The isomer shifts are reported with respect to metallic iron. The Mössbauer spectra displayed in the illustration show the data points with error bars and theoretical convolution curves of the spectral components. Stick diagrams indicate the identification of the different spectral components.

X-ray powder diffraction analyses

X-ray powder diffractograms of several samples were obtained using CuKα radiation and a Philips PW 1050/70 vertical goniometer equipped with a diffracted beam graphite monochromater. Following the procedure of Schulze (1981), the samples were treated with a mixture of dithionate, citrate, and bicarbonate (DCB) (Mehra and Jackson, 1960) to remove preferentially the iron oxides. Treated and untreated samples were step-scanned from 32° to 40°2θ at 0.02°2θ increments (counting time = 100 sec/increment). The diffractograms of the DCB-treated samples were least squares fitted with a series of Gaussian lines. To fit the diffraction diagrams of the corresponding untreated samples, positions, widths, and relative areas of the lines of the silicate minerals were held constant and only the line profile parameters of the iron oxides and the overall area of the silicate lines were allowed to vary. The latter parameter accounts for the different mass absorption properties of the treated and untreated samples. The lines of the soil iron oxides are obtained by subtracting the Gaussian lines of the silicate constituents in the diagram of the untreated sample.

MINERALOGICAL ANALYSIS

Bronger and Smolíková (1981) found no mineral weathering or clay mineral formation in *terrae rossae* from Dreveník, Ivanovce, or the three exposures near Levice. These soils therefore are lithomorphic in the sense of the "residual" theory described above. The clay content of the *terra rossa* from Ratnovce is high (87%), however, the residue from the underlying travertine itself consists of 75% clay. The weathering of feldspars and the considerable amount of phyllosilicates resulted in the formation of illite and kaolinite. However, the amount of clay formed in the *terra rossa* from Ratnovce is low in comparison with that of the much younger interglacial loess soils in the neighboring Carpathian Basin (cf. Bronger, 1976a; Bronger *et al.*, 1976). The largest part of the clay minerals in this *terra rossa* must also be regarded as inherited.

On the other hand, the amount of primary minerals >2 μm in the LR from Kolíňany Málok is very high (78%), and the clay content of the *terra rossa* is about twice that of the LR (47% vs. 22%). Although the total amount of clay formed is even less than that of a rubified Earthy Braunlehm[2] of middle Pleistocene age described

[2] Intensely weathered alfisol with very little clay illuviation.

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Table 1. Munsell soil color values, Fe_d values, Mössbauer parameters, and iron oxide content of the <0.2-μm fraction of *terrae rossae* and *terrae fuscae* samples.

	Sample locality (Slovakia)		Munsell color (dry)	Fe_d (%)	Mössbauer parameters: Hematite H[2] (kG)	Hematite RA[3] (%)	Goethite H (kG)	Goethite RA (%)	Doublet RA (%)	Hematite content (%)	Goethite content (%)	Al content of (goethite) (mole % ± 2)
A	Dreveník	*terra rossa*	5 YR 5/6	3.5	528	23.5	495	46.2	30.6	1.6	3.8	18
B		LR[1]	5 YR 5/6	3.7	526	14.0	493	58.7	27.3	1.0	4.8	22
C	Hradište pod Vrátnam	*terra fusca*	7.5 YR 6/6-8	5.9	—	—	486	58.0	42.0	—	9.4	≳32
D		LR	7.5 YR 6-7/6-8	6.2	—	—	485	83.0	17.0	—	9.9	≳32
E	Ivanovce	*terra rossa*	10 YR 7/6	3.9	527	5.2	493	76.1	18.7	0.3	5.9	22
F		LR	7.5 YR 6-7/6-8	4.3	527	4.8	494	80.1	15.1	0.3	6.5	20
G	Ratnovce	*terra rossa*	6.25 YR 7/6-8	4.7	529	9.2	495	75.0	13.8	0.7	6.7	18
H		LR	10 YR 7-8/6-8	4.6	526	1.0	495	81.0	15.0	0.2	7.1	18
K	Kolíňany-Málok	*terra rossa*	2.5 YR 5/8	4.5	525	39.0	493	31.0	30.0	3.6	3.3	22
L		LR	5 YR 5-6/8	4.5	522	17.0	492	57.0	26.0	1.5	5.6	25
M	Levice Zlatý onyx (lower left part)	*terra rossa*	3.75 YR 6/8	3.4	529	28.0	496	41.0	31.0	1.9	3.3	15
N		LR	7.5 YR 6/6	2.9	531	8.7	497	43.0	48.3	0.7	3.8	14
O	Levice Zlatý onyx (lower right part)	*terra rossa*	2.5 YR 5/8	5.5	531	51.8	497	28.3	19.8	5.2	3.2	14
P		LR	10 YR 6-7/6	4.4	532	2.8	496	43.3	53.8	0.3	6.7	15
Q	Levice Zlatý onyx (upper part) "Vo viniciach"	*terra rossa*	3.75 YR 5-6/8	3.9	527	26.0	495	39.8	34.2	2.2	3.8	18
R		LR (partly weathered)	5 YR 5/8	4.1	528	8.9	495	57.4	33.7	0.7	5.7	18
R″		LR (fresh)	10 YR 7-8/6	n.d.	—	—	497	92.3	7.7	n.d.	n.d.	14
X	Ludrová	*terra fusca*	7.5 YR 5-6/8	5.6	—	—	488	60.0	40.0	—	8.9	32
Y		LR	7.5 YR 6/8	6.3	—	—	491	92.0	8.0	—	10.0	28

[1] LR = limestone residue.
[2] H = effective magnetic field (at 5°K).
[3] RA = relative area fraction.

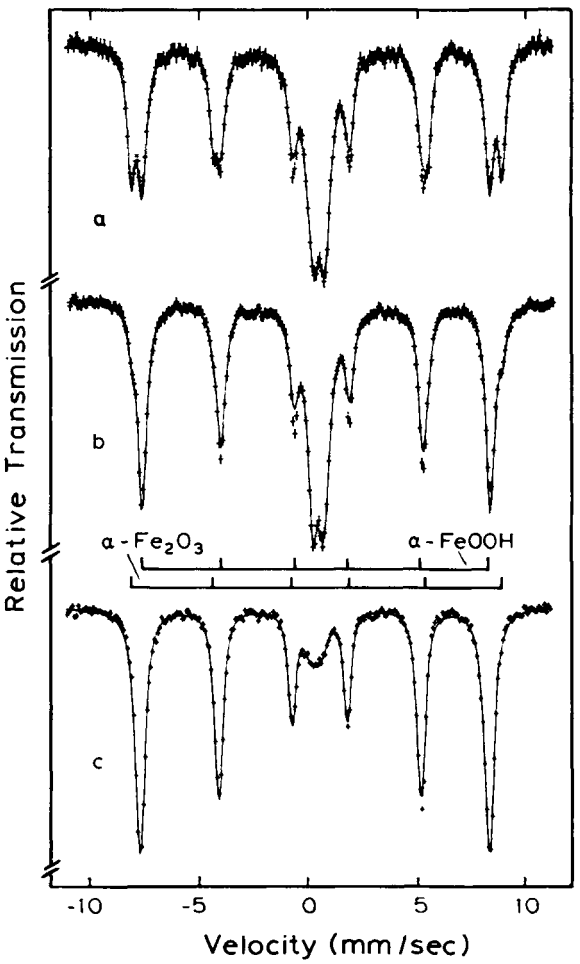


Figure 1. Mössbauer spectra (5°K) of (a) a terra rossa (Q), and its noncalcareous limestone residues from (b) weathered travertine (R) and (c) fresh bottom travertine (R″) of Pliocene age in the upper part ("Vo viniciach") of the exposure "Zlaty onyx" near Levice.

by Bronger *et al.* (1976), the weathering of most of the feldspar and phyllosilicates resulted in the formation of illite and, to a greater extent, kaolinite, contrary to the rubified Earth Braunlehms of middle and early Pleistocene age developed from loess, and in which almost no kaolinites were formed (Bronger, 1976a, 170–173, Figure 7B).

MÖSSBAUER ANALYSIS

Description of Mössbauer spectra

Mössbauer data for the LR and soil samples are listed in Table 1. The main feature of the room temperature spectra for most of the soil samples is a quadrupole doublet typical of paramagnetic Fe(III). Some of the spectra also show evidence of magnetic splitting. The Mössbauer parameters of a second low intensity doublet (sample G, H) are characteristic of paramagnetic Fe(II) ($\delta = 0.90$ mm/sec, $\Delta E_Q = 2.92$ mm/sec at 296°K).

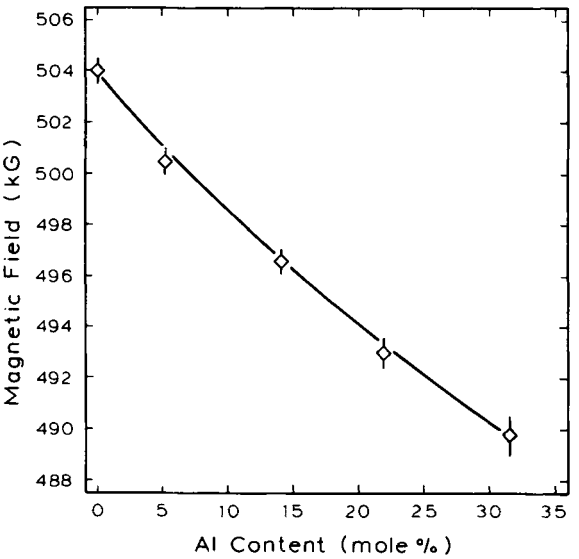


Figure 2. Variation of the magnetic hyperfine field (at 5°K) with Al substitution for synthetic α-$Al_xFe_{1-x}OOH$.

Representative 5°K spectra of *terrae rossae* samples are shown in Figure 1. These spectra are dominated by well-resolved magnetic hyperfine sextets. In all 5°K spectra of *terrae rossae* sample pairs, two, six-line patterns were detected, whereas only one magnetic sextet was observed in the spectra of the two *terrae fuscae* sample pairs. The paramagnetic Fe(III) quadrupole doublet persists in the low-temperature spectra, although less pronounced in some samples than in others (see Figure 1). This changeover from a doublet to a six-line pattern as the main component of the spectrum upon cooling is expected for very small antiferromagnetic or ferromagnetic particles (≤200 Å) which exhibit superparamagnetism (Kündig *et al.*, 1966).

Identification and quantitative analysis of the soil iron oxides

In principle, different iron oxides can be identified from their characteristic internal magnetic fields H_{eff} and quadrupole splittings ϵ (Greenwood and Gibb, 1971, p. 241). For soil iron oxides the analysis is complicated because both parameters depend on the particle size and the partial substitution of Fe(III) by nonmagnetic elements, commonly Al (Norrish and Taylor, 1961; Janot and Gibert, 1970). However, as will be shown below, the effect of particle size on the hyperfine field can be neglected at sufficiently low temperatures.

The Mössbauer spectra at 5°K of the soil samples indicate that hematite and/or goethite are present. The hyperfine fields of the oxides are reduced compared with those of pure goethite and hematite of 504 kG (Forsyth *et al.*, 1968) and 544 kG (Van der Woude, 1966), respectively; the values range from 486 to 497 kG for the soil goethites and from 522 to 532 kG for the soil hematites (Table 1). This reduction of the magnetic fields

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of the soil iron oxides is most probably due to partial substitution of Fe(III) by Al (Golden *et al.*, 1978; Fleisch *et al.*, 1980) causing a partial disruption of the magnetic coupling of Fe(III). To estimate the Al content, the decrease of H_{eff} as a function of substituted Al was calibrated with synthetic aluminous goethites (Figure 2). On this basis the Al concentrations of the goethite in the *terrae rossae* and *terrae fuscae* sample pairs range from 14 to 25 mole % and from 28 to ~32 mole %, respectively (Table 1). A corresponding calibration for aluminous hematite was communicated to the authors by L. H. Bowen (Department of Chemistry, University of North Carolina, Raleigh, North Carolina) that indicates an Al concentration of ~7 to 10 mole % in the hematite of our soil samples. These values agree with results obtained by Norrish and Taylor (1961) and Golden *et al.* (1979) for soil goethite, and by Schwertmann *et al.* (1979) for aluminous hematite synthetized under near pedogenic conditions.

The quadrupole interaction term ϵ for pure hematite changes sign and magnitude at the Morin temperature of 260°K (Van der Woude, 1966). The transition cannot be observed for hematite in the soil samples, in agreement with Bowen's results that synthetic hematite substituted by more than 7 mole % Al does not undergo the Morin transition. The same effect was found by Van der Kraan (1972) for small hematite particles ($\leq$120 Å in diameter). In all of the 5°K spectra a central quadrupole doublet was detected with different peak areas (see Table 1). This doublet probably derives from Fe(III) in clay silicates. The additional doublet (δ = 1.12 mm/sec, ΔE_Q = 3.25 mm/sec at 5°K) in two samples must be due to Fe(II) in the same structure.

On the basis of the peak areas of the different spectral components in the Mössbauer spectra at 5°K (Table 1), the relative amounts of hematite and goethite were estimated using the relative Mössbauer constants determined at 296°K by Meisel and Kreysa (1973). This analysis neglects the influence of Al concentration, particle size, and temperature on the proportionality constants; thus, the relative amounts of goethite are probably overestimated. To calculate the absolute hematite and goethite concentrations in the samples the total oxidic Fe (Fe_d) was determined (Table 1).

Mean particle size

As noted above, particle size and Al substitution affect the magnetic hyperfine fields of the iron oxides. A separation of these interrelated influences (Thiel, 1963) is possible on the basis of the following considerations: The internal magnetic field of a magnetically ordered compound is proportional to the magnetization which decreases with increasing temperature according to its magnetization curve. For very small particles the collective excitation of the magnetization vector of the particle leads to a further reduction of the magnetization at any temperature (Mørup and Topsøe, 1976). This reduction is given for uniaxial crystals by

$$M(T) = M_0(T)\langle \cos \theta \rangle_T, \quad (1)$$

where $M_0(T)$ is the magnetization of a large particle at temperature T and $\langle \cos \theta \rangle_T$ is the thermal average of the projection on the easy axis of the crystal. In the low temperature approximation $\langle \cos \theta \rangle_T$ decreases linearly with T, as follows:

$$\langle \cos \theta \rangle_T \simeq 1 - kT/2KV. \quad (2)$$

The slope is proportional to the inverse of the anisotropy energy KV of the particle of volume V. The corresponding equation for the internal magnetic field becomes

$$H(T) = H_0T(1 - kT/2KV). \quad (3)$$

The measured value of H represents an average of distributions of three crystal properties: (1) the internal field $H_0(T)$ which is determined by the Al substitution; (2) the anisotropy constant K which depends on various factors such as the size and shape of the crystals and probably the Al substitution; (3) the volume of the crystals. As a first approximation the dependence between the various distributions is neglected and the averages $\overline{H}_0$, $1/K_{av}$, and $1/V_{av}$ are taken. The volume distribution of the particles is assumed to be most important. A logarithmic Gaussian function

$$F(V) = \exp[-\ln(V/V_0)^2/b^2] \quad (4)$$

is assumed to be the best means of describing the natural size distribution of the oxide particles (V_0 = mean particle volume; b = shape parameter of the volume distribution). For this function $1/V_{av} = (1/V_0)\exp(b^2/4)$, which is approximately equal to $1/V_0$ for reasonable values of b ($b \leq 1$). Inserting the average values the equation

$$H(T) = \overline{H}_0(T)[1 - (KT/2)(1/K_{av})(1/V_0)] \quad (5)$$

depends on two parameters: $\overline{H}_0(T)$, the average internal field of the bulk material and $(1/K)_{av}V_0^{-1}$, the reciprocal of the anisotropy energy.

Without assumptions on the temperature dependence of $\overline{H}_0(T)$ the effect of the Al content and the particle size of the oxides on the internal field cannot be separated. The dependence of the reduced values $\overline{H}_0(T)/\overline{H}_0(T = 0)$ vs. the reduced temperature T/T_N is supposed to be independent of the Al concentration. The Neél temperature T_N is also an average value.

In a *terra fusca* sample the analysis for goethite at 7°K and 40°K proceeds as follows: The pure compound exhibits a reduced field value of ~1.0 at the reduced temperature T/T_N of ~0.2 for T = 78°K and $T_N \simeq 400$°K (Forsyth *et al.*, 1968). From the temperature dependent Mössbauer spectra of the soil sample, the Neél temperature is $\geq$200°K. Consequently, T/T_N is <0.2, and

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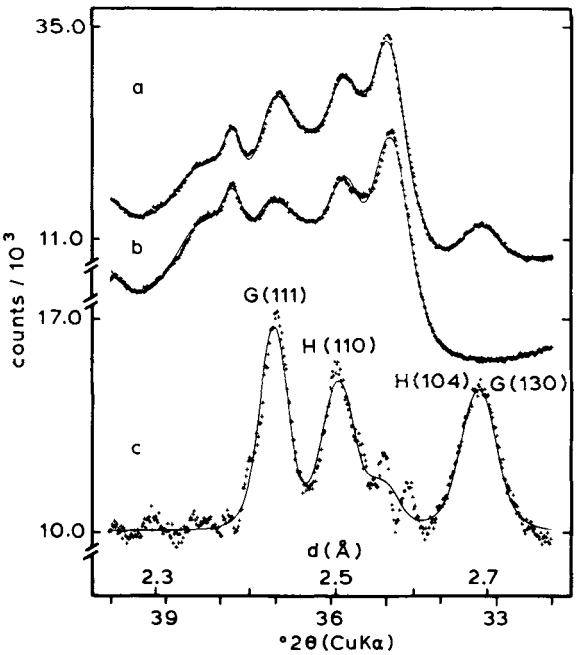


Figure 3. X-ray powder diffraction patterns of (a) untreated, (b) DCB-treated soil sample Q, and (c) X-ray diffractogram obtained from diagram (a) after subtraction of the reflections of the silicate minerals (solid line represents the theoretical convolution curve of the components; G = goethite and H = hematite).

$\overline{H}_0(40\ K)/\overline{H}_0(0)$ can be taken to be 1.0. Inserting the measured values of H(7°K) = 492 kG and H(40°K) = 486 kG in Eq. (5), $\overline{H}_0(0) = 492$ kG and $V_0(1/K)_{av}^{-1} = 2.8 \times 10^{-13}$ erg. A mean diameter of the particles of ~260 Å can be calculated using for $(1/K)_{av}^{-1}$ the value of the anisotropy constant of 1.5×10^4 erg/cm³ given by Shinjo (1966). This particle size can be taken as typical for the goethite microcrystals in all the soil samples on the basis of the similar temperature dependent Mössbauer spectra.

The collective excitation effect can be neglected at 4.2°K. The correction in this example is $\frac{1}{2} \times kT(1/K)_{av}(1/V)_{av} \simeq 2 \times 10^{-3}$ which would lead to an overestimation of the Al substitution in goethite of 2 mole %.

For a soil sample rich in hematite a mean diameter of the hematite microcrystals was determined to be ~95 Å (using the values $K = 0.6 \times 10^6$ erg/cm³ determined by Mørup and Topsøe (1976) for 120-Å α-Fe_2O_3 particles).

X-RAY POWDER DIFFRACTION ANALYSIS

Typical X-ray powder diffractograms of a soil sample are shown in Figure 3. The presence of hematite and/or goethite in the untreated sample (Figure 3a) are indicated by a peak at ~2.70 Å (goethite d(130) and hematite d(104) spacing). After subtraction of the peaks of the silicate constituents (Figure 3b) in the sample both soil oxides could be distinguished by the 111 peak of goethite at ~2.45 Å and the 110 peak of hematite at ~2.51 Å.

The dimensions of the iron oxide crystallites were estimated from the broadening of the 110 reflection of hematite and the 111 and 130 reflections of goethite, using Scherrer's formula (Klug and Alexander, 1954, 491–538). The measured widths at half height of the peaks were corrected for instrumental line broadening. For hematite in *terra rossa* sample O the dimension D(110), defined as the effective thickness of the crystallite in a direction perpendicular to the (110) reflecting planes, amounts to ~135 Å. This value is in good agreement with that of ~95 Å from the Mössbauer analysis. The dimensions D(111) and D(130) for goethite in a *terra fusca* sample are ~120 Å and ~205 Å, respectively, compared to the value of ~260 Å obtained from the Mössbauer analysis.

The estimation of the extent of substitution of Fe by Al in both oxides from the XRD line shifts is not possible, because of the great uncertainty (about ±0.07 Å) in the determination of the line positions.

DISCUSSION AND CONCLUSIONS

Only goethite was detected in the two *terrae fuscae* samples and their corresponding LR of strong brown to reddish yellow colors. In the seven *terrae rossae* sample pairs of strong red to reddish yellow colors different proportions of goethite and hematite were identified. Both iron oxides contain substitutional Al and occur as small crystallites. From the Mössbauer data and the Munsell colors of the *terrae rossae* sample pairs (Table 1), the gross coloration of the samples can generally be related to the proportions of both iron oxides. Similar findings were reported by Bigham *et al.* (1978) and Torrent *et al.* (1980). In our samples ranging in color from 5 YR to 2.5 YR the hematite content is ≥1.5%, e.g., the concentrations of 1.5%, 2.0%, and 3.6% were found for the 5 YR, 3.75 YR, and 2.5 YR hues, respectively. In the color range 10 YR to 6.25 YR, the hematite content is 0.2–0.7%, with two exceptions. *Terra rossa* (A) and its LR (B) from Dreveník show the same Munsell color in the <0.2-μm fraction (5 YR 5/6), but the hematite content is 1.6% in the *terra rossa* and only 1.0% in the LR. Also, the <0.2-μm fractions of *terra rossa* (Q) and its LR (R) in the "Vo viniciach" exposure from Levice show similar Munsell colors (3.75 YR 5-6/8 and 5 YR 5/8, respectively), but the hematite concentration is 2.2% in the *terra rossa* and only 0.7% in the LR (from a highly weathered travertine with lime content of ~96%). The LR of the fresh bottom travertine (R″) ($CaCO_3 > 99.1\%$), on the other hand, exhibits a Mössbauer spectrum of pure goethite (Figure 1). This observation agrees with the idea of Gebhardt *et al.* (1969) and Meyer and Kruse

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(1970) who explained the rubification as a process during decalcification ("Entkalkungsrötung").

Some silt fractions, especially the coarse silt fraction (63–20 μm) of two of the three *terrae rossae* from Levice (M and Q), are very red (2.5 YR 4/8). This observation implies that the iron oxides are also bound to the silt particles, at odds with the findings by Bresson (1974, p. 540) who observed only "strong bonding between iron oxides and clay minerals" in "Red Mediterranean soils."

All *terrae rossae* contain more hematite than their corresponding LR (Table 1). This general trend is most pronounced in the *terra rossa* sample pair O-P where the hematite content is 0.3% in the LR and 5.2% in the *terra rossa*. In these samples, however, the weathering of silicates and formation of clay minerals is negligible. A less pronounced increase of 0.2–0.7% hematite was found for the sample pair G-H, but here weathering of phyllosilicates and clay formation have taken place. In the *terra rossa* from Kolíňany-Málok (K), the only soil to have undergone intensive weathering and clay formation, the increase of the hematite content is intermediate (from 1.5% in the limestone to 3.6% in the *terra rossa*). In the *terra rossa* sample pair E-F from Ivanovce no change in the hematite content was observed. In this exposure, however, the material consists of a soil sediment which contains small fractions of distinct red color (10 R 4/6) in a predominantly brown matrix (7.5 YR 5/8). These fractions show a single Mössbauer six-line spectrum which can be attributed to Al-substituted hematite on the basis of the hyperfine field value of 529 kG at 5°K. Because weathering of silicate minerals was not detectable in most samples, the largest portions of the iron oxides probably result from the weathering of ankerite.

These investigations show that the extent of rubification of *terrae rossae* from Slovakia can be characterized, with some exceptions, by a greater hematite content than corresponding limestone residues, and that the rubification of *terrae rossae* is independent of weathering. Silicate weathering and clay formation was not detected in most of the *terrae rossae* examined. The assumption that the formation of hematite occurs only under subtropical or tropical climate with distinct dry seasons seems doubtful. Schwertmann *et al.* (1982) observed that in soils on calcareous gravels from the Würm glaciation in the humid temperate climate in southern Germany, goethite *and* hematite can be detected under specific lithogenic and microclimatic conditions.

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Резюме—Минералогический и ^{57}Fe Мессбауеровский спектральный анализы были проведены на семи образцах терра-росса и двух образцах терра-фюзе из эпохи от плиоцена до раннего плейстоцена в Словакии и на известняковых осадках из первоначальных материалов. В большинстве образцов ни выветривание, ни образование глинистых минералов не могут быть обнаружены при помощи оптической или порошковой рентгеновской диффракции по сравнению с их первоначальными известняковыми осадками. Только один образец терра-росса показал сильное выветривание первоначального фельдшпата и филлосиликатов и большую скорость образования глины, особенно каолинита. Мессбауеровские измерения между 5° и 300°K указали на то, что гематит и гетит являются главными цветовыми пигментами в красноватых образцах терра-росса и соответствующих им известняковых осадках. Средний размер частиц гематита и гетита был приблизительно оценен из данных эффектов Мессбауера и рентгеновской порошковой диффракции на 95 и 250 Å соответственно. Меньшие величины сверхтонких полей при 5°K почвенных окисей железа по сравнению с величинами чистых окисей указывают на частичную подстановку атомов Fe(III) атомами Al. Содержание гематита соответствует минселловскому цветному коду для 5 из 7 образцов терра-росса и соответствующих им известняковых осадков. Все образцы терра-росса имели большее содержание гематита, чем соответствующие им известняковые осадки. Это указывает на то, что покраснение таких материалов является независимым от степени выветривания. [E.G.]

Resümee—Sieben ausgewählte Terrae rossae pliozänen bis altpleistozänen Alters und zwei Terrae fuscae alt- bis mittelpleistozänen Alters und ihre jeweiligen Kalksteinlösungsrückstände aus der Slowakei wurden mineralogisch und mößbauerspektroskopisch untersucht. In fünf Terrae rossae ist im Vergleich zum jeweiligen Kalksteinlösungsrückstand keine Mineralverwitterung und Tonmineralbildung belegbar. In einer Terra rossa ist die Tonmineralbildung gering. Nur eine Terra rossa zeigt eine stärkere Verwitterung von primären Feldspäten und Phyllosilikaten und eine höhere Tonbildungsrate, insbesondere von Kaoliniten. Mößbauer-Messungen zwischen 5° und 300°K zeigen, daß Hämatite und Goethite die dominierenden Eisenoxide in den rubefizierten Terrae rossae einschließlich ihrer zugehörenden Kalksteinlösungsrückstände sind. Die mittleren Korngrößen von Hämatit und Goethit wurden aufgrund von Mößbauereffekt-Daten und Röntgenanalysen auf 95 bzw. 250 Å abgeschätzt. Reduzierte Werte der Hyperfeinfelder bei 5°K der Eisenoxide in den Böden im Vergleich zu reinen Eisenoxiden weisen auf eine partielle Substitution von Fe(III) durch Al hin. Bei fünf der sieben Terrae rossae und ihrer jeweiligen Kalksteinlösungsrückstände korreliert der Hämatitgehalt mit den Munsell-Farbwerten. Alle Terrae rossae zeigen höhere Hämatitgehalte als ihre jeweiligen Kalksteinlösungsrückstände. Das bedeutet, daß die Rubefizierung dieser Böden unabhängig von der Verwitterungsintensität ist.

Résumé—Des analyses minéralogiques et spectrographiques de Mössbauer ^{57}Fe ont été faites sur sept échantillons de *terrae rossae* et sur deux échantillons de *terrae fuscae* du pliocène et du haut pleistocène de Slovaquie et sur des résidus calcaires des matériaux d'origine. Dans la plupart des échantillons, aucune altération minéralogique ni de formation de minéral argileux ne pouvait être détectée par investigation optique ou de diffraction poudrée de rayons-X, comparé aux résidus calcaires d'origine; une seule *terra rossa* a montré une forte altération de feldspar primaire et des phyllosilicates, et un taux élevé de formation d'argile, spécialement de la kaolinite. Des mesures de Mössbauer entre 5° et 300°K ont montré que l'hématite et la goethite étaient les piments de coloration dominants dans les *terrae rossae* rubifiées et leurs résidus calcaires correspondants. La taille moyenne de la particule d'hématite et de goethite a été estimée à partir des effets de Mössbauer et des données de diffraction poudrée des rayons-X à 95 et 250 Å, respectivement. Des valeurs réduites des champs hyperfins à 5°K des oxides de fer de sols, comparé à celles d'oxides purs, indiquent une substitution partielle de Fe(III) par Al. Le contenu en hématite s'accorde avec la notation de couleur Munsell de 5 des 7 échantillons *terrae rossae* et leurs résidus calcaires correspondants. Tous les échantillons de *terrae rossae* ont montré des contenus en hématite plus élevés que leurs résidus calcaires correspondants, indiquant que la rubification de tels matériaux est indépendante de degré d'altération. [D.J.]

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