Relationship between Mineralogy and Elemental Composition in Strongly Developed Soils using Principal Components Analysis

M. T. García-González and F. J. Aragonese

Departamento de Geoquímica y Mineralogía, Centro de Ciencias Medioambientales, Serrano 115 Dpto, 28006-Madrid, Spain

Abstract

The distribution rate of major, minor and trace elements in different size fractions of highly developed soils of central Spain was determined and related to the mineralogy of the soils. Analysis of variance, factor analysis and contingency tables were used. The principal trace element carriers were the 2:1 phyllosilicates and the Fe and Mn-oxides; kaolinite did not play a role in this regard.

Factor analysis indicated that the principal difference is found between samples rich in clay-kaolinite- Al_2O_3 and samples rich in quartz- SiO_2 . Alkaline and alkaline-earth elements (K, Na, Rb, Ba and Sr) show a similar behaviour, being directly related to the contents of illite and feldspars. Co and Pb contents are found to be related to the Mn-oxides, while Cu and Zn showed a relatively erratic distribution. Vanadium content was clearly associated with the Fe-oxides, but other metals, such as Cr, Ni and La, showed distinct associations depending on particle size.

Keywords: Trace elements, phyllosilicates, statistical analysis, acid soils.

Introduction

We present here an statistical study, including analysis of variance and factor analysis, aimed to establish the relationship between mineralogy and elemental composition of several raña soils of Central Spain. These soils, highly developed, are infertile because of unfavourable physico-chemical and mineralogical properties. This has led to depopulation in these areas, which now lie at the limit of desertification (Martínez-Vega 1989). Our results are thus aimed to help other working teams to a better understanding of the potential fertility of these soils and facilitate appropriate actions for their reclamation. Other references to these types of soils are Espejo (1985, 1987), Vicente *et al.* (1986), Rodríguez-Pascual *et al.* (1987), García-González and Aragonese (1988, 1990), Sánchez-Camazano *et al.* (1988), Aragonese (1990), Aragonese and García-González (1991), García-Rodríguez *et al.* (1988), Jiménez-Ballesta *et al.* (1988) and Palomar *et al.* (1988).

Materials and Methods

The zone studied lies in the Province of Gndalajara in the north-east centre of the Iberian peninsula (Fig. 1) and comprises the four areas Membrillera, Robledo de Corpes,

Bustares y Mesa del Pino, subsequently abbreviated as ME, RC, BU and MP, respectively. Further description of the profiles studied as well as the methods used in the mineralogical identification can be found in previous papers (García-González and Aragonese 1990; Aragonese and García-González 1991).

Fig. 1. Map showing location of the study area and situation of the soil profiles.

Quantitative determinations of major, minor and trace elements (Si, Al, Fe, Mg, Ca, K, P, Ti, Mn, Na, Rb, Cu, Sr, Co, Ni, Zn, Zr, Ba, Pb, La, V and Cr) were carried out in all size-fractions by X-ray fluorescence spectrometry on pressed powder pellets with international rock standards being used for calibration. The K_{α} , K_{β} , L_{α} or L_{β} lines were measured using a Siemens SRS 300 sequential spectrometer (Rh end-window tube) connected to a PDP 11/23 micro-computer.

Pedogenic and amorphous Fe and Al were extracted from the clay fractions using dithionite-citrate-bicarbonate (Mehra and Jackson 1960) and HCl (Segalen 1968), respectively. Fe was determined with a Perkin-Elmer 403 atomic absorption spectrometer and Al with a Perkin-Elmer ICP/5500 plasma emission spectrometer.

The various statistical analysis were carried out with the BMDP (1985) statistical package. Variables were transformed beforehand for inducing normality; for those variables which, after different transformations, the hypothesis of normality was rejected (MnO, paragonite and

smectite), non-parametric procedures were used. The analyses carried out and the statistical programs used were:

- Description of groups and analysis of variance (BMDP-7D program). Welch statistic was used to study the differences between clay, fine-silt, and medium- and coarse-silt fractions. Pairwise *t*-test (separate variances) was used to compare each pair of fractions.

- Factor analysis (BMDP-4M program). In each size-fraction it was carried out according to the following criteria: (i) for the initial factor extraction, the principal components method was used, considering only those factors with eigenvalues greater than one; (ii) varimax orthogonal factor rotation was performed.

- Two-way frequency tables and measures of association (BMDP-4F program). For variables with a distribution far from normality (Mn, paragonite, smectite), contingency tables were obtained for testing the independence of the variable with respect to the size-fraction using the chi-square test. Likewise, the independence hypothesis was tested for the MnO content and some of the factors obtained after factor analysis.

Table 1. Mean values calculated with the 11 soil profiles and for the different size-fractions
Standard deviations in parentheses. Mineralogical composition and major and minor elements in wt%, trace elements in mg kg^{-1} . 2:1 Phyllos. = illite + smectite. — = values not determined.

	Soil	Clay	Fine-silt	Coarse + M-silt	Welch
SiO ₂	62.87(10.55)	41.64(3.85)	51.79(10.19)	71.17(9.60)	^B
Al ₂ O ₃	19.11(6.65)	26.21(3.20)	20.18(4.21)	10.25(4.24)	^B
Fe ₂ O ₃	6.37(3.47)	11.88(2.41)	10.44(4.84)	3.88(4.06)	^B
MgO	0.56(0.20)	0.79(0.27)	0.66(0.17)	0.32(0.12)	^B
CaO	0.34(0.12)	0.59(0.20)	0.53(0.37)	0.24(0.07)	^B
K ₂ O	1.75(0.58)	2.32(0.63)	2.98(0.87)	1.95(0.68)	^B
P ₂ O ₅	0.11(0.07)	0.52(0.44)	0.49(0.37)	0.29(0.19)	^B
TiO ₂	0.74(0.10)	0.93(0.23)	1.13(0.28)	1.11(0.22)	^B
MnO	0.05(0.10)	0.15(0.30)	0.11(0.23)	0.03(0.07)	^A
Na ₂ O	0.48(0.12)	0.24(0.26)	0.48(0.32)	0.44(0.26)	^a
Rb	106(40)	229(51)	186(33)	80(26)	^e
Cu	12(10)	123(131)	205(259)	62(94)	^e
Sr	70(27)	106(33)	129(42)	55(13)	ⁿ
Co	13(15)	28(39)	23(42)	9(15)	^B
Ni	26(19)	57(13)	37(16)	6(9)	^e
Zn	40(14)	160(84)	206(131)	50(38)	^B
Zr	311(103)	126(32)	220(76)	768(248)	^u
Ba	245(164)	670(308)	832(276)	426(185)	^B
Pb	36(13)	63(31)	66(26)	27(9)	^B
La	27(23)	103(11)	97(11)	75(15)	^B
V	111(45)	198(31)	191(42)	95(44)	^B
Cr	31(24)	62(16)	63(24)	10(21)	^B
Phyllosilicates	36(19)	84(6)	57(14)	16(11)	^B
Quartz	57(19)	8(7)	33(16)	77(12)	ⁿ
Feldspars	3(4)	1(1)	4(2)	4(4)	ⁿ
Goethite	3(3)	7(3)	6(5)	2(3)	ⁿ
Kaolinite	—	44(18)	20(13)	—	—
Illite	—	34(15)	31(12)	—	—
Paragonite	—	1(1)	1(1)	—	^A
Smectite	—	4(5)	5(9)	—	^A
2:1 Phyllos.	—	40(14)	37(8)	—	—

^A Distribution far from normality. ^B $P < 0.001$.

Results

Analysis of Variance

Table 1 shows the mean values of the chemical and mineralogical results for the 11 profiles and for the different size-fractions. The data obtained for the trace elements compare well with the results found in the literature (Vinogradov 1959; Kabata-Pendias and Pendias 1984; Sbaketle and Boerngen 1984), thus the existence of any contamination effect may be discarded. The total Fe and goethite contents accumulate in the finest fractions (clay and fine-silt). The elements K, Cu, Zn, Ba and Sr are present in their highest proportions in the fine-silt fraction, whereas Al, Rb, Fe and Ni accumulate in the clay fraction. The highest kaolinite content is found in the clay fraction, while illite is rather uniformly distributed between the clay and fine-silt fractions.

Most of the variables show significant differences in the three size fractions (clay, fine-silt and medium and coarse-silt), with a confidence interval greater than 99.9% (Table 1). Only the contents of smectite and paragonite fail to show differences in the clay and fine-silt fractions.

Factor Analysis

Total sample (≤ 2 mm)

Four factors, with eigenvalues greater than one, explain 84.3% of the total variance (Table 2).

Factor 1. This factor accounts for almost 60% of the total variance. Phyllosilicate and goethite contents are found to be positively correlated (significance level 99.9%) in this fraction. A large number of metallic elements (V, Cu, La, Sr, Cr, Zn and Ni) are positively correlated with phyllosilicate and goethite. On the other hand, negative loadings for Si, quartz, Zr and feldspars indicate a negative correlation with the foregoing variables.

Factor 2. This factor is a direct index of the abundance of alkaline and alkaline-earth metals. The variables with highest weights in this factor are Na, K, Ba and Rb. The distribution of Sr is uniform between factors 1 and 2.

Factor 3. The variables showing maximum correlation with this factor are P, Co and Pb. The existing relation between this factor and Mn content has been studied using contingency tables, owing to the fact that Mn has not a statistically normal behaviour. The chi-square test rejects the hypothesis of independence between both variables, with a confidence level of 99.9%; thus Mn and factor 3 are dependent.

Factor 4. No soil significance has been found for this factor, which includes the variables Ti, Mg and Ca.

The factor scores (cases grouped according to the type of horizon) for factor 1 plotted against factor 2 (Fig. 2), show that all the A horizons are found in the negative part of the X-axis, corresponding to horizons rich in Si, quartz and Zr, and poor in phyllosilicates, Al, Fe, goethite and other metals. Conversely, most of the B horizons appear in the positive X-axis.

Clay fraction ($\leq 2 \mu\text{m}$)

Factor analysis of the clay fraction leads to seven factors with eigenvalues greater than one, which explains 86.5% of the variance (Table 3).

Table 2. Loadings of the variables for the rotated factors. Total sample fraction
The 11 soil profiles have been used. Loading factors under 0.25 are shown thus (—)

	Factor 1	Factor 2	Factor 3	Factor 4
Al ₂ O ₃ /SiO ₂	0.928	—	—	0.263
Goethite	0.923	—	—	—
Fe ₂ O ₃	0.906	—	0.292	—
SiO ₂	-0.903	—	—	-0.328
Quartz	-0.889	—	—	-0.319
Phyllosilicates	0.888	—	—	0.328
Phyll/quartz	0.887	—	—	0.340
V	0.883	—	0.275	—
Al ₂ O ₃	0.882	—	—	0.301
Cu	0.784	0.395	—	—
La	0.783	—	—	—
Zr	-0.777	—	—	—
Sr	0.669	0.661	—	—
Cr	0.660	—	0.492	—
Zn	0.639	0.306	0.504	0.424
Ni	0.638	—	0.527	—
Feldspars	-0.604	0.497	0.522	—
Na ₂ O	—	0.922	—	—
K ₂ O	—	0.859	—	0.326
Ba	—	0.854	—	0.318
Rb	0.558	0.688	0.287	0.282
P ₂ O ₅	—	—	0.895	—
Co	—	—	0.865	—
Pb	0.260	0.295	0.785	0.308
TiO ₂	—	0.328	—	0.719
MgO	—	0.277	0.510	0.702
CaO	0.423	—	—	0.613

Factor 1. It may be remarked that the negative loading factor is for kaolinite and the positive ones are for illite, alkaline metals (K, Sr, Rb, Ba) and primary minerals. Illite and kaolinite are also negatively correlated ($r = -0.947$), indicating that the content of one of these minerals leads to a decrease of the other. The positive correlations (confidence level of 99.9%) between K-illite ($r = 0.879$), Rb-illite ($r = 0.818$) and Ba-illite ($r = 0.727$) are also noticeable.

Factor 2. This is related to the variables total Fe, V, Fe and Al (DCB method), but in general, the greater this factor is, the higher is the Fe content. The variables Cr and Si also show loadings for this factor above 0.5. The negative loading for Si indicates a negative correlation of this element with Fe content.

Factor 3. This factor is more difficult to define; it includes metals such as Mg, Co, Ni and Pb (positive correlation) and goethite (negative correlation). It is comparable with factor 3 of the total sample, with a marked dependence between the content of Mn and this factor (chi-square test significant).

Factor 4. The variables Zr and Ti have the greatest weight in this factor. Quartz shows a positive loading although it is lower than in factor 1. The negative loading for the variable Al indicates that the horizons rich in Zr and Ti are poor in Al and conversely.

Fig. 2. Plots of the factor scores. I, Total sample. II, Clay fraction. III, Fine-silt fraction. IV, Medium and coarse-silt fraction. A, B, C, and E: samples of A, B, C, and E horizons, respectively,

Factors 5, 6 and 7. The variables Cu, Ca and Zn are the most important ones in factor 5, while in 6 La and Na have the highest factor loadings, although Na is distributed between factors 6 and 1. Factor 7 includes Fe(DCB/total) and Fe(HCl), with positive and negative loadings respectively.

The plot of the factor scores for factor 1 *v.* factor 3 (Fig. 2) can be useful, since Co and Pb are the variables that discriminate most between types of horizons according to the results of discriminant analysis (Aragoneses 1990). Most A horizons are found to the right of the Y-axis, in the 'illite predominance' zone. In the third quadrant almost all cases are B or C horizons, characterized by high kaolinite and goethite contents.

Fine-silt fraction (2–8 μ m)

Six factors are obtained for this fraction, explaining 83.58% of the total variance (Table 4).

Factor 1. It is similar to factor 1 of the total sample. A high positive value indicates a high proportion of secondary minerals (phyllosilicates, kaolinite, goethite), and a high concentration of Fe and Al; a negative value indicates a high proportion of quartz, Zr and Ti. Here, the association Al-Fe and phyllosilicates-goethite is more important than in the clay fraction, Zr and Ti being included in this factor.

Table 3. Loadings of the variables for the rotated factors, clay fraction. The 11 soil profiles have been used

Loading factors under 0.25 are shown with (—)

	Fact 1	Fact 2	Fact 3	Fact 4	Fact 5	Fact 6	Fact 7
Kaolinite	-0.922	—	-0.255	—	—	—	—
K ₂ O	0.901	—	—	—	—	—	—
Illite	0.901	—	—	—	—	—	—
2:1 Phyll.	0.900	—	0.277	—	—	—	—
Feldspars	0.817	—	—	—	—	—	-0.265
Sr	0.784	-0.290	—	0.290	—	—	—
Rb	0.771	—	0.491	—	—	—	—
Ba	0.738	—	0.425	—	—	0.251	—
Quartz	0.719	—	0.319	0.482	—	—	—
Phyllosil.	-0.707	-0.287	—	-0.526	—	—	—
Al ₂ O ₃ /SiO ₂	-0.675	0.261	-0.357	-0.432	—	—	—
Cr	0.652	0.594	—	—	—	—	—
SiO ₂	0.615	-0.558	—	—	—	0.265	—
Fe ₂ O ₃	—	0.910	—	—	—	—	—
V	—	0.864	—	0.337	—	—	—
Al (DCB)	—	0.829	—	—	—	—	—
Fe (DCB)	—	0.756	—	0.298	—	—	0.492
MgO	0.338	—	0.783	—	0.270	—	—
Co	0.326	—	0.782	—	—	—	—
Ni	—	0.496	0.645	0.281	—	—	—
Coethite	-0.438	0.480	-0.630	—	—	—	—
Pb	0.357	0.440	0.542	0.329	—	—	-0.305
Zr	—	—	—	0.921	—	—	—
TiO ₂	—	—	—	0.917	—	—	—
Al ₂ O ₃	-0.262	—	-0.407	-0.630	—	0.426	—
Cu	—	—	—	—	0.892	—	—
CaO	0.309	—	—	—	0.709	—	—
Zu	0.378	—	0.381	0.368	0.642	—	—
La	—	—	—	—	—	0.882	—
Na ₂ O	0.565	—	—	—	0.272	0.667	—
Fe (DCB/Tot)	—	0.270	—	-0.256	—	—	0.768
Fe (HCl)	0.260	—	0.387	—	—	-0.459	-0.554
Al (HCl)	0.332	0.370	0.466	—	—	-0.290	-0.416
P ₂ O ₅	0.372	0.290	0.470	0.426	0.269	0.344	—

Factor 2. In this factor the most important variables are 2:1 phyllosilicates (illite+smectite), illite, Rb and K contents. It must be emphasized that, while in the clay fraction, factor 1 distinguishes between illite-kaolinite, in this fraction the principal distinction is between quartz-kaolinite, illite following an independent distribution.

Factors 3 and 4. As in previous fractions factor 3 again is related to the Mn content. La and Ca are associated in factor 4.

Factor 5. Ba and feldspars are found to be associated in this factor. The participation of K, Mg, P and Na is important. In fact, although K-feldspars and K-illite correlations are significant, the correlation coefficient in the first case ($r = 0.737$) is greater than in the second ($r = 0.599$). This is also true for

Table 4. Loadings of the variables for the rotated factors. Fine-silt fraction. The 11 soil profiles have been used

Loading factors under 0.25 are shown (—)

	Fact 1	Fact 2	Fact 3	Fact 4	Fact 5	Fact 6
Quartz	-0.955	—	—	—	—	—
Al ₂ O ₃ /SiO ₂	0.945	—	—	—	—	—
Zr	-0.932	—	—	—	—	—
Phyllosilicates	0.919	—	—	—	-0.272	—
TiO ₂	-0.897	—	—	—	—	—
SiO ₂	-0.874	—	—	—	0.261	—
Al ₂ O ₃	0.857	—	-0.367	—	—	—
V	0.822	-0.278	—	0.356	—	—
Kaolinite	0.804	-0.368	—	—	-0.335	—
Fe ₂ O ₃	0.794	-0.359	—	—	—	—
Goethite	0.783	-0.285	-0.275	0.378	—	—
Cr	0.778	—	—	0.455	—	—
Na ₂ O	-0.635	—	—	—	0.376	—
2:1 Phyll.	0.280	0.850	—	—	—	—
Illite	—	0.814	—	—	—	—
Rb	—	0.739	0.366	—	—	—
K ₂ O	—	0.636	—	-0.269	0.607	—
Co	-0.276	0.281	0.808	—	—	—
Pb	-0.325	—	0.787	0.252	—	—
MgO	—	—	0.710	—	0.390	0.266
Sr	-0.318	0.414	-0.692	—	—	—
Ni	0.458	—	0.636	0.409	—	—
La	—	—	—	0.780	—	—
CaO	—	-0.406	—	0.545	—	0.299
Ba	-0.473	0.273	—	—	0.634	—
Feldspars	-0.536	0.352	—	—	0.563	—
Cu	—	—	—	—	—	0.907
Zn	—	—	—	—	—	0.861
P ₂ O ₅	-0.361	—	0.461	—	0.328	—

Ba, although Rb shows the opposite trend: (Rh-illite, $r = 0.726$; Rb-feldspars, $r = 0.423$).

Factor 6. This factor resembles factor 5 of the clay fraction (although with less participation of Ca), pointing out the similar behaviour of Cu and Zn.

The plot of the factor scores (factor 1 *v.* factor 2) are shown in Fig. 2. All samples of quadrant III are A horizons with the exception of one E horizon. They are rich in primary minerals but poor in 2:1 phyllosilicates. Most of the cases that appear to the right of the Y-axis are B and C horizons, rich in kaolinite.

Medium and coarse-silt fraction (8–50 μ m)

The six factors extracted (Table 5) explain 84.96% of the variance.

Factors 1, 2 and 3. These are similar to the same factors of the total sample.

Factors 4, 5 and 6. Ca and Cr are contained in factor 4; Ni, goethite and total Fe show important loadings. Factor 5, shows that the association Cu–Zn is the same here as in the finer fractions. Factor 6 groups variables P and Na.

Table 5. Loadings of the variables for the rotated factors, medium and coarse-silt fraction.
The 11 soil profiles have been used

Loading factors under 0.25 are shown thus (—)

	Fact 1	Fact 2	Fact 3	Fact 4	Fact 5	Fact 6
Al ₂ O ₃ /SiO ₂	0.911	—	—	—	—	—
Quartz	-0.894	—	—	-0.257	—	—
Phyllosilicates	0.891	—	—	—	0.264	—
Al ₂ O ₃	0.884	—	0.268	—	—	—
SiO ₂	-0.830	-0.365	—	-0.260	—	—
V	0.824	—	—	0.386	—	—
Fe ₂ O ₃	0.747	—	—	0.573	—	—
Zr	-0.730	—	—	—	—	-0.340
Goethite	0.659	—	-0.287	0.619	—	—
Sr	0.632	—	0.294	—	—	0.292
Ni	0.624	—	-0.254	0.619	—	—
MgO	0.542	—	0.526	—	0.514	—
Co	—	0.820	—	—	—	—
Pb	—	0.734	—	0.394	—	—
TiO ₂	—	-0.697	-0.267	—	0.395	—
La	—	0.678	—	—	0.454	—
Feldspars	-0.441	0.533	0.417	—	—	0.302
Ba	—	—	0.890	—	—	—
K ₂ O	—	0.370	0.887	—	—	—
Rb	0.282	0.578	0.659	—	—	0.259
CaO	—	—	—	0.823	—	—
Cr	0.519	—	—	0.650	—	—
Cu	0.326	—	—	—	0.845	—
Zn	0.348	—	—	0.368	0.782	—
P ₂ O ₅	—	—	—	—	—	0.839
Na ₂ O	-0.409	—	0.395	—	—	0.745

The plot of the factor scores (Fig. 2) points up clearly that in quadrants I and II (horizons rich in secondary minerals) all but one are B and C horizons; in quadrant IV (horizons rich in feldspars, Co, K and quartz) A horizons dominate.

Discussion

Among the four studied areas, ME (lower raña and away from RC, BU and MP) shows the more significant differences with respect to the others. It contains the highest content of Mn and Co (in all size-fractions) and of Mg (total soil and fine fractions). ME and RC can be distinguished from BU and MP by a higher Na content in the total soil fraction and by the presence of paragonite in the fine fractions. RC shows higher content in Na, K, Sr, Ba and Rb (total soil and clay fractions) than the other areas. On the contrary, MP is rather poor in K and Ba.

In general, MP and BU are the more similar areas, although their heavy metal contents can differentiate between them. For example, MP profiles show an enrichment in Ni (clay and silt fractions) while BU has a significant lower content in La (fine- and medium- and coarse-silt fractions) and a higher Zr content in the 8–50 μ m fraction.

Taking into account the mineralogical results, ME is the area with the highest illite and lower kaolinite contents, just the reverse situation to that occurring

in MP. Both phyllosilicates show intermediate contents in BU and RC areas. Finally, MP shows significantly the highest goethite content.

Depending on the particle size distribution, the variables can be divided into the following groups:

(1) Variables with the highest content in the finest fractions (clay and/or fine-silt), within which we can distinguish between:

(a) Those whose content in the clay fraction is significantly higher than in the fine-silt fraction (*t*-test). Phyllosilicates and kaolinite as well as Al, Mg, Ca, Rb, Ni and La are included in this group.

(b) Those variables having significant higher contents in the fine-silt than in the clay fraction (K, Sr and Ba).

(c) Those variables whose contents in the clay and fine-silt fractions are not significantly different (Fe, P, Cu, Co, Zn, Pb, V, Cr, goethite, illite, and 2:1 phyllosilicates). Mn, paragonite and smectite, which do not follow a normal distribution, can also be included in this group, given their similar contents in the clay and fine-silt fractions (chi-square test).

(2) Variables with the highest content in the coarse fractions. For Si, Zr and quartz the contents vary according to the sequence: medium and coarse-silt > fine-silt > clay, all these differences being significant. Somewhat different are the cases of Ti, Na and feldspars, where the contents are similar in the two silt fractions.

There are associations among the variables that recur for almost all particle size. Thus the content of Si is always included in the same factor as quartz; Al is related, except in the clay fraction, to the phyllosilicate content. In the clay fraction, the different content of Al in the two major minerals (kaolinite and illite) implies that this element is not clearly related to any of these minerals. The principal factor distinguishes between secondary minerals (phyllosilicates, kaolinite) and primary minerals (quartz), thus being related to concepts such as degree of alteration, eluviation/illuviation and particle size. A high positive value of factor 1 corresponds to horizons rich in secondary minerals with fine granulometry, which have suffered illuviation processes; an elevated negative value for this factor is typical of leached horizons with resistant minerals, where the coarser particle sizes predominate. Factors 1 and 2 are quite similar to those obtained by Monra and Kroonenberg (1988) when studying tropical soils, despite the important differences between the profiles in the two cases.

Although kaolinite is the major mineral in the clay fraction, its negative correlation with Sr, Rb, Ba and Cr indicates that kaolinite plays no role as a trace elements carrier (Mosser 1983; García-González and Recio 1988). This phyllosilicate holds a very small proportion of trace elements because it has very few isomorphous substitutions and a very low exchange capacity (Dixon 1989). Illite, Fe and Mn compounds are the principal trace elements carriers in these soils.

The illite content is always related to K, Rb and, to a smaller degree, with Sr and Ba. Kaolinite and illite show a negative correlation in the clay fraction, in which the principal factor groups together illite and quartz. Nevertheless, in the fine-silt fraction no correlation is observed between kaolinite and illite. No significant correlation is found between Na and paragonite, owing to the fact that feldspars are the principal Na-sources in these soils (García-González and Aragoneses 1990).

Alkaline and alkaline-earth metals show a close relationship in all fractions. K and Rb are always related, as can be expected from the similarity of both elements which provides for ready substitution of Rb for K in mica minerals (Jones 1989). Ba is also included in the alkaline and alkaline-earth factor in all size-fractions except in the fine-silt, in which its distribution is more related to the feldspar content (factor 5). In the total sample, K and Ba show the highest correlation ($r = 0.946$), since in geochemical processes usually Ba^{2+} is associated with K^+ due to their similar ionic radii (Kabata-Pendias and Pendias 1984). Mg, Ca, Na and Sr exhibit a more complex behaviour; in some of the fractions they behave similarly to K, Rb and Ba, but in other cases they are comprised in other factors. Although Sr is usually associated with Ca and to a lesser extent with Mg (Kabata-Pendias and Pendias 1984), these relationships are not clear in the soils studied.

The distribution of total Fe and goethite in the clay is markedly different from that in the other fractions. In the total sample and in the silt fractions they are included in the principal factor, showing positive correlation with the secondary minerals. On the other hand, in the clay fraction, total Fe is included in a specific factor, indicating an independent distribution from other minerals. The fact that goethite and total Fe are not directly correlated indicates that other Fe compounds (probably non-crystalline) may also be present. The small particle size of non-crystalline iron oxides (Schwertmann and Taylor 1989), points out the importance of these components in the fine fractions. In coarser fractions Fe-oxides act as an important source of trace elements; it is known that many elements are strongly retained by goethite and by less crystalline forms of Fe-oxides (Koons *et al.* 1980), and may be present adsorbed at the surface or as isomorphous substitutions (Schwertmann 1988). However, in the present study, Fe-oxides do not seem to be the principal source of trace elements (except for V closely related to Fe), these being more related to illite and Mn-oxides. Trivalent V^{3+} may replace both Fe^{3+} and Mn^{3+} , but as Fe^{3+} is more abundant than Mn^{3+} , and because the oxide stoichiometry M_2O_3 is the same for Fe and V, these may explain the greater enrichment of V in the high iron phases (Dawson *et al.* 1985).

Co and Pb appear associated in all the fractions, although sometimes Mg, Ni, La and P have an important participation in the same factor. The notable relation to the Mn content suggests the association Mn-Co-Pb. The Co content would be directly related to the proportion of Mn-oxides, a fact well documented in the literature (Taylor and McKenzie 1966; Jarvis 1984; McLaren *et al.* 1986; Norvell 1988; McKenzie 1989).

Ti and Zr show close relation in all fractions except in the total sample. Although Ti and Zr normally occur in specific mineral forms, they can also be present in the structure of other minerals (Milnes and Fitzpatrick 1989). In the silt fractions, these elements are enclosed in the principal factor, being included in primary minerals resistant to alteration. In the clay fraction, they form a specific factor, in spite of the greater mobility of Ti over Zr in soils (Kaup and Carter 1987).

Other metals (Ni, La and Cr) show a more complex behaviour. Ni seems to be related to illite in the clay fraction (positive loading for factor 1), to the factor 3 in the fine-silt and to the phyllosilicate content in the medium- and coarse-silt fraction. In the total sample, it is distributed between the factors 1

and 3, suggesting a competition between phyllosilicates and Mn-oxides for Ni retention. Although Tiller *et al.* (1984) found out that in clay fractions Ni shows a greater affinity for kaolinite than for other clay minerals, this association is not supported by the present study. In a similar way, no correlation is found between La and kaolinite contents, in good agreement with the results of Prudêncio *et al.* (1989) when studying Cretaceous and Pliocene sediments.

Cr is found in factor 1 (clay fraction), possibly illite being the principal Cr source. However, in the fine-silt the association of Cr with Fe-oxides appears to be more important, in agreement with Cary *et al.* (1977) and Grove and Ellis (1980); in the medium and coarse-silt fraction Cr behaviour differs from that of other heavy metals (e.g. association with Ca). There is Cr-Ni relation in the total sample, as found by Berrow and Reaves (1986), but this association is not evident in the fine fractions.

Cu and Zn show a special behaviour in these soils, and although they are associated with each other in all size fractions, their distribution does not follow any of the above patterns. Only in the total sample do they form part of the principal factor. This situation allows us to define a specific factor which differentiates these two metals from other trace elements. Their marked accumulation in specific horizons makes their distribution difficult to explain. Both Cu and Zn are very versatile trace cations, and in soils they exhibit a great ability to chemically interact with mineral and organic components (Kabata-Pendias and Pendias 1984).

Acknowledgments

We wish to thank Mr A. Gómez and Mrs M. P. Lázaro for technical assistance, and Mrs L. Barrios for statistical advice. FJA thanks the Ministerio de Educación y Ciencia (Spain) for providing a FPI fellowship. This research was supported by CAICYT (Spain) under project PR84/0140/C06.

References

- Aragoneses, F. J. (1990). Geoquímica y mineralogía de las fracciones finas de suelos tipo raña en la provincia de Guadalajara. Ph.D. Thesis. Universidad Autónoma de Madrid, Spain, 296 pp.
- Aragoneses, F. J., and García-González, M. T. (1991). High-charge smectite in Spanish "raña" soils. *Clays Clay Miner.* **39**, 211-18.
- Berrow, M. L., and Reaves, G. A. (1986). Total chromium and nickel contents of Scottish soils. *Geoderma* **37**, 15-27.
- BMDP (1985). Statistical software manual. (University of California Press: Berkeley, U.S.A.)
- Cary, E. E., Allaway, W. H., and Olson, O. E., 1977. Control of chromium in food plants. 2. Chemistry of chromium in soils and its availability to plants. *J. Agric. Food Chem.* **25**, 305-9.
- Dawson, B. S. W., Fergusson, J. E., Campbell, A. S., and Cutler, E. J. B. (1985). Distribution of elements in some Fe-Mn nodules and an iron-pan in some gley soils of New Zealand. *Geoderma* **35**, 127-43.
- Dixon, J. B. (1989). Kaolinite and serpentine group minerals. In 'Minerals in Soil Environments'. (Eds J. B. Dixon and S. B. Weed.) pp. 357-404. (Soil Sci. Soc. of Am.: Madison, U.S.A.)
- Espejo, R., 1985. The ages and soils of two levels of "Raña" surfaces in Central Spain. *Geoderma* **35**, 223-39.
- Espejo, R., 1987. The soils and ages of the "Raña" surfaces related to the Villuerca and Altamira Mountain ranges (western Spain). *Catena* **14**, 399-418.

- García-González, M. T., and Aragonese, F. J., (1988). Relación entre la mineralogía y el tamaño de partícula en snelos sobre formaciones pliocuaternarias en el área de Membrillera (Guadalajara). In 'II Congr. Nac. Ciencia del Suelo, Sevilla, Spain, 1988'. (Ed C. Roquero.) pp. 529-34. (Soc. Esp. Ciencia del Suelo: Madrid, Spain.)
- García-González, M. T., and Aragonese, F. J. (1990). Paragonite in Spanish 'raña' soils. *J. Soil Sci.* 41, 313-23.
- García-González, M. T., and Recio, P. (1988). Geochemistry and mineralogy of the elay fraction from some Spanish Terra Rossa. *Agrochimica* 32, 161-70.
- García-Rodríguez, M. P., Forteza, J., García-Rodríguez, A., and Lorenzo, L. F., (1988). Dinámica del hierro y del aluminio en suelos desarrollados sobre rañas en la provincia de Salamanca. In 'II Congr. Nac. Ciencia del Suelo, Sevilla, Spain, 1988'. (Ed C. Roquero.) pp. 396-401. (Soc. Esp. Ciencia del Suelo: Madrid, Spain.)
- Grove, J. H., and Ellis, B. G., (1980). Extractable chromium as related to soil pH and applied chromium. *Soil Sci. Soc. Am. J.* 44, 238-42.
- Jarvis, S. C. (1984). The association of cobalt with easily reducible manganese in some acidic permanent grassland soils. *J. Soil Sci.* 35, 431-8.
- Jiménez-Ballesta, R., Ibáñez, J. J., Monturiol, F., Alcalá, L., and Palomar, M. L., (1988). Fraccionamiento y distribución de óxidos de hierro en superficies de tipo raña y altas terrazas al sur del Macizo de Ayllón y Somosierra (Sistema Central). *An. Edaf. Agrobiol.* 47, 1365-378.
- Jones, R. L., 1989. Rubidium in surface horizons of Illinois soils. *Soil Sci. Soc. Am. J.* 53, 588-91.
- Kabata-Pendias, A., and Pendias, H. (1984). 'Trace Elements in Soils and Plants'. (CRC Press: Boca Raton, U.S.A.) 293 pp.
- Kaup, B. S., and Carter, B., 1987. Determining Ti source and distribution within a paleosol by micromorphology, submicroscopy and elemental analysis. *Geoderma* 40, 141-56.
- Koons, R. D., Helmke, P. A., and Jackson, M. L. (1980). Association of trace elements with iron oxides during rock weathering. *Soil Sci. Am. J.*, 44, 155-9.
- Martínez-Vega, J. (1989). Aplicación de la teledetección a la cartografía del medio ambiente: transformaciones del paisaje agrario. Ph.D. Thesis. Universidad Complutense, Madrid, Spain. 336 pp.
- McKenzie, R. M. (1989). Manganese oxides and hydroxides. In 'Minerals in Soil Environments'. (Eds J. B. Dixon and S. B. Weed.) pp. 439-65. (Soil Sci. Am.: Madison, Wisc.)
- McLaren, R. G., Lawson, D. W., and Swift, R. S. (1986). The forms of cobalt in some Scottish soils as determined by extraction and isotopic exchange. *J. Soil Sci.* 32, 247-56.
- Mehra, O. P., and Jackson, M. L. (1960). Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* 5, 317-27.
- Milnes, A. R., and Fitzpatrick, R. W. (1989). Titanium and zirconium minerals. In 'Minerals in Soil Environments'. (Eds J. B. Dixon and S. B. Weed.) pp. 1131-1205. (Soil Sci. Soc. of Am.: Madison, Wisc.)
- Mosser, C. (1983). Elements traces des argiles: des marqueurs. *Clay Miner.* 18, 139-51.
- Moura, M. L., and Kroonenberg, S. B. (1988). Major and minor elements, geochemistry and mineralogy of four soil profiles from Aracuaara, Colombian Amazonas. *Catena* 15, 81-97.
- Norvell, W. A. (1988). Inorganic reactions of manganese in soils. In 'Manganese in Soil and Plants'. (Eds R. D. Graham, R. J. Hannam and N. C. Uren.) pp. 37-58. (Kluwer Academic Publ.: Dordrecht, The Netherlands.)
- Palomar, M. L., Jiménez-Ballesta, R., Monturiol, F., and Guerra, A. (1988). Dinámica del Fe y Al en raña bajas y terrazas en la provincia de Guadalajara. *An. Edaf. Agrobiol.* 47, 1541-52.
- Prudêncio, M. I., Figueiredo, M. O., and Cabral, J. M. P. (1989). Rare earth distribution and its correlation with clay mineralogy in the clay-sized fraction of Cretaceous and Pliocene sediments (central Portugal). *Clay Miner.* 24, 67-74.
- Rodríguez-Pascual, C., Galván, B., and Galván, J. (1987). Mineralogical properties of soils on "raña" formations in the province of Guadalajara (Spain). In 'Proc. 6th European Clay Groups, Sevilla, Spain, 1987'. (Eds E. Galán, J. L. Pérez-Rodríguez and J. Cornejo.) pp. 467-9. (Soc. Esp. Arcillas: Sevilla, Spain.)

- Sánchez-Camazano, M., Sánchez-Martín, M. J., and Vicente, M. A. (1988). Características de la fracción arcilla en los suelos de raña al norte del Sistema Central. In 'II Congr. Nac. Ciencia del Suelo, Sevilla, Spain, 1988'. (Ed. C. Roquero.) pp. 548-53. (Soc. Esp. Ciencia del Suelo: Madrid, Spain.)
- Schwertmann, U. (1988). Some properties of soil and synthetic iron oxides. In 'Iron in Soils and Clay Minerals'. (Eds J. W. Stucki, B. A. Goodman and U. Schwertman.) pp. 203-50. (Reidel: Dordrecht, The Netherlands.)
- Schwertman, U., and Taylor, R. M. (1989). Iron oxides. In 'Minerals in Soil Environments'. (Eds J. W. Dixon and S. B. Weed.) pp. 379-438. (Soil Sci. Soc. Am.: Madison, Wisc.)
- Segalen, P. (1968). Note sur une méthode de détermination des produits minéraux amorphes dans certains sols à hydroxydes tropicaux. *Cah. ORSTOM, sér. Pédol.* **6**, 105-26.
- Shacklett, H. I., and Boerngen, J. C. (1984). Element concentrations in soils and other surficial materials of the conterminous United States. U.S. Geol. Surv. Prof. Pap. 1237.
- Taylor, R. M., and McKenzie, R. M. (1966). The association of trace elements with manganese minerals in Australian soils. *Aust. J. Soil Res.* **4**, 29-39.
- Tiller, K. C., Gerth, J., and Brümmer, C. (1984). The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. *Geoderma* **34**, 17-35.
- USDA (1975). Soil Taxonomy. Agricultural Handb. No. 346. (U.S. Government Printing Office: Washington, D.C.)
- Vicente, M. A., Molina, E., and García-Rodríguez, M. P. (1986). Mineralogical study of the <2 μm clay fraction of raña type soils of the northern Meseta (Spain). In 'Trans. 13th Congr. Int. Soc. Soil Sci., Hamburg, 1986'. (Ed. K. H. Hartge.) pp. 1490-91. (Int. Soc. Soil Sci.: Wageningen.)
- Vinogradov, A. P., (1959). 'The Geochemistry of Rare and Dispersed Chemical Elements in Soils'. (Consultants Bureau: New York.) 209 pp.