

THE QUANTITATIVE MINERALOGY OF CERAMIC GRADE KAOLIN FROM THE ST AUSTELL GRANITE AND ITS RELATIONSHIP TO CHEMISTRY AND PHYSICAL PROPERTIES.



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Kaolin products from the St Austell Granite with different physical and chemical properties are used in porcelain, bone china, earthenware and sanitaryware. Six refined clays, taken from Wheal Prosper, Goonvean and Rostowrack China Clay Pits, chosen to represent the complete range of properties, show a close correlation between increase in strength, as measured by the modulus of rupture, and the methylene blue index, the latter being an approximate measure of the cation exchange capacity. There is no significant correlation between the size distribution of the clays and the other physical properties. Quartz, K-feldspar (microcline), and mica are present in all samples and smectite occurs in the stronger clays. The chemistry can be accounted for largely in terms of the quantitative mineralogy, determined by X-ray diffraction. Increased amounts of CaO and MgO in the stronger clays are attributed to the presence of smectite, although in clays which do not contain smectite, these elements are probably associated with kaolinite. Lip and F are accounted for in mica. A very good linear relationship exists between the strength of the clay and the smectite content. Using a procedure for accounting for the chemistry in terms of the mineralogy, it can be shown that the smectite is a dioctahedral montmorillonite of Otay-type, in which about one-third of octahedral sites are occupied by Mg.

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INTRODUCTION

The kaolinised granites of the St Austell area, Cornwall, are an important source of kaolin (china clay) for use in porcelain, bone china, earthenware and sanitaryware, a range of clays with different properties being made to suit the various applications. Products come from either a single china clay pit or are made to have specific properties by blending material from more than one locality and adjusting the refining process. The differences in physical properties are largely a consequence of the variation in mineralogy between products.

Refined kaolin from three locations, Goonvean and Rostowrack

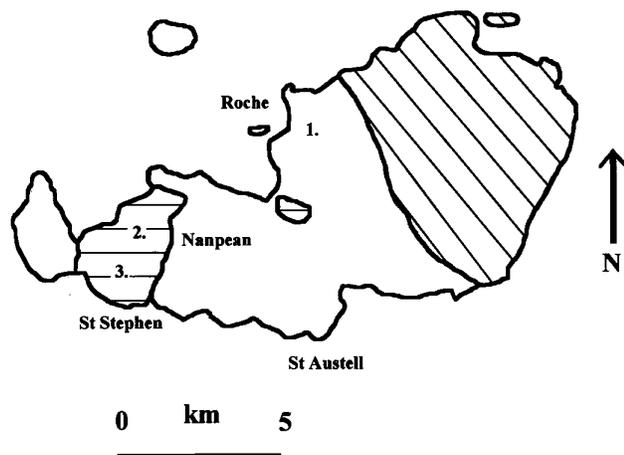


Figure 1. Geological map of the St Austell Granite, showing locations of china clay pits for sampling. Geology simplified after Bristow and Exley (1994). Diagonal ornament: biotite granite. Horizontal ornament: topaz granite with pockets of fluorite granite. No ornament: Li-granite with some biotite granite. 1, Wheal Prosper Pit. 2, Rostowrack Pit. 3, Goonvean Pit.

Pits, close to Nanpean in the west of the kaolinised zone, and Wheal Prosper Pit, near Roche to the east (Figure 1), have been used in the present study. Production and laboratory samples were chosen to represent as complete a range of physical properties as possible. Goonvean and Rostowrack Pits lie within the Type E, Topaz Granite, with some Type F, Fluorite Granite (Bristow and Exley, 1994). The mineralogical composition of refined clay extracted from these pits includes kaolinite, K-feldspar, mica and quartz. Smectite is usually present and is particularly abundant in the partially kaolinised granite adjacent to Prosper China Stone Quarry, which abuts Rostowrack Pit. Wheal Prosper Pit is within Type D, Megacrystic Li-mica Granite (Bristow and Exley, 1994). Kaolinisation is more complete, with K-feldspar and smectite virtually always absent in refined kaolin products. Large tourmalinite veins are common in this pit.

The objective has been to establish the quantitative mineralogy of a range of refined kaolin clays and to use these data to interpret the observed chemical differences and changes in physical properties of the clays. In addition, by using a procedure for accounting for the chemistry of the clays using the composition and proportions of minerals, it has been possible to estimate the type and mineral chemistry of the smectite phase.

PHYSICAL PROPERTIES OF CERAMIC KAOLINS

The physical properties of kaolin are of paramount importance to the ceramic manufacturer, who requires an appropriate product to blend with the other ingredients to give specific properties to the plastic clay mass or clay slip, and subsequent green and dry body. The properties include plasticity, strength, size distribution, cation exchange capacity, surface area, and casting rate (rheology) (Noble *et al.*, 1979). All of these are dependent on the mineralogy of the clay, each mineral component contributing in a positive or negative way to each physical property. The fired colour of a ceramic clay is also very important. This property is largely controlled by the amount of Fe₂O₃ present in the clay, although other transition elements and TiO₂ also

have an effect on the colour of the fired clay.

Kaolin from the St Austell Granite can be refined and blended to produce eminently suitable raw materials for use in all the major ceramic industries in the UK and rest of the world. For the tableware, bone china and porcelain sectors, plastic kaolins are selected and refined to concentrate smectites in the fine fraction. These kaolins are naturally very low in TiO₂ (approximately 0.02%), and Fe₂O₃ is reduced to low levels by careful selection in the pit and refining by hydrocyclones and high intensity magnetic separators. This ensures a high level of whiteness and translucency in the ceramic product. Plasticity is also important for kaolins for sanitaryware, but this must be balanced by a requirement for fast casting rates. Thick opaque glazes are applied to sanitaryware. Thus these kaolins may contain higher levels of Fe₂O₃ and give an off-white fired colour.

The unfired strength of the kaolin, as measured by the modulus of rupture (MOR), is used throughout the ceramic industry as a guide to the plasticity of the clay. It is measured by the three-point bending strength of an extruded bar at 0.5 inch diameter, dried at 110°C. The MOR is closely related to the plasticity, a decrease indicating a less plastic body (Ryan and Radford, 1987). Typical ranges of values for china clays and ball clays, which are more plastic and have a higher MOR, are given in Table 1.

The methylene blue index (MBI) is a convenient and rapid method for estimating the cation exchange capacity (CEC) of a clay, its validity depending on there being a linear relationship between the surface area and the CEC (eg. Poole and Kelk, 1971; Ryan and Radford, 1987; Ingleshorpe *et al.* 1993). The MBI is measured by

<i>Modulus of Rupture</i>	lb/in ²
china clay	50-750
ball clay	700-1500
<i>Methylene blue index</i>	meq/100g
china clay	2-9
ball clay	15-40
(smectite)	70-120)
<i>Surface area</i>	m ² /g
china clay	8-14
ball clay	15-35
(smectite)	>500)
<i>Particle size distribution</i>	%<2microns
china clay	30-70
ball clay	70-95

Table 1. Ranges of values of physical properties of ceramic kaolins. Data taken from Ryan and Radford (1987), and clay company literature. (1 lb/in² = 0.006895 MPa)

adsorption by the clay of methylene blue dye from an aqueous solution. Kaolinite clays have a low MBI, but this increases as the crystal structure becomes more disordered (eg. as in Ball Clays) (Table 1). Smectites have a very high MBI.

The surface area, which is measured by adsorption of nitrogen gas onto the solid surface of the mineral particles, varies with the particle size distribution of the clay, and the nature of the clay mineral. Smectites, with very high structural disorder and corresponding very small crystal size, have extremely high surface areas (Table 1) when in a fully dispersed state.

The casting rate, which is essentially the speed at which water is drawn from the ceramic slip into the plaster mould, is a major factor in the production of ceramic bodies, notably sanitaryware. Faster casting clays are usually characterised by a coarse particle size distribution and a low level of smectite, which retains water during the casting process. A balance of properties is required to maintain acceptable casting characteristics and strength for subsequent handling of the green and dry product.

Ceramic kaolins can vary considerably in their particle size distribution, measured here using a Sedigraph X-ray sedimentometer. The ceramic industry often takes the proportion of <2 micron particles to give an indication of strength as measured by MOR, larger amounts giving a stronger clay body.

The physical properties of six refined kaolins from Goonvean, Rostowrack and Wheal Prosper China Clay Pits are given in Table 2. A is a coarse, low strength, low viscosity clay product derived entirely from Wheal Prosper. B and C are blended products containing different proportions of clays from the three pits. D is a blended product of moderate strength from Rostowrack Pit. E is a very fine grained highly refined clay from Rostowrack and Goonvean Pits, processed through a high intensity magnetic separator to remove iron oxide bearing minerals. It has high strength and a high brightness fired colour. F is taken from Rostowrack Pit adjacent to Prosper China Stone Quarry. It has extremely high strength and was chosen because

	MOR	MBI	Surface area	Particle size distribution				
				>20	>10	<2	<1	<0.5
				(microns)				
A	91	2.7	9.3	%	%	%	%	%
B	155	3.2	10.1	3	17	46	34	18
C	241	4.5	11.3	12	29	41	30	18
D	367	5	11.3	1	12	50	38	22
E	367	5	12.2	3	16	49	38	19
D	590	7.6	14.4	1	5	67	51	32
F	838	9.2	14	1	11	51	39	27

Table 2. Physical properties of six kaolin clays from Goonvean, Rostowrack and Wheal Prosper china clay pits. Details of sample locations given in the text.

it is known that clays from this area contain significant amounts of smectite.

MOR and MBI values increase from A to F, and there is a close linear correlation (Figure 2a. Correlation coefficient, r²=0.986). Such a trend could be explained by an increasing degree of disorder in the kaolinite crystal lattice, which would usually be accompanied by a corresponding decrease in the particle size, particularly the proportion of particles <2 micron. A similar relationship exists between these two properties and the surface area, except for sample F, where significantly higher MOR and MBI compared with sample E are accompanied by a lower surface area. The particle size distribution data show no systematic variation between samples. There are wide variations in both the >10 micron and <2 micron fractions, and pairs of samples with similar size distribution data (C and F, and A and D) have very different other physical properties. Although there is an increase in the <0.5 micron fraction in the clays with the higher MOR (ie. E and F), only a poor correlation exists (r²=0.631). There is no significant correlation between the <2 micron fraction and the other physical properties (eg. for MOR and % <2 micron, r²=0.336). This indicates that the variation in proportions of the individual mineral components has a stronger control on the subsequent physical properties of the clay product than the variation in particle size distribution that can be achieved by extended processing.

CHEMICAL AND MINERALOGICAL ANALYTICAL TECHNIQUES

The chemistry of the six refined kaolin clays and <0.5 micron fractions, separated from each of the clays by deflocculated sedimentation according to Stokes' Law, was determined by X-ray fluorescence spectrometry using a Philips PW1400 and a fusion bead technique, except for F and Li. A separate loss on ignition (LOI) was determined on the dried powders. F was measured by selective ion electrode: and Li by atomic absorption spectrophotometry (AAS). A sample of 'gilbertite' mica from Rostowrack Pit, and fine grained tourmaline from a tourmalinite from Goonbarrow Pit, adjacent to Wheal Prosper, were also analysed using the same procedures, except that Rb and Mg were determined by AAS for the mica. For Mg this was necessary as the level is much lower than in the clay samples, and

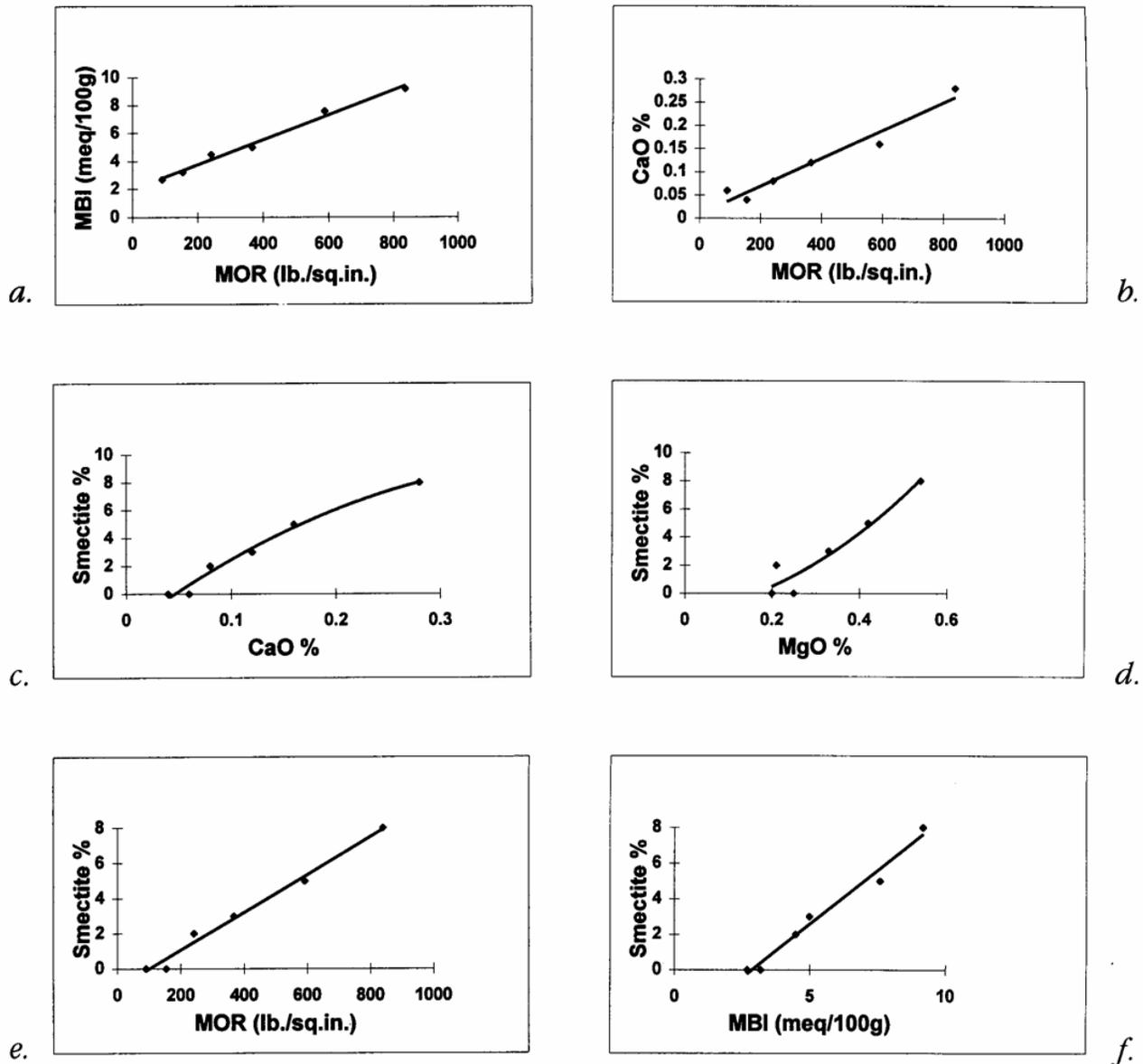


Figure 2. Plots to show correlation between physical properties, chemistry and mineralogy of ceramic clays.

a. Modulus of rupture v. methylene blue index. b. Modulus of rupture v. CaO. c. CaO v smectite. d. MgO v smectite. e. Modulus of rupture v smectite. f. Methylene blue index v smectite.

an accurate value was required for use in the calculation of the smectite chemistry.

The qualitative mineralogy of the clays and the <0.5 micron fractions was determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer. Reference patterns of quartz, K-feldspar, 'gilbertite' mica and tourmaline, collected from the St Austell area were also made, and apart from tourmaline which is present in only very minor amounts in two samples, these minerals were used in the preparation of standards for the quantitative mineralogy. The K-feldspar appears to be an ordered microcline, a close match being achieved with PDF datafile 220687. The tourmaline is schorl closely matching with PDF datafile 41-1497.

The quantitative mineralogy of K-feldspar, quartz and smectite was determined by XRD, using a procedure of making known additions of the pure mineral phases (spiking) for the preparation of calibration curves and randomly orientated powder mounts in the diffractometer. A pure Wyoming Bentonite (montmorillonite) was used as a standard for the smectite calibration, and measurements were made in the air-

dried state, the kaolin samples being run immediately following the standards to avoid any changes in the position and intensity of diffraction maxima due to humidity variations. The following peaks were chosen for the calibration: K-feldspar, 3.24Å, 27.5°2θ; quartz 4.26Å, 20.8°2θ and 2.46Å, 36.5°2θ; smectite 15Å, 5.8°2θ. At equilibrium in the air-dried state, the 15Å peak from the bentonite gave close correspondence with the (001) smectite peak in the kaolin samples. The most intense peak for quartz at 3.343Å could not be used for calibration as there is overlap with mica. The 4.26Å quartz peak is between two kaolinite peaks and it is difficult to measure a true background. This creates problems when the kaolinite proportion is not similar to that in the samples to be measured. A second, but much less intense quartz peak was measured as a check on the data. An attempt to quantify the mica content by XRD, was abandoned as a usable calibration curve could not be obtained. Two reasons may account for this: platy mica crystals are difficult to grind to a suitable fine grain size, coarse particles giving anomalous intensities and a heterogeneous powder mixture; preferred orientation may be present in the powder mounts. Preferred orientation effects were not apparent

with the smectite calibration, probably as the bentonite remained as aggregates in the calibration mixtures, rather than as individual crystals.

The quantitative mica content of the clays was determined by calculation from the chemical analysis, using the quantitative XRD data for quartz, K-feldspar and smectite, and matching the K₂O and F content of the clays with an amount of mica to give no remainder. A stoichiometric formula was assumed to attribute an appropriate amount of K₂O to K-feldspar and the measured chemistry of 'gilbertite' mica was used in the calculation, which was made using a spreadsheet. Although his electron microprobe analyses show a considerable variation in mineral chemistry of micas from the St Austell Granite, Bray's (1980) data for secondary muscovites are similar to the 'gilbertite' mica. Thus, use of this mica composition in the calculation seems reasonable. Checks were made that a balance between a calculated and measured chemistry also was achieved with the other elements as far as possible. Although Li is present in only very minor amounts in the clay, and is likely to be entirely in the mica, a close correspondence was achieved between the measured value of Li and a calculated value, giving further confidence to the quantitative procedure. Other minerals which account for the presence of some of the minor elements (eg. Ti, P) are assumed to be present only in very minor proportions, and much less than 1%, in the clay.

QUALITATIVE MINERALOGY AND CHEMISTRY

The qualitative XRD data confirm the presence of mica with kaolinite in all six samples. There are also minor, but variable amounts, of quartz and K-feldspar throughout. Tourmaline, in amounts only just above the detection limit, is identifiable in the X-ray patterns of samples A and B. Smectite occurs only in samples C-F. The kaolinite in the <0.5 micron fractions gives much lower intensity and broader diffraction peaks compared with the whole samples. These fractions contain very minor amounts of mica, the (001) peak being very broad. Smectite is identifiable in samples B-F. Quartz occurs in very minor amounts in the <0.5micron fractions of samples B, C, D and F. Feldspar is absent in all <0.5 micron fractions.

Pure kaolinite has the chemical composition: SiO₂, 46.55%; Al₂O₃, 39.49%. LOI (H₂O), 13.96%. As would be expected the chemical analyses of the clay samples (Table 3) show increased amounts of SiO₂, partly accountable as quartz, and less Al₂O₃, as a consequence of the presence of other minerals. Other elements also occur in significant quantities, notably K₂O, reflecting the presence of mica and feldspar. Fe₂O₃, which is highest in samples A and B, is partly accounted for in tourmaline (Table 4; see also analyses of tourmaline in Manning (1991)) and in mica, and probably partly as Fe and FeTi oxides. Minor amounts of Fe, Ti and K may substitute into the kaolinite structure, be present as surface coatings or as random interleaving of other phyllosilicates (Jepson and Rowse, 1975; Giese, 1988; Schroeder and Pruet, 1996). CaO and MgO are present in small amounts in all samples, and can be attributed mainly to smectite, particularly in samples D-F. Small amounts of MgO may be present in kaolinite (Giese, 1988), perhaps as an exchangeable cation, and the same may apply to Ca. Similar amounts of MgO (around 0.2%) are reported in paper coating, quality kaolin, in which no smectite can be present. Given the amounts of Ca and Mg in the mica and tourmaline (Table 4; see also analyses in Chaudhry and Howie (1973) and Manning (1991)), only a very minor proportion of the measured amounts of these elements can be attributed to these minerals.

Na₂O is probably accounted for partly as tourmaline, especially in samples A and B, partly as minor substitution for K in K-feldspar, and possibly as an exchangeable cation associated with the smectite. It is also possible that minor albite could be present, particularly in sample F. Li₂O is attributed entirely to mica, as is fluorine, there being insufficient CaO in the analyses to account for the fluorine as fluorite, except possibly for a small amount in sample F, where both CaO and fluorine values are increased relative to the other samples. The presence of very minor fluorite might be expected in sample F, given its location adjacent to the China Stone Quarry. There is insufficient

Ca in the clays to account for the observed amounts of P₂O₅ as apatite. Very minor amounts of U, Th and REE phosphates are known to

A. REFINED KAOLIN						
%	A	B	C	D	E	F
SiO ₂	46.70	47.78	47.88	49.29	49.69	51.74
TiO ₂	0.03	0.01	0.02	nd	nd	0.04
Al ₂ O ₃	36.22	35.95	35.95	34.60	33.90	30.29
Fe ₂ O ₃	1.23	1.37	0.74	0.84	0.43	0.54
MgO	0.25	0.20	0.21	0.33	0.42	0.54
MnO	0.01	0.03	0.01	0.01	0.01	0.01
CaO	0.06	0.04	0.08	0.12	0.16	0.28
BaO	0.04	0.03	0.03	0.04	0.02	0.01
Li ₂ O	0.04	0.08	0.04	0.08	0.03	0.05
Na ₂ O	0.07	0.07	0.08	0.09	0.08	0.17
K ₂ O	2.11	2.64	2.30	3.03	2.94	4.69
P ₂ O ₅	0.13	0.12	0.14	0.14	0.15	0.18
F	0.27	0.37	0.30	0.40	0.33	0.43
S	0.01	nd	nd	nd	0.01	nd
LOI	12.11	11.60	12.61	11.55	12.16	10.44
Total	99.26	99.99	100.39	100.52	100.33	99.41
B. <0.5 MICRON FRACTION.						
%	A	B	C	D	E	F
SiO ₂	46.40	46.59	46.35	47.31	47.45	47.49
TiO ₂	0.03	0.06	0.01	0.02	0.04	0.02
Al ₂ O ₃	37.78	37.20	35.85	35.18	33.80	29.37
Fe ₂ O ₃	1.19	1.27	0.67	0.64	0.38	0.53
MgO	0.25	0.33	0.51	0.66	0.67	1.24
MnO	nd	nd	nd	nd	nd	nd
CaO	0.09	0.10	0.15	0.18	0.19	0.34
BaO	nd	0.01	0.01	0.01	0.01	0.01
Li ₂ O	0.01	0.02	0.01	0.02	0.01	0.01
Na ₂ O	0.05	0.09	0.12	0.12	0.11	0.24
K ₂ O	1.00	0.97	1.00	1.44	0.92	1.98
P ₂ O ₅	0.22	0.24	0.18	0.16	0.13	0.14
S	0.01	0.01	0.01	0.01	0.01	0.01
LOI	12.91	12.69	14.33	14.11	14.91	18.39
Total	99.94	99.58	99.20	99.86	98.63	99.78

Table 3. Chemical analyses of six refined kaolin clays from Goonvean, Rostowrack and Wheal Prosper china clay pits, and <0.5micron fractions. nd = below detection limit. LOI = loss on ignition.

	MICA			TOURMALINE			
	%		formula		%		formula
SiO ₂	48.47	Si	6.5592	SiO ₂	35.7	Si	6.0425
TiO ₂	0.11	Al(IV)	1.4408	TiO ₂	0.1	Al(IV)	6
Al ₂ O ₃	31.96	Al(VI)	3.6565	Al ₂ O ₃	36.50	Al(VI)	1.281
FeO	2.74	Ti	0.0112	FeO	13.77	Ti	0.0127
MnO	0.07	Fee.	0.3101	MnO	0.12	Fee*	1.9491
MgO	0.07	Mn	0.008	MgO	0.48	Mn	0.0172
CaO	0.11	Mg	0.0141	CaO	0.06	Mg	0.1211
Na ₂ O	0.22	Ca	0.0159	Na ₂ O	1.71	Ca	0.0109
K ₂ O	10.48	K	1.8091	K ₂ O	0.02	Na	0.5612
Li ₂ O	0.35	Na	0.0577	LOI	3.56	K	0.0043
Rb ₂ O	0.66	Li	0.0952			OH	4.0201
LOI	4.48	Rb	0.0287				
F	1.47	OH	4.0448				
O=F	0.61	F	0.6291				
Total	100.58						

Table 4. Chemical analysis of gilbertite' mica and partial chemical analysis of tourmaline, and structural formulae. All Fe is expressed as FeO. LOI = loss on ignition plus allowance for oxidation of Fe²⁺ to Fe³⁺ during ignition, assumed to be H₂O for calculation of formula. Formula calculated on basis of Si+Ti+Al+Fe²⁺+Mn+Mg = 12 for mica, and Si+Ti+Al'+Fe²⁺+Mn+Mg+Ca+Na+K = 16 for tourmaline.

occur as accessory minerals in Cornish granites, and might account for the P_2O_5 values.

The chemical data of the <0.5 micron fractions (Table 3) support the above discussion. Increased amounts of MgO and CaO would support the argument that Mg and Ca is present in smectite, and the same would apply to Na from the increased amounts of Na_2O in samples C-F. K_2O is present in lower amounts in the <0.5 micron fraction as would be expected from the absence of K-feldspar and, at best, only a very broad (001) reflection, barely above the detection limit, is present for mica in the XRD data for the fine fractions in samples A-C and E. However, at approximately 1% (samples A-C and E), 1.5% (sample D) and 2% (sample F) K_2O , the chemistry would indicate around 10%, 15% and 20% muscovite respectively in the fine fractions, if all the K_2O is attributed to this mineral, and even more, if a structurally disordered mica occurs, say illite, as would be present in this size fraction. A preferred interpretation is that the K is present, at least in part, as an exchangeable cation associated with smectite and, possibly associated with a random interleaving of illite within kaolinite and/or smectite. The presence of similar amounts of Fe_2O_3 in the fine fraction as in the whole clay for each sample could indicate that Fe is distributed through several minerals, but the argument that Fe is present in the lattice of kaolinite is also supported by this data.

Some systematic changes occur in the chemical analyses between samples. SiO_2 increases from A through F, and there is a corresponding decrease in Al_2O_3 ($r^2=0.922$). Although levels are overall very low, CaO and MgO also generally show an increase with SiO_2 . Other elements vary less systematically, but sample F contains increased amounts of K_2O , Na_2O , P_2O_5 and fluorine compared with the other samples. There is a very good correlation between CaO, MgO and SiO_2 with MOR ($r^2 = 0.984, 0.919$ and 0.960 respectively, Figure 2b), and an inverse correlation of Al_2O_3 with MOR ($r^2 = 0.960$).

%	quartz	K-feldspar	mica	smectite	kaolinite
A	3	1	19	0	77
B	3	1	23	0	73
C	2	2	17	2	77
D	4	4	20	3	69
E	5	6	16	5	68
F	7	12	21	8	52

Table 5. Quantitative mineralogy of the refined kaolin clays. Quartz, feldspar and smectite determined by quantitative X-ray diffraction, mica by matching K_2O and F with chemical analysis, after allowance made for K-feldspar. The kaolinite value is by difference. The error is estimated at ± 296 for each mineral.

QUANTITATIVE MINERALOGY AND RELATIONSHIP TO CHEMISTRY AND PHYSICAL PROPERTIES

The quantitative mineralogical data are given in Table 5. Minor amounts of quartz and K-feldspar are present in all samples with amounts increasing from A to F. The smectite content also increases from C to F. Mica is the major phase after kaolinite, and shows some variation between samples. The coarsest clay (sample B) contains the most, and the finest clay (sample E) the least amount of mica. This would be expected in kaolin products where mica has an overall larger crystal size than kaolinite. The kaolinite content also varies somewhat, almost half of sample F, the strongest clay with the highest MOR, being made up of minerals other than kaolinite.

There is a clear relationship between CaO and MgO and the amount of smectite (Figures 2c and 2d), a positive intercept leaving around 0.05% CaO and 0.2% MgO to be accounted for in other minerals. Figures 2e and 2f show that a good linear relationship exists between MOR and smectite ($r^2 = 0.980$) and MBI and smectite ($r^2 = 0.961$) respectively over the range of values given by the data.

CHEMISTRY OF THE SMECTITE

An estimation of the mineral chemistry of the smectite can be made by calculation using the quantitative mineral data and the chemical analysis of the clays containing smectite, and apportioning each element to mineral species. Ideally, the remainder, after accounting for quartz, mica, K-feldspar and kaolinite, should approximate to a smectite composition. Although several other assumptions are made, not least that errors in the data have not accumulated in the remainder and the presence of small amounts of other minerals are ignored, an acceptable estimate for the smectite composition can be achieved. The result is particularly sensitive to minor changes in the quartz value, minor variations creating major changes in the SiO_2 content of the remainder. However, the Al_2O_3 and MgO contents of the remainder are less sensitive to variations in the data, which is fortunate, as the sub-division of smectites is largely controlled by differences in these elements.

The estimated smectite composition along with approximate chemical formula is given in Table 6. It is a dioctahedral type with about one third of the octahedral sites occupied by Mg. There is no tetrahedral substitution. Using the subdivisions in Newman and Brown (1987) the smectite is a montmorillonite of Otay type, which is defined as having <15% tetrahedral substitution and a layer charge >0.85. A dioctahedral smectite is to be expected during the weathering of granitic rock (Velde and Meunier, 1987).

	%		Formula
SiO_2	54	Si	8.07
Al_2O_3	16	Al	2.82
MgO	5	Mg	1.11
RO+ R_2O	5	$R^+ + R^{2+}$	0.8-1.5
H_2O	20		

Table 6. Estimate of mineral chemistry of smectite in kaolin clays from the St Austell area. Formula calculated on basis of $Si+Al+Mg=12$. R is one or more exchangeable cations. $R^+ + R^{2+}$ varies with the proportion of different exchangeable cations.

CONCLUSIONS

The variation in the physical properties of different kaolin products made from the kaolinised St Austell Granite can be explained by quantitative variations in mineralogy. Quartz, K-feldspar, smectite and mica occur in varying amounts in the clay, and occasionally tourmaline is recognisable. The mica is a Li and F rich dioctahedral type. An increase in the smectite content of the clay corresponds with an increase in the strength of the clay as measured by the MOR, and the cation exchange capacity, determined by the MBI. The particle size distribution of the clay, particularly the <2 micron fraction, is not a reliable indication of the likely MOR of clay bodies.

Kaolin with a high smectite content occurs adjacent to partly kaolinised areas, where there is also a significant amount of K-feldspar in the refined clay products. The smectite is a dioctahedral montmorillonite.

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REFERENCES

BRAY, C.J. 1980. *Mineralisation, greisenisation and kaolinisation at Goonbarrow China Clay Pit, Cornwall, UK*. Unpublished D.Phil. Thesis, University of Oxford, 2vols, 174pp.

- BRISTOW, C.M. and EXLEY, C.S. 1994. Historical and geological aspects of the china clay industry of South-West England. *Transactions of the Royal Geological Society of Cornwall*, **21**, 247-314.
- CHAUDHRY, M.N and HOWIE, R.A. 1973. Muscovite ('gilbertite') from the Meldon Aplite. *Proceedings of the Ussher Society*, **2**, 480-481.
- GIESE, R.F. 1988. Kaolin minerals: structures and stabilities Pp.29-66 in BAILEY, S.W. (Ed.) *Hydrous phyllosilicates*. Reviews in Mineralogy, Volume 19. Mineralogical Society of America, 725pp.
- INGLETHORPE, S.D.J., MORGAN, D.J., HIGHLEY, D.E., and BLOODWORTH, A.J. 1993. *Industrial minerals laboratory manual: bentonite*. Technical Report WG/93/20, British Geological Survey, 116pp.
- JEPSON, W.B. and ROWSE, J.B. 1975. The composition of kaolinite - an electron microscope microprobe study. *Clays and Clay Minerals*, **33**, 1-14.
- MANNING, D.A.C. 1991. Chemical variation in tourmalines from S.W. England. *Proceedings of the Ussher Society*, **7**, 327-332.
- NEWMAN, A.C.D. and BROWN, G. 1987. The chemical constitution of clays. Pp.1- 128 in NEWMAN, A.C.D. *Chemistry of clays and clay minerals*. Mineralogical Society Monograph No. 6, 480pp.
- NOBLE, F.R., ROWSE, J.B. and GOLLEY, C.R.L. 1979. Studies on the mineralogy of ceramic clays. *Mineralogy of ceramics* pp. 117-126. British Ceramic Society.
- POOLE, E.G. and KELK, B. 1971. *Calcium montmorillonite (fuller's earth) in the Lower Greensand of the Baulking area, Berkshire*. Report No. 71/4. Institute of Geological Sciences, 56pp.
- RYAN, W. and RADFORD, C. 1987. *Whitewares: production, testing and quality control*. Pergamon Press on behalf of Institute of Ceramics, 333pp.
- SCHROEDER, P.A. and PRUETT, R.J. 1996. Fe ordering in kaolinite: ^{29}Si and ^{27}Al MAS NMR spectroscopy. *American Mineralogist*, **81**, 26-38.
- VELDE, B. and MEUNIER, A. 1987. Petrologic phase equilibria in natural clay systems. Pp.423-458 in NEWMAN, A.C.D. *Chemistry of clays and clay minerals*. Mineralogical Society Monograph No. 6, 480pp.