

Red soil geochemistry in a semiarid Mediterranean environment and its suitability for vineyards

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Abstract A geochemical study of a red soil derived from plioquaternary materials was carried out. The soil was located in a region of complex geomorphology and pedologic evolution, with particular characteristics of a Mediterranean climate associated with processes of alteration, rubification, gleying (hydromorphism) and argillization. The depth distribution of 27 trace elements was studied in order to determine the amounts of these elements in the soil and its tendency. The mineralogy of the clay fraction was also studied along with other physico-chemical properties to elucidate in terms of attributes meaningful for viticulture. The geochemical composition of the horizons was studied. The effect of human activities on the soil was investigated as well as the geographical origin of Mancha wines. It was found that these activities did not give rise to significant

variations of trace elements, although a discontinuity related to the accumulation of new materials was detected. Ultimately, using established productivity standards, suitability for the cultivation of vines on these soils was determined.

Keywords Pedogenesis · Geochemical · Trace elements · Red soils · Vineyard

Introduction

The coexistence of geological forms of different origins and ages, as well as the current existence of active morphogenesis, has led to a varied soil covering that is expressed in different taxonomic levels in the Tagus basin, a semiarid region of central Spain. Some soils of the region show an intense degree of pedologic development, with processes of argillization, rubification and hydromorphism. A number of aspects of these soils have been studied in relation to the geomorphology of the region (Pardo 1995).

As a general rule, the “natural background” concentrations of trace elements in soils can be seen as a function of their concentrations in the parent material. The trace elements are always present in the soil, but some human (anthropic) activities can add to the initial content, thus modifying the original balance. The variations that are observed in the concentration of trace elements at different depths

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can be related to mineralogical changes and conditions of pH and Eh. In the superficial horizons, the high concentrations of some trace elements can interfere with certain processes that establish the quality of the soil and these can also be of concern for the health of living beings.

It has been suggested recently that trace elements could be used to identify the origin of wines of certain regions (Almeida and Vasconcelos 2003; Taylor et al. 2003) regardless of the influence of sanitary treatments (Kment et al. 2005) and the system of production (Nicolini et al. 2004; Gremaud et al. 2004). The aim of the work described here was to assess the quality of the soil from a geochemical point of view. The potential for the use of this soil for the cultivation of vines is also discussed, particularly in conjunction with modern, non-traditional techniques.

Materials and methods

The profile under investigation is located in Malpica de Tajo (Toledo, Spain) and represents a proportion of the soils developed in one of the formations termed “raña” in the region, i.e. a zone that is preserved from erosion, is flat or with a slight slope (between 0 and 2% approximately) and has horizons at a depth affected by water saturation (hydromorphism). The surface and parent materials are located in the south-western border of the basin, between the river Tagus and the Toledo mountains. The materials that shape this area are from the plioquaternary age and originate from the erosion of Palaeozoic materials (Toledo mountains) that are metamorphic in nature, e.g. slate, schists, and gneisses amongst others. The rainfall regime is xeric throughout the region and the climatic vegetation is the Mediterranean forest. The traditional agricultural use has been cereal (without irrigation) and pasture with isolated trees, called “dehesa”, which is very suitable for extensive cattle farming.

Relevant information for the profile and its morphology is gathered in Tables 1 and 2.

Sampling

Samples were taken in soil, which were dug by hand. The soil samples were collected with a steel blade

Table 1 Information on the soil profile

Soil type FAO/soil taxonomy	Location/coordinates	Parent material	Vegetation/ use	Topography	Slope	Drainage	Stoniness
Cutanic Luvisol (Oxyaquic/Rhodic)/typic Rhodoxeralf	Bodegas Solaz Malpica de Tajo 39°51'03" (N) 04°40'08" (W), 0357309 (X)—4412751 (Y)	Pliocuaternary materials	Vineyard	Plane	C-1 Nearly level	C-2 Weakly drained	C-0 No stoniness

Table 2 Descriptions of the horizons

Horizons depth (cm)	Colour (dry)	Structure	Consistence	Roots	Pores	Limit	Stoniness (%)
A _p (0–50)	5 YR 4/6	Strong, subangular blocky, coarse	Sticky, plastic, friable and soft	Common fine and medium	Many fine and few medium	Gradual and wavy	10
B _{1t} (50–110)	10 Y 3/6	Strong, prismatic, coarse	Sticky, very plastic, firm and hard	Common fine and medium	Without pores	Diffuse and wavy	10
B ₂ (110–142)	Mixed colours 7,5 YR 6/4 and 10 R 3/6			Without roots	Without pores	Diffuse and wavy	30
B ₁ /C _k (142–161)	10 YR 4/6 mottled 7,5 YR 5/4	Strong, subangular blocky,	Stickily, plastic, hard	Without roots	Without pores	Diffuse	20
2C _{gk} (161–185)	10 YR						
2C _k (>185)	10 R 4/6	Similar to the horizon immediately above	Similar to the horizon immediately above	Very fine	Without pores		10

and transferred into polyethylene bags for shipment to laboratory.

The samples were air-dried and sieved to remove rock fragments, roots, etc. Care was taken in sampling, preparation and storage to avoid accidental contamination. Soil samples were dried under 40°C and disaggregated.

Analytical methods

The analytical determinations were carried out according to SCS-USDA (1972). In particular, soil texture was determined using the hydrometer method (Gee and Bauder 1986) with three replicates. Soil pH was measured in H₂O and in 0.1 M KCl using a 1:2.5 soil/solution ratio. Electrical conductivity was measured in a 1:5 soil:water extract. For calcium carbonate determination CO₂ was measured using a calcimeter. The active calcium carbonate equivalent (ACCE) or “active lime” was determined with NH₄-oxalate as described by Drouineau (1942). The method of Olsen et al. (1954), which is based on extraction with 0.5 M NaHCO₃, was used to estimate available P. Soil organic matter was determined by potassium dichromate oxidation and titration of remaining dichromate with ammonium ferrous(II) sulfate (Anne 1945). Exchangeable cations were determined using an ammonium acetate extraction method (Thomas 1982). Exchangeable Na, K, Ca and Mg were determined by atomic absorption spectrometry. Total nitrogen content was determined by the Kjeldahl method (Bremner and Mulvaney 1982). All samples were extracted and analysed in duplicate.

The semi-quantitative mineralogical analyses were carried out by X-ray diffraction (XRD) techniques: about 2 g of sample was hand-milled to below 53 µm in an agate mortar and used for the determination of the bulk mineralogy (random powder method). For the detailed study of phyllosilicates, 100 g of sample was treated to remove components that prevent complete dispersion (e.g. carbonates, sulfates, organic matter, etc.). The <2 µm (clay fraction) particles were extracted by sedimentation techniques and analysed on “thick” glass slides by XRD according to Moore and Reynolds (1989). Samples were chemically treated (with ethylene glycol to detect expandable minerals, and with dimethyl sulfoxide to differentiate chlorite and kaolinite) and thermally treated (550°C for 2 h to study the behaviour of phyllosilicates). The

samples were analysed using a CuK α radiation source (Philips-Panalytical X-PERT diffractometer) with a graphite monochromator, 40 kV and 40 mA, and sensitivity of 2×10^3 cps. The ranges measured were $2-75^\circ$ or $2-50^\circ 2\theta$, with a goniometer speed of 0.04 or 0.05 and a time constant of 0.4 or 1 s for random powder or glass slides, respectively. The chemical compositions of whole samples were determined using an X-ray fluorescence spectrometer (PHILIPS PW 2404) in solid mode.

Results and discussion

The chemical and physicochemical results for the horizons of the analysed soil are shown in Tables 3, 4 and 5.

The clay fraction is quantitatively the most important (Table 3), showing an enrichment in horizons B (reaching more than 50% in some cases); the sand and silt contents are similar (around 25%), providing a balanced texture that is favourable for the traditional cultivation methods. The cationic exchange capacity (C.E.C.) is in the range 32.2–38.2 cmol/kg (Table 4) and this value is relatively high. The changed cations are dominated by Ca^{2+} , showing total saturation in the aforementioned element. The pH values for all horizons are shown in Table 5. The values are neutral or moderately basic and do not vary significantly along the profile. The calcium carbonate content in horizons B_t increases proportionally with depth. The percentage in active limestone is insignificant. The free oxides of iron denote a rubification process. The content of the aforementioned element (2.4–2.5%

Table 3 Particle size distribution and textural class

Horizon	(%) Gravels	(%) Sand	(%) Silt	(%) Clay	Textural classification
A _p	28.0	37.3	29.3	33.4	Loam-clay
B _{t1}	10.0	27.3	25.3	47.4	Clay
B _{t2}	14.6	24.6	24.0	51.4	Clay
B _t /C _k	19.9	27.8	23.3	48.9	Clay
2C _{gk}	52.7	37.1	24.0	38.9	Clay
2C _k	59.7	29.1	22.0	48.9	Clay

Table 4 Data for organic matter (O.M.), nitrogen (N), phosphorus (P), cation exchange capacity (C.E.C.) and base saturation average (V)

Horizon	O.M. (%)	N (%)	C/N	P Olsen	Exchangeable cations (cmol/kg)				C.E.C. (cmol/kg)	% V
					Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺		
A _p	1.7	0.11	6.9	2.4	17.3	2.6	0.5	2.0	32.2	100
B _{t1}	0.7	0.05	5.9	0.5	18.1	5.2	0.2	2.7	36.2	100
B _{t2}	0.5	0.04	5.9	0.2	31.4	3.6	0.2	3.0	38.2	100

Table 5 Data for pH, electrical conductivity (E.C.), carbonate, active limestone and free iron oxides

Horizon	pH H ₂ O (1:2.5)	pH KCl (1:2.5)	E.C. (dS/m)	Carbonate (%)	Active limestone (%)	Free iron oxides (%)
A _p	8.2	7.2	0.48	10.4	3.4	
B _{t1}	8.2	7.2	0.46	2.1	1.4	2.5
B _{t2}	8.0	7.0	0.34	1.9	1.8	2.4
B _t /C _k	7.9	7.4	1.02	20.8	2.8	
2C _{gk}	7.9	7.3	1.20	34.9	3.1	
2C _k	7.9	7.3	1.26	38.6	4.1	

in Fe_2O_3) guarantees plant nutrition and prevents the potential blocking of iron in the cultures (particularly in vineyard).

Pedogenetic processes

The general geomorphologic characteristics and the predominance of a xeric Mediterranean regime, with a tendency to water saturation (aquic), determine the evolution of the pedologic processes. Migration of components in suspension (argiluviation) and migration of components in solution (decarbonation) are both processes that enable intense rubification.

The surface under investigation is arranged, for the most part, on a plioquaternary material called “raña”. The stability of this type of geomorphologic surface means that pedogenetic processes typical of the Mediterranean area can occur over long periods of time on the initial material. As a result, this soil shows features of intense evolution with a clear trend towards flatness (horizontalization). These horizontalization processes can be loss-addition and/or transformation in nature. In the former process decarbonation and illuviation of clays predominate whereas in the latter case rubification is the most important process.

Decarbonation in this soil leads to a decrease in the pH in the top horizons and this causes the initiation of the genesis and illuviation of the clay, both common processes in soils developed on fluvial terraces and “rañas”. This process begins with the dispersion of the clay fraction, after which there is a flow down as a suspension in the wash water and subsequent deposition. Flocculation occurs easily when the wash solution arrives in the horizon, with a major concentration of flocculant cations and carbonates. Nevertheless, it must be borne in mind that the textural contrast between the argillic horizon and the overlaying material is not clearly defined (texturally both are clayey). It should be pointed out that there are other possible reasons for this genesis; this change can occur through a differential deposition process.

On the other hand, it was found that weathering caused the liberation of iron from the primary minerals. For the same reason, the rubification process leads to an intense red colour in the soil, indicating a warm temperature regime and low rainfall. Finally, water saturation at depth leads to

the loss of the red colour and this is also favoured by the presence of carbonates. In fact, a large proportion of the soils in the zone present, to a greater or lesser extent, gleyic features at depth as a consequence of the existence of a hung layer with low hydraulic conductivity.

Trace elements

The term ‘trace elements’ is applied to those chemical elements that have a low concentration under natural conditions in the soil. Nevertheless, diverse anthropogenic activities (manufacturing, mining, farming, cattle, etc.) can give rise to an increase in the levels of these elements and, as a result, pollution can enter the food chain. As a consequence, the study of these subjects has become more intense in recent years.

In the study described here, the vertical distributions of several trace elements were analysed. In the initial approach a search for possible heterogeneity in the parent materials was undertaken. The Ti/Zr ratio, which is a habitually used criterion, proves the existence of a lithological discontinuity between deeper horizons and the superficial ones. The information is represented in Fig. 1.

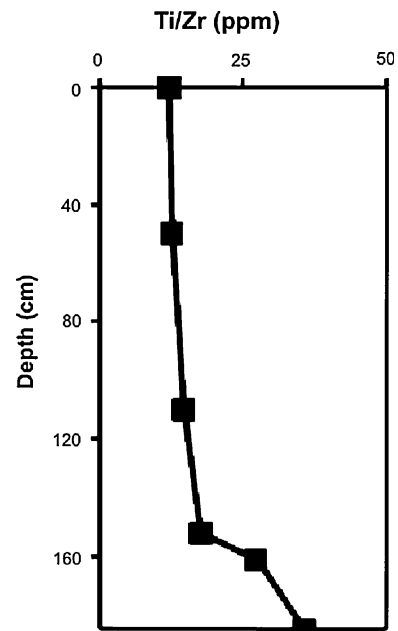


Fig. 1 Variations in Ti/Zr along the profile

Once the discontinuity had been identified, the distribution patterns of the different trace elements analysed was represented graphically. The results obtained are shown in Fig. 2.

The order of the contents of elements in soils approximately corresponds to the general order of the contents of elements in soil of the world (Kabata-Pendias and Pendias 1984) and the region (Jiménez Ballesta et al. 2009).

It can be seen that U, Th, Hf, Ce, La, Ba, Cs, Nb, Zr, Y, Zn, Co, Ni, Cr, V, Sc and Nd show similar behaviour; the concentrations of these elements diminish with depth, a finding that is related to the abundance of carbonates and/or the effect of water saturation (hydromorphism). In contrast, Pb, W, As and Ta show a discontinuity at depth. A similar trend is observed for Sn, Mo, Sr and Cu but in reverse order. Finally, the Ga content remains almost uniform throughout the profile.

Numerous studies aimed at reliably determining the origin of wines have been carried out all around the world. To achieve this aim, efforts to relate the contents of trace elements in the wine to those in the soils could be of great interest; this hypothesis has been verified in studies carried out in Oporto (Almeida and Vasconcelos 2003). Nevertheless, in some studies in Canada (Taylor et al. 2003) a linear correlation between the soil and the wine was not identified for the content of any element studied. One must bear in mind the process for the production of wine (Nicolini et al. 2004; Gremaud et al. 2004) and the influence of other factors, e.g. climatologic (Gremaud et al. 2004) and anthropic (Kment et al. 2005), amongst others.

The results described here provide the first values for trace elements in a soil dedicated to grapevine harvest in the zone under investigation. Changes in concentrations were not observed as a result of human activity (e.g. pesticide treatment, the use of machinery) (Kment et al. 2005) in superficial horizons for elements that usually accumulate through these agricultural practices (Cu, As, Pb, Cr, etc.). It should be noted, however, that the study was carried out on very young plantations (i.e. less than 10 years old).

Possibilities for use of the soil in vineyards

The soil under investigation has characteristics that are very different from other soils in Castilla-La

Mancha (central Spanish region) dedicated to vineyard culture. Due to the moderately alkaline nature and the low percentage of limestone in these soils, the choice of rootstock is not limited and it is therefore possible to focus on other important aspects such as control of the vigour, the affinity with the *vinifera* variety and the resistance to eelworm (Chomé 2003). It is necessary, however, to bear in mind that in cases where the limestone increases with depth, the thickness of the colluvial deposit of red soil is very superficial, as occurs in Villarrubia de los Ojos (Carlevalis et al. 1992). This structure has been detected in soils of other zones of the same central Spanish region, including Carrión de Calatrava and Malagón, amongst others (De la Horra et al. 2008).

The water logging of the soil is important because of the depth and clay content (Hidalgo 2002; Porta et al. 2008). This character increases the vigour, delays the end point of the growth (Huglin 1998) and thus delays ripeness. This delay in ripeness could be exploited in a hot climate (the plot is located in a Zone III or IV; Winkler 1965). As the harvest continues during September for each vintage, the nights become fresher and this factor can improve the biosynthesis and accumulation of phenolic and aromatic compounds (Jackson and Lombard 1993). Moreover, it may be of interest to study the influence of the reflectivity of the soil on the synthesis of anthocyanins (Bergquist et al. 2001) since the nature of the light reflected by the red soils is different from that reflected by other soils with clearer tonalities (calcareous or clear-brown). Similar soils have been described in Castilla-La Mancha (Hidalgo 1980) that have a territorial extension of 5.5% and are called “red Mediterranean soils over calcareous materials”. Such soils are found in areas where the colluvial quartzite deposits have slipped over surrounding Miocene materials.

The fertility of the soil, in general terms, is considered acceptable. The levels of the principal fertilizer elements (N, P, K) are normal for an agricultural soil and expensive amendments would therefore not be required. The quantities of nutrients are very suitable for the vineyard since the levels of nitrogen are not excessive. High nitrogen levels would induce excessive vigour that would be difficult to control. Potassium, which is a quality factor for wine production, is present in sufficient and suitable levels so that luxury consumption is not produced.

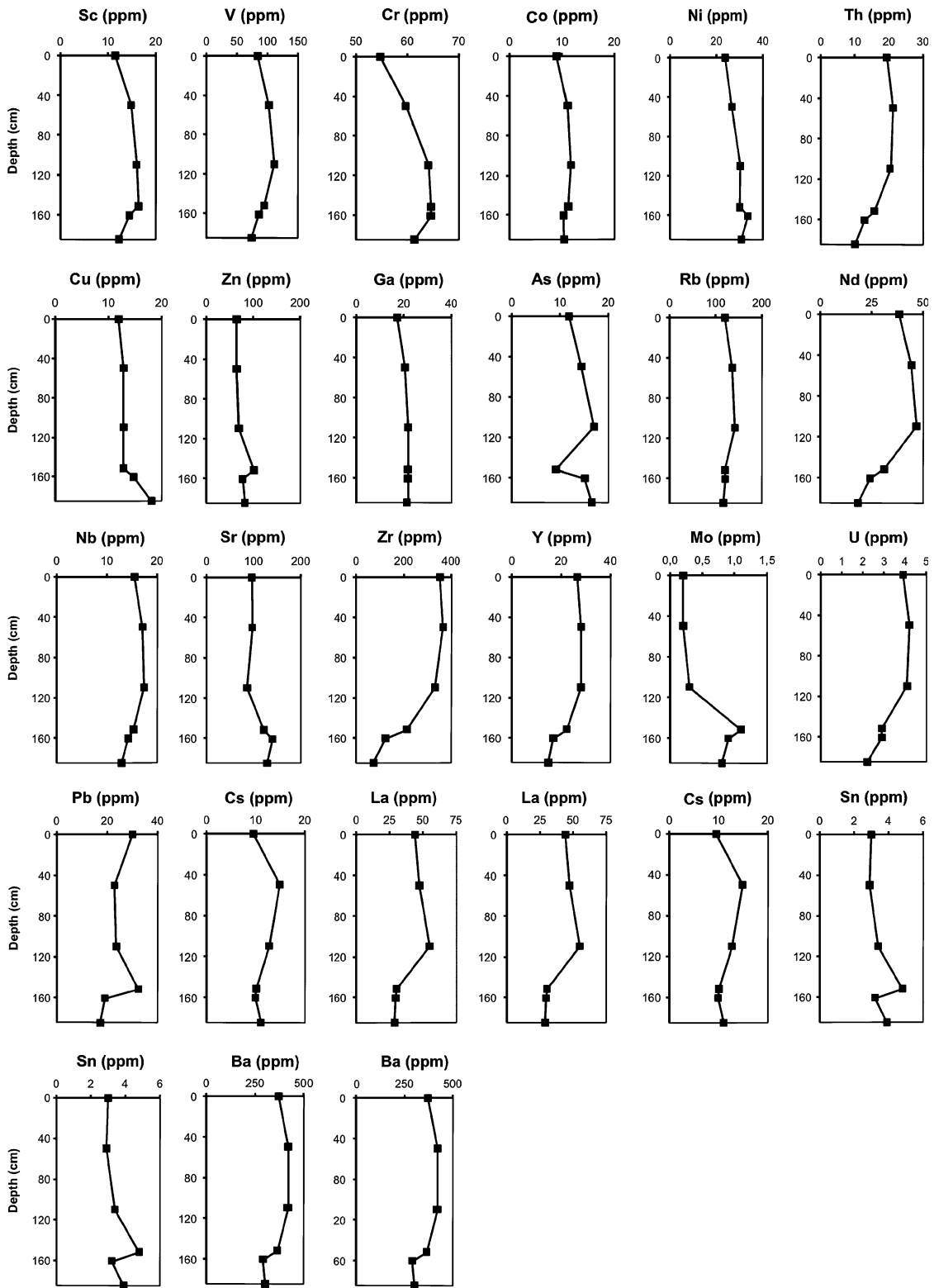


Fig. 2 Evolution of trace elements with depth along the profile. The concentrations (mg/kg) are shown at the *top* of each graph

Mineralogy of the clay fraction

The results of the mineralogical study by X-ray diffraction are shown in Table 6. It is necessary to highlight the high levels of phyllosilicates contained in horizons B_t, a finding that is consistent with the leaching (illuvial) nature of this horizon. The high content in calcium carbonate in the horizon B_t/C can be inferred as being due to a process of accumulation by CaO washing, which gives rise to the neoformation of this mineral. The presence of quartz and feldspar indicates the origin of these materials from the erosion of the surrounding reliefs. The existence of illite and kaolinite is consistent with the detritic character, whereas the high content in smectite can be related to the occurrence of weathering processes “in situ”.

The presence of significant quantities of illite (up to 45%) guarantees the presence of native K (Dixon 1991), which is very important for the production of quality wines. The content in smectite reaches similar levels to those obtained in other wine-growing zones of Castilla-La Mancha (Carlevalis et al. 1992).

The diffractograms obtained for the total fine earth fraction are shown in Fig. 3. The pattern reveals the mineralogical homogeneity of the different horizons. The diffractograms of orientated aggregates are shown in Fig. 4.

General discussion

To increase the discrimination between geographical origins, the use of elemental analysis was proposed by several authors (Martin et al. 1995 and 1999). During the mid-1990s, several studies indicated that trace elements in wines might be used to determine the origin of their grapes at vineyard and regional levels. The geochemical behavior of trace elements in soil suggests that a common mechanism, the effect of climate on trace element solubility, affects trace-element concentration patterns. Further, regional average concentrations of most trace elements must be available.

The total element content in wine has two major sources. The first is a natural source and is supposed

Table 6 Semiquantitative analysis from total soil and from clay fraction

Horizon	Bulk mineralogy				Clays mineralogy		
	Calcite	Quartz	Feldspar	Phyllosilicates	Kaolinite	Illite	Smectites
A _p (M-01)	13	20	11	56	11	25	20
B _{t1} (M-02)	0	23	14	63	11	26	26
B _{t2} (M-03)	0	13	Traces	87	14	45	28
B _t /C (M-04)	20	7	5	68	15	28	25

Fig. 3 X-ray diffractogram of the total fraction

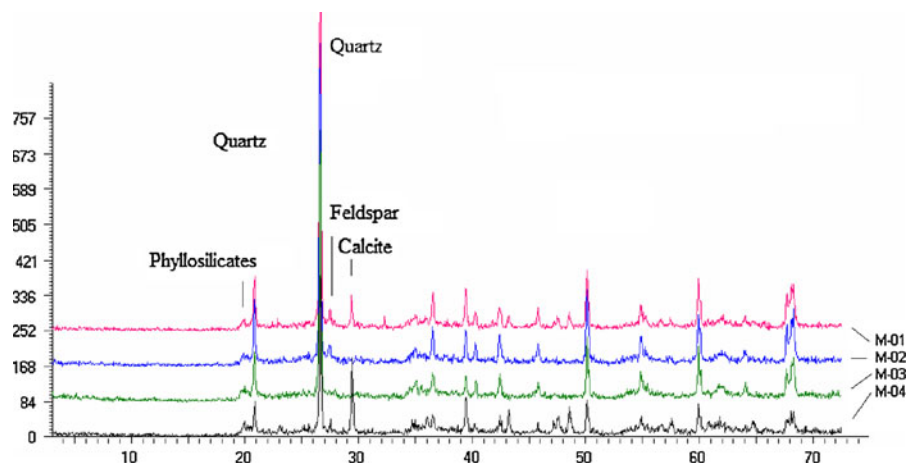
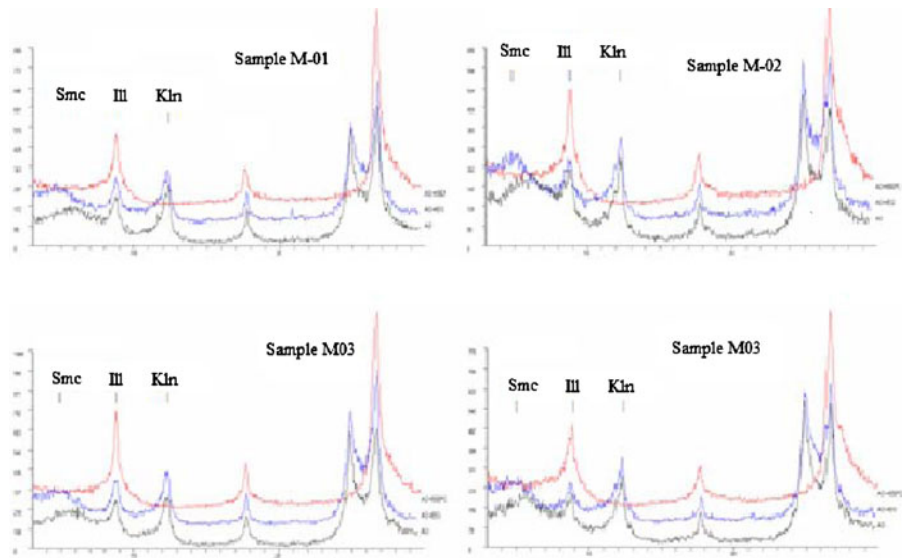


Fig. 4 XRD patterns of the clay fraction with appropriate treatments



to include the soils, resulting from the weathering of their parent materials. The second is an anthropogenic source and may be divided into three subgroups:

1. Application of organic and mineral fertilizers, inorganic pesticides and other substances employed in growing practices (Ramachandran and D’Souza 1998). Pesticides may increase the contents of Cu, As and Zn.
2. Pollution of the surrounding environment, which is not directly associated with viticulture practice.
3. Application of food additives, machinery and other operations employed in the production of wine from grapes (Frías et al. 2001).

Three factors appear to demonstrate the closest links between soil and wine: landscape, the underlying rock (*sensu lato*) and the specific soils. The contribution made by landscape comprises a number of interrelated components, each of which has an influence on the local climate. The soil conditions must, however, be such that heat is stored during the day, generally in pebbles or stone fragments, so that it can be re-radiated during cooler periods at night.

Our trace-element analyses can be used as a test for the hypothesis that wines can be regionally “fingerprinted”. Thus, terroir-related climate and soil differences lead to quantifiable trace-element fingerprints for La Mancha wines by region.

Conclusions

The work described here concerned a study of the soil performance in a Mediterranean climate with processes of alteration, reddishment (rubification), gleying (hydromorphism) and argillization. The depth distribution of 27 elements in the soil revealed that the majority of the elements show little enrichment/loss. Nevertheless, a discontinuity was detected, from the geochemical composition of the horizons, in the profile and this is due to the accumulation of new materials. Human activity such as soil management, the addition of fertilizers, etc. was not an important source of trace elements. The mineralogy of clays is composed of illite and smectite, accompanied by kaolinite, and this reveals a conservative environment.

On the other hand, it can be concluded that the soil under investigation is suitable for vineyard cultivation, with some recommendations. The texture and the stoniness lead us to recommend alternative systems of maintenance for the soil (temporary cover crop, no tillage with bare soil) as this will improve access to the plot (mechanical harvest) and prevent excessive erosion. It should always be borne in mind that the transitory water saturation could adversely affect the root zone (improving natural drainage will be a priority). Soil fertility is sufficient in terms of most macronutrients for the grapevine, with very suitable levels of potassium. Finally, with this soil it is possible to choose between a wide range of

rootstock, avoiding the excessively vigorous ones, and it is always compatible with red varieties of medium-long cycle.

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