

MINERALOGY, GEOCHEMISTRY, AND ORIGIN OF THE UNDERCLAYS OF THE CENTRAL COAL BASIN, ASTURIAS, SPAIN

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Abstract—Samples of underclays corresponding to nine different coal beds of the María Luisa coal seam in the Aller valley (Asturias, Spain) were collected to determine whether their mineralogy and geochemistry could be used for correlation. The underclays are dominated by illite, with an average abundance of 46%, and contain smaller amounts of chlorite, kaolinite (chlorite always more abundant), paragonite, pyrophyllite, mixed-layer illite/smectite (I/S), and mixed-layer muscovite/paragonite. This mineralogical association along with the illite “crystallinity” values (mean values of “crystallinity” in air-dried and ethylene glycol-solvated illite are 0.48° and $0.35^\circ 2\theta$, respectively) suggest that the samples have undergone very low-grade metamorphism. No consistent variation in the mineral components with increasing depth below the coal was noted. The presence of chlorite and K-feldspar precludes the development of the underclays by extensive leaching by acid swamp waters and thereby suggests that their mineral composition was determined largely by provenance.

Thirty-seven mineralogical and geochemical variables were treated by stepwise discriminant analysis. The variables that best served as discriminators between the underclays were: illite + I/S contents of both the whole rock and clay fraction, illite “crystallinity” of the clay fraction in both air-dried and glycolated patterns, pH of the samples, and the elements (in order of atomic number) Na, Al, K, Ca, Ti, V, Sr, Zr, Nb, Ba. The Molino underclay is clearly distinct from the other eight underclays, suggesting its potential use in regional correlation.

Key Words—Chlorite, Diagenesis, Illite, Illite/smectite, Paragonite, Pyrophyllite, Underclay.

INTRODUCTION

The María Luisa horizon in the Central Coal Basin of Asturias, Spain, contains the maximum thickness of workable coal beds in the basin. As many as nine principal coal beds plus several thin beds have been found (Figure 1). Most of the studies in the Central Coal Basin since the pioneer works of Ezquerro del Bayo (1841), Schulz (1837, 1858), and Barrois (1882) have focused on stratigraphy, stratigraphic nomenclature, sedimentology, and palaeontology, and, with the exception of Aller and Brime (1985), no mineralogical-geochemical studies have been reported. The mineralogy and origin of the underclays in this basin have not been investigated.

The term underclay is used in this paper to mean a non-laminated argillaceous rock commonly found beneath beds of coal. Generally, underclays contain plant roots and randomly orientated slickensides. The contact between the underclay and the coal is usually sharp, but the lower contact is generally gradational. Two hypotheses have been proposed for the origin of underclays and whether or not they have undergone post-depositional alteration. Grim and Allen (1938) and Schultz (1958) suggested that the composition of the underclays is controlled essentially by the source from which they were derived and, therefore, is related to depositional processes. Plant action and leaching may have been operable, but only to a slight degree. Huddle

and Patterson (1961), on the other hand, and later Rimmer and Eberl (1982) and Hughes *et al.* (1987) held that underclays acquire their peculiar characteristics in a water-logged swamp environment. Plant roots and continued leaching by acid swamp waters were proposed to be the major modifying influences of the initial sediments.

The present investigation was conducted to examine the mineralogy and geochemistry of the underclays of the principal coal beds in the María Luisa horizon in order to establish their paragenesis and to see whether or not individual underclays could be used as marker beds throughout the basin.

MATERIALS AND METHODS

Sixty-three unweathered samples from the nine principal underclays in the horizon were collected (Figure 1) from the underground galleries of the San Antonio, Aller, and Santiago workings of the Empresa Hulleras del Norte Sociedad Anónima (HUNOSA) in the Aller River Valley (Figure 2).

Mineral identification

All samples were ground and dispersed in deionized water; the $<2\text{-}\mu\text{m}$ size fractions were separated by differential settling. Oriented mounts for X-ray powder diffraction (XRD) of both whole-rock and $<2\text{-}\mu\text{m}$ size fractions were prepared using the suction technique

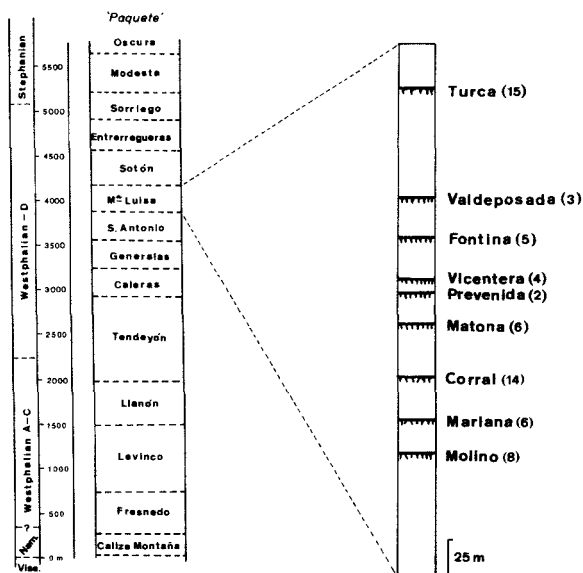


Figure 1. Vertical distribution of the different coal horizons of the Central Coal Basin of Asturias, Spain, and location of the underclays of the María Luisa coal horizon. Numbers in parentheses = number of samples studied from each underclay.

described by Brime (1981). The samples were examined in the air-dried state, after ethylene glycol treatment and after heating at 550°C, using a Philips 1410 diffractometer, operated at 40 kV and 20 mA, and Fe-filtered $\text{CoK}\alpha$ radiation, a time constant of 2, a 1° divergence slit, a 0.1-mm scatter slit, and a 1° receiving slit. The scan speed was 1°/2 θ /min, and the chart speed was 1 cm/min.

Clay minerals were identified from their periodic 00l reflections determined from XRD patterns. Their relative proportions were estimated by the XRD method described by Schultz (1960, 1964), which was slightly modified to determine the paragonite content of the samples.

The presence of illite/smectite (I/S) mixed-layer clay was recognized by the broad shoulder on the low-angle side of the 001 illite reflection on XRD traces of air-dried mounts (Figure 3). To differentiate the respective I/S and illite peaks, glycolation was required, and the illite peak area and shape were therefore measured using glycolated mounts. The I/S was identified using the methods of Reynolds and Hower (1970), Reynolds (1980), and Hower (1981).

In addition, a second mixed-layer mineral consisting of muscovite/paragonite (Figures 3 and 4) was identified. A strong basal reflection at 3.25 Å and a weaker reflection at 1.96 Å are characteristic of this mineral (Frey, 1969).

The sodic mica paragonite was identified by the three periodic reflections at 9.6, 4.8, and 3.2 Å. The reflection

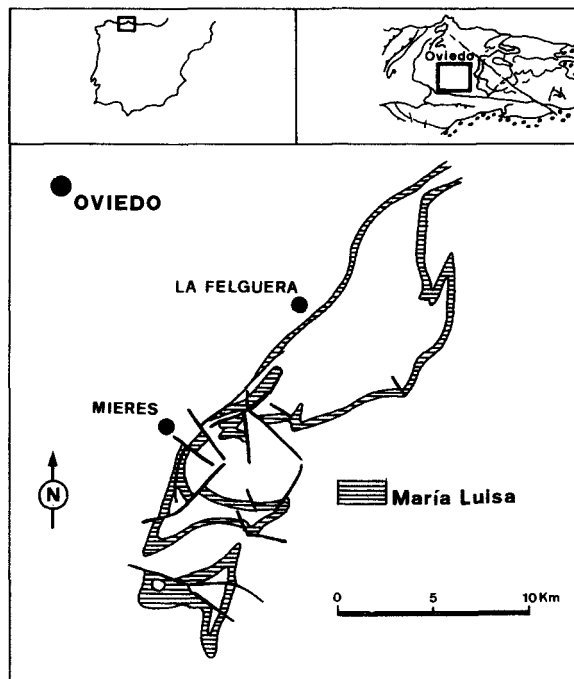


Figure 2. Location and distribution of the María Luisa coal seam in the Central Coal Basin of Spain.

at 3.2 Å was clearly visible in the patterns of all samples, but, because the paragonite content was low, the other two peaks were not always identified (Figure 4). The 9.6-Å peak appeared as a small shoulder on the low-angle side of the illite peak; the 4.8-Å peak was commonly masked by the chlorite 003 reflection and the muscovite/paragonite phase.

The composition of chlorite, identified by its peaks at 14, 7, 4.72, 3.56, and 2.8 Å, was obtained using the empirical method of Nieto *et al.* (1983), based on the variation of the ratios between the structure factors of the 004/003 and 004/005 basal reflections. This method takes into account not only the presence of heavy atoms but also the chlorite di-trioctahedral character.

The first-order basal reflection of kaolinite coincided in most of the samples with the 002 reflection of chlorite, but the second-order basal reflection at 3.60 Å was resolved from the 004 reflection of chlorite at 3.56 Å (Figure 5).

Pyrophyllite was easily detected by its basal reflections at 9.2, 4.6, and 3.06 Å (Figure 3). This mineral was found in many samples but in very small quantities.

Determination of the illite "crystallinity"

The "crystallinity" of illite, i.e., the width of the first-order illite basal reflection at half-height above background (Kubler, 1964; Dunoyer de Segonzac, 1969), was measured from the patterns of both air-dried and

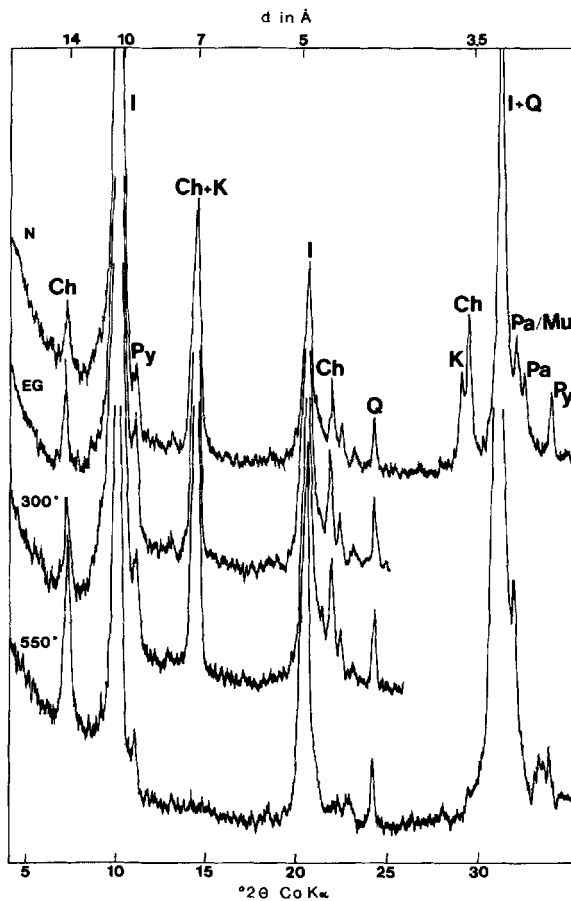


Figure 3. X-ray powder diffractograms of the orientated <2- μm fraction of sample 33, untreated (N), glycolated (EG), and heated at 300° and 550°C. Ch = chlorite; I = illite; I/S = illite/smectite mixed layer; K = kaolinite; Pa = paragonite; Pa/Mu = paragonite/muscovite mixed layer; Py = pyrophyllite; Q = quartz.

glycolated samples (Persoz and Remane, 1976; Frey *et al.*, 1980; Brime and Perez-Estaún, 1980; Brime, 1981, 1985; Kisch, 1983, 1987; Frey, 1987). The numerical value decreases with improving "crystallinity" and is given in $\Delta 2\theta^\circ$. The measurements were standardized by two methods: (1) against samples of known "crystallinity" (provided by G. Dunoyer de Segonzac), which were prepared by the same method as the unknowns; and (2) against a set of polished slate slabs (provided by H. Kisch).

The transient zone ("anchizone" of Kubler, 1967) between diagenesis (*sensu lato*) and the green schist facies ("epizone" of Kubler, 1967) is defined by $\Delta 2\theta^\circ$ indices between 0.42° and 0.25° 2θ , respectively (Kisch and Frey, 1987).

Chemical analysis

The following elements were analyzed on each sample: (1) Nb, Zr, Y, Sr, Rb, Zn, Cu, Ni, Co, Cr, V, and

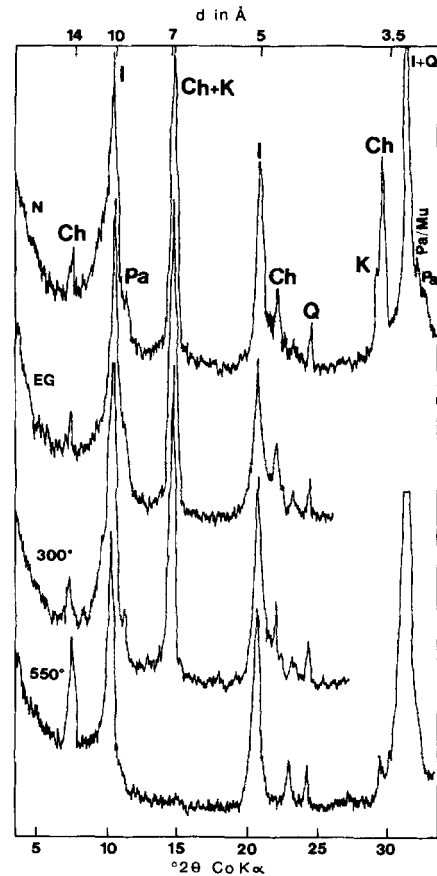


Figure 4. X-ray powder diffractograms of the orientated <2- μm fraction of sample 43. For abbreviations see Figure 3.

Ba were analyzed by X-ray fluorescence spectrometry; (2) Si, Al, Fe, Mg, Mn, Ca, Na, and K were analyzed by atomic absorption using a Zeeman flame spectrometer; (3) Ti and P were analyzed by colorimetry.

XRF samples were prepared with phenolic resin (Durite F-103) and heated at 112°C for 30 min. The samples were analyzed in a Philips fluorescence spectrometer PW1410 using a rhodium tube and a LiF (220) crystal for the analysis of Nb, Zr, Y, Sr, and Rb; the remaining elements were analyzed using a LiF (200) crystal.

Determination of pH

The underclay pH was determined using a "micropH 2001 meter." One gram of ground clay was mixed with 10 ml of deionized water, and the pH read when stable, usually after 1 min.

Statistical analysis

Discriminant analyses using the program 7M (Jennrich and Sampson, 1983) of the Statistical Package BMDP were performed on the data. The chemical and mineralogical variables were treated separately and then

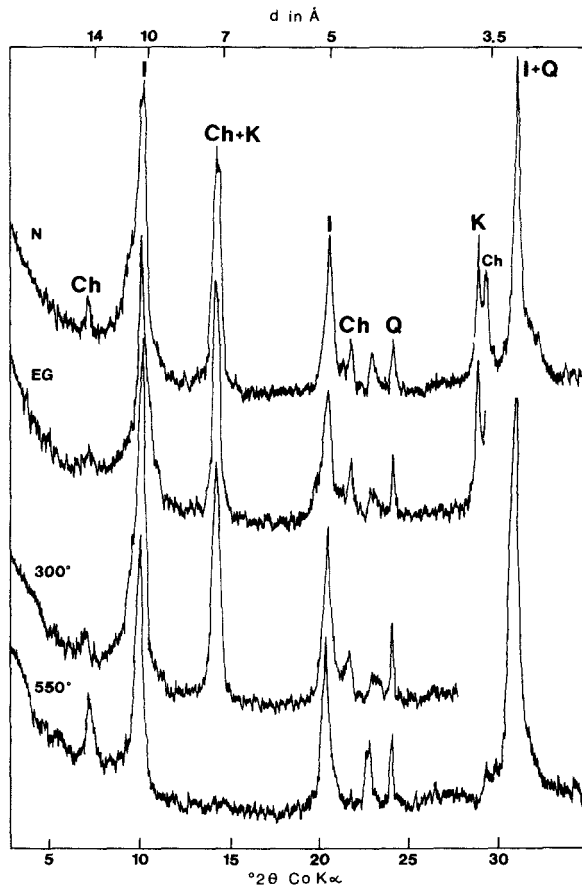


Figure 5. X-ray powder diffractograms of the orientated <2- μm fraction of sample 7. For abbreviations see Figure 3.

combined with all other variables to determine whether each of the nine underclays carried a unique and identifiable "fingerprint."

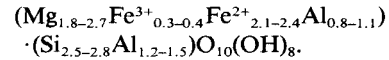
RESULTS AND DISCUSSION

The underclays studied from the María Luisa coal horizon consist chiefly of illite with considerable amounts of quartz, chlorite, kaolinite, pyrophyllite, paragonite, and mixed-layer muscovite/paragonite and illite/smectite (I/S) (Figures 3–5). Potassium feldspar also was detected in most of the samples, but only in small quantities. In some of the samples siderite, calcite, anhydrite, and (in one sample) pyrite were also identified. No discrete smectite was found in any of the underclays.

Illite was by far the dominant clay mineral identified in the underclays, in amounts ranging from 22% to 67% and averaging 46%. Discrete illite was invariably found to be associated with I/S, which was an ordered variety and had <30% expandable layers. In some of the underclays studied, the illite was slightly less abun-

dant, especially if the sample had been collected immediately below the coal.

Chlorite compositions determined for four samples using the method of Nieto *et al.* (1983) correspond to the following structural formula:



Peak intensities before and after heat treatment also indicated a relatively Fe-rich chlorite in all the samples; the amounts ranged from 5% to 17%, with an average of 11%.

The two groups of three reflections of kaolinite at 2.55, 2.52, and 2.49 and 2.37, 2.33, and 2.38 Å were commonly present in randomly oriented samples, but the doublet at 4.17 and 4.12 Å was not resolved, suggesting that the kaolinite in the underclays was intermediate between well-crystallized and poorly crystallized fireclay kaolinite. Kaolinite, although present in all the samples, was less abundant than chlorite.

Five underclays were sampled from top to bottom at about 20-cm intervals to determine whether their major mineral constituents showed any vertical variation. The data showed no consistent vertical variation, with the exception of a slight increase in the illite content towards the bottom of the underclays (Figure 6). These data agree with the observations of Grim and Allen (1938), Schultz (1958), and Wilson (1965), who concluded that post-depositional leaching was not a major factor in underclay formation.

In addition to this lack of a consistent vertical variation, the presence of chlorite in all the samples is further evidence against a major leaching phase, inasmuch as the mineral is sensitive to leaching (Rimmer and Eberl, 1982). Furthermore, the amount of chlorite is greater in the whole sample than in the <2- μm fraction. Therefore, most of the chlorite in the underclays is probably of primary origin.

These underclays clearly could not have been greatly affected by leaching and weathering processes; thus, the slight differences found between them were probably due to differences in the prevailing conditions of the source area and/or their derivation from different source areas. In support of this idea is the fact that the mineral suite found in these underclays is similar to that described by Aller and Brime (1985) for pelitic rocks of the southern part of the Central Coal Basin, not directly associated with coals.

The mineralogy of the underclays studied here bears a marked resemblance to the underclay profiles of the type K and L described by Odom and Parham (1968) from Pennsylvanian underclays in Illinois, in which mineralogical variations were related to depositional processes.

According to Wilson (1965), the almost invariable association of coal with underclay can be explained if underclays are interpreted as representing the transi-

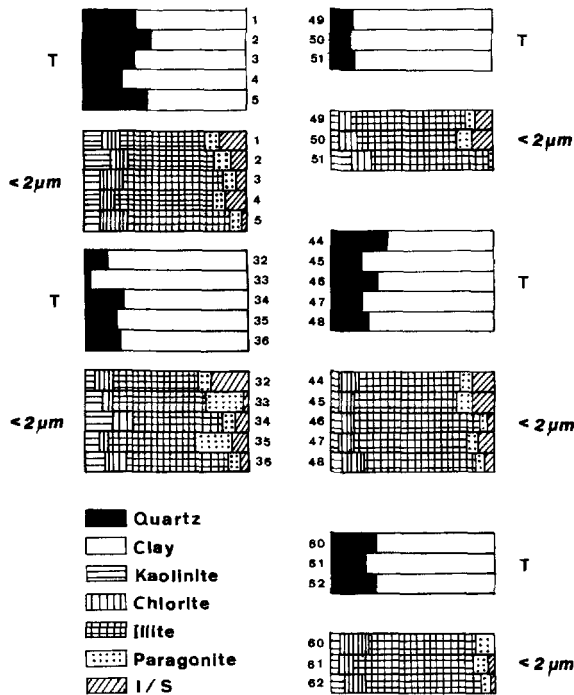


Figure 6. Mineralogical variation of the five underclays sampled from top to bottom. T = whole sample. Samples 1–5 correspond to Turca underclay; samples 32–36 to Corral underclay; samples 49–51 to Mariana underclay; samples 44–48 and 60–62 to Molino underclay.

tion from the oxidizing conditions of the shales and sandstones below the underclay to the reducing conditions of the coal. The measured values of the illite “crystallinity” (Table 1 and Figure 7) indicate that the underclays have been subjected to very low grade metamorphism. The presence of minerals such as paragonite, pyrophyllite, and mixed-layer muscovite/paragonite is also characteristic of the transient zone between diagenesis (*sensu lato*) and the green schist facies (Frey, 1970, 1987).

The chemical analysis and pH values of the samples are listed in Table 1. As in the mineral component study, no consistent vertical variation was found in the chemical data of the five underclays sampled from top to bottom (Table 1).

In the discriminant analysis, the 62 samples analyzed were grouped so as to consider together all the samples belonging to underclays below the same coal bed. These groups were identified by the name of the overlying coal bed (Table 3). The discriminant analysis, using the mineralogical variables and the pH, established that 8 of the 12 variables were useful discriminators. The variables with discriminant power were: illite and I/S content of the clay fraction, the illite “crystallinity” in both the air-dried and the glycolated pattern, the contents of chlorite, illite, and I/S of the whole sample,

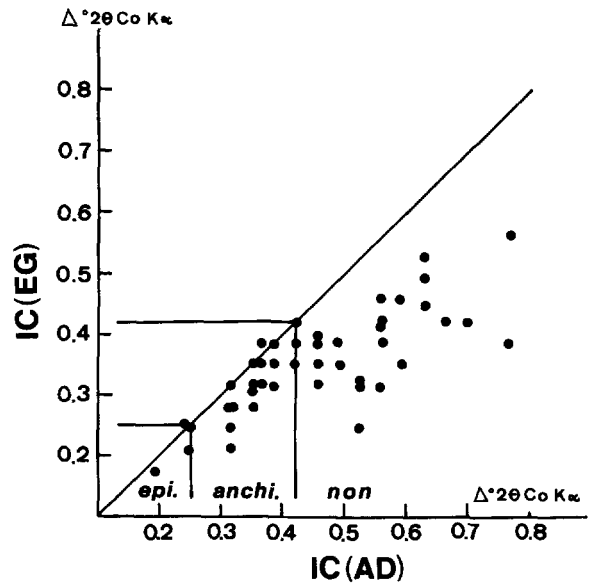


Figure 7. Illite “crystallinity” of air-dried samples vs. illite “crystallinity” of ethylene glycol-solvated samples.

and the pH of the sample. Using the variables mentioned above, correct classification of 67% of the control-group samples was obtained, and all the samples of the Molino underclay were correctly classified. The differences between the groups were significant for only four samples (Table 3).

If the discriminant analysis was performed using the 22 chemical variables, the model established 12 significant variables: TiO₂, Al₂O₃, MgO, CaO, Na₂O, K₂O, weight loss, Nb, Zr, Sr, V, and Ba. Correct classification of 64% of the control-group samples was obtained using the 12 elements mentioned above. Within the groups the best results were obtained for the Molino underclay with 7 of 8 samples correctly classified. The differences between the control-group samples was significant for 7 samples (Table 4).

If both the mineralogical and chemical variables were entered together in the analysis, the discriminant model found 18 of the 37 variables to be significant discriminators: illite and I/S content of both whole rock and clay fraction, illite “crystallinity” of both air-dried and glycolated samples, pH of the samples, and the elements (in order of atomic number) Na, Al, K, Ca, Ti, V, Sr, Zr, Nb, and Ba. The analysis performed in this way increased the separation between the groups, mainly in those comparisons involving the Molino underclay (Table 5).

The representation of canonical variate analysis plotted on a scatter diagram shows the separation among the underclay groups (Figure 8). As expected from the F matrices shown in Tables 3–5, the Molino underclay is clearly separated from all others by the second canonical variable in which the original variable with

Table 1. Chemical results on underclays. (Underclays sampled from top to bottom are underlined.)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO ₂	65.35	70.13	60.28	58.93	62.25	55.58	62.82	58.92	57.76	59.14	66.32	63.75	65.36	56.40	59.95	60.25
TiO ₂	1.01	0.88	0.79	1.04	0.89	0.82	0.89	1.00	1.13	1.13	0.94	0.99	1.07	1.01	0.88	1.19
Al ₂ O ₃	16.82	16.07	16.11	19.79	14.12	15.00	16.37	20.08	21.92	21.83	17.74	17.34	15.6	19.29	16.58	21.56
FeO	2.38	3.27	10.42	4.45	5.31	8.51	5.09	4.42	4.42	2.48	3.75	5.22	4.00	5.11	4.71	3.47
MgO	0.96	0.98	1.87	1.48	1.40	1.83	1.34	1.50	1.36	0.96	1.26	1.21	1.15	0.01	1.65	1.13
MnO	0.08	0.03	0.02	0.04	0.11	0.13	0.08	0.05	0.07	0.03	0.02	0.07	0.02	0.07	0.07	0.05
CaO	0.40	0.31	1.17	0.72	3.25	3.08	1.65	0.98	0.67	0.86	0.15	0.59	2.02	3.35	3.54	0.51
Na ₂ O	0.51	0.62	0.66	0.62	0.76	0.66	0.78	0.60	0.64	0.89	0.62	0.74	0.70	0.93	0.87	0.66
K ₂ O	2.07	2.33	2.01	3.68	1.62	2.45	2.01	3.72	3.26	3.14	3.02	2.88	1.79	3.85	2.84	3.16
P ₂ O ₅	0.11	0.64	0.14	0.77	0.18	0.53	0.19	0.57	0.21	0.33	0.52	0.42	0.21	0.45	0.56	0.21
Total	89.69	95.26	93.47	91.52	89.89	88.59	91.22	91.84	91.44	90.79	94.34	93.21	91.92	90.47	91.65	92.19
Nb	22	22	18	24	16	19	20	23	23	21	22	20	23	21	19	24
Zr	292	333	216	180	311	244	281	177	179	144	296	275	200	176	274	199
Y	34	35	41	38	33	35	36	38	37	33	41	38	31	198	33	34
Sr	124	134	123	177	148	140	139	171	173	138	142	137	164	195	165	163
Rb	129	119	119	184	100	107	121	175	179	202	149	144	193	1367	134	170
Zn	95	149	100	149	137	111	137	151	148	133	159	150	128	121	120	188
Cu	50	51	40	48	32	35	38	47	43	43	53	47	0	47	45	54
Ni	55	48	47	78	42	48	49	68	67	59	60	76	50	53	52	75
Co	3	0	20	20	13	0	14	12	22	15	13	29	20	5	3	28
Cr	147	152	137	145	135	140	134	163	144	150	146	140	141	138	133	152
V	181	219	204	211	176	198	174	0	222	179	183	200	122	197	195	197
Ba	639	722	562	725	520	781	490	488	689	569	640	619	451	815	615	621
Ign. loss	9.98	4.10	6.11	7.53	9.62	10.22	8.54	8.21	8.32	8.54	5.36	6.68	7.91	9.22	7.97	7.26
pH	9.65	9.09	9.79	9.11	10.12	9.81	10.11	9.73	9.78	10.20	9.14	8.94	10.20	9.50	9.74	9.58
IC(AD) ¹	0.46	0.56	0.38	0.70	0.32	0.38	0.45	0.49	0.63	0.77	0.38	0.53	0.46	0.52	0.32	0.63
IC(EG) ²	0.31	0.42	0.31	0.42	0.25	0.35	0.38	0.35	0.46	0.38	0.38	0.32	0.35	0.25	0.31	0.49

Table 1. Continued.

	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
SiO ₂	54.49	57.46	53.52	67.74	64.83	61.33	46.37	48.00	59.85	53.23	56.08	53.54	58.69	70.00	60.00	62.55
TiO ₂	1.05	1.01	1.18	0.66	1.14	1.01	0.91	0.80	1.14	0.65	1.22	0.90	1.08	0.85	0.94	0.74
Al ₂ O ₃	20.13	21.85	25.52	11.09	20.70	20.76	19.77	16.15	20.22	10.29	24.71	21.65	19.77	17.09	20.08	16.64
FeO	6.22	3.73	1.71	3.98	1.58	3.65	5.93	6.95	2.69	4.31	2.52	5.08	6.17	3.19	4.27	5.30
MgO	1.41	1.43	0.86	0.91	0.88	1.30	1.06	1.98	1.06	11.30	1.15	1.18	1.60	1.05	1.43	1.99
MnO	0.07	0.02	0.03	0.05	0	0.02	0.08	0.09	0.03	0.07	0.02	0.02	0.15	0.08	0.02	0.03
CaO	1.26	0.28	0.24	0.52	0.07	0.09	1.65	9.13	1.65	6.24	0.22	0.51	1.87	0.71	0.18	1.87
Na ₂ O	0.44	0.87	0.62	0.55	0.78	0.74	0.49	0.72	0.69	0.57	0.58	0.58	0.51	0.34	0.74	0.42
K ₂ O	2.93	4.30	3.37	1.77	3.76	3.72	2.91	2.82	2.95	1.61	3.78	3.43	2.87	2.71	4.34	2.81
P ₂ O ₅	0.34	0.30	0.36	0.64	0.38	0.42	0.87	0.48	0.28	0.58	0.16	0.36	0.16	0.05	0.45	0.12
Total	88.34	90.95	87.41	87.91	94.12	93.04	80.40	87.12	90.56	88.85	90.44	87.25	92.87	96.07	92.45	92.47
Nb	19	21	26	10	23	21	16	16	22	10	21	17	20	17	18	18
Zr	160	146	182	192	185	164	117	125	203	329	144	126	163	243	159	282
Y	32	33	32	22	42	29	27	31	37	24	33	29	35	29	37	35
Sr	149	191	216	83	186	182	184	286	199	172	108	160	174	109	153	121
Rb	153	196	183	80	117	168	163	130	173	73	202	181	155	145	183	137
Zn	180	173	104	83	59	150	153	124	208	105	174	153	132	123	127	135
Cu	46	56	43	21	35	34	44	42	54	29	60	48	42	56	59	51
Ni	64	69	62	30	47	45	73	60	66	39	74	59	59	50	83	52
Co	22	18	0	9	12	21	169	21	0	0	22	21	25	21	27	40
Cr	160	153	158	189	129	144	161	129	127	146	161	156	163	168	150	155
V	210	226	155	101	179	156	764	148	618	111	223	238	216	151	212	126
Ba	689	803	951	359	533	412	2473	553	2751	435	782	774	721	600	767	540
Ign. loss	11.72	7.90	12.32	12.31	6.04	6.35	19.74	11.04	9.33	10.38	9.29	13.00	7.29	4.41	6.69	7.02
pH	9.93	9.51	8.95	9.40	9.50	9.45	9.82	9.79	10.28	9.96	9.65	9.49	10.18	9.07	8.66	9.71
IC(AD) ¹	0.66	0.49	0.77	0.35	0.52	0.49	0.45	0.35	0.49	0.45	0.46	0.56	0.38	0.70	0.32	0.38
IC(EG) ²	0.42	0.38	0.56	0.28	0.42	0.35	0.38	0.35	0.35	0.38	0.31	0.42	0.31	0.42	0.25	0.35

¹ IC(AD) = Illite "crystallinity," air-dried sample; ² IC(EG) = Illite "crystallinity," ethylene glycol-solvated sample.

Table 1. Continued.

	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SiO ₂	57.66	58.55	59.27	57.8	59.60	53.51	58.84	51.84	51.55	57.00	51.00	65.64	57.16	56.58
TiO ₂	1.01	0.99	1.03	1.00	1.14	0.91	0.84	1.09	0.79	0.94	0.88	1.05	1.07	0.94
Al ₂ O ₃	18.99	19.32	22.55	20.01	23.05	20.08	22.10	20.13	20.43	21.61	19.29	16.55	19.64	20.08
FeO	5.89	5.60	3.22	5.22	3.91	4.79	4.68	5.53	7.04	3.81	8.19	5.01	2.38	5.67
MgO	1.53	1.43	1.11	1.38	1.12	1.55	1.24	1.51	1.55	1.26	1.90	1.36	0.96	1.75
MnO	0.08	0.04	0.08	0.05	0.03	0.06	0.04	0.06	0.11	0.03	0.16	0.11	0.08	0.06
CaO	1.27	1.32	0.30	0.43	0.33	1.87	0.57	3.00	0.83	0.34	2.58	2.31	0.40	0.92
Na ₂ O	0.82	0.55	0.71	0.80	0.69	0.64	0.84	1.00	0.95	0.97	0.80	0.58	0.51	0.95
K ₂ O	3.30	2.58	3.10	3.50	3.28	3.50	3.89	3.18	3.80	4.17	3.36	2.01	2.07	4.15
P ₂ O ₅	0.60	0.21	0.20	0.51	0.10	0.52	0.18	0.55	0.61	0.50	0.63	0.25	0.11	0.71
Total	91.15	90.59	91.57	90.70	93.25	87.43	93.22	87.89	87.66	90.63	88.79	94.87	84.32	91.81
Nb	20	20	21	21	23	20	15	19	19	21	18	19	19	20
Zr	202	193	164	198	170	141	110	163	118	126	136	275	151	149
Y	40	34	33	37	40	31	29	37	30	30	31	35	35	35
Sr	162	145	172	174	173	175	145	208	183	181	165	151	137	145
Rb	151	144	180	170	179	175	187	161	184	189	156	115	165	178
Zn	126	123	169	120	170	140	135	172	129	122	117	128	148	141
Cu	38	43	56	48	45	48	52	55	41	54	26	44	47	45
Ni	64	59	66	66	72	70	61	65	58	61	48	56	67	57
Co	1	30	15	3	22	11	18	23	18	11	9	18	20	14
Cr	139	136	149	154	155	157	141	146	154	152	130	135	145	143
V	239	179	217	237	213	257	190	222	255	234	221	151	245	212
Ba	803	532	607	775	707	884	862	698	10,720	796	578	492	0	683
Ign. loss	8.03	9.09	6.70	8.40	6.62	10.19	6.80	12.64	11.89	8.87	10.10	4.87	9.98	7.77
pH	9.12	9.90	9.06	8.90	9.41	9.73	9.60	10.08	9.16	8.28	9.81	10.08	8.89	9.48
IC(AD) ¹	0.56	0.42	0.56	0.42	0.56	0.42	0.32	0.32	0.7	0.36	0.59	0.35	0.35	0.56
IC(EG) ²	0.45	0.38	0.38	0.42	0.42	0.35	0.32	0.28	0.42	0.38	0.35	0.28	0.28	0.32

Table 1. Continued.

	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62
SiO ₂	54.47	56.65	52.02	54.83	54.11	58.86	61.90	64.80	63.43	71.96	65.96	47.30	59.50	60.99	62.33	61.78
TiO ₂	0.93	0.93	0.97	0.96	1.10	1.14	0.87	0.55	0.90	1.02	0.90	0.84	0.93	0.94	0.96	0.79
Al ₂ O ₃	18.14	17.89	21.83	20.56	21.47	19.50	15.63	9.60	17.00	12.37	15.57	15.72	18.25	20.84	19.96	17.62
FeO	4.98	6.26	8.53	7.04	5.42	6.05	5.50	4.16	4.61	3.47	4.33	15.25	5.98	3.99	3.31	7.13
MgO	2.67	2.44	1.58	1.68	1.57	1.62	1.38	1.08	1.27	1.29	1.40	1.40	1.61	1.36	1.27	1.41
MnO	0.06	0.08	0.09	0.08	0.09	0.08	0.07	0.09	0.06	0.06	0.04	0.07	0.07	0.09	0.01	0.04
CaO	2.74	2.83	0.96	0.59	1.87	1.43	3.10	7.16	1.80	0.38	1.78	1.45	2.22	0.36	0.01	0.51
Na ₂ O	0.62	0.51	0.51	0.91	0.51	0.58	0.84	0.59	0.64	0.58	0.78	0.93	0.62	0.49	0.74	0.47
K ₂ O	4.05	2.98	3.06	3.93	3.12	2.62	2.55	1.51	2.09	3.53	1.96	2.70	2.75	3.26	4.63	1.88
P ₂ O ₅	0.21	0.14	0.19	0.63	0.31	0.17	0.52	0.70	0.20	0.18	0.14	0.64	0.18	0.10	0.51	0.20
Total	88.87	90.71	89.74	91.21	89.57	92.05	92.36	90.24	92.00	94.84	92.86	94.84	92.86	92.42	93.73	91.76
Nb	18	17	17	21	21	22	18	10	19	18	17	14	16	20	17	17
Zr	166	200	139	95	99	193	302	158	306	162	282	201	216	224	160	259
Y	32	32	34	35	35	35	33	22	36	31	33	27	35	28	34	37
Sr	129	119	157	165	166	158	152	154	148	158	123	102	136	102	146	107
Rb	161	144	170	175	165	148	110	62	121	193	119	118	143	172	197	145
Zn	115	121	115	136	146	127	112	98	113	139	131	94	122	148	170	128
Cu	49	45	35	46	47	42	44	29	42	57	58	51	47	60	74	55
Ni	60	53	58	66	64	57	54	41	50	69	56	77	55	57	74	54
Co	14	48	68	20	26	18	16	10	11	22	15	43	19	13	23	21
Cr	141	152	159	161	159	141	147	175	167	154	146	157	139	155	187	156
V	184	127	159	246	214	172	162	113	187	205	187	168	188	209	250	172
Ba	719	487	355	692	599	598	448	436	556	867	753	645	705	851	885	694
Ign. loss	9.11	9.91	10.18	8.20	10.18	7.94	7.24	10.04	7.59	5.77	7.06	11.96	8.50	7.03	5.62	8.17
pH	9.38	9.74	9.66	9.22	10.09	10.10	9.87	9.71	10.14	9.45	10.04	9.25	10.09	9.34	9.24	9.41
IC(AD) ¹	0.45	0.49	0.63	0.77	0.32	0.35	0.49	0.36	0.24	0.49	0.68	0.36	0.32	0.24	0.38	0.35
IC(EG) ²	0.38	0.35	0.46	0.38	0.32	0.32	0.45	0.35	0.24	0.35	0.17	0.32	0.28	0.24	0.35	0.32

Table 2. Mineralogical and geochemical composition of the samples grouped by underclays.

	Turca	Valdeposada	Fontina	Vicentera	Prevenida	Matona	Corral	Mariana	Molino
<i>Whole sample</i>									
Quartz	30	21	16	12	13	20	28	17	25
Clay	66	77	80	75	80	60	68	76	73
Kaolinite	6	8	6	5	5	6	6	6	7
Chlorite	11	12	13	9	9	5	12	12	12
Illite	43	50	53	52	58	41	44	53	49
I/S	6	7	8	9	8	8	6	5	5
Ign. loss	7.88	8.12	7.74	10.90	11.55	10.77	8.45	9.67	7.24
pH	9.66	9.53	9.34	9.40	9.10	9.93	9.69	9.71	9.36
SiO ₂	61.53	58.82	57.82	53.80	52.27	54.86	61.23	54.86	61.10
TiO ₂	0.96	0.93	0.98	0.92	0.89	0.96	0.94	1.01	0.88
Al ₂ O ₃	17.64	19.96	21.56	19.43	20.47	17.94	17.38	20.62	18.53
FeO	4.90	4.97	4.36	5.32	5.63	4.57	5.01	5.88	4.80
MgO	1.26	1.36	1.28	1.57	1.54	2.98	1.28	1.49	1.70
MnO	0.06	0.06	0.05	0.07	0.09	0.07	0.06	0.08	0.05
CaO	1.52	1.03	0.70	2.77	1.54	3.53	1.60	1.00	1.09
Na ₂ O	0.71	0.68	0.74	0.88	0.69	0.60	0.69	0.64	0.54
K ₂ O	2.71	3.01	3.45	3.52	3.39	2.68	2.82	3.21	3.33
P ₂ O ₅	0.39	0.34	0.40	0.58	0.49	0.44	0.36	0.38	0.22
Total	91.68	91.16	91.34	88.86	87.00	88.19	91.37	89.17	92.24
Nb	21	21	20	20	17	17	18	20	18
Zr	238	198	134	150	131	199	204	132	212
Y	47	36	34	32	30	109	153	121	129
Sr	151	157	168	194	162	188	154	153	123
Rb	228	155	178	165	168	143	137	168	160
Zn	132	146	147	134	135	149	117	144	133
Cu	41	45	50	48	37	45	43	44	56
Ni	57	66	67	58	53	61	55	63	60
Co	13	20	14	13	15	38	17	28	26
Cr	143	142	151	143	143	143	154	154	158
V	177	205	223	221	229	336	172	214	179
Ba	568	652	767	654	677	579	627	503	693
<i><2-μm fraction</i>									
Kaolinite	14	8	7	6	7	9	9	7	6
Chlorite	10	7	9	7	9	10	12	9	11
Illite	56	64	62	74	65	66	60	70	69
Paragonite	7	6	8	4	6	5	9	4	7
I/S	13	15	14	9	13	10	10	10	7
IC(EG) ¹	0.35	0.44	0.38	0.37	0.35	0.38	0.35	0.34	0.35

¹ IC(EG) = Illite "crystallinity," ethylene glycol-solvated sample.

Table 3. F matrix (degrees of freedom 8, 47; F_{1%} = 3.28) of the groups for the mineralogical variables.

	Turca	Valdeposada	Fontina	Vicentera	Prevenida	Matona	Corral	Mariana	Molino
Valdeposada	1.33								
Fontina	1.07	0.49							
Vicentera	3.36*	1.12	1.18						
Prevenida	1.33	1.45	0.99	1.04					
Matona	1.94	0.71	0.96	1.35	1.81				
Corral	2.05	2.03	1.31	3.61*	2.10	1.55			
Mariana	1.71	0.94	0.84	0.89	0.89	1.24	2.70		
Molino	3.87*	2.24	1.49	1.33	0.84	2.93	4.62*	1.24	

* = Significant value.

Table 4. F matrix (degrees of freedom 12, 43; $F_{1\%} = 2.95$) of the groups for the chemical variables.

	Turca	Valdeposada	Fontina	Vicentera	Prevenida	Matona	Corral	Mariana
Valdeposada	1.97							
Fontina	2.26	1.70						
Vicentera	2.27	2.50	1.94					
Prevenida	1.27	1.30	0.38	1.07				
Matona	5.39*	3.17*	2.01	2.77	1.06			
Corral	1.29	2.13	1.17	2.14	0.59	3.95*		
Mariana	1.15	1.55	0.40	2.20	0.26	2.49	1.33	
Molino	5.04*	2.98	2.62	4.63*	1.17	4.53*	3.62*	2.45

* = Significant value.

Table 5. F matrix (degrees of freedom 18, 37; $F_{1\%} = 2.69$) of the groups for all variables (chemical and mineralogical).

	Turca	Valdeposada	Fontina	Vicentera	Prevenida	Matona	Corral	Mariana
Valdeposada	1.82							
Fontina	1.74	1.71						
Vicentera	2.83*	2.28	2.58					
Prevenida	1.24	1.81	0.61	1.45				
Matona	3.66*	2.33*	1.84	3.04*	1.45			
Corral	2.62	2.46	1.39	4.19*	1.46	1.92		
Mariana	1.29	1.37	0.60	2.11	0.60	2.15	1.93	
Molino	4.29*	2.69*	2.63	3.48*	1.37	3.34*	3.88*	1.96

* = Significant value.

greater weight is the K content, followed by the Na and Al contents. Contribution from all other variables was considerably smaller. Only the underclays belonging to the Molino coal bed could therefore be distinctively characterized by means of the 19 variables introduced in the model.

SUMMARY AND CONCLUSIONS

The main mineralogical component of the underclays studied was illite with smaller amounts of I/S, chlorite, kaolinite, pyrophyllite, paragonite, and muscovite/paragonite. The non-clay minerals identified were quartz, K-feldspar, calcite, siderite, anhydrite, and, in one sample, pyrite. This mineral suite is similar to that described by Aller and Brime (1985) for pelitic samples in the southern part of the Central Coal Basin, not related directly with coals.

The mineral suite and the illite "crystallinity" of the <2- μ m fractions of the samples suggest that the rocks have been subjected to very low grade metamorphic conditions, thereby explaining the low kaolinite content of the samples (Kisch, 1987). The underclays do not display a consistent vertical variation in either mineral components or chemical content. The absence of vertical zonation, the high pHs found, and the presence of chlorite and K-feldspar preclude an origin for the underclays by extensive leaching by acid swamp waters. Their mineral composition appears to have been determined largely by provenance.

The Molino underclay can clearly be differentiated from the other eight underclays, suggesting its potential use as a marker bed in correlation, provided its lateral homogeneity can be demonstrated.

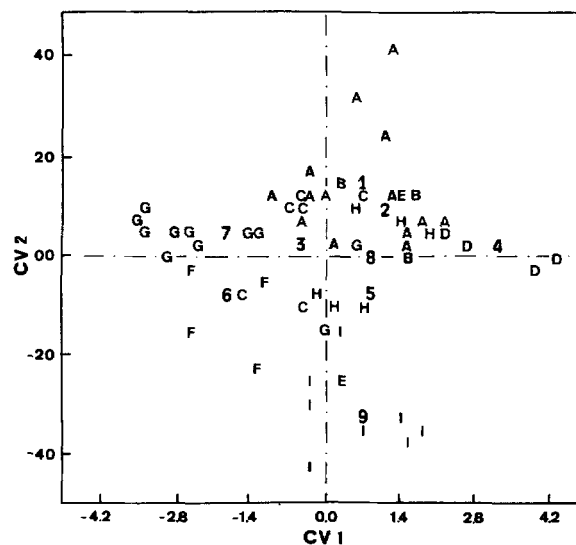


Figure 8. Canonical analysis of the different underclays of the María Luisa coal horizon using all the variables. Letters are the symbols for samples, and numbers refer to the average values of different underclays as follows: A, 1 Turca; B, 2 Valdeposadas; C, 3 Fontina; D, 4 Vicentera; E, 5 Prevenida; F, 6 Matona; G, 7 Corral; H, 8 Mariana; and I, 9 Molino.

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