INFLUENCE OF CLIMATE ON THE IRON OXIDE
MINERALOGY OF *TERRA ROSSA*

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Abstract—*Terra rossa* samples were taken from the B horizons of soil profiles and from cracks within limestone in Italy. The average annual temperature (AAT) of the sites ranged from 8.4 to 20.3°C and the average annual precipitation (AAP) from 511 to 3113 mm, with either a 5–6 month water deficit or a large water surplus. Goethite and hematite were identified in all the samples. Under a moist (>1700 mm AAP) and cool (13°C AAT) climate, a xeric, hematitic pedoenvironment was preserved by the well-litified carbonate rock. Hematite occurred in trace amounts, even with an AAT of 8.4°C and an AAP of 3300 mm, confirming the specific role of the hard limestone on the pedoclimate of *terra rossa*. The lowest mean crystallite dimension of goethite and hematite was found in the samples from the wettest sites, and in these samples hematite was nearly free of Al substitution. Rubification in *terra rossa* appeared to be due to the specific pedoenvironment. The hematite cannot be considered a relict phase formed under another climate. Illite and kaolinite were the main clay minerals in samples from xeric sites whereas more weathered clays, such as Al-interlayered vermiculite, occurred in cool, moist sites. We postulate that the processes of rubification and vermiculitization could have taken place at the same time.

Key Words—Goethite, Hematite, Pedoclimate, *Terra rossa*, XRD.

Terra rossa is a red soil very common in areas of mediterranean climate. It forms a discontinuous and shallow cover on hard carbonate rock. The characteristic bright red color is due to the high pigmenting power of hematite, which masks the coexisting yellow of goethite (Torrent *et al.,* 1983; Barron and Torrent, 1986; Schwertmann, 1988; Boero and Schwertmann, 1989).

Red hematitic soils are generally considered the result of intense mineral weathering under subtropical and tropical climates. Therefore, the *terra rossa* that occur under temperate climates have been considered *relict soils,* formed under warmer paleoclimates (see Bronger *et al.,* 1983 for references). However, hematite has been demonstrated to form in axeric temperate areas, provided there is a dry pedoclimate during part of the year (Bresson, 1974, 1976; Schwertmann *et al.,* 1982). Therefore, the relict hypothesis is not the only explanation for the occurrence of hematite in *terra rossa.*

Boero and Schwertmann (1989) have recently identified the crucial role of limestone in determining the specific pedoclimate under which the hematite of a *terra rossa* can form. The high internal drainage of the rock controls the water and air regime of the overlying soil. This generates a xeric environment and the preferential formation of hematite over goethite, i.e., rubification. This conclusion was further supported by the observation that neighboring soils of equal age, on

weakly-permeable parent rock, showed no rubification. However, no *terra rossa* is formed above certain altitudes where lower temperatures and higher precipitation prevail, even on hard limestone. This suggests the existence of a threshold for the association of climate and hard limestone that determines the xeric conditions for hematite crystallization. Furthermore, it is not known how this association might be relevant for the weathering processes of clay minerals in *terra rossa.*

The aim of this work is to elucidate the role of the climate-hard limestone association on the mineralogy of iron oxides and clay minerals in *terra rossa.*

MATERIALS AND METHODS

Soils and climate

Sixteen *terra rossa* samples were taken from the B horizons of soil profiles and from cracks in carbonate rocks in Sardinia (Italy) and NE Italy (Figure 1). Samples (10–20 kg) were also taken from the underlying rock, mainly well-lithified limestone or dolomite, sometimes also fossiliferous, entirely or partially recrystallized with a micritic structure.

Temperature and rainfall data were collected at the meteorological stations closest to the sites. Average annual temperatures (AAT) ranged from 8.4 to 20.3°C; average annual precipitation (AAP) from 511 to 3313 mm. The number of rainy days per year ranged from
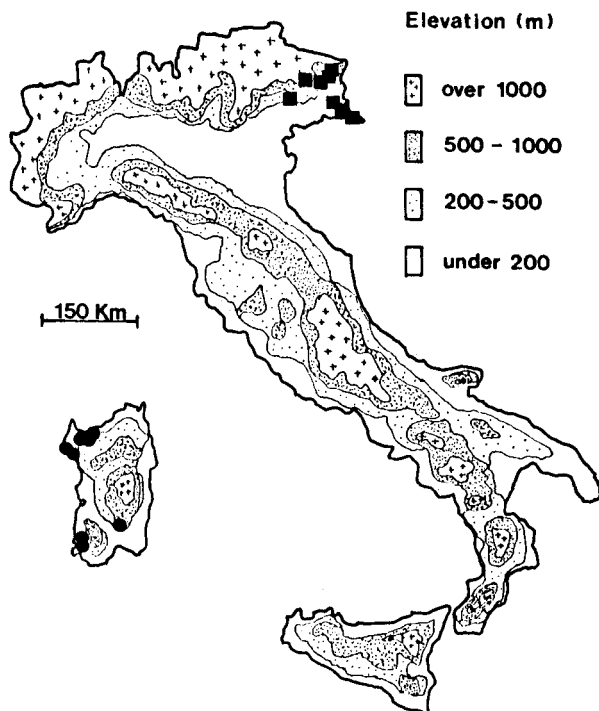
Elevation (m)

over 1000

500 - 1000

200 - 500

under 200

150 Km

Figure 1.   Location of the samples from Sardinia (●) and NE Italy (■).

Table 1.   Meteorological data for the sampling sites.

Sample no.	Elevation (m)	AAT[1] (°C)	AAP[2] (mm)	Rainfall (days/y)	Water deficit[3] (months/y)
Sardinia					
8B	75	16.1	511	66	6.4
17B	2	20.3	581	62	6.6
6TR	85	16.1	599	74	5.8
3D	125	17.4	655	(*)	6.1
I120	39	17.1	665	(*)	5.6
I110	20	16.2	688	51	5.5
15	20	16.2	688	(*)	5.5
14	763	15.9	791	64	4.7
NE Italy					
205	5	14.2	1078	95	2.7
206	131	13.2	1387	103	1.3
204	150	13.3	1415	102	1.1
211	200	13.0	1741	107	0
209	1050	8.4	1820	130	0
210b	1050	8.4	1820	130	0
208	550	11.0	2246	99	0
207	852	12.8	3313	129	0

[1] AAT = Average annual temperature.
[2] AAP = Average annual precipitation.
[3] Water deficit (rainfall minus evapotranspiration).
* Not available.

51 to 130, and water balance from 5 to 6 months of water deficit (rainfall minus evapotranspiration) to a large water surplus (Thornthwaite, 1948) (Table 1).

Physical and chemical methods

The soil samples were air dried and sieved to <2 mm after crushing the aggregates in a porcelain mortar. Particle size analysis was carried out by the pipette method after dispersion in water with Na-hexametaphosphate. Organic matter was removed by digestion with H_2O_2 and iron oxides by the Na-dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960).

The pH was measured potentiometrically in soil : water suspensions (1:2.5). Dry color of the <2-mm fraction was estimated using the Munsell Color charts and then converted to a redness rating index as proposed by Torrent *et al.* (1980). The carbonate content of the soil samples was determined with a Dietrich Fruhling pressure-calcimeter. Total iron (Fe_t) and total Manganese (Mn_t) were determined after acid attack with $HCl : HNO_3$ (3:1, 2 hr boiling). DCB-extractable Fe (Fe_d) and Mn (Mn_d) were determined as described in Boero and Schwertmann (1989).

In order to determine the percent of insoluble residue of the rock underlying the *terra rossa,* selected rock samples were ground to pass a 2-mm sieve. Subsamples of 500 g were treated with a pH 4.5 CH_3COONa buffer solution to remove the carbonates (Rabenhorst and Wilding, 1984). The insoluble residues were kept in the acid solution until pH did not change. After centrifugation, Fe and Mn were determined in the clear supernatant. The residue was washed free of salts, dried at 40°C and weighed.

X-ray analyses

Iron oxides. The <2-μm fraction was separated by sedimentation from NaOH (pH = 9) dispersed and sonicated aqueous suspensions of <2 mm soil. These suspensions were then washed free of salts and oven-dried at 40°C. The powders were X-rayed using Fe-filtered CoKα radiation and a Philips diffractometer (PW1729 generator, PW1820 vertical goniometer equipped with a PW1710 control unit). Differential X-ray diffraction (DXRD) patterns between 23.5 and 45°2θ with 0.02°2θ steps and 40 s counting time per step, were obtained by subtracting step-scanned powder diffractograms of the sample before and after DCB (Schulze, 1981). Heights (h), widths at half height (WHH), and positions of diffraction lines were measured on DXRD spectra.

The hematite/goethite ratios were approximated by using the DXRD line intensities after multiplying the 110 peak area (WHH·h) of hematite (Hm) by 1.41 and the 111 peak area of goethite (Gt) by 1.25. The mean crystallite dimension of goethite perpendicular to 111 (MDC_{111}) was calculated from WHH_{111}, and that of hematite (MCD_a, plate diameter) from WHH_{110} using the Scherrer formula.

The Al substitution in goethite was determined from the unit cell dimension c_0 (obtained from d_{110} and d_{111}), using the equation Al (mole %) = $1730 - 572c_0$ (Schulze, 1984). Al substitution in hematite was estimated from

Table 2. Color, redness rating, pH, carbonates and clay content of *terra rossa* samples.

Sample no.	Color (dry)	RR[1]	pH (H_2O)	Carbonates (%)	Clay[2] (%)
Sardinia					
8B	5 YR 4/6	7.5	7.6	0.4	64.9
17B	5 YR 3/6	10.0	7.1	0.4	39.6
6TR	5 YR 3/4	6.7	7.9	0.2	48.3
3D	2.5 YR 4/6	11.2	8.1	7.1	59.4
I120	5 YR 5/6	6.0	7.5	0.2	63.7
I110	5 YR 5/8	8.0	7.6	0.2	63.1
15	7.5 YR 5/6	3.0	7.4	1.4	47.1
14	5 YR 3/6	10.0	8.3	1.6	24.9
NE Italy					
205	2.5 YR 4/6	11.2	8.0	1.4	73.0
206	5 YR 4/6	7.5	6.9	0.2	80.9
204	5 YR 5/8	8.0	7.5	0.2	80.3
211	2.5 YR 3/6	10.0	7.8	0.8	97.1
209	7.5 YR 6/6	2.5	6.9	0.4	87.1
210b	7.5 YR 6/6	2.5	6.6	0.4	81.1
208	7.5 YR 6/6	2.5	8.0	0.8	58.7
207	5 YR 5/6	6.0	7.5	0.2	62.6

[1] Redness rating.
[2] <2-μm fraction after DCB treatment.

the a_0 dimension (obtained from d_{110}) using the equation Al (mole %) = $3109 - 617.1a_0$ (Schwertmann *et al.*, 1979).

Clay minerals. The <2-μm fraction was separated from dispersed suspensions of H_2O_2- and DCB-treated <2-mm soil. The clay fraction was subjected to the usual procedures for the identification of clay minerals. X-ray diffraction analysis was carried out using a Philips PW1730 instrument with CoKα Fe-filtered radiation

on oriented specimens at a scanning rate of 1.2°2θ/min. Hydroxy interlayers, if present, were removed from subsamples by boiling with 1 N NH_4F for 10 min (Rich and Obenshain, 1955). Diffractograms of these NH_4-saturated samples as well as of the NH_4-saturated and heated-to-550°C samples were recorded.

RESULTS

<2-mm fractions

General properties. All samples had neutral or alkaline reactions and low carbonate contents (Table 2). Samples from NE Italy had a significantly higher average clay content than those from Sardinia (78 *versus* 51%) and were free of reductomorphic features, including sample 211 which had 97.1% clay.

The Munsell hue ranged from 7.5 YR to 2.5 YR and the redness rating ranged from 2.5 to 11.2, indicating the occurrence of hematite (Schwertmann, 1988; Torrent *et al.*, 1983). The correlations between redness rating and AAP, water deficit and number of rainy days per year were poor and not significant. However, correlation between redness rating and AAT (r = .61) was significant (p = .99).

Forms of iron. In *terra rossa* samples the total amount of pedogenic iron oxides and the degree of weathering (Table 3), as judged from the Fe_d/Fe_t ratio, were similar to those reported for other *terra rossa* (Boero and Schwertmann, 1989). Sample 3D from Sardinia has a relatively high Fe_d content directly related, possibly, to the high Fe content of underlying limestone (0.25%), which might have played an important role as the Fe source. Similarly in this sample, the high amount of

Table 3. Fe and Mn in <2-mm *terra rossa* and in the underlying limestone.

Sample no.	<2-mm *terra rossa*				Limestone		
	Fe_d (%)	Fe_t (%)	Mn_d (%)	Fe_d/Fe_t	Fe ppm	Mn ppm	Residue[1] (%)
Sardinia							
8B	4.35	5.95	0.090	0.73	nd	nd	nd
17B	4.20	5.85	0.590	0.72	nd	nd	nd
6TR	3.07	4.98	0.074	0.62	62	23	<1
3D	8.76	10.86	1.090	0.81	2508	756	10
I120	3.65	6.22	0.068	0.59	650	66	<1
I110	2.85	5.48	0.034	0.52	124	17	0.01
15	3.10	4.80	0.050	0.64	nd	nd	nd
14	3.11	4.37	0.050	0.71	nd	nd	nd
NE Italy							
205	5.19	7.06	0.083	0.74	40	13	<1
206	5.18	6.94	0.069	0.75	40	13	0.12
204	5.33	6.92	0.189	0.77	nd	nd	nd
211	4.97	7.08	0.032	0.70	33	10	nd
209	3.22	5.81	0.042	0.56	nd	nd	nd
210b	3.78	6.42	0.075	0.59	64	13	1.35
208	3.93	5.32	0.104	0.74	29	34	0.13
207	3.39	6.26	0.077	0.54	41	13	nd

[1] Solid residue obtained after dissolution of the carbonate.
nd = not determined.

Table 4. Fe oxide and clay mineralogy of <2-μm fraction of *terra rossa* samples.

| Sample no. | Fe oxides | | | | | |
| | MCD$_{111}$ (nm) | MCD$_a$ | Al substitution (mole %) | | Hm/(Hm + Gt) | Clay minerals |
	Gt	Hm	Gt	Hm		
Sardinia						
8B	21	36	12	2	0.24	I ≫ K > CHL
17B	23	28	6	4	0.65	I ≫ K > CHL
6TR	49	20	9	2	0.52	I ≫ K
3D	32	26	5	5	0.49	I ≫ K > CHL
I120	26	21	12	11	0.44	I ≫ K > CHL
I110	19	20	16	14	0.45	I ≫ K > CHL
15	23	20	14	4	0.68	I ≫ K > CHL
14	42	53	4	0	0.57	I > K > CHL ≃ HIV
NE Italy						
205	17	12	12	0	0.75	HIV ≫ K ≃ I
206	19	12	13	2	0.76	HIV ≫ K ≃ I
204	21	11	10	2	0.66	HIV ≫ K ≃ I
211	21	12	15	0	0.60	HIV ≫ K ≃ I
209	15	(*)	16	(*)	(**)	HIV ≫ K ≃ I
210b	19	(*)	16	(*)	(**)	HIV ≫ K ≃ CHL
208	19	(*)	12	(*)	(**)	HIV ≫ K ≃ I
207	17	(*)	17	(*)	(**)	HIV ≫ K ≃ I

Gt = goethite; Hm = hematite; MCD = mean crystallite dimension; I = illite; K = kaolinite; CHL = chlorite; HIV = hydroxy interlayered vermiculite.
* Non-measurable peak.
** Traces of hematite.

Mn extractable in DCB seems closely related to the lithogenic Mn. The correlations between Fe_d/Fe_t and the climatic parameters were poor ($r < .51$) and not significant.

0.2444nm
0.2515nm
130 Gt
104 Hm
111 Gt
110 Hm
2000
1000
counts
0.2518 nm
0.2441nm
1000
44   43   °2θ (Co Kα)   39   38

Figure 2. DXRD traces of <2-μm fraction: goethite (Gt) and hematite (Hm) of well-crystallized (above, sample 3D) and poorly-crystallized (below, sample 206) samples.

<2-μm fractions

Hematite and goethite occurred in all the samples (Table 4). Hematite was detected only as traces in some samples from the sites with a water surplus (AAT < 13°C; AAP > 1800 mm).

Goethite, and especially hematite, had, on the average, lower MCDs in the samples from wet sites (MCD$_{111}$ of goethite = 18 nm, MCD$_a$ of hematite = 12 nm) than those from dry sites (MCD$_{111}$ of goethite = 29 nm, MCD$_a$ of hematite = 28 nm). In the DXRD traces the peaks of hematite and goethite from moist and cool sites are broader and less intense than those from dry and warm sites (Figure 2).

Goethite had a medium level of Al substitution (9–17 mole %) except in three samples from Sardinia in which Al substitution was only 4, 5 and 6 mole %. Hematite was nearly free of Al substitution in most of the samples.

These data are in contrast with the observation that in soils the Al substitution in hematite and goethite is usually close to a ratio of 1:2 (Schwertmann, 1988).

Illite and kaolinite were the main clay minerals found in the samples from Sardinia, with a marked prevalence of the former. Chlorite occurred as traces in most of these samples (Table 4). In the xeric climate of this region the weathering of the clay fraction appears only slight. A greater clay weathering seems to characterize the samples from NE Italy where hydroxy-interlayered vermiculite is the dominant phase (Figure 3). Under wetter climates a vermiculitization of the 2:1 silicates
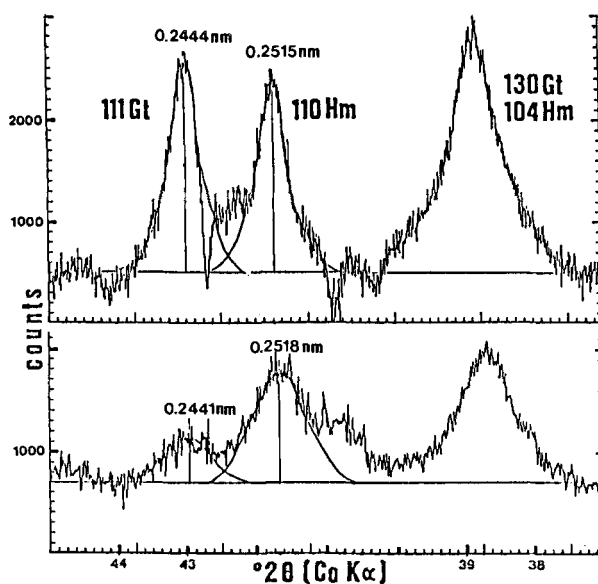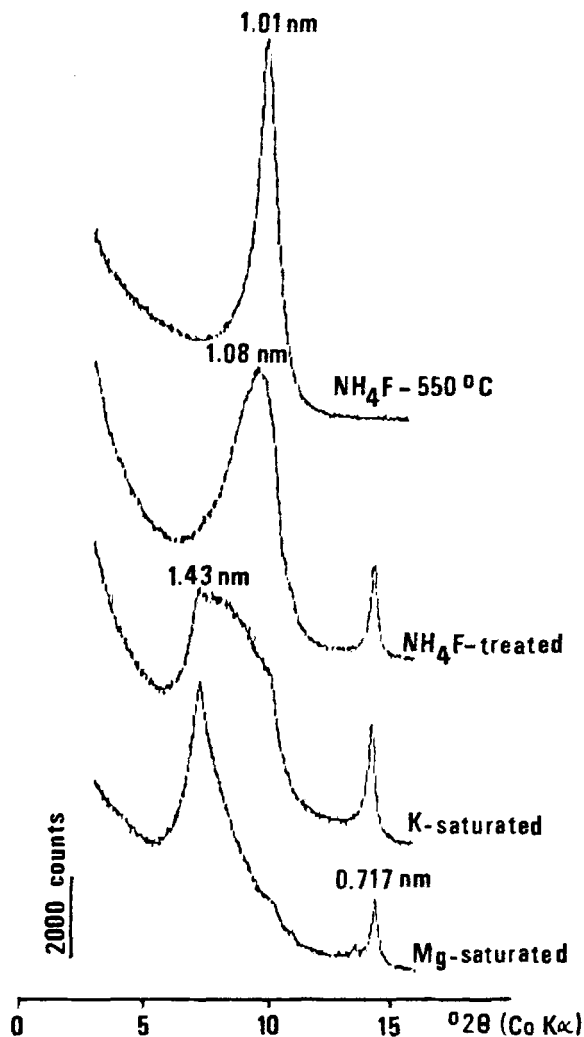
Figure 3. X-ray diffraction traces of the oriented DCB- and DCB-NH$_4$F-treated <2-μm fraction of sample 208.

and a precipitation of hydroxypolymers in the interlayers might occur.

DISCUSSION AND CONCLUSIONS

The influence of climate is reflected in the nature of the clay minerals, which are less preserved in the moist environment. However, uncertainty on the origin of clay minerals in *terra rossa* limits their use as climatic indicators. The occurrence of hematite is irrespective of climate, and hematite may be the dominant iron oxide even in sites with 13°C AAT and up to 1700 mm AAP. This confirms the specific role of the well-lithified limestone in maintaining a hematitic pedoenvironment. However, the climate affects the MCDs of iron oxides; hematite and goethite being better crystallized in the xeric environment. The goethite Al-substitution/hematite Al-substitution ratio is variable, but tends to increase in *terra rossa* of moist environments because

of the very low level of Al substitution in the hematite. These data suggest a different origin for the two oxides in a moist environment. However, hematite does not appear as a residual phase. In fact, it is not characterized by high MCDs and high Al substitution as was found for residual hematite crystals in yellowed *terra rossa* (Boero and Schwertmann, 1987).

A possible explanation for the low Al substitution in the hematite of the moist environment of NE Italy could be its formation in association with vermiculite formation. The processes of rubification and vermiculitization could have taken place at the same time, the vermiculite acting as a preferential trap for Al and thus preventing a high Al substitution in the oxide.

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