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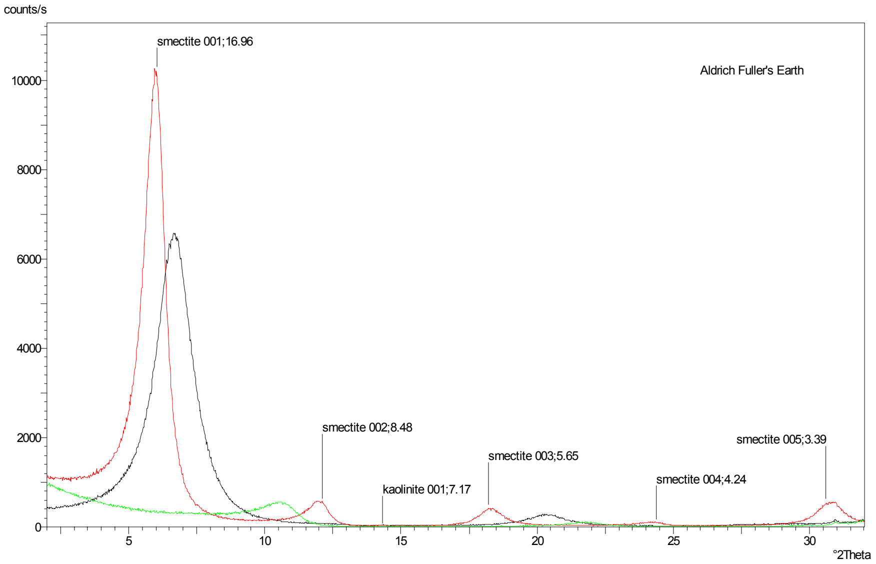
Mineralogical, geochemical and physico-chemical characterisation of compact clays

Development of Capability Programme

Internal Report IR/04/155



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/04/155

Mineralogical, geochemical and physico-chemical characterisation of compact clays

S J Kemp, D Wagner and B P Vickers

Key words

Standard clays, mineralogy, chemistry, cation exchange capacity, surface area.

Front cover

<2 micron X-ray diffraction traces for Aldrich Fuller's Earth

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Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU
☎ 01793-411500 Fax 01793-411501
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1 Introduction

This report summarises the results of mineralogical, geochemical and physico-chemical characterisation of a suite of clay-rich materials that were undergoing pore-squeezing tests as part of the Development of Capability subproject 'Characterisation of Compact Clays – pilot Study'.

A sample list is shown in Table 1.

X-ray diffraction (XRD, whole-rock and <2 µm fraction) analyses were performed to determine the mineralogy of the samples while 2-ethoxyethanol (ethylene glycol monoethyl ether, EGME) surface area analyses and cation exchange capacity (CEC) determinations were carried out to assess the physico-chemical properties of the materials. The major and selected trace-element geochemistry of the samples was also investigated using X-ray fluorescence (XRF) spectroscopy.

Table 1. Sample list

BGS code	Sample name	Description
MPLJ883	Bentonite	Light grey pelleted clay
MPLJ884	Baulking Blue Fuller's Earth	Medium grey clay
MPLJ885	Ball clay	Light grey clay
MPLJ886	Kaolinite Grade 'B'	White powdered clay
MPLK166	Aldrich Fuller's Earth	Light grey powdered clay

2 Laboratory methods

2.1 SAMPLE PREPARATION

Approximately half of the submitted material was first dried at 55°C overnight and where necessary crushed to <2 mm diameter. Half of this crushed material was then subsampled and tema-milled to <0.12 mm for whole-rock XRD analysis, surface area analysis and CEC determinations. A subsample of the crushed material was agate tema –milled for geochemical analysis.

2.2 X-RAY DIFFRACTION ANALYSIS

In order to achieve a finer and uniform particle-size for whole-rock XRD analysis, approximately 3 g portions of the tema-milled material was micronised under acetone for 5 minutes and dried at 55°C. The dried material was then disaggregated in a pestle and mortar and back-loaded into a standard aluminium sample holder for analysis.

Approximately 7.5 g subsamples of the jawcrushed material were dispersed in distilled water using a reciprocal shaker combined with ultrasound treatment. The suspension was then sieved on 63 µm and the <63 µm material placed in a measuring cylinder and allowed to stand. In order to prevent flocculation of the clay crystals, 1 ml of 0.1M 'Calgon' (sodium hexametaphosphate) was added to each suspension. After a time period determined from Stokes' Law, a nominal

<2 µm fraction was removed and dried at 55°C. 100 mg of the <2 µm material was then re-suspended in a minimum of distilled water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. The mounts were Ca-saturated using 0.1M $CaCl_2.6H_2O$ solution and washed twice to remove excess reagent.

XRD analysis was carried out using a Philips PW1700 series diffractometer fitted with a cobalt-target tube and operated at 45kV and 40mA. Whole-rock samples were scanned from 3-50 °2θ at 0.69 °2θ/minute. The <2 µm samples were scanned from 2-32 °2θ at 0.54 °2θ/minute as air-dry mounts, after glycol-solvation and after heating to 550°C for 2 hours.

Diffraction data were firstly analysed using PANalytical X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on a PC system.

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) using Siroquant v.2.5 software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier *et al.*, 2001). Where a phase was detected but its concentration was indicated to be below 0.5%, it is assigned a value of <0.5%, since the error associated with quantification at such low levels becomes too large.

In order to gain further information about the nature of the clay minerals present in the samples, modelling of the XRD profiles was carried out using Newmod-for-Windows™ (Reynolds and Reynolds, 1996) software.

Modelling was also used to assess the relative proportions of clay minerals present in the <2 µm fractions by comparison of sample XRD traces with Newmod-for-Windows™ modelled profiles. The modelling process requires the input of diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the selection of different sheet compositions and chemistries. In addition, an estimate of the crystallite size distribution of the species may be determined by comparing peak profiles of calculated diffraction profiles with experimental data. By modelling the individual clay mineral species in this way, *mineral reference intensities* were established and used for quantitative standardization following the method outlined in Moore and Reynolds (1997).

2.3 X-RAY FLUORESCENCE ANALYSIS

XRF analysis was carried out using sequential, fully automatic wavelength-dispersive spectrometers (2 x Philips PW2400 and 1 x Philips PW2440) controlled via PCs running SuperQ (version 3.0H) XRF application package.

Fused beads for major element analysis were prepared by fusing 0.9 g sample plus 9.0 g flux (66/34 $Li_2B_4O_7$ and $LiBO_2$) at 1200°C. Loss on ignition (LOI) was determined on *c.*1 g sample heated at 1050°C for one hour.

2.4 CATION EXCHANGE CAPACITY DETERMINATION

Cation exchange capacity (CEC) determinations were carried out using tema-milled material and a $BaCl_2$/triethanolamine (pH 8.1) titration method based on that proposed by Bascomb (1964). BGS experience has shown that this modified method appears to give a slightly increased CEC value compared to that indicated by the methylene blue method. Data for standard materials analysed with the samples indicates that values might be increased by 10%.

2.5 SURFACE AREA DETERMINATION

Surface area determinations were performed on all samples using the 2-ethoxyethanol (ethylene glycol monoethyl ether, EGME) technique (Carter *et al.*, 1965). The method is based on the formation of a monolayer of EGME molecules on the clay surface under vacuum. Aluminium dishes containing approximately 1.1 g hammer-milled sample/clay standard (Patterson Court Blue bentonite) were placed in a desiccator containing anhydrous phosphorus pentoxide. The desiccator was evacuated and allowed to stand overnight before the dishes were reweighed. The samples were then saturated with 2-ethoxyethanol and placed in a second desiccator containing dry calcium chloride. After 1½ hours, the desiccator was evacuated and left overnight. The sample was then rapidly re-weighed and the weight of 2-ethoxyethanol absorbed determined and the surface area calculated. Finally, a correction based on the Patterson Court Blue standard was applied.

Smectite has a surface area of *c.*800 m^2/g while other clay minerals and quartz have surface areas typically less than 100 m^2/g and 1 m^2/g respectively. Such a difference in value means that the surface area of a sample can provide a useful estimate of its smectite content.

3 Results

The results of all analyses are summarised in Tables 2 to 5 and labelled whole-rock and <2 µm X-ray diffraction traces are shown in the Appendix.

Due to the presence of cement minerals in the pelletised ‘bentonite’, and the lack of such cementitious phases in the Siroquant database, no quantification of the whole-rock mineralogy was possible for this sample.

Table 2. Summary of whole-rock XRD analyses

BGS code	Sample name	%mineral									
		quartz	‘mica’	smectite	K-feldspar	kaolinite	calcite	hatrurite	gismondine	gypsum	pyrite
MPLJ883	Bentonite	tr	nd	maj	nd	nd	min	min	?tr	tr	nd
MPLJ884	Baulking Blue Fuller's Earth	3.1	0.8	93.2	1.7	nd	1.2	nd	nd	nd	nd
MPLJ885	Ball clay	5.7	36.6	3.0	0.2	54.5	nd	nd	nd	nd	nd
MPLJ886	Kaolinite Grade ‘B’	0.9	12.4	0.9	4.5	81.3	nd	nd	nd	nd	nd
MPLK166	Aldrich Fuller’s Earth	2.3	nd	95.2	nd	nd	2.5	nd	nd	nd	<0.5

KEY		
	nd	not detected
	maj	major component
	min	minor component
	tr	trace component
	‘mica’	undifferentiated mica species possibly including muscovite, biotite, illite, illite/smectite etc

Table 3. Summary of <2 µm XRD analyses

BGS code	Sample name	%clay mineral		
		smectite	illite	kaolinite
MPLJ883	Bentonite	100	nd	nd
MPLJ884	Baulking Blue Fuller's Earth	100	nd	nd
MPLJ885	Ball clay	2	32	66
MPLJ886	Kaolinite Grade 'B'	<1	8	91
MPLK166	Aldrich Fuller's Earth	100	nd	<<1

KEY nd not detected

Table 4. Summary of CEC and surface area data

BGS code	Sample name	CEC (meq/100g)	Surface area (m^2/g)
MPLJ883	Bentonite	97.1	356
MPLJ884	Baulking Blue Fuller's Earth	76.3	756
MPLJ885	Ball clay	16.5	130
MPLJ886	Kaolinite Grade 'B'	5.1	34
MPLK166	Aldrich Fuller's Earth	89.3	793

Table 5. Summary of XRF geochemical and loss on ignition data

BGS code	Sample name	% oxide											
		SiO2	TiO2	Al2O3	Fe2O3t	Mn3O4	MgO	CaO	Na2O	K2O	P2O5	SO3	LOI
MPLJ883	Bentonite	39.40	0.35	9.95	7.34	0.05	2.14	24.00	1.81	0.56	0.09	0.8	12.92
MPLJ884	Baulking Blue Fuller's Earth	59.81	0.90	17.13	6.74	<0.01	3.51	2.72	0.16	0.62	0.12	0.5	7.76
MPLJ885	Ball clay	50.99	0.87	31.90	1.40	<0.01	0.60	0.22	0.32	2.89	0.06	<0.1	9.92
MPLJ886	Kaolinite Grade 'B'	48.06	0.03	35.96	0.90	0.02	0.22	0.02	<0.05	2.23	0.15	<0.1	11.92
MPLK166	Aldrich Fuller's Earth	57.43	0.86	16.47	7.09	<0.01	3.50	3.33	1.37	0.59	0.12	0.6	7.66

BGS code	Sample name	% oxide							
		Cr2O3	SrO	ZrO2	BaO	NiO	CuO	ZnO	PbO
MPLJ883	Bentonite	<0.01	0.05	0.05	0.18	<0.01	<0.01	0.02	<0.01
MPLJ884	Baulking Blue Fuller's Earth	<0.01	0.11	0.09	0.03	<0.01	<0.01	0.01	<0.01
MPLJ885	Ball clay	0.02	0.02	<0.02	0.07	<0.01	<0.01	0.01	<0.01
MPLJ886	Kaolinite Grade 'B'	<0.01	0.02	<0.02	0.02	<0.01	0.01	<0.01	<0.01
MPLK166	Aldrich Fuller's Earth	<0.01	0.08	0.10	0.03	<0.01	<0.01	0.02	<0.01

4 Discussion

4.1 BENTONITES

Whole-rock XRD analysis suggest that all three bentonite samples ('bentonite', Baulking Blue Fuller's Earth and Aldrich Fuller's Earth) contain large proportions of smectite. 'Contaminant' phases in the Baulking and Aldrich fuller's earths include quartz, 'mica', K-feldspar, calcite and pyrite.

<2 μm fraction XRD analyses indicate almost pure smectite clay mineral assemblages for all three samples. [A trace of kaolinite was detected in the Aldrich Fuller's Earth.] Each of the samples produces the typically broad, rational smectite basal spacings. The air-dry smectite d_{001} peaks for the Baulking and Aldrich fuller's earths appear at *c.*15Å, 'swell' to *c.*17Å on glycolation and collapse to *c.*10Å on heating as would be expected of a standard smectite. However, despite showing similar glycol-solvated and heated peak positions, the pelletised bentonite is characterised by an air-dry d_{001} peak at *c.*19.5Å. Such a large spacing for the air-dry peak suggests that the smectite contains three layers of interlayer water rather than the usual two. On glycolation and heating, this excess water is driven out and the structure returns the more characteristic smectite peak spacings.

CEC values for the two fuller's earth samples are high (76.3 meq/100g for the Baulking sample and 89.3 meq/100g for the Aldrich sample). These compare well with standard montmorillonite values of between 76.4 and 120 meq/100g (van Olphen & Fripiat, 1979). 2-ethoxyethanol surface areas are also high for the fuller's earth samples (756 and 793 m^2/g) and close to the 'standard' smectite value of 800 m^2/g. The Baulking Fuller's earth surface area appears to validate the XRD quantification results considering the *c.*5% non-clay mineral contaminants identified. However, the major amounts of 'mica' identified in the Aldrich Fuller's Earth do not correspond with its high CEC and surface area and suggest that the 'mica' content should be included in the smectite total. A cross-plot of CEC versus surface area shows a good correlation between these parameters for the fuller's earths (Figure 1).

However, the pelletised bentonite has a surface area approximately only half as large as the fuller's earth samples (356 m^2/g) probably due to the major presence of lower surface area calcite and cement minerals. The very large CEC for this sample (97.1 meq/100g) and the fact that this sample falls away from the correlation line between surface area and CEC (Figure 1) is most likely the result of the high exchange capacity of cement minerals (e.g. Delattre Louvel *et al.*, 1993).

The major element chemistry of the bentonites also indicates the similarity between the two fuller's earth samples and the presence of cementitious materials in the pelletised bentonite. The major oxide for the two fuller's earths show very similar distributions but the pelletised bentonite shows relatively higher levels of Ca and LOI, similar levels of Fe, K and Na but significantly lower levels of Si, Al and Mg (Figure 2).

4.2 KAOLINITE-BEARING SAMPLES

Whole-rock XRD analysis indicates that both the ball clay and kaolinite Grade 'B' samples are predominantly composed of kaolinite with variable amounts of 'mica' (major in the ball clay and minor in the Grade 'B') and minor-trace amounts of quartz, smectite and K-feldspar.

<2 μm fraction XRD analyses indicate clay mineral assemblages dominated by kaolinite with minor amounts of illite and traces of smectite. The ball clay kaolinite has a much smaller average crystallite-size, revealed by the broader XRD basal spacings (e.g. d_{001} full width at half maximum (FWHM) = 0.74°2θ) compared to a FWHM of 0.26°2θ for the Grade 'B' sample. Newmod-for-Windows™ modelling suggests a mean defect-free distance of seven 7Å units and a range of 1 to 35 7Å units for the ball clay kaolinite compared to a mean defect-free distance of twenty 7Å units and a range of 1 to 100 7Å units for the Grade 'B' kaolinite. The illite and smectite present in both samples have approximately similar crystallite-size distributions.

Both kaolinite-bearing samples present relatively low CEC values (ball clay = 16.5 meq/100g and Grade 'B' = 5.1 meq/100g) reflecting the lack of cation exchange from the dominant 1:1 kaolinite structure. However, these are higher than published values for standard kaolinites (typically *c.*3 meq/100g, van Olphen & Fripiat, 1979) due to the presence of 2:1 clay minerals. The higher value for the ball clay indicates the significant presence of illite and to a lesser extent smectite in this material. Surface area values of 130 and 34 m^2/g show a good correlation with the CEC values (Figure 1).

The Al and Si-dominated major element chemistry of both the ball clay and Grade 'B' samples reflects their kaolinite-dominated mineralogy. The greater LOI figure for the Grade 'B' sample indicates the greater kaolinite concentration in this sample. The slightly enhanced K concentration in the ball clay reflects the greater mica content of this sample but is partially compensated by the K-feldspar in the Grade 'B' sample. Higher Ca, Mg, Na concentrations in the ball clay probably mirror its greater smectite component while the similarly enhanced Fe and Ti contents may indicate the greater occurrence of Fe- and Ti-oxides in the ball clay.

5 Conclusions

Five samples undergoing pore-squeezing tests have been characterised using mineralogical, geochemical and physico-chemical analyses. These have revealed that:

- The two fuller's earth samples (Baulking Blue and Aldrich) are smectite-rich with surface areas and cation exchange capacities similar to published values. They contain minor contaminant phases such as quartz, 'mica', K-feldspar, calcite and pyrite. Both have similar major-element geochemistries.
- The pelletised bentonite is also smectite-rich but contains major amounts of calcite and cementitious material producing a more Ca-rich geochemistry. Such a mineralogy is also responsible for a very high cation exchange capacity but a surface area only half as large as the fullers earth samples. The smectite present in the pelletised bentonite is an unusual tri-hydrate species.
- The ball clay sample is composed of major amounts of kaolinite and 'mica' with minor amounts of quartz, smectite and K-feldspar. The kaolinite and 'mica' are 'poorly crystalline', having small defect-free distances and low range crystallite-size distributions. The ball clay's CEC and surface area are low but greater than expected for a standard kaolinite due to the presence of illite and smectite. Enhanced levels of K, Ca, Mg and Na are also due to the presence of these clay minerals.
- The Grade 'B' kaolinite is predominantly composed of a 'well-crystallised' kaolinite which has a large mean defect-free distance and extended range crystallite-size distribution. Minor-trace levels of 'mica', K-feldspar, quartz and smectite were also detected. It has a low CEC and surface area value but these are slightly higher than those obtained from pure kaolinites due to the detected impurities.

6 References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

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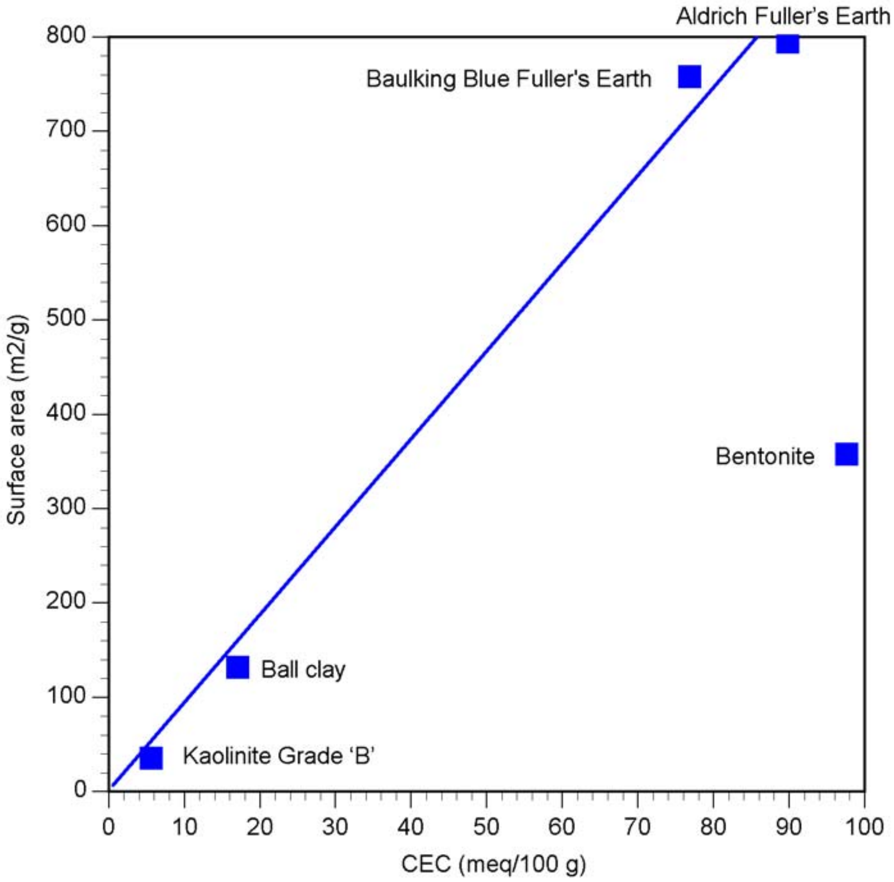


Figure 1. Cross-plot of CEC versus surface area for the compact clay samples.

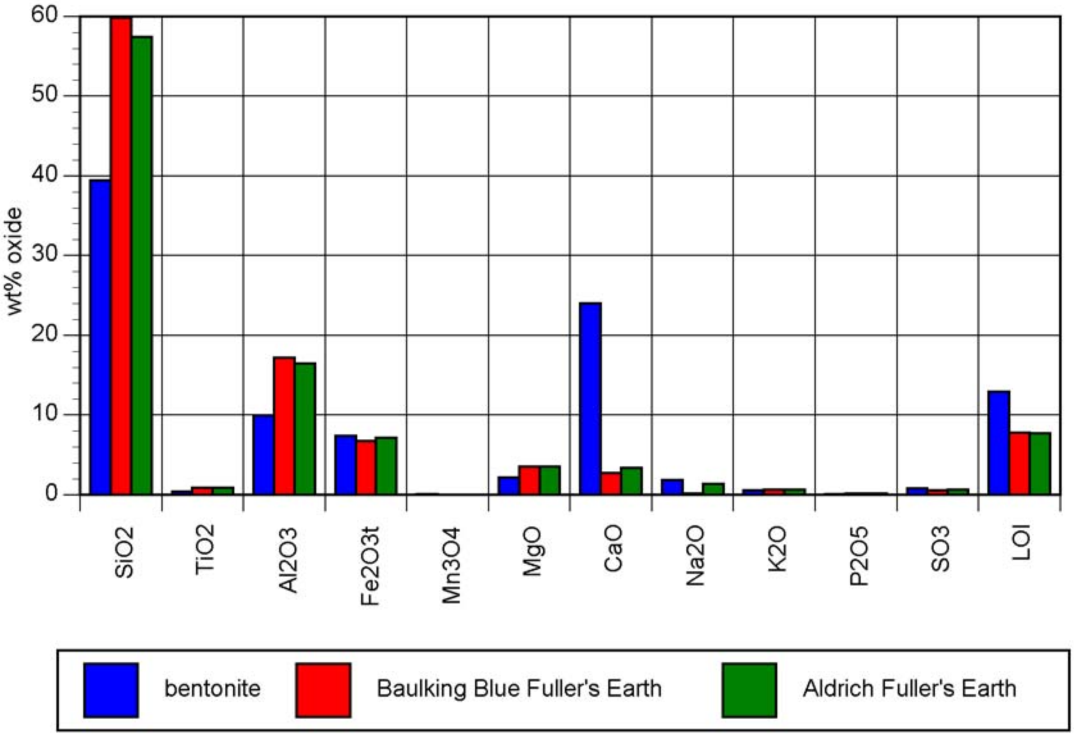


Figure 2. Summary of bentonite major element chemistry and loss-on-ignition (LOI)

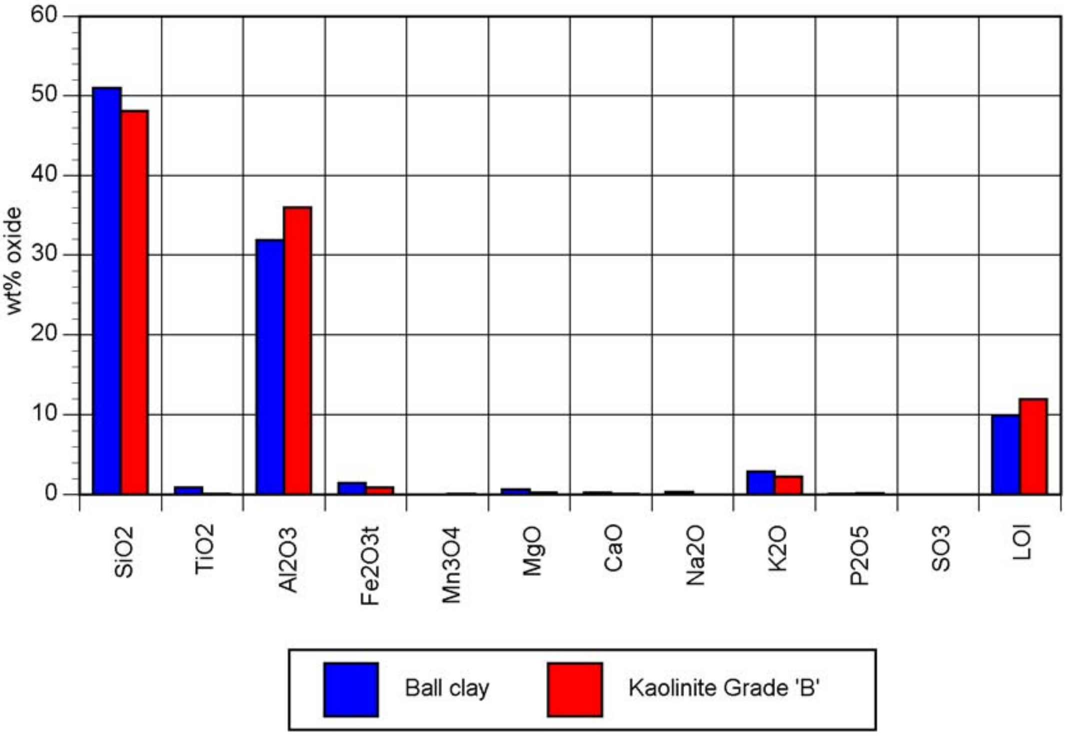


Figure 3. Summary of kaolinite major element chemistry and loss-on-ignition (LOI)

Appendix 1: X-RAY DIFFRACTION TRACES:

KEY

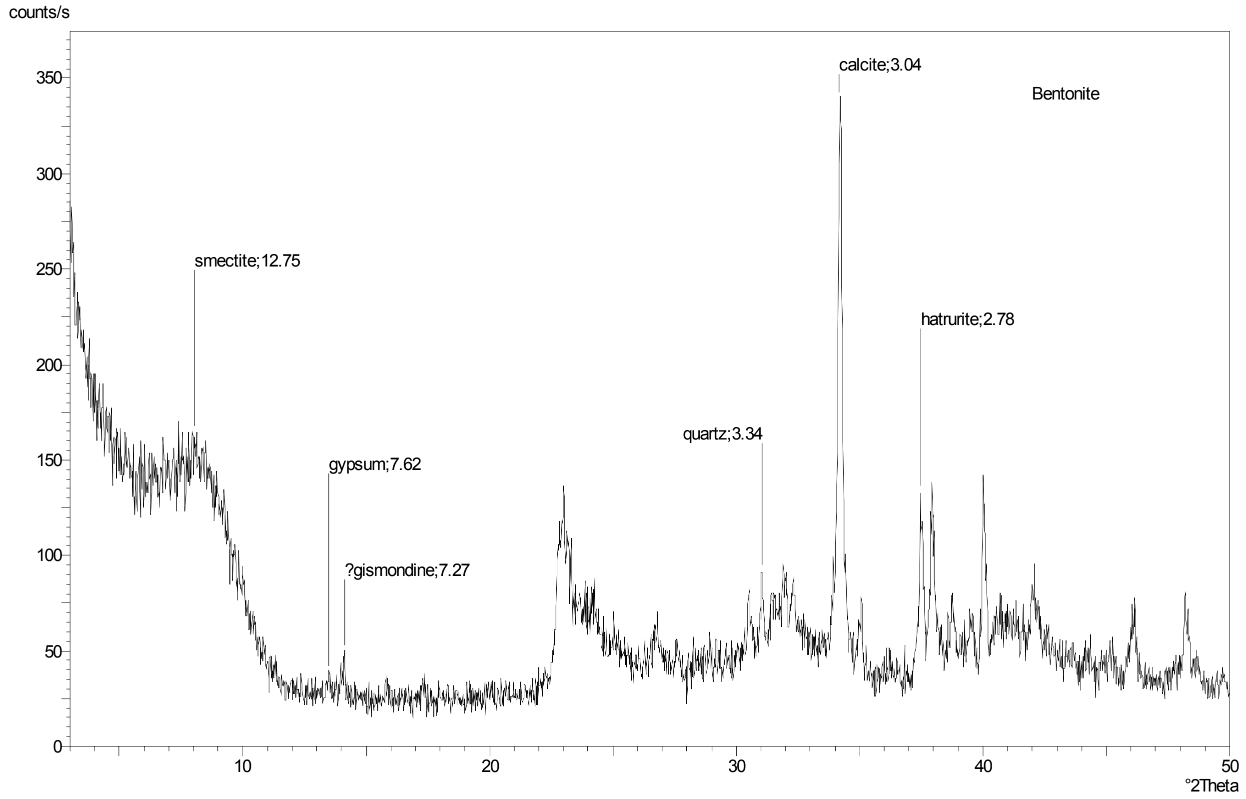
Vertical axis – Intensity (counts per second)

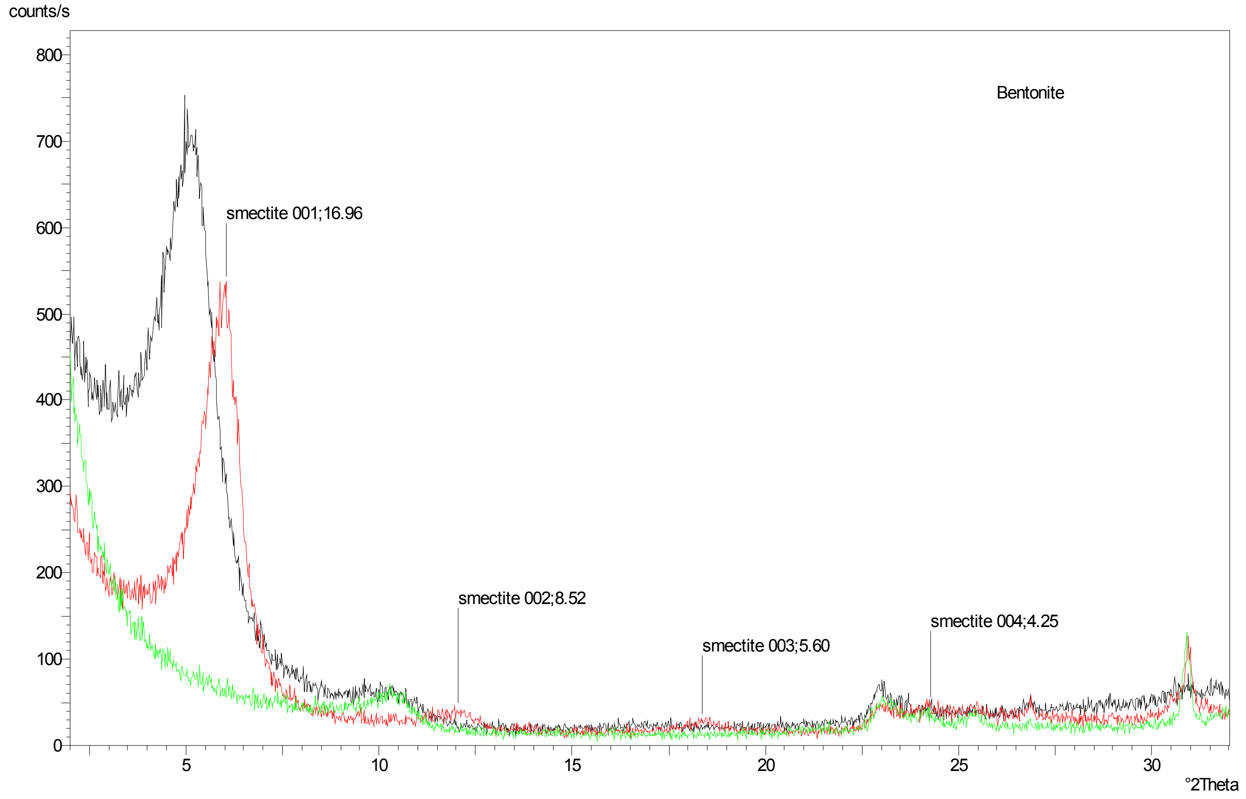
Horizontal axis - °2θ Co-Kα

For the whole-rock traces, only the most intense/diagnostic peak of each identified mineral is labelled.

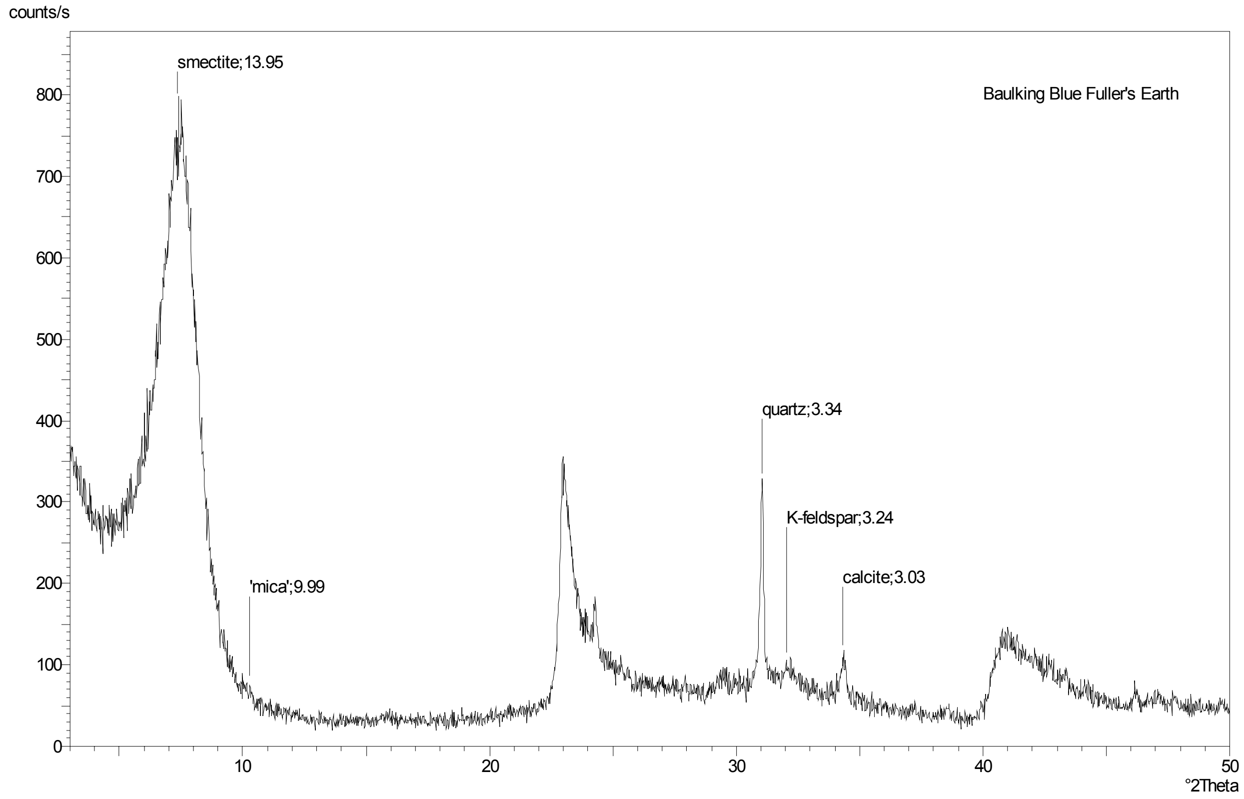
For the <2 µm traces. Black trace (air-dry), red trace (glycol-solvated) and green trace (heated 550°C/2 hours).

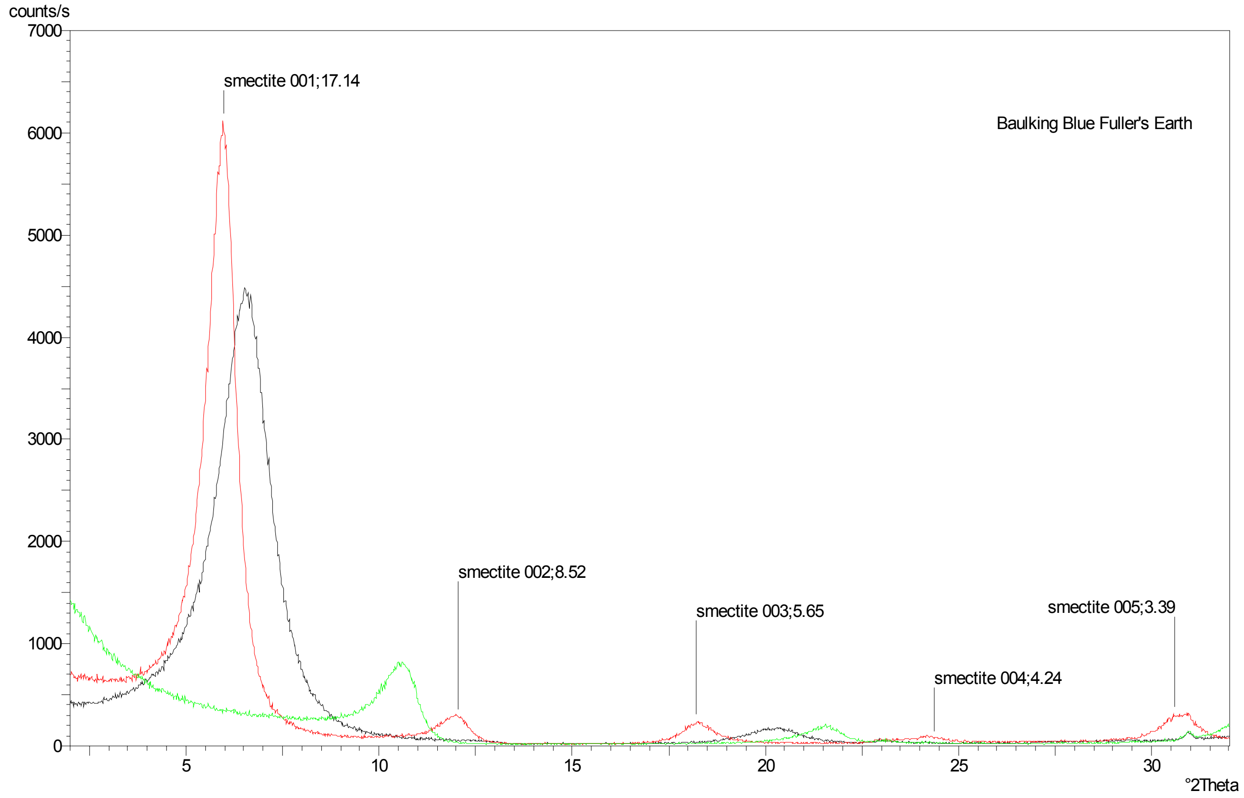
MPLJ883, Bentonite



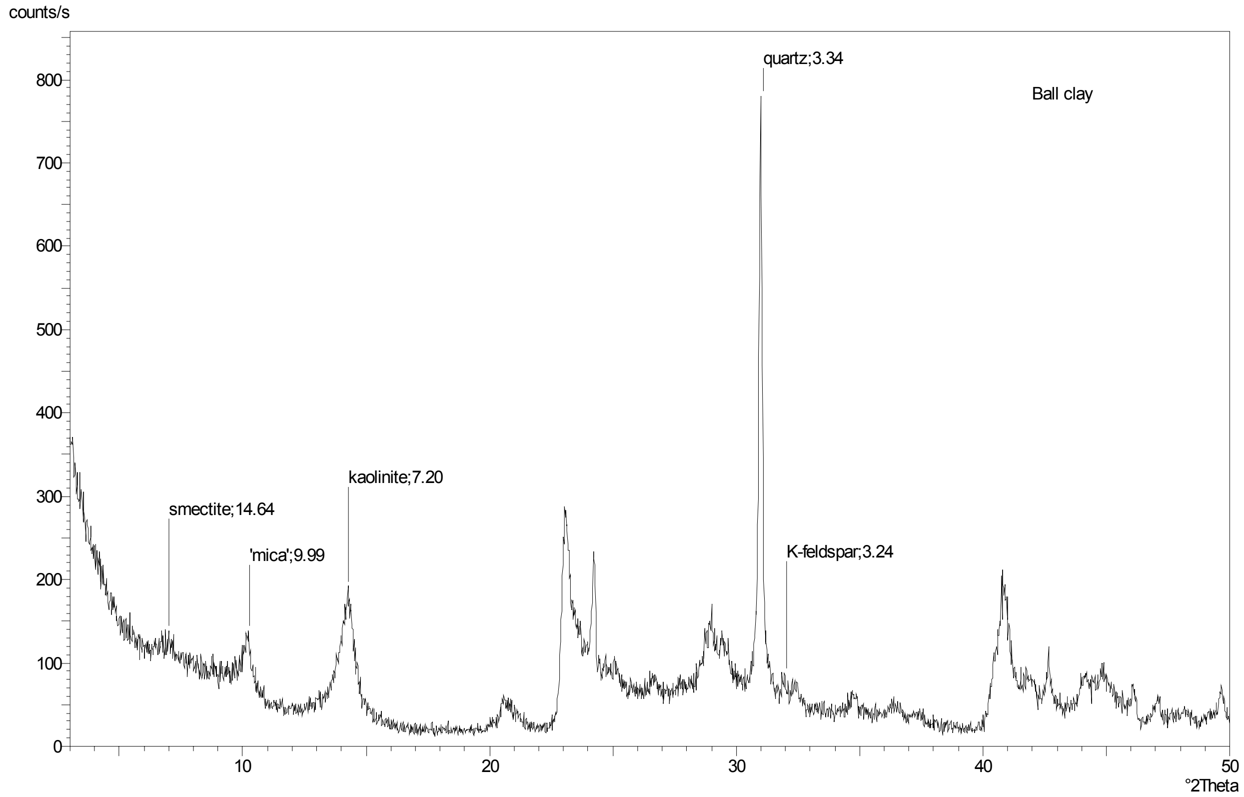


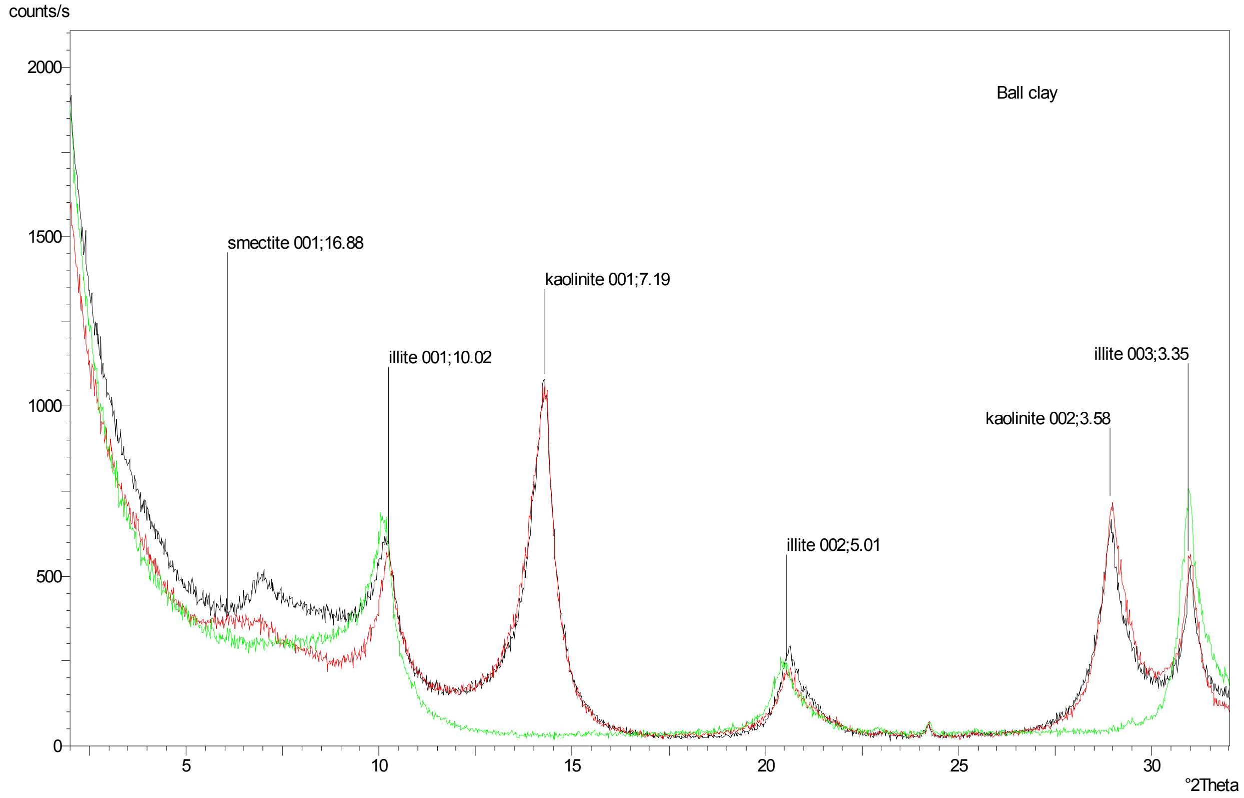
MPLJ884, Baulking Blue Fuller's Earth



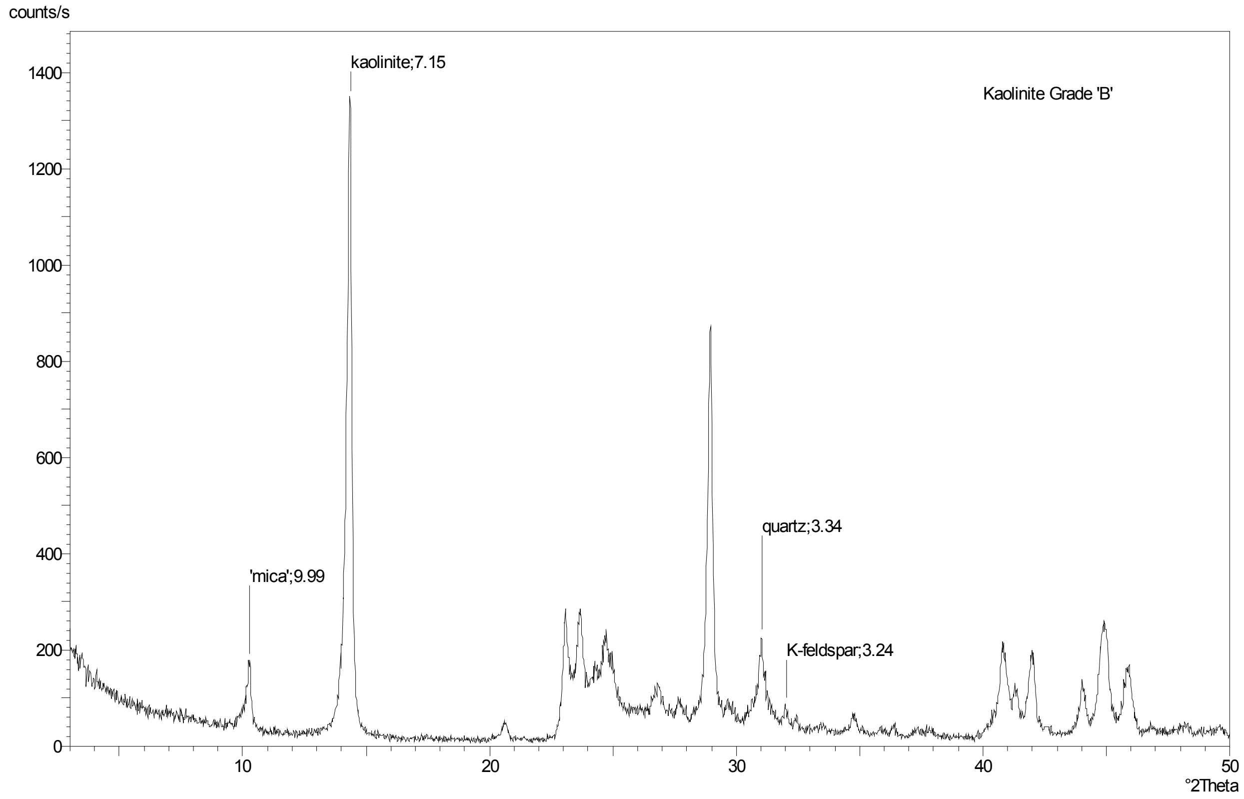


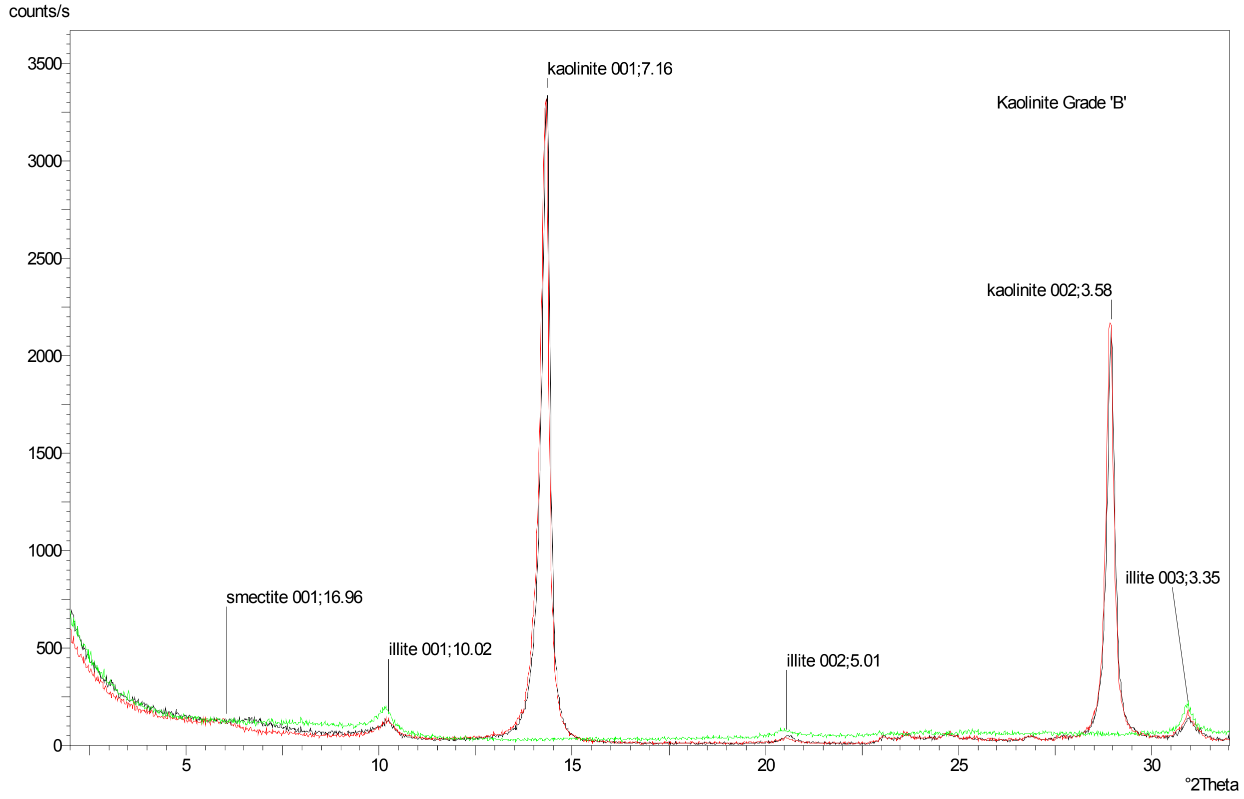
MPLJ885, Ball clay





MPLJ886, Kaolinite Grade 'B'





MPLK166, Aldrich Fuller's Earth