Clays and Clay Minerals, Vol. 47, No. 1, 12–27, 1999.

MINERALOGICAL INTERFERENCE ON KAOLINITE CRYSTALLINITY INDEX MEASUREMENTS

PATRICIA APARICIO AND EMILIO GALÁN

Departmento de Cristalografia, Mineralogía y Química Agrícola, Universidad de Sevilla, Apdo. 553, 41071 Sevilla, Spain

Abstract—This study examines the influence of minerals and amorphous phases associated with kaolin and kaolinitic rocks on kaolinite crystallinity indices (KCI) derived from X-ray diffraction (XRD) data in order to select the best index for systematic studies of commercial kaolins or geological sequences. For this purpose, 8 kaolins of differing structural order were chosen and used to prepare mixtures containing different weight fractions of quartz, feldspar, illite, smectite, chlorite, halloysite and iron hydroxide and silica gels. An additional 17 samples of kaolin were also studied to test the results and evaluate the restrictions. KCIs used included Hinckley (HI), Range and Weiss (QF), Lièтard (R2), Stoch (IK), Hughes and Brown (H&B) and Amigó et al. (full width at half maximum, FWHM), and the "expert system" of Plançon and Zacharie.

Based on more than 15,000 KCI determinations, the HI and QF are influenced by quartz, feldspar, iron hydroxide gels, illite, smectite and halloysite. IK can be used in the presence of quartz, feldspar and iron hydroxide and silica gels. Also, R2 is the only KCI that could be measured in the presence of halloysite; FWHM indices should not be used in the presence of chlorite and/or halloysite; and H&B should only be used with pure kaolinite samples. The "expert system" of Plançon and Zacharie is strongly affected by the presence of other mineral phases, particularly with more than 25% of well-ordered kaolinite. Their system is less sensitive to other mineral phases when only disordered kaolinite is present, and it should not be used with kaolinite of medium order-disorder because the well-ordered phase is present in an inappreciable proportion (<10%). KCI is only measurable in kaolinitic rocks if kaolinite is >20 wt% and the precision increases with an increase in the quantity of kaolinite. In all cases, the reliability will depend on the other minerals present. When a KCI can be measured accurately, the others can be obtained by using the empirical relationships reported in this paper.

Key Words—Kaolinite Crystallinity Index, Mineralogical Interferences.

INTRODUCTION

Kaolinite chemistry differs little from the ideal formula, $Al_4Si_4O_{10}(OH)_8$, but kaolinite crystal structure is highly complex as a result of the large number of stacking faults that may appear during its formation and growth. These structural defects are not easy to detect. The XRD and spectroscopic methods usually employed to study kaolinite order only provide an approximation of the real structure. Mathematical modeling of XRD data can improve the description of various structural defects and polytypes (Drits and Tchoubar 1990; Artioli et al. 1995). However, it is difficult to implement in routine studies of kaolins and kaolinite samples. So, when knowledge of kaolinite structural variations is necessary for industrial applications such as the correlation with plasticity (Chávez and Johns 1995), brightness (Velho and Gomes 1991; Galán et al. 1998) and viscosity (Murray and Lyons 1956; Bundy et al. 1963; Velho and Gomes 1991; Yvon et al. 1980); or for geological interpretations (Ferraro and Kubler 1964; Maxwell and Hower 1967; Schroeder and Hayes 1968; Galán et al. 1977; Köster and Brandl 1991; Ruiz Cruz 1994), a simple and expeditious procedure based on XRD-derived crystallinity indices is useful.

The most widely used among these indices are those based on changes in 2 groups of XRD reflections, namely: 1) the 02*l* and 11*l* sequence (20–23 °2θ using Cu*K*α), which is sensitive to random and specific interlayer displacements of type *b*/3 and 2) the 13*l* and 20*l* sequence (35–40 °2θ using Cu*K*α) which is affected by random displacements (Cases et al. 1982). Alternatively, Plançon and Zacharie (1990) have proposed an "expert system" based on multiple measurements from the diffraction pattern, which describes the structural defects of kaolinite and provides a global abundance estimate of translation defects.

KCIs measured by XRD are influenced by associated minerals (such as quartz and feldspars) and amorphous phases such as silica and iron hydroxide gels (Galán et al. 1994), but direct assessments of their interference are lacking. The purpose of this study is to extend the study of mineralogical interferences on KCIs to include common phyllosilicates in kaolins, that is, halloysite, smectite, illite and chlorite, and to use a greater number of kaolin samples to include a more complete range of kaolinite structural order. The goal of this investigation is to identify the most suitable KCI for use with samples of

Copyright © 1999, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 1. Description of kaolins and kaolinitic rock samples.

Location	Genesis/age	Structural order	References
Montecastelo (Spain)	Granite weathering	High	Galán (pers. com. 1994)
Alvaraes (Portugal)	Granite weathering	Medium	Gomes et al. (1990)
Bustelo (Portugal)	Gneiss weathering	Medium	Gomes et al. (1990)
Mevaiela (Angola)	Hydrothermal alteration of anorthosite	High	Gomes et al. (1994)
St. Austell (UK)	Hydrothermal alteration of granite	High	Bristow (1993)
Poveda de la Sierra (Spain)	Sedimentary (Cretaceous)	Medium-High	Galán et al. (1977)
Warren (Georgia, USA)	Sedimentary (Tertiary)	Medium-Low	Patterson and Murray (1975) Van Olphen and Fripiat (1979)
La Guardia (Spain)	Sedimentary (Tertiary)	Low	Galán (1975)
Clays (10) and sandstones (4) from Campo de Gibraltar area (Spain)	Aquitanian flysch	—	Rodríguez Jiménez and Ruiz Cruz (1988)
Shale from Zalamea de la Serena (Spain)	Devonian	—	Mesa (1986)
Raw kaolin from Montecastelo (Spain)	Granite weathering	—	Galán (pers. com. 1994)
Raw kaolin from Reillo (Spain)	Sedimentary (Cretaceous)	—	Galán (1975)

varying mineralogical composition and to statistically assess the mineralogical interferences. The results are also applied to assess kaolinite structural order determination in 17 kaolinitic rocks, to test their general applicability.

MATERIALS AND METHODOLOGY

Materials

Eight kaolins of different structural order and genesis were selected (Table 1). Most were industrial (washed) kaolin samples used in ceramics, as a filler or coating in paper, or in plastics and paints. Table 1 also identifies the source of the additional kaolinitic samples used for evaluation.

Minerals and amorphous phases to be mixed with kaolins were: commercial silica gel (Riedel-De Haen 3712); iron hydroxide gel (synthesized in the laboratory from Fe acid dissolution and later precipitation at pH 10); quartz and feldspars from the Geological Museum of the University of Sevilla; halloysite from Grossetto (Tuscany, Italy, described by Mattias et al. 1994); illite from Fithian (Illinois, USA, Kerr 1949;

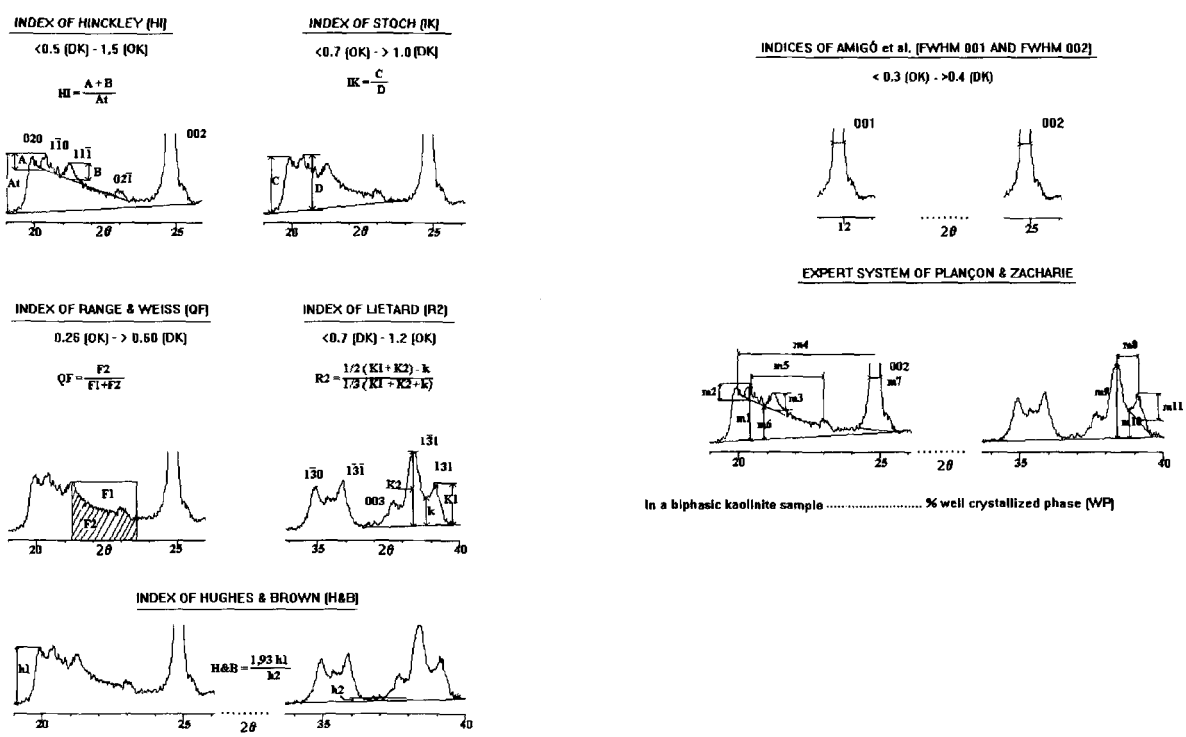


Figure 1. Methods for the XRD determination of kaolinite crystallinity indices.

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

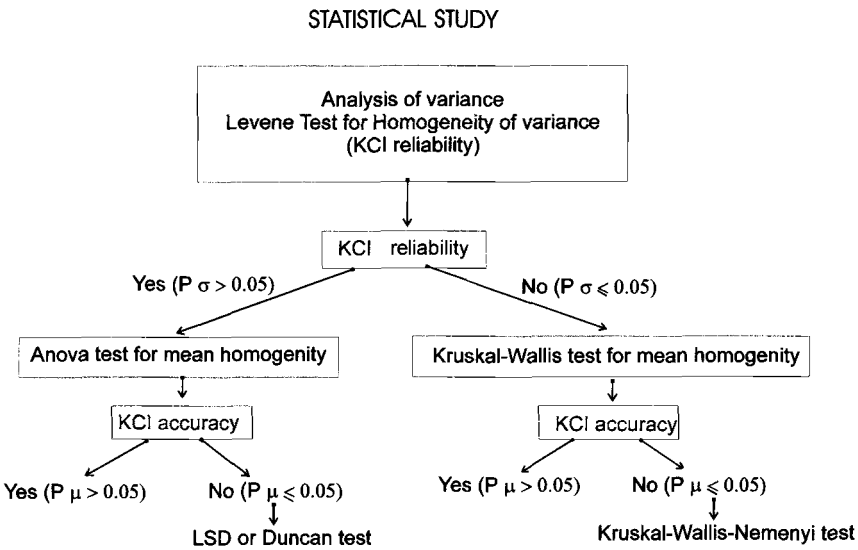


Figure 2. Statistical study flow sheet.

smectite from Los Trancos (Almeria, Spain, bentonite deposit, Martín Vivaldi and Linares 1969); and chlorite (clinochlore) from Bayarque, Almeria (described by Nieto and Rodríguez Gallego 1981).

Methodology

Kaolins and other materials were characterized by XRD (powder method) using a Philips PW 1130/90 diffractometer with Ni-filtered Cu*K*α radiation and a theta-compensating automatic slit. Chemical analyses by atomic absorption spectrometry (Al, Fe, Ti, Ca, Mg) and emission spectrometry (Na, K) were carried out on a Perkin-Elmer model 640 instrument. Si was determined by UV-Vis spectrometry on a Pye Unicam, SP6-400 instrument. Loss on ignition at 1000 °C was measured gravimetrically. Particle size distribution was determined by X-ray absorption on a Sedigraph 5100 microanalyzer.

Table 2. Kaolin mineralogical composition (fraction <4 μm) and % <4 μm fraction.

Sample	% K	% H	% Q	% Fd	% I	% SiO_2	% Fe	<4 μm
Montecastelo	98	—	tr	—	tr	—	—	93
Alvaraes	95	tr	<5	—	—	—	—	75
Bustelo	92	tr	5	—	<5	—	—	88
Mevaiela	85	12	—	—	—	tr	—	94
St. Austell	95	tr	tr	—	tr	tr	—	100
Poveda	97	tr	<5	—	<5	?	tr	84
Warren	98	tr	—	—	—	—	tr	95
La Guardia	83	tr	5	tr	10	tr	—	87

K: Kaolinite; H: Halloysite; Q: Quartz; Fd: Feldspar; I: Illite; SiO_2: amorphous silica; Fe: amorphous iron hydroxide; tr: present in quantities <2%.

Whole sample quantitative mineralogical analyses were carried out with the Schultz method (1964) after adjusting the mineral factors for an automatic slit (M. Ortega, personal communication, Department of Cristalografia y Mineralogia, Universidad de Granada). Clay minerals were studied in oriented aggregates using standard methods involving drying at room temperature, solvation with ethylene glycol and heating at 550 °C for 2 h. Phases were quantified by the method of Martín Pozas (1975), also corrected for automatic slit, and with mineral intensity ratios reported by Galán and Martín Vivaldi (1973). Halloysite was distinguished from kaolinite by intercalation of N-methyl formamide at 60 °C for 24 h (Martín Vivaldi et al. 1972). Mineralogy was also tested by transmission electron microscopy (TEM), observing in some samples the presence of amorphous silica and iron oxides.

After characterization, larger volume samples were gently ground to avoid structural modification (La Iglesia and Aznar 1996) and sieved through a 50-μm sieve. Further size separation (by sedimentation) was used to obtain the <4-μm aliquots of kaolin and other phyllosilicates and the <10-μm fractions of amorphous materials, quartz and feldspar. They were combined to prepare various mixtures of kaolin containing different weight percentages of the "contaminant" (between 5 and 50 wt%). Grain sizes selected for the mixtures were close to those present in many kaolinitic rocks. The <4-μm fraction of kaolins was mineralogically similar to the <2-μm fraction (Galán et al. 1994) and is close to the mean particle size of amorphous phases, quartz and feldspar.

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

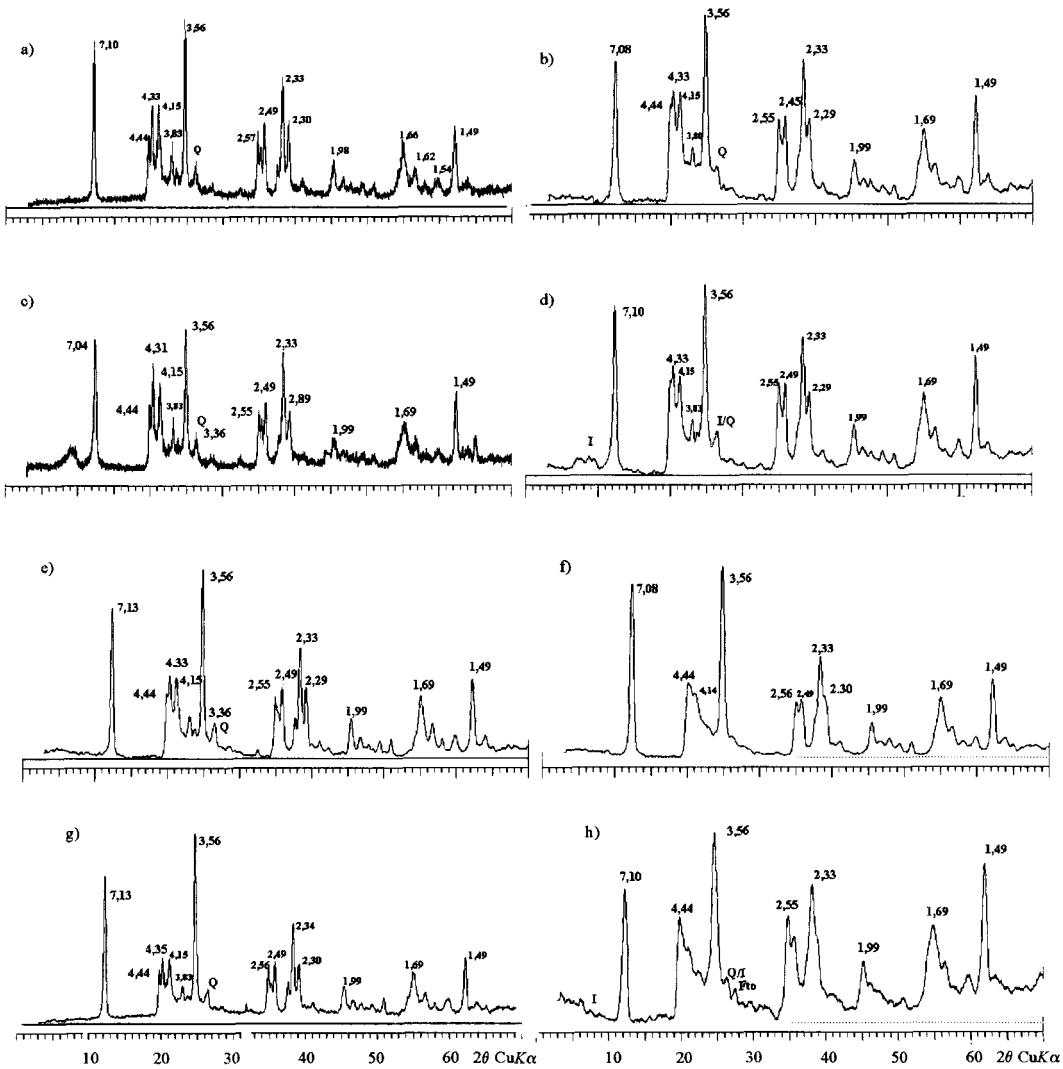


Figure 3. XRD pattern of kaolins: a) Montecastelo (Spain), b) Alvaraes (Portugal), c) Mevaiela (Angola), d) Bustelo (Portugal), e) St. Austell (UK), f) Warren (Georgia, USA), g) Poveda de la Sierra (Spain) and h) La Guardia (Spain).

The structural order-disorder of kaolinite was determined by XRD using a side-loading sample holder to minimize mineral orientation. The scan range was from 19 to 40 °2θ (powder KCI) and from 10 to 26 °2θ (oriented aggregate KCI) at 2 °2θ/min. The KCIs employed are illustrated in Figure 1 and briefly described below.

1) HI (Hinckley 1963) is one of the most widely used indices. As illustrated in Figure 1a, it is the ratio of the height above background of the $1\bar{1}0$ and $11\bar{1}$ peaks above the band of overlapping peaks occurring between 20–23 °2θ compared to the total height of the $1\bar{1}0$ above background. Normal values ranges from <0.5 (disordered) to 1.5 (ordered).

2) QF (Range and Weiss 1969) is another widely used KCI. It compares the area of the diffraction band between the $11\bar{1}$ and $02\bar{1}$ peaks to the total area of a rectangle formed with the height of the $11\bar{1}$ peak and the distance separating the $11\bar{1}$ and $02\bar{1}$ peaks as the base (Figure 1b). Reported values range from >0.6 (disordered) to 0.26 (ordered).

3) IK (Stoch 1974) is measured in the same zone as HI and QF. It is the ratio of 020 and $1\bar{1}0$ peak heights above background (Figure 1c). Normal values range from >1.0 (disordered) to <0.7 (ordered).

4) R2 (Lièrtard 1977), which according to Cases at al. (1982) is sensitive to the presence of random defects only, is calculated with the $1\bar{3}1$ and 131 peak intensities and the counts in the valley between them (Figure 1d). Reported values range from <0.7 (disordered) to 1.2 (ordered).

5) H&B (Hughes and Brown 1979) utilizes the ratio between the height of the 020 reflection and the height of the background between the $1\bar{3}1$ and 003 reflections

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 3. Kaolinite crystallinity index mean (X) and standard deviation (σ_{n-1}).

	HI		IK		R2		QF		H&B	
	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}
Montecastelo	1.04	0.0207	0.64	0.072	0.72	0.034	0.40	0.1236	930	195.59
Alvaraes	0.79	0.0457	0.76	0.0235	0.58	0.1494	0.45	0.0666	41	6.6523
Bustelo	0.72	0.0630	0.79	0.0229	0.54	0.023	0.43	0.0266	33	10.303
Mevaiela	1.00	0.0252	0.64	0.084	0.57	0.0476	0.34	0.007	80	27.49
St. Austell	0.89	0.0149	0.69	0.0233	0.79	0.0236	0.45	0.0391	43	4.8443
Poveda	0.89	0.0343	0.80	0.0430	0.83	0.0358	0.51	0.0189	99	38.7780
Warren	0.56	0.0277	1.02	0.0251	0.68	0.0350	0.58	0.0219	25	3.4762
La Guardia	0.30	0.0343	1.18	0.0530	0.55	0.0643	0.72	0.0643	15	1.9531

HI, Hinckley Index; IK, Stoch index; R2, Lièrard index; QF, Range and Weiss index; H&B, Hughes and Brown index; FWHM, Amigò indices; %wp, percentage of well-crystallized sample (expert system, the values with * are of percentage of translation defect with a single kaolinite phase); X: mean value; σ_{n-1}: standard deviation.

(Figure 1e). This index was defined for kaolinite in soils.

6) The Amigó et al. (1987) indices, FWHM (001) and FWHM (002), are the only ones derived from oriented aggregates. They are determined as the width at half height of the 001 and 002 reflections in degrees (Figure 1f). Normal values range from >0.4 (disordered) to <0.3 (ordered).

7) The "expert system" of Plançon and Zacharie (1990) was also used. The 11 proposed measurements are listed below. For the the 02*l* and 11*l* sequence: m1, $1\bar{1}0$ reflection height; m2 and m3, $1\bar{1}0$ and $11\bar{1}$ intensities, respectively; m4, distance between the 020 and 002 reflections; m5, distance between the $1\bar{1}0$ and the $02\bar{1}$ reflections; m6, the height of the background between the $1\bar{1}0$ and $11\bar{1}$ reflections; and m7, FWHM of the 002 reflection. For the 13*l* and 20*l* sequence: m8, distance between the $1\bar{3}1$ and 131 reflections; m9, $1\bar{3}1$ height; m10, height of the background between the $1\bar{3}1$ and 131 reflections; and m11, 131 intensity (Figure 1g). The first structural parameter determined is the number of different phases in the sample. The "expert system" describes kaolinite defects and provides a global abundance of translation defects but cannot distinguish between the t_0 translation (roughly $t_1 - b/3$) and the t_2 translation (roughly $t_1 + b/3$). This system indentifies the number of different phases in the sample (1 or 2). For a biphase system, it establishes the percentage of low-defect phase or well-ordered phase (%wp). For single-phase samples, the system fixes the amount of the C layers (*Wc*), the variation of interlayer translation about the mean values (δ), the proportion of translation defects (p), and the mean number of layers (M). The results of this system are acceptably consistent with the theoretical and experimental diffractograms for kaolinite (Plançon and Zacharie 1990).

KCI measurements were repeated 5 times to obtain better estimates of mean values and their standard deviation in kaolins and the mixtures as in Galán et al. (1994). Data were compared following a statistical evaluation of homogeneity of variances and means as outlined in Figure 2. First we applied the Levene test to determine the homogeneity of the variance (Kotz and Johnson 1983). If the variance is homogeneous, KCIs are reproducible. Next, we applied the analysis of variance (ANOVA) test to compare the means (Muller 1981). If the means match or are very close, KCIs are accurate. Then we used the LSD test or Duncan test to determine which percentages of impurities interfere with the accuracy of the KCI measurement. If the variances are not homogeneous, the homogeneity of means must be assessed by the Kruskal-Wallis test (Montgomery 1976). When the means are matched or similar, the KCIs are accurate. If the means are different, the test of Kruskal-Wallis-Nemenyi (Muller 1981) should be applied to determine the impurity weight percentages that prevent accurate measurement of KCI (Figure 2).

RESULTS

Sample Characterization

KAOLINS. Kaolinite accounted for 80–97 wt% of all the samples. It was accompanied by halloysite in trace amounts in many samples, except for Mevaiela kaolin, which contained 12 wt% of this mineral. Quartz and illite were minor components. Feldspars, and silica and iron hydroxide gels, were rare. The <4-μm fractions were richer in kaolinite but the impurities persisted (Table 2). The chemical composition of the finer fraction (<4-μm) was consistent with the mineralogy. The following findings are worthy of special note: 1) the iron content in Alvaraes (1.19%) and La Guardia (1.12%) kaolins, 2) the TiO_2 content in Georgia kaolin (1.2%), 3) the K_2O content in La Guardia kaolin (1.78%) and 4) the higher SiO_2/Al_2O_3 ratio in the St. Austell (1.3), La Guardia (1.21) and Alvaraes (1.33) kaolins.

Figure 3 shows XRD patterns of kaolins. Their structural order-disorder as reflected in mean KCIs are recorded in Table 3. Most kaolins can be considered as 2-phase complexes containing 14% to 31 wt% of a well-ordered phase as determined by the "expert sys-

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 3. Extended.

$FWHM_{001}$		$FWHM_{002}$		%wp	
X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}
0.226	0.012	0.245	0.021	29	2.039
0.360	0.016	0.464	0.126	14	0.976
0.322	0.062	0.367	0.046	15	3.200
0.272	0.026	0.355	0.016	31	1.030
0.274	0.019	0.210	0.019	24	0.933
0.282	0.061	0.275	0.043	26	1.687
0.258	0.012	0.244	0.018	—	—
0.438	0.014	0.452	0.009	0.25*	0*

tem" of Plançon and Zacharie (1990). The system could not be applied to the Warren kaolin because the well-ordered phase is present in such small quantities (<10 wt%). The results obtained for La Guardia kaolin suggest that the sample consists of a single, disordered phase.

Gonzalez et al. (1997) compared the KCI values for these samples and detected a strong correlation between the following pairs of indices: HI and IK; HI and QF; HI and FWHM (001), IK and QF; R2 and FWHM (002); and FWHM (001) and (002) (Table 4). The highest correlation coefficients are between those indices determined with the same sequence of reflections: HI and IK, and IK and QF. The first correlation

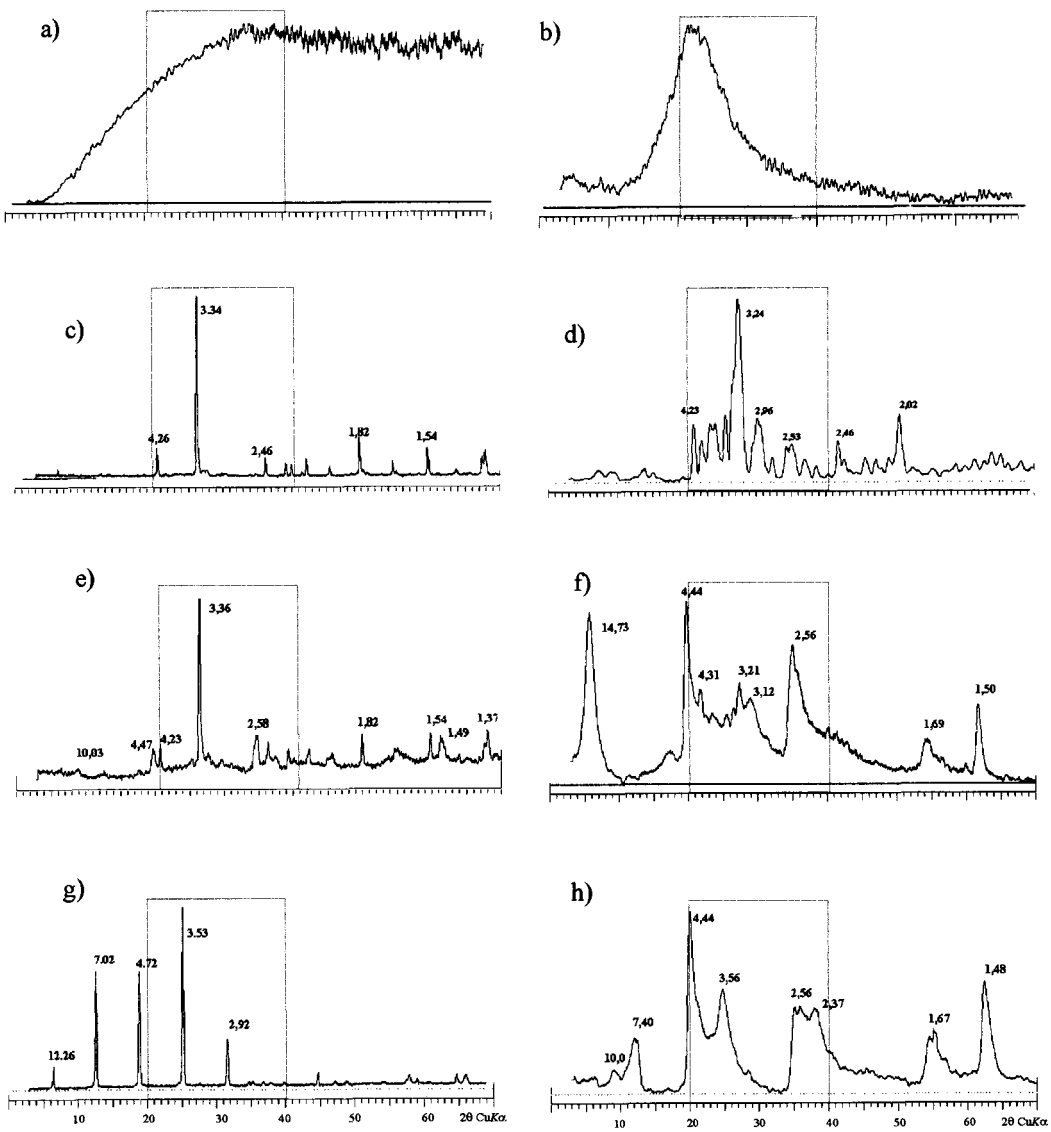


Figure 4. XRD patterns of minerals and amorphous phases: a) Iron hydroxide, b) Silica gel, c) Quartz, d) Feldspar, e) Illite, f) Smectite, g) Chlorite and h) Halloysite.

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 4. Relations between KCIs.

x vs. y ($y = ax + b$)	a	b	Correlations coefficient
Hinckley vs. Stoch	1.3776	−0.7329	−0.9465
Hinckley vs. Range & Weiss	0.82138	−0.4518	−0.8398
Hinckley vs. Amigó et al. $FWHM_{001}$	0.45917	−0.2047	−0.7403
Stoch vs. Range & Weiss	−0.0440	0.6363	0.9159
Lièrtard vs. Amigó et al. $FWHM_{002}$	0.6806	−0.5491	−0.7172
$FWHM_{001}$ vs. $FWHM_{002}$	0.0367	1.1836	0.8281
Hinckley vs. "expert system"	−21.3800	50.2170	0.8532
Amigó et al. $FWHM_{001}$ vs. "expert system"	81.4387	−204.0816	−0.7957

coefficient is positive and the second negative, because HI increases when the kaolinite is better ordered and IK and QF decrease. The "expert system" of Plançon and Zacharie (1990) was highly correlated with HI and FWHM (001), but this correlation excluded the Warren and La Guardia kaolins because the numerical values for these single-phase kaolinites could not be compared directly with the others.

AMORPHOUS PHASES AND OTHER MINERALS. XRD patterns of the "contaminants" illustrate where potential interference with the KCIs may occur (Figure 4). Quartz is mineralogically pure with 99 wt% < 10-μm fraction. Feldspar is mainly potassic with 88 wt% < 10-μm fraction. Silica gel shows an XRD band between 15 and 30 °2θ, and more than 80 wt% is <4-μm. Iron gels increase the background noise of XRD

Table 5. Kaolinitic rocks mineralogical composition shown as % (bulk, <20 μm and <2 μm fractions).

Sample	Q	K	I	I–S	S	Fd	$CO_3^=$	Sample	Q	K	I	I–S	S	Fd
C1								C10						
Total	25	44	6	<5	24	tr	—	Total	22	14	9	tr	55	—
<20 μm	14	51	7	<5	24	tr	—	<20 μm	18	15	10	tr	57	—
<2 μm	<5	58	6	<5	31	—	—	<2 μm	13	16	10	tr	61	—
C2								SH						
Total	20	38	14	18	10	tr	—	Total	16	82	<5	—	—	tr
<20 μm	15	41	15	19	10	tr	—	<20 μm	6	89	<5	—	—	tr
<2 μm	<5	46	17	21	12	tr	—	<2 μm	2	96	<5	—	—	tr
C3								K1						
Total	35	45	10	10	—	tr	—	Total	80	20	—	—	—	—
<20 μm	15	59	14	13	—	tr	—	<20 μm	11	89	—	—	—	—
<2 μm	6	65	15	14	—	tr	—	<2 μm	6	94	—	—	—	—
C4								K2						
Total	18	49	20	8	<5	<5	—	Total	90	10	—	—	—	tr
<20 μm	16	50	21	8	<5	<5	—	<20 μm	8	92	tr	—	—	tr
<2 μm	6	52	21	9	<5	<5	—	<2 μm	<5	95	tr	—	—	—
C5								S1						
Total	19	28	23	—	10	—	19	Total	99	tr	—	—	—	—
<20 μm	12	35	28	—	12	—	13	<20 μm	40	51	9	—	—	tr
<2 μm	5	40	33	—	14	—	7	<2 μm	25	64	11	—	—	tr
C6								S2						
Total	15	21	9	tr	54	—	—	Total	80	13	<5	<5	—	<5
<20 μm	15	21	9	tr	54	—	—	<20 μm	36	36	9	12	—	<5
<2 μm	5	24	10	tr	61	—	—	<2 μm	<5	60	14	20	—	tr
C7								S3						
Total	11	19	13	tr	53	<5	—	Total	81	<5	—	—	—	14
<20 μm	8	20	14	tr	57	tr	—	<20 μm	62	15	20	—	—	<5
<2 μm	8	20	10	tr	57	tr	—	<2 μm	22	30	45	—	—	tr
C8								S4						
Total	15	21	9	<5	51	—	—	Total	100	—	—	—	—	—
<20 μm	15	21	9	<5	51	—	—	<20 μm	85	12	<5	tr	—	—
<2 μm	14	22	9	<5	52	—	—	<2 μm	25	60	15	tr	—	—
C9														
Total	15	19	12	—	54	—	—							
<20 μm	15	19	12	—	54	—	—							
<2 μm	10	20	13	—	58	—	—							

C: clay; S: sandstone; SH: shale; K: raw kaolin; Q: Quartz; K: Kaolinite; I: Illite; I–S: I–S mixed layered; S: Smectite; Fd: Feldspars; $CO_3^=$: Calcite; tr: present in quantities <2%.

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 6. Hinckley KCI data obtained for the mixtures prepared, and the standard deviation (significance level of 5% or 95% probability).

		Montecastelo		Mevaiela		St. Asutell		Poveda		Alvaraes		Bustelo		Warren		La Guardia	
		X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}
		1.04	0.021	1.00	0.025	0.89	0.011	0.89	0.034	0.79	0.046	0.72	0.063	0.56	0.028	0.30	0.034
Quartz	5%	1.08	0.039	0.95	0.026	0.87	0.030	1.01	0.081	0.73	0.130	0.76	0.049	0.56	0.044	0.42	0.050
	10%	1.11	0.063	0.96	0.030	0.85	0.043	0.99	0.071	0.86	0.089	0.73	0.027	0.51	0.035	0.31	0.020
	20%	1.17	0.052	1.09	0.010	0.90	0.037	0.97	0.032	0.85	0.035	0.89	0.039	0.61	0.049	nd	
Feldspar	5%	1.10	0.021	0.94	0.084	0.83	0.041	1.03	0.043	0.71	0.065	0.67	0.035	0.56	0.050	0.56	0.114
	10%	1.10	0.047	1.03	0.071	0.85	0.031	1.03	0.078	0.74	0.029	0.69	0.019	0.57	0.049	0.60	0.095
Silica gel	5%	1.05	0.024	0.98	0.039	0.83	0.035	0.93	0.045	0.72	0.028	0.70	0.031	0.59	0.031	0.36	0.108
	10%	1.05	0.054	0.93	0.033	0.83	0.033	0.97	0.073	0.71	0.070	0.65	0.013	0.60	0.041	0.36	0.027
Iron gel	5%	1.06	0.023	0.93	0.040	0.80	0.044	1.04	0.057	0.72	0.028	0.68	0.029	0.53	0.044	0.37	0.030
	10%	1.05	0.052	0.95	0.070	0.85	0.034	1.04	0.029	0.73	0.053	0.67	0.033	0.65	0.035	0.34	0.011
Illite	5%	1.06	0.036	0.99	0.053	0.82	0.029	0.83	0.042	0.75	0.031	0.71	0.034	0.47	0.025	0.37	0.064
	10%	1.02	0.012	0.95	0.037	0.79	0.033	0.57	0.040	0.71	0.079	0.62	0.071	0.49	0.054	0.31	0.038
	15%	0.98	0.048	0.89	0.093	0.79	0.044	0.55	0.074	0.65	0.037	0.64	0.038	0.52	0.043	0.26	0.082
	20%	0.95	0.029	0.88	0.033	0.77	0.028	0.52	0.071	0.60	0.065	0.58	0.030	0.55	0.058	nd	
Smectite	5%	1.07	0.053	0.96	0.048	0.80	0.041	0.71	0.019	0.72	0.074	0.69	0.043	0.48	0.192	0.41	0.158
	10%	0.98	0.041	0.88	0.074	0.76	0.027	0.72	0.048	0.68	0.021	0.64	0.036	0.52	0.051	0.29	0.047
Chlorite	5%	1.10	0.043	0.99	0.050	0.80	0.021	0.92	0.055	0.79	0.029	0.72	0.038	0.49	0.044	0.35	0.081
	10%	1.09	0.049	0.98	0.034	0.85	0.012	0.93	0.057	0.79	0.057	0.72	0.039	0.47	0.027	0.40	0.680
	15%	1.09	0.050	1.02	0.038	0.84	0.037	0.92	0.035	0.71	0.050	0.72	0.033	0.50	0.054	0.53	0.192
	20%	1.05	0.129	0.97	0.041	0.84	0.043	0.97	0.064	0.76	0.023	0.72	0.040	0.52	0.046	0.40	0.063
Halloysite	5%	1.02	0.032	0.94	0.053	0.80	0.038	0.88	0.055	0.74	0.030	0.68	0.050	0.46	0.021	0.35	0.036
	10%	0.95	0.044	0.88	0.054	0.71	0.027	0.84	0.018	0.67	0.027	0.66	0.014	0.44	0.046	0.34	0.076
	25%	0.78	0.042	0.73	0.036	0.59	0.052	0.69	0.018	0.45	0.040	0.52	0.063	0.31	0.025	0.37	0.063
	50%	0.53	0.414	0.46	0.032	0.38	0.036	0.46	0.096	0.44	0.091	0.31	0.044	0.37	0.065	0.30	0.093

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 7. Amigó (FWHM 001) KCl data obtained for the mixtures prepared, and the standard deviation (significance level of 5% or 95% probability).

		Montecastelo		Mevaiela		St. Austell		Poveda		Alvaraes		Bustelo		Warren		La Guardia	
		X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}
		0.23	0.012	0.27	0.026	0.27	0.019	0.28	0.61	0.36	0.016	0.32	0.062	0.26	0.201	0.44	0.014
Quarrtz	5%	0.24	0.027	0.26	0.014	0.24	0.043	0.30	0.041	0.35	0.072	0.36	0.111	0.26	0.046	0.43	0.068
	10%	0.21	0.015	0.27	0.032	0.24	0.023	0.27	0.016	0.35	0.056	0.40	0.121	0.26	0.066	0.44	0.074
	20%	0.20	0.134	0.26	0.023	0.23	0.051	0.29	0.031	0.34	0.126	0.38	0.200	0.28	0.046	0.40	0.056
Feldspar	5%	0.25	0.018	0.28	0.084	0.24	0.024	0.30	0.057	0.40	0.201	0.37	0.078	0.27	0.072	0.44	0.066
	10%	0.23	0.022	0.27	0.030	0.25	0.018	0.28	0.024	0.40	0.046	0.37	0.077	0.26	0.056	0.46	0.046
Silica gel	5%	0.25	0.044	0.24	0.040	0.24	0.034	0.30	0.025	0.40	0.033	0.40	0.098	0.26	0.126	0.44	0.031
	10%	0.24	0.145	0.25	0.183	0.24	0.033	0.28	0.055	0.40	0.017	0.38	0.112	0.26	0.201	0.41	0.015
Iron gel	5%	0.25	0.043	0.24	0.042	0.26	0.029	0.30	0.024	0.40	0.079	0.36	0.082	0.27	0.025	0.45	0.095
	10%	0.25	0.048	0.26	0.169	0.25	0.041	0.30	0.074	0.39	0.065	0.36	0.088	0.25	0.055	0.47	0.081
Illite	5%	0.23	0.084	0.27	0.216	0.24	0.012	0.30	0.045	0.38	0.057	0.37	0.113	0.25	0.024	0.46	0.093
	10%	0.22	0.098	0.23	0.009	0.25	0.023	0.32	0.042	0.39	0.030	0.38	0.136	0.25	0.074	0.47	0.018
	15%	0.22	0.078	0.27	0.014	0.26	0.036	0.30	0.048	0.38	0.027	0.37	0.146	0.27	0.031	0.46	0.035
	20%	0.23	0.057	0.26	0.053	0.25	0.021	0.32	0.022	0.34	0.091	0.36	0.099	0.27	0.015	0.41	0.032
Smectite	5%	0.25	0.099	0.24	0.124	0.24	0.026	0.30	0.013	0.40	0.033	0.34	0.117	0.28	0.082	0.44	0.027
	10%	0.21	0.120	0.26	0.011	0.25	0.022	0.30	0.026	0.39	0.126	0.32	0.171	0.28	0.088	0.44	0.080
Chlorite	5%	0.26	0.007	0.31	0.018	0.19	0.011	0.27	0.051	0.35	0.070	0.29	0.026	0.25	0.030	0.34	0.042
	10%	0.26	0.025	0.23	0.038	0.22	0.033	0.26	0.024	0.30	0.065	0.16	0.015	0.24	0.027	0.30	0.094
	15%	0.27	0.018	0.23	0.053	0.18	0.036	0.25	0.014	0.26	0.074	0.14	0.11	0.23	0.091	0.25	0.081
	20%	0.27	0.100	0.15	0.146	0.19	0.033	0.16	0.055	0.16	0.068	0.11	0.145	0.18	0.027	0.26	0.071
Halloysite	5%	0.25	0.210	0.39	0.034	0.28	0.079	0.28	0.026	0.40	0.091	0.43	0.022	0.26	0.080	0.43	0.058
	10%	0.23	0.053	0.35	0.038	0.29	0.078	0.27	0.032	0.39	0.021	0.44	0.015	0.27	0.033	0.46	0.047
	25%	0.25	0.075	0.36	0.050	0.30	0.087	0.27	0.039	0.41	0.011	0.42	0.026	0.28	0.126	0.48	0.063
	50%	0.25	0.078	0.46	0.127	0.31	0.061	0.28	0.030	0.43	0.021	0.51	0.058	0.26	0.058	0.48	0.038

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 8. Expert system of Plançon and Zacharie data obtained for the mixtures prepared, and the standard deviation (significance level of 5% or 95% probability).

		Montecastelo		Mevaicla		St. Austell		Poveda		Alvaraes		Bustelo		La Guardia	
		X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	X	σ_{n-1}	Y	σ_{n-1}
		29	2.039	31	1.030	24	0.933	26	1.687	14	0.976	15	3.200	0.35	0
Quarrtz	5%	27	3.160	24	2.234	19	3.442	25	1.517	15	6.098	13	1.466	0.33	0.016
	10%	26	2.253	23	2.242	16	2.502	18	3.701	15	4.088	12	0.704	0.33	0.027
	20%	21	4.585	22	2.457	13	0.699	14	0.682	1 Phase		13	1.313	0.30	0
Feldspar	5%	30	1.128	30	2.489	21	4.717	31	1.775	13	0.589	12	1.600	0.33	0.0192
	10%	31	1.420	29	2.889	17	2.842	30	1.760	12	1.383	12	1.600	0.35	0.018
Silica gel	5%	31	2.096	30	0.362	18	4.606	27	2.349	13	0.450	13	0.772	0.34	0.0109
	10%	29	1.774	30	1.456	21	4.098	27	3.721	12	0.861	13	0.977	0.34	0.0308
Iron gel	5%	32	2.453	31	1.659	21	4.219	32	0.972	13	0.828	15	2.829	0.35	0.016
	10%	32	2.532	30	1.882	26	2.190	31	1.927	13	1.049	13	0.912	0.35	0.025
Illite	5%	30	2.160	31	1.640	22	2.138	21	2.471	13	0.454	13	0.873	0.35	0.014
	10%	28	1.985	27	1.592	21	1.539	15	1.092	12	1.126	11	2.144	0.35	0
	15%	25	2.153	27	1.296	21	1.679	17	4.191	10	1.458	11	0.466	0.35	0
	20%	21	3.932	25	0.786	16	3.185	13	2.071	10	2.089	10	1.340	0.35	0
Smectite	5%	31	2.086	34	5.128	21	3.406	16	4.153	13	1.256	14	0.819	0.35	0.022
	10%	30	1.750	29	1.828	22	0.912	16	3.923	11	0.680	13	0.834	0.35	0
Chlorite	5%	31	2.388	33	2.158	18	4.509	23	2.471	14	0.556	16	2.167	0.33	0.081
	10%	32	1.840	34	2.099	24	1.521	21	1.092	15	2.742	14	0.237	0.33	0.065
	15%	35	3.808	35	1.481	23	1.139	22	4.191	15	3.239	16	3.288	0.33	0.192
	20%	33	2.774	34	1.327	24	1.781	29	2.071	14	0.795	15	2.650	0.35	0.063
Halloysite	5%	31	2.549	34	3.648	21	1.875	22	4.198	14	0.837	15	3.049	0.37	0.027
	10%	28	2.549	31	3.355	17	3.173	21	4.658	13	1.457	15	2.679	0.36	0.022
	25%	28	2.831	1 Phase		13	1.595	15	2.608	1 Phase		13	1.000	0.34	0.018
	50%	18	4.356	1 Phase		1 Phase		1 Phase		1 Phase		1 Phase		0.37	0.0274

Table 9. KCl summary for the mixtures (p_μ = statistical value for the means, p_σ = statistical value for the standard deviation).

		Montecastelo		Mevaiela		St. Austell		Poveda		Alvaraes	
		p_μ	p_σ	p_μ	p_σ	p_μ	p_σ	p_μ	p_σ	p_μ	p_σ
HI	Quartz	0.014		0.010	0.002			0.023			0.043
	Feldspar	0.013						0.001	0.043		
	Silica gel		0.003	0.022		0.013					
	Iron gel		0.030			0.005		0.000			
	Illite	0.001		0.001		0.000		0.000		0.000	
	Smectite	0.002		0.010		0.006	0.009	0.000		0.014	
	Chlorite					0.017		0.001	0.000		
	Halloysite	0.000		0.000		0.000	0.039	0.012	0.000	0.000	
IK	Quartz										
	Feldspar					0.026					0.017
	Silica gel										
	Iron gel				0.002	0.019		0.032			
	Illite		0.014	0.000		0.001		0.000		0.002	
	Smectite					0.026				0.000	
	Chlorite							0.001	0.000		
	Halloysite	0.000		0.000		0.000		0.014	0.002	0.000	
R2	Quartz	0.000		0.004		0.002		0.002			
	Feldspar	0.013						0.006			
	Silica gel						0.008				0.034
	Iron gel	0.019	0.031			0.013					
	Illite	0.000									
	Smectite			0.002							0.043
	Chlorite	0.048	0.008	0.006		0.000		0.001	0.000		
	Halloysite		0.001			0.013		0.001	0.002		
QF	Quartz		0.022					0.001		0.035	
	Feldspar		0.026				0.021	0.007			
	Silica gel		0.033	0.005		0.013		0.002			
	Iron gel		0.029	0.001		0.024		0.000			
	Illite		0.007		0.048	0.044		0.000			
	Smectite		0.025		0.002	0.033		0.001			
	Chlorite		0.009	0.032	0.003			0.000	0.001		
	Halloysite		0.008	0.005		0.000		0.003	0.001		0.017
H&B	Quartz	0.042			0.003			0.045		0.044	0.002
	Feldspar	0.008	0.025	0.043	0.000			0.021	0.030		
	Silica gel	0.000					0.000		0.001	0.000	
	Iron gel	0.009	0.002	0.014	0.001		0.033	0.012	0.003		0.047
	Illite	0.006	0.000	0.002	0.000	0.002		0.005	0.002	0.001	
	Smectite	0.021	0.000	0.037	0.000				0.000		0.000
	Chlorite	0.001	0.002	0.000	0.000		0.006	0.019	0.000		0.000
	Halloysite	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Expert	Quartz	0.035		0.000		0.001	0.005	0.001	0.008		0.027
	Feldspar		0.005			0.013		0.019		0.012	
	Silica gel		0.032		0.021		0.015			0.003	
	Iron gel	0.019						0.001			
	Illite	0.001		0.000		0.001		0.001	0.000	0.001	
	Smectite				0.000	0.047		0.000		0.011	
	Chlorite	0.009		0.028			0.001	0.007			
	Halloysite	0.000				0.001	0.020	0.001			
$FWHM_{001}$	Quartz										
	Feldspar										
	Silica gel										
	Iron gel										
	Illite										
	Smectite										
	Chlorite	0.002		0.002		0.002		0.005		0.000	
	Halloysite			0.000		0.018				0.038	
$FWHM_{002}$	Quartz										
	Feldspar										
	Silica gel										
	Iron gel										
	Illite										
	Smectite										
	Chlorite	0.009		0.002		0.001		0.001		0.000	
	Halloysite	0.032		0.006		0.007				0.003	

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 9. Extended.

Bustelo		Warren		La Guardia	
p_μ	p_σ	p_μ	p_σ	p_μ	p_σ
0.033		0.007		0.003	
				0.002	
	0.001				0.012
	0.008				0.014
0.001					0.034
					0.004
				0.022	
0.000		0.000	0.002		
					0.021
0.000			0.038	0.021	0.002
					0.047
		0.000		0.039	
0.000		0.005		0.041	
		0.000			
		0.021		0.000	
0.031			0.047		
	0.000	0.000		0.016	
0.000		0.011		0.000	
0.018	0.025		0.001		
				0.043	
		0.001		0.000	
		0.034		0.007	
0.020	0.007	0.000		0.000	
0.000		0.000		0.014	0.013
	0.029			0.027	
0.039	0.002				
	0.008	0.038		0.045	
0.002				0.031	0.033
	0.007				
0.000			0.000	0.014	0.015
0.013	0.022	0.001	0.006	0.000	
0.0149					
0.000		0.002		0.000	
0.000				0.035	
0.000		0.005		0.001	
0.004		0.034		0.003	

patterns and are 94 wt% < 10-μm fraction and 85 wt% <4-μm. Illite is mostly the 1*M* polytype but contains 25 wt% 2*M* mica, a very low proportion of smectite layers, and less than 10 wt% quartz and kaolinite; more than 80 wt% is less than 1 μm. Smectite is a montmorillonite (beidellite–montmorillonite series), with some feldspars. Chlorite is a clinochlore and particle-size distribution of the sample used ranges between 15 and 3 μm. Halloysite is mineralogically pure and 94 wt% is less than 4 μm.

Most of the minerals have moderately high intensity peaks in the 2θ intervals where the indices are calculated and directly interfere with the intensity measurement. The amorphous materials exhibit broad bands in the same areas, complicating the determination of the peak height above background.

KAOLINITIC ROCKS. The selected clays (C) and sandstones (S) consist of quartz (11–100 wt%) and varying quantities of phyllosilicates (kaolinite: tr–49 wt%; illite: tr–23 wt%; smectite: tr–55 wt% and I–S: tr–18 wt%), with some feldspar. Percentages of kaolinite in the <20-μm and <2-μm fraction range between 12 and 65 wt%. The shale (SH) is essentially kaolinitic (>80 wt%) with illite (<5 wt%), quartz (16 wt%) and traces of feldspars. Raw kaolins are kaolinitic sand (>80 wt% quartz) (K) with up to 20 wt% kaolinite; this proportion is reversed for the finer fractions (Table 5).

Influence of Sample Composition on KCI Determination

Table 6, Table 7 and Table 8 illustrate the statistical analysis result for the HI, Amigo (001) index and the "expert system" of Plançon and Zacharie (1990), respectively. Means and standard deviations presented in the first row of data are for the pure sample. Subsequent rows record the mean KCI and the standard deviation when the indicated quantities of mineral contaminants were added to the original samples. Values that are not significantly different from the original have a plain background. Shaded values in the mean column indicate an inaccurate KCI determination, that is, those that are significantly different from the KCI of the pure sample. Shaded values in the standard deviation column indicate the KCIs were not reproducible when compared to the pure sample (within 95% error). Values within each subtreatment block with identical shading are different from the results for the untreated sample but cannot be distinguished from one another. For example, the mean HI for the Montecastelo kaolinite with 5 wt% or 10 wt% feldspar is statistically different from the original but the results for the 2 additions are similar (Table 6). In other experiments, the results for all subsets were significantly different, as indicated by the different levels of shading for the halloysite additions to the Mevaiela kaolinite (Table 6). Usually, higher proportions of impurities

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

produce more difficulties for the KCI measurement. A general comparison of the number of shaded blocks in the tables suggests that the Amigo index is less subject to interference by other minerals and the HI most prone to interference.

In Table 9, a summary of the complete statistical study is presented. Values given are those for which the similarity of means, or variance, are not satisfied at a significance level of 5% (probability 95%). Blank areas are those where the values for the various added minerals were similar to the original sample and thus exhibited no interference effects.

From the statistical study, the following generalizations can be derived:

1) The HI is influenced by quartz, chlorite and halloysite and to a lesser degree by feldspar (>10%), illite and smectite (>5%).

2) The QF index could be used in the presence of feldspars (<10%), smectite and chlorite, but it is necessary to repeat the measurement at least 5 times, because the variance of the measurement can be large.

3) The IK index can be used in presence of quartz, feldspar and amorphous silica and iron, but not in the presence of other phyllosilicates.

4) The R2 index is the only one which could be used in the presence of halloysite. It can also be used when amorphous silica, iron gels and smectite are present.

5) The Amigó et al. indices should not be used in presence of chlorite and/or halloysite, but they are appropriate in the presence of other contaminants (quartz, feldspars, silica and iron gels, illite and smectite).

6) The H&B index is the most subject to interference. It should never be used when other phases are present.

7) The "expert system" of Plançon and Zacharie is interference-free when only a disordered kaolinite is present (La Guardia kaolin). The most severe interferences were noted when the percentage of well-crystallized kaolinite was approximately 25% of the kaolinite total (Poveda). Results for the other samples are highly variable. The addition of halloysite often affects the determination of the number of phases present.

Application to Kaolinitic Rocks

The KCI means for kaolinitic rock are presented in Table 10. Some KCI could not be measured because the reflections were too weak. According to data reported in Table 10 and taking in mind those of Table 9, at least one of the KCIs is measurable in rocks containing more than 20 wt% kaolinite. The accuracy of this measurement will improve with a higher content of kaolinite, but in any case the accuracy of an individual method will depend on the specific types of mineral interferences. For example, quartz strongly affects the HI and QF indices and prevents the measurement or produces erroneous results; in this case the IK or Amigo indices should be used.

In geological series, rocks containing less than 20% kaolinite cannot be tested directly, and any discussion on the basis of a KCI is completely speculative. Moreover, those indices greatly influenced by other minerals (Table 11) should not be used.

DISCUSSION

The summary presented in Table 11 addresses the question of interference in terms of a simple YES/NO response, or lists the quantity of the contaminant required to produce a significant interference. YES indicates that the interference is not significant.

The responses to interferences are generally predictable by considering how the index is measured and where peaks or diffraction bands are produced by potential contaminants. For example, HI and QF are affected by quartz because the 100 reflection at 4.26 Å interferes with the $11\bar{1}$ kaolinite reflection. Illite, smectite, chlorite and halloysite produce erroneous values in the measure of IK, because their peaks overlap in the 020 kaolinite reflection. Halloysite and chlorite both interfered with the FWHM indices because they produce peaks with similar *d*-values. It seems that FWHM indices are the best because they are not severely influenced by other minerals. But the Amigo indices are not generally recommended because the values are very small.

When a KCI can be measured accurately, we can obtain an approximation for the others, taking into account the relationship between them depicted in Table 4. In the presence of quartz, HI and QF cannot be measured reliably, but it is possible to obtain their value from the IK or FWHM (001) indices since they are not affected by quartz. For example, samples C5 and C6 contain kaolinite, quartz, illite and smectite (Table 5), and accordingly HI, QF and IK should not be used. The indices affected by the contaminants indicated poorly ordered kaolinite but the FWHM value indicated medium-ordered kaolinite (Table 10). The recalculated indices are more indicative of medium order.

The results show many choices for the selection of optimal KCI calculation procedures. When quartz is the major contaminant, only IK, H&B and FWHM (001 and 002) should be used. In the presence of feldspar, IK, FWHM (001 or 002) and QF are acceptable, but for QF it is necessary to repeat the measurement at least fivefold ($n > 5$) because the variance can be large. IK, R2, FWHM (001 and 002) and HI ($n > 5$) can be used with amorphous gels (iron hydroxide and silica). With illite, FWHM (001 and 002), R2 for medium-ordered kaolinite and QF for ordered or disordered kaolinite could be used. FWHM (001 and 002) and R2 ($n > 5$) could be employed with smectite. Chlorite does not affect the measurement of QF ($n >$

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Table 10. Kaolin crystallinity index (mean of 5 determinations) for kaolinitic rocks.

Sample	%K	HI	IK	QF	$FWHM_{001}$	Sample	%K	HI	IK	QF	$FWHM_{001}$
C1						C10					
Total	30	0.26	1.12	0.61	0.368	Total	7	nd	nd	nd	0.237
<20 μm	35	0.54	1.10	0.50	0.367	<20 μm	7	nd	nd	nd	0.235
<2 μm	42	0.29	1.29	0.55	0.315	<2 μm	8	nd	nd	nd	0.231
C2						SH					
Total	40	0.10	1.12	0.48	0.412	Total	82	0.27	0.98	0.45	0.360
<20 μm	43	0.11	1.23	0.51	0.399	<20 μm	89	0.28	0.97	0.46	0.357
<2 μm	50	0.20	1.23	0.58	0.393	<2 μm	96	0.48	0.93	0.50	0.216
C3						K1					
Total	40	nd	1.09	nd	0.415	Total	20	nd	0.60	nd	0.248
<20 μm	47	0.22	1.18	0.51	0.398	<20 μm	89	0.99	0.67	0.37	0.218
<2 μm	53	0.12	1.07	0.61	0.393	<2 μm	94	1.14	0.58	0.38	0.216
C4						K2					
Total	58	0.18	1.16	0.62	0.402	Total	10	nd	0.69	nd	0.323
<20 μm	62	0.18	1.18	0.63	0.387	<20 μm	97	1.17	0.59	0.43	0.235
<2 μm	66	0.19	1.21	0.64	0.337	<2 μm	99	1.21	0.59	0.42	0.230
C5						S1					
Total	23	nd	1.12	nd	0.347	Total	tr	nd	nd	nd	nd
<20 μm	29	nd	1.29	nd	0.354	<20 μm	51	nd	1.08	nd	0.289
<2 μm	32	0.29	1.45	0.68	0.341	<2 μm	64	0.59	1.04	0.50	0.263
C6						S2					
Total	13	nd	1.17	0.48	0.335	Total	15	nd	nd	nd	nd
<20 μm	13	nd	1.17	0.44	0.331	<20 μm	42	0.03	1.17	0.36	0.400
<2 μm	15	0.09	1.25	0.62	0.328	<2 μm	63	0.03	1.09	0.56	0.380
C7						S3					
Total	9	nd	1.16	0.57	0.328	Total	tr	nd	nd	nd	nd
<20 μm	10	nd	1.30	0.63	0.287	<20 μm	20	nd	1.17	nd	0.131
<2 μm	10	nd	1.12	0.99	0.286	<2 μm	27	nd	nd	nd	0.114
C8						S4					
Total	12	nd	nd	nd	0.273	Total	tr	nd	nd	nd	nd
<20 μm	13	nd	nd	nd	0.270	<20 μm	9	nd	nd	nd	0.239
<2 μm	14	0.10	nd	nd	0.267	<2 μm	55	0.67	1.02	0.45	0.237
C9											
Total	9	nd	nd	nd	0.287						
<20 μm	10	0.17	1.76	0.65	0.275						
<2 μm	10	0.17	1.70	0.72	0.266						

C: clay; S: sandstone; SH: shale; K: raw kaolin; nd: not determined.

5), and IK could be used with ordered kaolinite and H&B with medium or disordered kaolinite. Finally, only R2 could be measured in the presence of halloysite.

SUMMARY

To determine the kaolinite order-disorder in kaolinitic rocks and kaolins by XRD, the indices influenced by other minerals should not be used. KCIs can only be measured when more than 20 wt% of kaolinite is present. The other minerals must be identified in order to select the KCI with least interference. Statistical analysis used to assess the heterogeneity of the means and standard deviation of experiments using added quantities of quartz, feldspar, illite, smectite, chlorite, halloysite and iron hydroxide and silica gels provide a reliable measure of the limitations of KCIs commonly reported

Table 11. Key for applying KCI determination in kaolin samples in presence of different impurities. KCI only could be used in poor (D), medium (M) or well (O) ordered kaolinite. N = number of measurements by XRD in presence of minerals and amorphous phases.

	Quartz	Feldspars	Amorphous silica	Amorphous Fe	Illite	Smectite	Chlorite	Halloysite
Amigó 001 and 002	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Stoch	Yes	Yes	Yes	Yes	No	D	O	No
Lièrtard	No	No	Yes	Yes	M	$n > 5$	No	$n > 5$
Hinckley	No	<10%	$n > 5$	$n > 5$	<5%	<5%	No	No
Range & Weiss	O/D	<10% $n > 5$	No	No	O/D	$n > 5$	$n > 5$	No
Hughes & Brown	Yes	No	No	No	No	No	M/D	No
"Expert system" of Plançon and Zacharie	D	D	D	M/D	D	D	M/D	D

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

in the literature. The HI and QF indices are influenced by quartz, feldspar, iron hydroxide gels, illite, smectite and halloysite. IK can be used in the presence of quartz, feldspar and iron hydroxide and silica gels. Also, R2 is the only one that could be measured in the presence of halloysite; Amigo indices should not be used in the presence of chlorite and/or halloysite; and H&B should only be used with pure kaolinite samples. The "expert system" of Plançon and Zacharie is highly affected by the presence of other phases and should only be used with a single-phase kaolinite (disordered kaolinite) or with a pure kaolinite sample.

ACKNOWLEDGMENTS

We are grateful to R. Ferrell for carefully reviewing this paper and making helpful comments. This work was partially supported by the Junta de Andalucía through Research Group RNM 135. Also the authors thank to the referees M. Batchelder and J. Elzea for improving the manuscript.

REFERENCES

Amigó JM, Bastida J, García Agramut MJ, Sanz M, Galván J. 1987. Crystallinity of Lower Cretaceous kaolinites of Teruel. In: Galán E, Pérez-Rodríguez JL, Cornejo J, editors. EUROCLAY Conf; Sevilla '87; Sevilla, Spain. p 74–75.

Artioli G, Belloto M, Gualtieri A, Pavese A. 1995. Nature of structural kaolinites: A new model based on computer simulation of powder diffraction data and electrostatic energy calculation. Clays Clay Miner 4:438–445.

Bristow CM. 1993. The genesis of China Clays of South-West England. A multistage story. In: Murray H, Bundy W, Harvey C. Kaolin, genesis and utilization. Boulder, CO: Clay Miner Soc. p 171–203.

Bundy WM, Johns WD, Murray, HH. 1963. Physico chemical properties of kaolinite and relationship to paper coating quality. TAPPI 48. p 688–696.

Cases, JM, Lièrard O, Yvon J, Delon JF. 1982. Étude des propiértés cristallochimiques, morphologiques, superficielles de kaolinites désordonnées. Bull Mineral 105:439–455.

Chàvez CL, Johns W. 1995. Mineralogical and ceramic properties of refractory clays from central Missouri (USA). Appl Clay Sci 9:407–424.

Drits V, Tchoubar C. 1990. The modellization method in the determination of structural characteristic of some layer silicates: internal structure of the layer, nature and distribution of stacking faults. In: X-ray diffraction by disorded lamellar structures. Theory and applications to micro divided silicates and carbons. Berlin: Springer-Verlag. p 231–253.

Ferraro J, Kubler B. 1964. Presence de dickite dans les gres Cambrienes d'Hassi Messaoud. Bull Serv Carte Geol Alsace-Lorraine 17:247–261.

Galán E. 1975. Caolines españoles. Geología, mineralogía y génesis [Tesis Doctoral Ed]. Soc Esp Ceram Vidr Madrid. 144 p.

Galán E, Aparicio P, González I, La Iglesia A. 1994. Influence of associated components of kaolin on the degree of disorder of kaolinite as determined by XRD. Geologica Carphatica. Series Clays 45:59–75.

Galán E, Aparicio P, González I, Miras A. 1998. Contribution of multivariate analysis to the correlation of some properties of kaolin with its mineralogical and chemical composition. Clay Miner 33:65–75.

Galán E, Martín Vivaldi JL. 1973. Caolines españoles. Geología, mineralogía y génesis (I). Bol Soc Esp Ceram Vidr 12:79–98.

Galán E, Mattias PP, Galván J. 1977. Correlation about kaolin genesis and age of some Spanish kaolinites. In: Galán E, editor. Proc 8th Int Symp and Meet on Alunite; Madrid-Rome. Madrid: Ministerio de Industria y Energía. K-8, 8 p.

Gomes C, Velho JA, Delgado H. 1990. Kaolin deposits of Portugal Geociências Rev Univ Aveiro 5:75–89.

Gomes C, Velho J, Guimaraes F. 1994. Kaolin deposit of Mevaíela (Angola) alteration product of anorthosite: Assessment of kaolin potentialities for applications in paper. Appl Clay Sci 9:97–106.

González I, Aparicio P, Galán E. 1997. Correlation between the most frequently used XRD crystallinity indices for kaolinite. Their accuracy and reproducibility. Abstr 11th Int Clay Conf; Ottawa, Canada. A32.

Hinckley D. 1963. Variability in "crystallinity" values among the kaolin deposits of the Coastal Plain of Georgia and South Carolina. Clays Clay Miner 11:229–235.

Hughes JC, Brown G. 1979. A crystallinity index for soil kaolins and its relation to parent rock, climate and soil nature. J Soil Sci 30:557–563.

Kerr PF. 1949. Reference clay minerals: Preliminary report. American Petroleum Institute. Project 49, Columbia Univ, New York.

Köster HM, Brandl M. 1991. Mineralogy and geochemistry of primary kaolins and related kaolinitic clays in NE-Bavaria. In: Stor E, Henning KH, Adolphi P, editors. Proc 7th Euroclay Conference; Dresden. p. 641–647.

Kotz S, Johnson NI. 1983. Encyclopedia of statistical sciences, vol. 4. New York: J Wiley. 672 p.

La Iglesia A, Aznar AJ. 1996. Crystallinity variations in kaolinite induced by grinding and pressure treatments. J Mater Sci 31(17):4671–4677.

Lièrard O. 1977. Contribution à l'étude des propiétés phisicochimiques, cristallographiques et morphologiques des kaolins [Ph. D. thesis]. Nancy, France. 345 p.

Mattias P, Crocetti G, Barrese E, Falco F. 1994. Halloysite and other hydrothermal related minerals of Capalbio Grosseto (Tuscani-Central Italy). Abstr 16th General Meet IMA; Pisa, Italy; 1994. p 269–270.

Martin Vivaldi JL, Linares González J. 1969. Las bentonitas de Cabo de Gata III. Consideraciones sobre la mineralogía y génesis de los yacimientos estudiados. Bol Geol y Min LXXX-I:74–80.

Martin Vivaldi JL, Pozzuoli A, Mattias P, Galan Huertos E. 1972. The swelling of layer minerals: I-Interaction with DMSO and NMFA. In: Serratosa JM, editor. Preprints Int Clay Conf: 1972; Madrid. p 455–468.

Martín Pozas JM. 1975. Análisis cuantitativo de fases cristalinas por DRX. In: Saja J, editor. Método de Debey-Scherrer. ICE. Universidad de Valladolid.

Maxwell DT, Hower J. 1967. High-grade diagenesis and low-grade metamorphism in the Precambrian Belt series. Am Mineral 52:843–857.

Mesa JM. 1986. Contribución al estudio mineralógico de las pizarras alumínicas (Tierras Blancas) del Paleozoico de la provincia de Badajoz. [Ph. D. thesis]. Univ de Sevilla. 318 p.

Montgomary DC. 1976. Design and analysis of experiments. New York: J. Wiley.

Muller RG. 1981. Simultaneous statistical inference. Berlin: Springer Verlag. p 165–172.

Murray HH, Lyons SC. 1956. Correlation of paper-coating quality with degree of crystal perfection of kaolinite. In: Swineford A, editor. Clays Clay Miner, Proc 4th Natl Conf; 1955.

Nieto F, Rodríguez Gallego M. 1981. Alteración experimental de cloritas. Revista de la Academia de Ciencias de Granada 1:108–124.

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press

Patterson SH, Murray HH. 1975. Clays. In: Lefond SJ, editor. Industrial minerals and rocks, 4th ed. New York: AIME. p 519–585.

Plançon A, Zacharie C. 1990. An expert system for the structural characterization of kaolinites. Clay Miner 25:249–260.

Range KJ, Weiss A. 1969. Uber das Verhalten von kaolinitit bei hohen Drücken. Ber Deut Keram Ges 46:231–288.

Rodríguez Jimenez P, Ruiz Cruz MD. 1988. Mineralogía y génesis de las arcillas de las unidades del campo de Gibraltar. I. Areniscas del Aljibe. Estudios Geológicos 44:31–46.

Ruiz Cruz MD. 1994. Diagenetic development of clay and related minerals in deep water sandstones (S. Spain): Evidence of lithological control. Clay Miner 29:93–104.

Schroeder RJ, Hayes JB. 1968. Dickite and kaolinite in Pennsylvanian limestone of southeastern Kansas. Clays Clay Miner 16:41–49.

Schultz LG. 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. US Geol Survey Prof Paper 391-C

Stoch L. 1974. Mineraly Ilaste ("Clay Minerals"). Warsaw: Geological Publishers. p 186–193.

Van Olphen H, Fripiat JJ. 1979. Data handbook for clay materials and other non-metallic minerals. Oxford: Pergamon Pr.

Velho JA, Gomes C. 1991. Characterization of Portuguese kaolins for the paper industry: Beneficiation through new delamination techniques. Appl Clay Sci 6:155–170.

Yvon J, Cases JM, Liètard O, Garin P, Lhote F. 1980. Influence des propriétés des charges kaolinitiques sur les performances des caoutchoucs naturels charges. Clay Miner 15:351–368.

(Received 3 April 1998; accepted 29 May 1998; Ms. 98-044)

https://doi.org/10.1346/CCMN.1999.0470102 Published online by Cambridge University Press