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The mineralogy and major-element geochemistry of samples of the Lias Group of England and Wales

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The mineralogy and major-element geochemistry of samples of the Lias Group of England and Wales

J A McKervey and H A Murphy

Key words

Lias Group, XRD analysis, surface area, mineralogy, geochemistry.

Front cover

Shrinkage cracks in sediment from the Whisby quarry.

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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 presents the results of X-ray diffraction (XRD) analysis, X-ray fluorescence (XRFS) analysis and surface area determinations of rocks from the Lias Group of England and Wales. It forms part of an ongoing project entitled Ground Movements: Shrink/Swell which aims to investigate the relationship between the shrinkage and swelling properties of UK clays and mudrocks (e.g. Jones, 2001). The aim of this report is to provide mineralogical and geochemical characterisation of the samples of the Lias Group collected by this project (see also Bouch, 2003 for SEM characterisation of these samples). The reader is also referred to Kemp and McKervey (2001) for a recent review of the mineralogy of the Lias Group in relation to its engineering properties.

2 Sampling

The outcrop of the Lias Group of England and Wales has been sub-divided into four main depositional areas: the Cleveland Basin, East Midlands Shelf, Worcester Basin (including the Bristol-Radstock shelf) and the Wessex Basin (including some parts of Somerset and south Wales) (Cox et al., 1999). In this study samples from each of the four depositional areas have been analysed: Cleveland Basin (n=5), East Midlands Shelf (n=13), Worcester Basin (n=5) and the Wessex Basin (n=11) (Table 1). In comparison to the study of Kemp and McKervey (2001), this study presents a less detailed view of the Cleveland Basin; new and similar locations of the East Midlands Shelf and Worcester Basin; and new locations in Somerset and south Glamorgan in the Wessex Basin.

3 Sample preparation and analysis

Representative portions of each sample were dried at 55 °C and then either hand-crushed in a pestle and mortar or jaw-crushed. Approximately ½ of this material was tema-milled to provide a powder sample for XRD, XRFS and surface area analysis. The remaining crushed material was retained for XRD analysis of the <2 μm fraction.

3.1 SURFACE AREA ANALYSIS

The surface area of each sample was determined using the 2-ethoxyethanol (ethylene glycol monoethyl ether, EGME) technique. Approximately 1.1 g of sample powder was weighed into an aluminium dish and placed in a desiccator containing anhydrous phosphorous pentoxide alongside a clay standard sample (Patterson Court Blue bentonite). The desiccator was evacuated and allowed to stand overnight before re-weighing the samples. The samples were then saturated with 2-ethoxyethanol and placed in the desiccator containing dry calcium chloride. After approximately 1.5 hours the desiccator was evacuated and left overnight. The samples were then weighed and the weight of 2-ethoxyethanol absorbed was determined and the surface area calculated. Finally, a small correction was applied to the surface area based on the result of the clay standard.

Smectite has a surface area of 800 m^2/g whereas 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.

3.2 XRD ANALYSIS: WHOLE ROCK AND < 2 μm FRACTION

Whole rock preparation: Approximately 3 g of the powdered sample was micronised under acetone for 10 minutes to provide a finer and more uniform particle size. The powder was then back-loaded into a standard aluminium sample holder for whole-rock XRD analysis.

<2 μm fraction preparation: The presence of carbonate cement in sedimentary rock samples can 'tie-up' clay minerals and prevent their release during sample preparation of the <2 μm fraction. Therefore where significant quantities of carbonate were identified by whole rock XRD analysis, carbonates were dissolved by the addition of sodium acetate/acetic acid buffer (pH 5.3) prior to the separation of the <2 μm fraction. Approximately 30 g of the crushed sample was placed in a plastic bottle and ~ 250 ml of the sodium acetate/acetic acid buffer solution added. The sample was treated with ultrasound for ~ 3 mins and placed in a water bath maintained at 60 °C stirring regularly. After 6 hours the sample was again treated with ultrasound for a further ~ 3 mins and left to stand overnight. When no further reaction between the sample and freshly added sodium acetate/acetic acid buffer was detected the sample was washed in deionised water using a centrifuge.

Either the carbonate-free material or approximately 15 g of jaw crushed material was dispersed in ~ 150 ml of de-ionised water using a reciprocal shaker overnight followed by ultrasound treatment for ~ 4 mins. The suspension was then wet sieved on 63 μm and the >63 μm fraction dried and retained. The <63 μm fraction was placed in a measuring cylinder and allowed to stand. To prevent flocculation, 1 ml of 0.1M 'Calgon' (sodium hexametaphosphate) was added to each cylinder. After a period determined from Stokes' Law, a nominal <2 μm fraction (the 'clay' fraction) was removed and dried at 55°C. The 2-63 μm fraction was also collected, dried and retained. 100 mg of the <2 μm material was then re-suspended in ~ 3 ml of deionised water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. The mounts were then Ca-saturated using 2 ml 0.1M $CaCl_2.6H_2O$ solution and finally 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 45 kV and 40 mA. The whole-rock samples were scanned from 3-50 °2θ at 0.7 °2θ/minute. The <2 μm oriented mounts were scanned from 2-32 °2θ at 0.55 °2θ/minute as air-dried mounts, after glycol-solvation and after heating to 550°C for two hours. Diffraction data were analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on a Gateway personal computer system.

3.3 XRFS ANALYSIS

XRFS analysis was performed on a subset of twelve samples at the BGS Analytical Geochemistry Laboratories for SiO_2, TiO_2, Al_2O_3, Fe_2O_3t, Mn_3O_4, MgO, CaO, Na_2O, K_2O, P_2O_5, Cr_2O_3, SrO, ZrO_2, BaO, SO_3, NiO, CuO, ZnO, PbO and loss on ignition (LOI) by fused glass bead analysis (procedure AGN 2.1.4). Fe_2O_3t represents total iron expressed as Fe_2O_3, and SO_3 represents sulphur retained in the fused bead after fusion at 1200°C. LOI was determined after 1 hour at 1050°C.

4 Results

Sample-by-sample results are given in Table 2 (whole rock XRD and surface area analysis), Table 3 (<2 μm fraction XRD analysis) and Table 4 (XRFS analysis). In addition, annotated XRD traces for each sample are illustrated in the Appendix. To provide semi-quantitative whole-rock XRD analyses, identified mineral phases are marked as major, minor or trace

constituents on the basis of relative X-ray intensity. Phases are classified as detected (d) or not detected (-) for the <2 μm fraction XRD analysis.

The minerals most commonly present are quartz, calcite, feldspar (albite and K-feldspar), 'mica' (undifferentiated mica species), chlorite, kaolinite and pyrite. Less commonly present are smectite, goethite, gypsum, dolomite, hematite, ?mixed-layer illite/smectite and more rare occurrences of ?siderite and jarosite are also found. Quartz, calcite and, in the ironstone samples, goethite are the dominant mineral phases. The twelve samples analysed for major element oxides display a range of SiO_2 from 37.66 to 76.25 wt %, broadly negatively correlated with a range in CaO from 0.01 to 19.25 wt %, illustrating the negative correlation between quartz and calcite content in these samples.

Clay mineral assemblages contain illite, kaolinite and chlorite in the main. Smectite has been identified from a number of samples and a mixed-layer illite/smectite has commonly been suggested to be present. The mixed layer illite/smectite is identified by the presence of a 'bridge' in the air-dried <2 μm fraction analysis between the chlorite 001 and illite 001 peaks. The range in Al_2O_3 content from 10.98 to 25.03 wt % in the samples analysed by XRFS points to range in clay mineral and /or 'mica' content, although variations in feldspar content may also occur. In general the samples from the south (e.g. Wessex and Worcester) are more likely to contain smectite and/or illite/smectite, whereas for the more northerly samples (e.g. East Midlands Shelf and Cleveland Basin) illite/smectite predominates. Similar regional variations in clay mineralogy were reported by Kemp and McKervey (2001), who suggested that such variations are related to differences in burial history and the increased burial of the northern basins compared to those in the south.

EGME surface areas range from 40 to 355 m^2/g, with a mean of 122 m^2/g. These results suggest that the clay mineral content of the samples varies considerably. This may be of particular interest to the engineering properties of the samples because the presence of clay minerals, most notably smectite or mixed layer illite/smectite, are commonly cited as the cause of shrink-swell behaviour in fine-grained sedimentary rocks. Combining the surface area results of this study with those of Kemp and McKervey (2001) suggests a mean surface area for the Lias Group of England and Wales of 110 m^2/g (n=61) with a range from 23 to 355 m^2/g.

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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Table 1: Summary of samples from the Lias Group of England and Wales.

Location	Sample	MPL code	NGR	Basin	Stratigraphy		Detailed location	Sample Description
					Formation	Member		
Dimmer, Somerset (landfill)	DM1	H279	ST 615 313	Wessex	Blue Lias/Charnmouth?	-	A new cell under construction	massive, mottled orange and light grey mudstone
Lake View, Somerset (quarry)	Lake View	H600	ST 548 304	Wessex	Blue Lias/Charnmouth	-	-	loosely cemented, massive, medium grey mudstone
Lliswerry, south Glam (quarry)	Rhoose	H601	ST 032 679	Wessex	Blue Lias	Porthkerry	-	poorly fissile, green-grey mudstone
Barry, south Glam (quarry)	Aberthaw	H604	ST 038 672	Wessex	Blue Lias	Porthkerry	-	loosely cemented, dark grey-black mudstone
Somerton, Somerset (quarry)	Station	H602	ST 532 290	Wessex	Blue Lias/Charnmouth	-	-	fissile, dark grey – black mudstone
Hamdon Hill, Somerset (quarry)	Hamdon	H603	ST 482 162	Wessex	Bridport Sand	-		massive, light brown ?mudstone/carbonate
Seatown	Seatown (Green ammonite)	J163	SY 412 918	Wessex	Charmouth Mudstone	Green ammonite beds	3m AOD	poorly fissile, dark grey mudstone
Seatown	Seatown (Eype clay)	J166	SY 425 915	Wessex	Dyrham Formation	Eype clay	2m AOD	poorly-fissile, grey, ?mudstone/carbonate
Black Ven	Black Ven (Belemnite marls)	J165	SY 355 932	Wessex	Charmouth Mudstone	Belemnite marls	74m AOD	massive, light grey, ?mudstone/carbonate
Black Ven	Black Ven (marls)	J162	SY 355 932	Wessex	Charmouth Mudstone	Black Ven marls	65m AOD	poorly-fissile, dark grey, mudstone
Black Ven	Black Ven (Shales with beef)	J161	SY 355 932	Wessex	Charmouth Mudstone	Shales with beef	24m AOD	fissile, grey, mudstone
Bishops Cleeve, Gloucs (landfill)	BC1	H284	SO 946 272	Worcester	Blue Lias	-	A new cell under construction	poorly fissile, medium grey mudstone
Bishops Cleeve, Gloucs (landfill)	BC2	H285	SO 946 272	Worcester	Blue Lias	-	A new cell under construction	massive, medium grey mudstone
Robin's Wood Hill, Gloucs (inactive brick pit)	RW2	H289	SO 836 149	Worcester	Marlstone Rock/Dyrham/Lower Lias	-	-	poorly fissile, light green-grey mudstone
Robin's Wood Hill, Gloucs (inactive brick pit)	RW3	H290	SO 836 149	Worcester	Marlstone Rock/Dyrham/Lower Lias	-	-	poorly fissile, light green-grey mudstone
Bishops Sutton, Avon (quarry)	Stowey	H609	ST 598 687	Worcester	White Lias or Blue Lias	-		massive, medium grey mudstone

Table 1 continued: Summary of samples from the Lias Group of England and Wales.

Location	Sample	MPL	NGR	Basin	Stratigraphy		Detailed location	Sample Description
Alkerton, Oxon (quarry)	AL1	H287	SP 395 429	?Worcester	Marlstone Rock	none	-	massive, light brown ?mudstone/carbonate
Hornton Grounds, Oxon (quarry)	HT1	H288	SP 382 449	?Worcester	Marlstone Rock	none	Base of the south face	massive, orange-brown ?mudstone/carbonate
Brixworth, Northants (landfill)	BW1	H280	SP 757 720	?E-Mids Shelf	Whitby Mdst	-	A new cell under construction	poorly fissile, medium-grey mudstone, rare fossil fragments
Sidegate Lane, Northants (landfill))	SL2	H282	SP 916 703	?E-Mids Shelf	Whitby Mdst	-	Cleared face at base of quarry and hand-dug pit	poorly fissile, medium-dark grey mudstone
Sidegate Lane, Northants (landfill)	SL1	H281	SP 916 703	?E Mids Shelf	Whitby Mdst	-	Cleared face at base of quarry and hand-dug pit	poorly fissile, medium-dark grey mudstone
old Southham Cement Works, Warcs (quarry)	SH1	H283	SP 419 630	E Mids Shelf	-	-	Base of east face of quarry	fissile, medium-dark grey mudstone
Edge Hill, Warcs (quarry)	EH1	H286	SP 375 474	?E Mids Shelf	Marlstone Rock	none	Base of the south face of quarry	orange-brown ?mudstone/carbonate
Barnstone quarry	Barnstone	J449	SK 735 335	E Mids Shelf	Scunthorpe Mudstone	Barnstone Limestone	25m AOD (0.2 bgl)	fissile, greenish grey, mudstone
Conesby quarry	Conesby S1	J450	SK 895 145	E Mids Shelf	Charmouth Mudstone	-	15m AOD (5m bgl)	massive, dark grey, mudstone
Conesby quarry	Conesby S2	J452	SK 895 147	E Mids Shelf	Charmouth Mudstone	-	21m AOD (9m bgl)	massive, dark grey, mudstone
Flixborough quarry	Flixborough	J453	SK 877 142	E Mids Shelf	Scunthorpe Mudstone	-	46m AOD (2m bgl)	poorly-fissile, some shell fragments, dark grey mudstone
Norton Bottoms	Norton Bottoms	J454	SK 867 360	E Mids Shelf	Scunthorpe Mudstone	-	11m AOD (9m bgl)	massive, grey, mudstone
Whisby quarry	Whisby	J455	SK 896 668	E Mids Shelf	Scunthorpe Mudstone	-	19m AOD (11m bgl)	massive, dark grey, mudstone
Kettleness, north Yorks (brick pit –cliff)	Kettleness	H605	NZ 833 160	Cleveland	Cleveland Ironstone	-	-	fissile, dark grey-black, mudstone
Runswick Bay, north Yorks (cliff)	Runswick	H606	NZ 817 154	Cleveland	Cleveland Ironstone or Whitby Mudstone	-	-	poorly fissile, dark grey-black mudstone
Robin Hood's Bay, north Yorks (cliff)	Robins Hood's Bay	H607	NZ 954 042	Cleveland	Redcar Mudstone	-	-	poorly cemented, massive, dark grey mudstone
Ravenscar, north Yorks (quarry)	Ravenscar	H608	NZ 971 015	Cleveland	Whitby Mudstone	Alum shale	-	fissile, dark grey-black mudstone
Ravenscar – 2	Ravenscar– 2	J164	NZ 971 015	Cleveland	Whitby Mudstone	Alum Shale	140m AOD (10m bgl)	poorly cemented, mottled, greenish-grey mudstone

Table 2: Summary of results of whole-rock XRD analysis and surface area determinations.

Basin	Sample	MPL code		quartz	calcite	albite	K-feldspar	'mica'	chlorite	kaolinite	smectite	goethite	gypsum	dolomite	pyrite	hematite	illite/smectite	siderite	jarosite	surface area (m2/g)
Wessex	Dimmer, DM1	H279		mj	mj	mi	mi	mi	mi	mi	-	-	-	mi	-	?tr	?mi	-	-	141
Wessex	Lake View	H600		mi	mj	-	-	mi	?tr	?tr	-	-	-	tr	mi	-	-	-	-	45
Wessex	Rhoose	H601		mj	mj	-	-	mi	?tr	?tr	-	-	-	-	-	-	-	-	-	40
Wessex	Aberthaw	H604		mj	mj	tr	-	mi	tr	?tr	-	-	-	tr	mi	-	-	-	-	124
Wessex	Station	H602		mi	mj	-	-	mi	-	-	-	-	-	-	mi	-	-	-	-	48
Wessex	Hamdon	H603		mj	mi	mi	mi	tr	-	-	?tr	-	-	tr	-	?tr	-	-	-	53
Wessex	Seatown (Green Ammonite)	J163		mj	mi	tr	tr	mi	mi	mi	-	-	-	-	mi	-	-	-	-	96
Wessex	Seatown (Eype Clay)	J166		mj	tr	mi	tr	mi	mi	mi	-	-	-	-	tr	-	?tr	-	-	91
Wessex	Black Ven (Belemnite Marls)	J165		mi	mj	-	tr	mi	mi	mi	-	-	-	mi	mi	-	-	-	-	69
Wessex	Black Ven (Marls)	J162		mj	mj	tr	tr	mi	mi	mi	-	-	tr	mi	mi	-	-	-	-	136
Wessex	Black Ven (Shales with Beef)	J161		mj	mi	tr	tr	mi	mi	mi	?tr	-	mi	tr	mi	-	-	-	-	216
Worcester	Bishops Cleeve, BC1	H284		mj	mj	mi	mi	mi	tr	mi	-	-	-	mi	tr	-	-	-	-	140
Worcester	Bishops Cleeve, BC2	H285		mj	mj	mi	mi	mi	mi	mi	-	-	-	mi	tr	-	-	-	-	88
?Worcester	Alkerton, AL1	H287		tr	mj	-	-	-	?mi	?tr	?tr	mi	-	-	-	-	-	?mi	-	129
Worcester	Robin's Wood Hill, RW2	H289		mj	--	mi	tr	mi	?mi	mi	?tr	-	mi	-	-	-	-	-	-	132
Worcester	Robin's Wood Hill, RW3	H290		mj	--	mi	tr	mi	?mi	mi	-	-	-	-	-	-	-	-	-	73
?Worcester	Horton, HT1	H288		mi	mi	-	-	-	?tr	?tr	?tr	mj	-	-	-	-	-	-	-	199
Worcester	Stowey	H609		mj	mj	-	tr	mi	mi	?tr	mj	-	-	-	mi	-	-	-	-	355
?E-Midlands Shelf	Brixworth, BW1	H280		mj	-	mi	mi	mi	mi	mi	-	-	tr	-	mi	-	-	-	-	98

Table 2 continued: Summary of results of whole-rock XRD analysis and surface area determinations.

Basin	Sample	MPL code		quartz	calcite	albite	K-feldspar	'mica'	chlorite	kaolinite	smectite	goethite	gypsum	dolomite	pyrite	hematite	illite/smectite	siderite	jarosite	surface area (m^2/g)
?E-Midlands Shelf	Sidegate Lane, SL1	H281		mj	-	mi	mi	mi	mi	mi	-	-	tr	-	mi	-	?tr	-	-	126
?E-Midlands Shelf	Sidegate Lane, SL2	H282		mj	-	tr	mi	mi	tr	mi	-	-	tr	-	mi	-	-	-	-	124
E-Midlands Shelf	Southam, SH1	H283		mi	mi	mi	mi	mi	tr	mi	?mi	-	tr	mi	mi	-	?tr	-	-	208
?E-Midlands Shelf	Edgehill, EH1	H286		-	mj	-	-	-	?mi	?tr	?tr	mi	-	-	-	-	-	?mi	-	146
E-Midlands Shelf	Barnstone	J449		mi	mj	-	-	mi	mi	?tr	-	-	-	mi	tr	-	-	-	-	89
E-Midlands Shelf	Conesby, S1	J450		mj	-	tr	tr	mi	mi	mi	-	-	-	-	tr	-	?tr	-	-	165
E-Midlands Shelf	Conesby, S2	J452		mj	mi	?tr	-	mi	mi	mi	-	-	-	-	mi	-	?tr	-	-	137
E-Midlands Shelf	Flixborough	J453		mj	mi	-	?tr	mi	mi	mi	-	-	-	?tr	tr	-	?tr	-	-	131
E-Midlands Shelf	Norton Bottoms	J454		mj	mj	tr	tr	mi	mi	mi	-	-	-	-	tr	-	?tr	-	-	123
E-Midlands Shelf	Whisby	J455		mj	mi	tr	tr	mi	mi	mi	-	-	-	-	tr	-	?tr	-	-	143
Cleveland	Kettleness	H605		mj	-	tr	-	mi	mi	mi	-	-	-	-	tr	-	?mi	-	-	122
Cleveland	Runswick	H606		mj	mi	mi	-	mi	mi	mi	-	-	-	-	mi	-	?tr	-	-	70
Cleveland	Robin Hood's Bay	H607		mj	-	mi	-	mi	?tr	mi	-	-	-	-	-	-	?tr	-	-	64
Cleveland	Ravenscar	H608		mj	-	mi	-	mi	tr	mi	-	-	-	-	-	-	?tr	-	-	116
Cleveland	Ravenscar - 2	J164		mj	-	tr	-	mi	mi	mi	-	-	-	-	-	-	?mi	-	mi	121

mj=major component; mi=minor component; tr=trace component.
- = not detected

Table 3: Summary of results of <2 μm fraction XRD analysis.

Basin	Sample	MPL code		smectite	illite	chlorite	kaolinite	illite/smectite	quartz	goethite	feldspar	jarosite
Wessex	Dimmer, DM1	H279		-	d	d	d	?d	d	d	-	-
Wessex	Lake View	H600		-	d	d	d	?d	d	-	-	-
Wessex	Rhoose	H601		?d	d	-	-	?d	d	-	-	-
Wessex	Aberthaw	H604		?d	d	d	d	?d	d	-	?d	-
Wessex	Station	H602		-	d	d	d	?d	d	-	?d	-
Wessex	Hamdon	H603		?d	d	d	d	?d	-	d	-	-
Wessex	Seatown (green ammonite)	J163		d	d	d	d	-	d	-	-	-
Wessex	Seatown (eype clay)	J166		d	d	d	d	-	d	-	-	-
Wessex	Black Ven (belemenite marls)	J165		-	d	d	d	?d	d	-	?d	-
Wessex	Black Ven (marls)	J162		-	d	d	d	?d	d	-	-	-
Wessex	Black Ven (shales with beef)	J161		d	d	d	d	-	d	-	-	-
Worcester	Bishops Cleeve, BC1	H284		-	d	d	d	?d	d	-	-	-
Worcester	Bishops Cleeve, BC2	H285		-	d	d	d	?d	d	-	-	-
?Worcester	Alkerton, AL1	H287		?d	-	d	d	-	-	d	-	-
Worcester	Robin's Wood Hill, RW2	H289		d	d	d	d	?d	d	-	-	-
Worcester	Robin's Wood Hill, RW3	H290		?d	d	d	d	?d	d	-	-	-
?Worcester	Hornton, HT1	H288		d	d	?d	d	-	-	d	-	-
Worcester	Stowey	H609		d	d	d	d	-	d	-	-	-
?E-Midlands Shelf	Brixworth, BW1	H280		-	d	d	d	?d	d	-	-	-

Table 3 continued: Summary of results of <2 μm fraction XRD analysis.

Basin	Sample	MPL code		smectite	illite	chlorite	kaolinite	illite/smectite	qtz	goethite	feldspar	jarosite
?E-Midlands Shelf	Sidegate Lane, SL1	H281		-	d	d	d	?d	d	-	-	-
?E-Midlands Shelf	Sidegate Lane, SL2	H282		-	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Southam, SH1	H283		d	d	d	d	?d	d	-	-	-
?E-Midlands Shelf	Edgehill, EH1	H286		d	d	-	d	-	-	d	-	-
E-Midlands Shelf	Barnstone	J449		-	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Conesby, S1	J450		-	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Conesby, S2	J452		?d	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Flixborough	J453		-	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Norton Bottoms	J454		-	d	d	d	?d	d	-	-	-
E-Midlands Shelf	Whisby	J455		-	d	d	d	?d	d	-	-	-
Cleveland	Kettleness	H605		-	d	d	d	?d	d	-	-	-
Cleveland	Runswick	H606		-	d	d	d	?d	d	-	-	-
Cleveland	Robin Hood's Bay	H607		-	d	d	d	?d	d	-	-	-
Cleveland	Ravenscar	H608		-	d	d	d	?d	d	-	-	-
Cleveland	Ravenscar - 2	J164		-	d	d	d	?d	d	-	-	d

d = detected

- = not detected

Table 4: Results of results of XRFS analysis (in wt% oxide).

Basin	Sample	MPL code	SiO_2	TiO_2	Al_2O_3	Fe_2O_3t	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cr_2O_3	SrO	ZrO_2	BaO	NiO	CuO	ZnO	PbO	LOI	Total
Wessex	Dimmer, DM1	H279	39.73	0.72	15.23	5.13	0.09	1.72	15.75	0.27	2.64	0.18	<0.1	0.01	0.04	<0.02	0.03	<0.01	<0.01	0.01	<0.01	18.05	99.60
Worcester	Bishops Cleeve, BC2	H285	37.66	0.60	10.98	5.19	0.12	2.18	19.25	0.37	2.00	0.09	1.0	0.02	0.04	0.03	0.04	<0.01	<0.01	<0.01	<0.01	19.77	99.34
Worcester	Robin's Wood Hill ,	H289	58.23	1.03	19.15	5.48	0.02	1.44	1.52	0.72	2.79	0.18	0.9	0.02	0.02	0.02	0.05	<0.01	<0.01	<0.01	<0.01	8.31	99.88
Worcester	Stowey	H609	51.61	0.74	17.13	5.82	0.04	3.53	5.67	0.10	3.61	0.04	<0.1	0.02	0.03	<0.02	0.05	0.01	<0.01	<0.01	<0.01	10.68	99.08
?E Mids Shelf	Brixworth , BW1	H280	56.15	1.04	19.17	6.94	0.03	1.61	1.05	0.28	2.96	0.22	0.2	0.02	0.01	0.03	0.05	<0.01	<0.01	0.01	<0.01	9.63	99.40
?E Mids Shelf	Sidegate Lane , SL1	H281	55.48	1.03	19.99	6.82	0.02	1.73	0.70	0.26	3.10	0.15	0.3	0.02	0.02	0.03	0.05	0.01	<0.01	0.01	<0.01	9.75	99.47
E Mids Shelf	Southam, SH1	H283	45.13	0.80	18.15	6.29	0.06	2.73	7.69	0.35	2.92	0.12	0.6	0.02	0.05	<0.02	0.04	0.01	<0.01	0.01	<0.01	14.26	99.23
E Mids Shelf	Conesby, S1	J452	42.25	0.81	18.02	7.26	0.11	1.53	9.30	0.22	2.42	0.06	0.3	0.02	0.04	0.02	0.04	<0.01	<0.01	0.01	<0.01	17.04	99.45
E Mids Shelf	Flixborough	J453	54.90	0.93	17.45	6.97	0.05	1.80	3.63	0.22	2.72	0.12	0.3	0.02	0.02	0.03	0.04	<0.01	<0.01	0.01	<0.01	10.21	99.42
Cleveland	Robin Hood's Bay	H607	76.25	0.96	12.02	2.25	<0.01	0.56	0.29	0.45	1.49	0.06	<0.1	0.02	<0.01	0.08	0.04	<0.01	<0.01	<0.01	<0.01	4.49	98.96
Cleveland	Ravenscar	H608	53.19	1.05	25.03	4.25	<0.01	1.27	0.01	0.14	3.34	0.10	<0.1	0.02	0.02	<0.02	0.05	<0.01	<0.01	<0.01	<0.01	11.00	99.47
Cleveland	Ravenscar - 2	J164	55.94	1.13	21.70	5.74	0.01	1.22	0.04	0.28	3.08	0.14	0.1	0.02	0.02	0.03	0.05	<0.01	<0.01	<0.01	<0.01	10.10	99.60

Appendix

Annotated whole-rock and <2 μm fraction X-ray diffraction traces are presented for each sample. Only the most intense/characteristic peak is labelled for each mineral.

Key to the whole-rock X-ray diffraction traces:

X-axis: °2θ Co-Kα

Y-axis: (Intensity) counts per second

Peak Labels: mineral and d-spacing (Å)

Blue trace: whole-rock powder

Key to the <2 μm diffraction traces:

X-axis: °2θ Co-Kα

Y-axis: (Intensity) counts per second

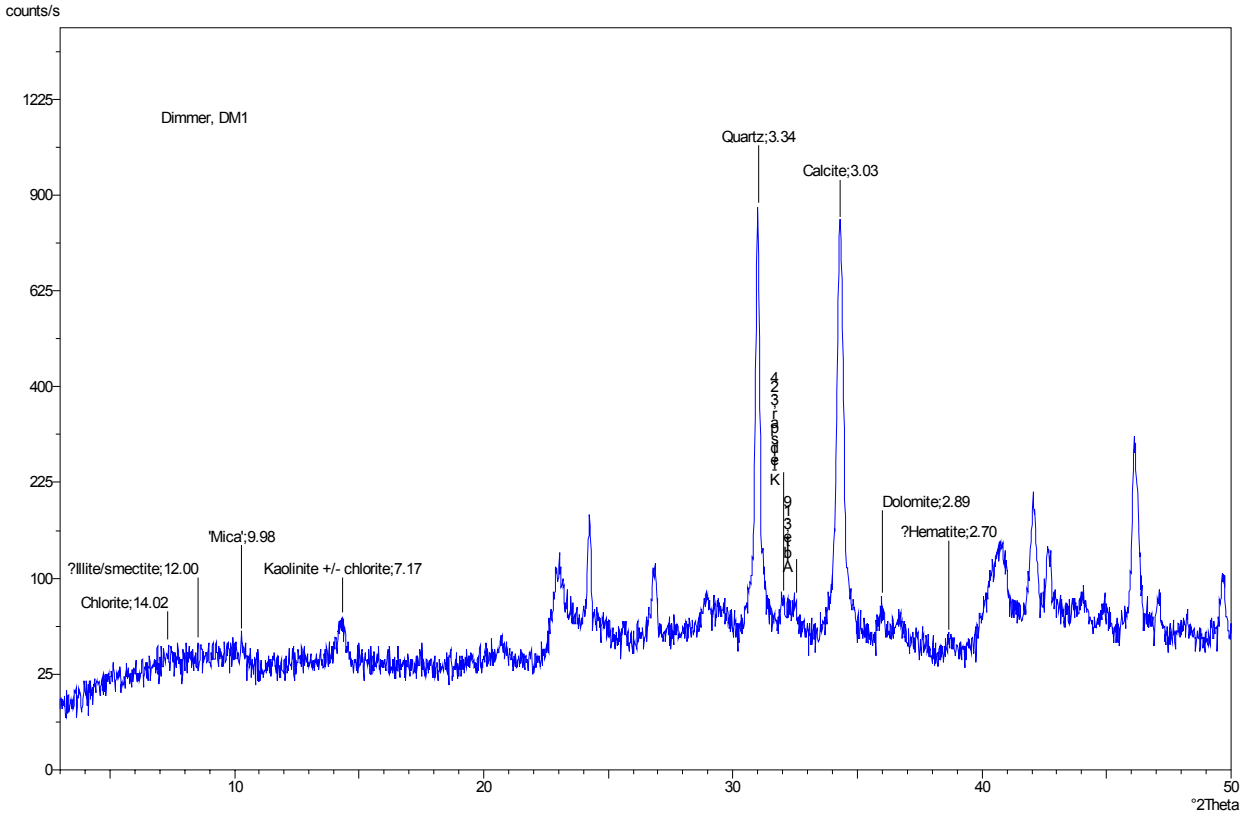
Peak Labels: mineral and d-spacing (Å)

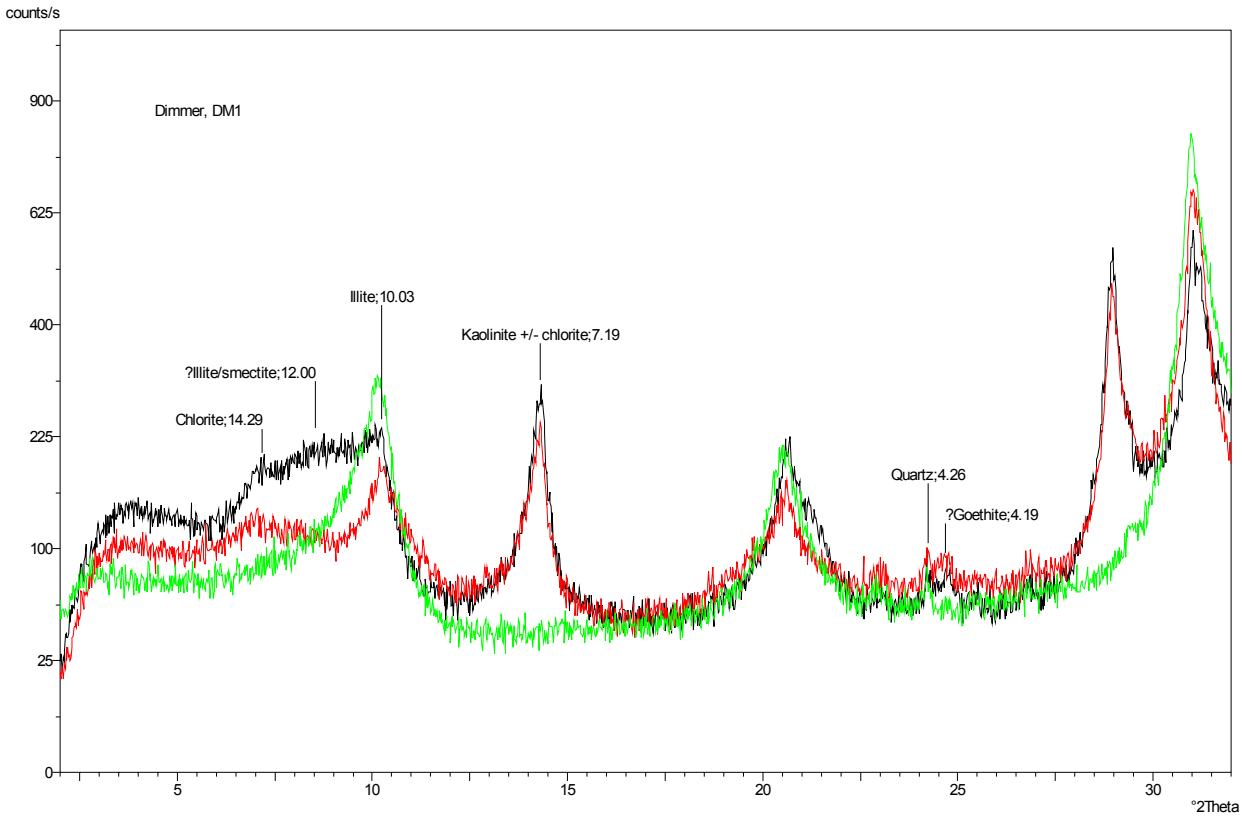
Black trace: air-dried oriented mount

Red trace: glycol-solvated oriented mount

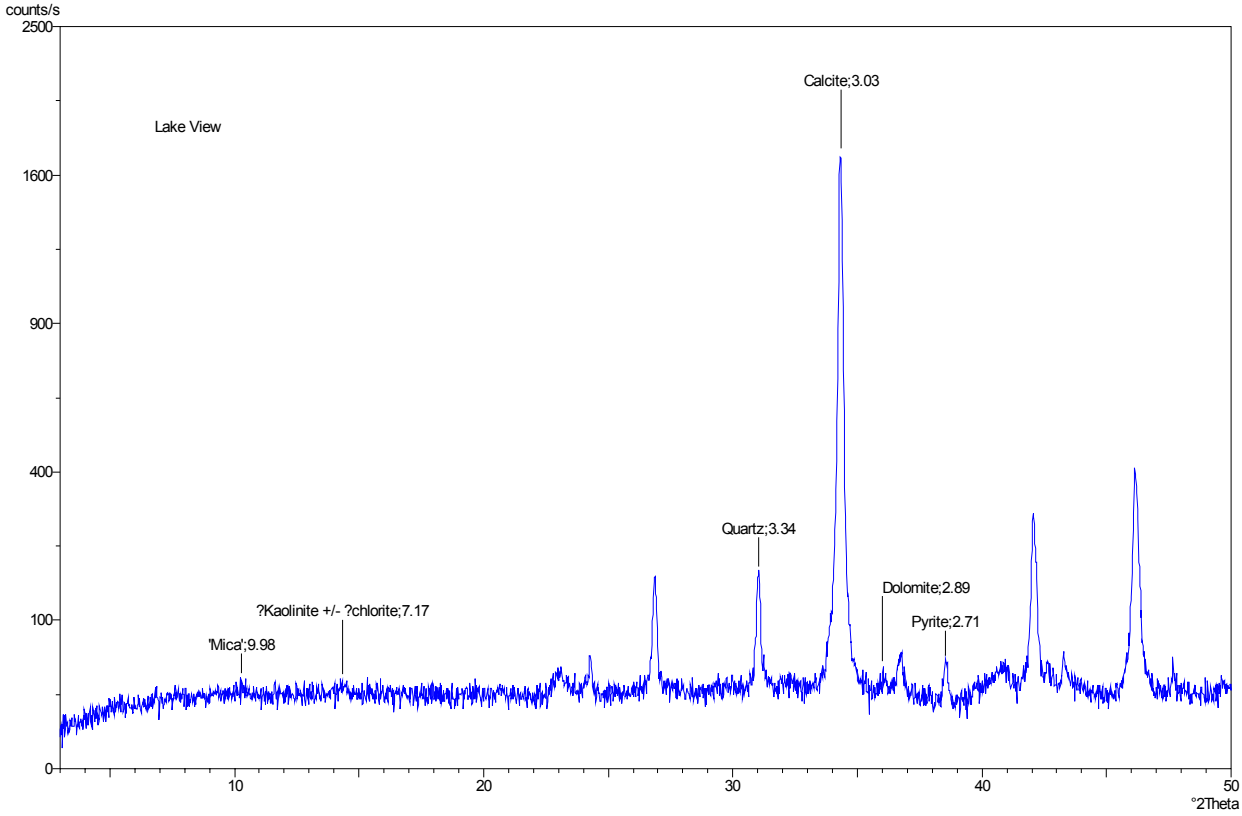
Green trace: heated (550°C for 2 hours) oriented mount

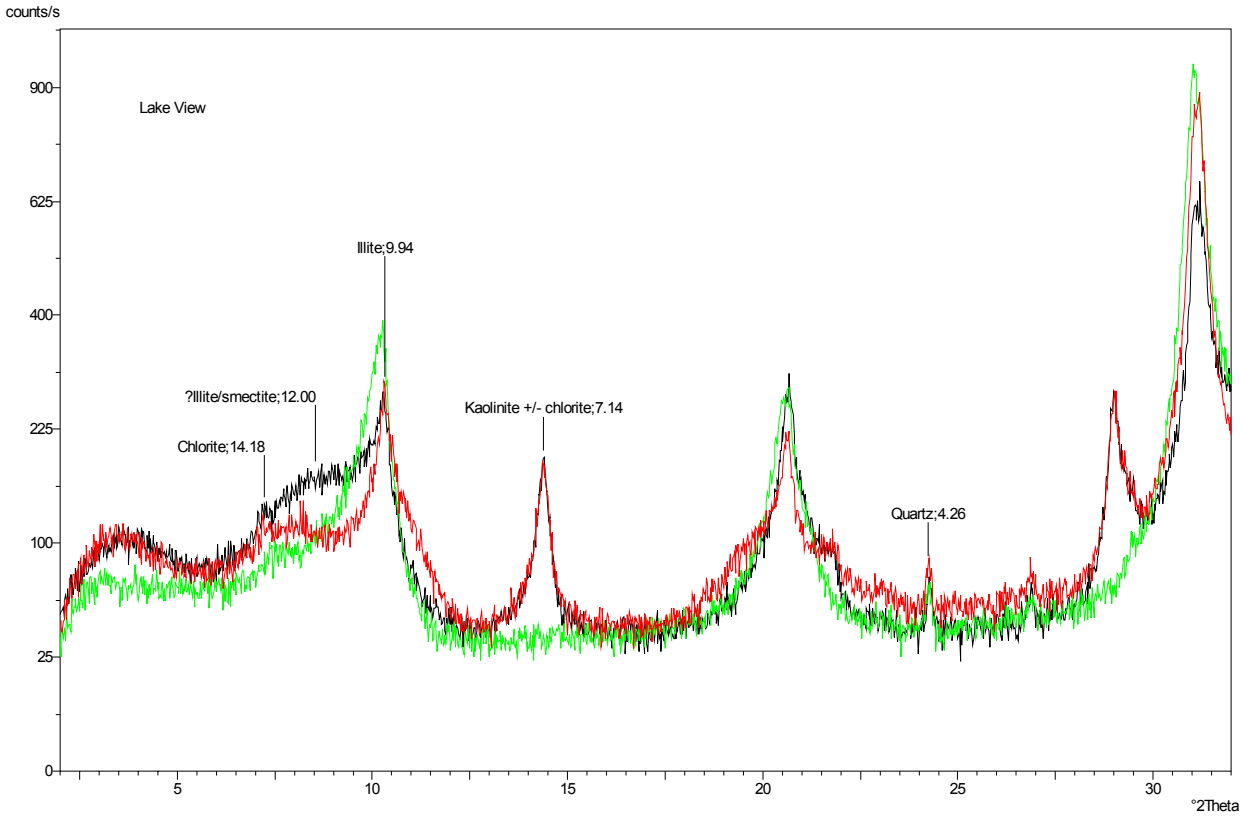
Dimmer, DM1


counts/s
Dimmer, DM1
Quartz;3.34
Calcite;3.03
Dolomite;2.89
?Hematite;2.70
'Mica';9.98
?Illite/smectite;12.00
Kaolinite +/- chlorite;7.17
Chlorite;14.02
°2Theta

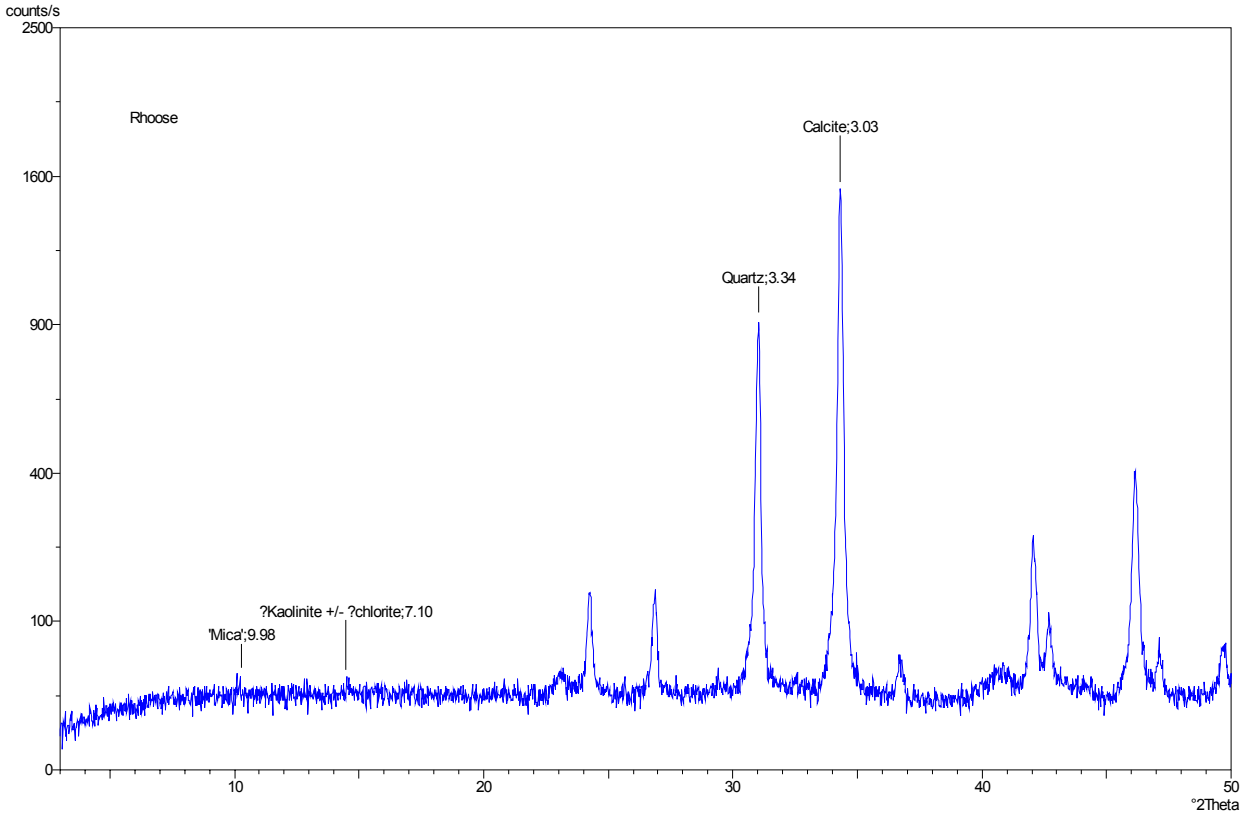

counts/s
Dimmer, DM1
Illite;10.03
Kaolinite +/- chlorite;7.19
?Illite/smectite;12.00
Chlorite;14.29
Quartz;4.26
?Goethite;4.19
°2Theta

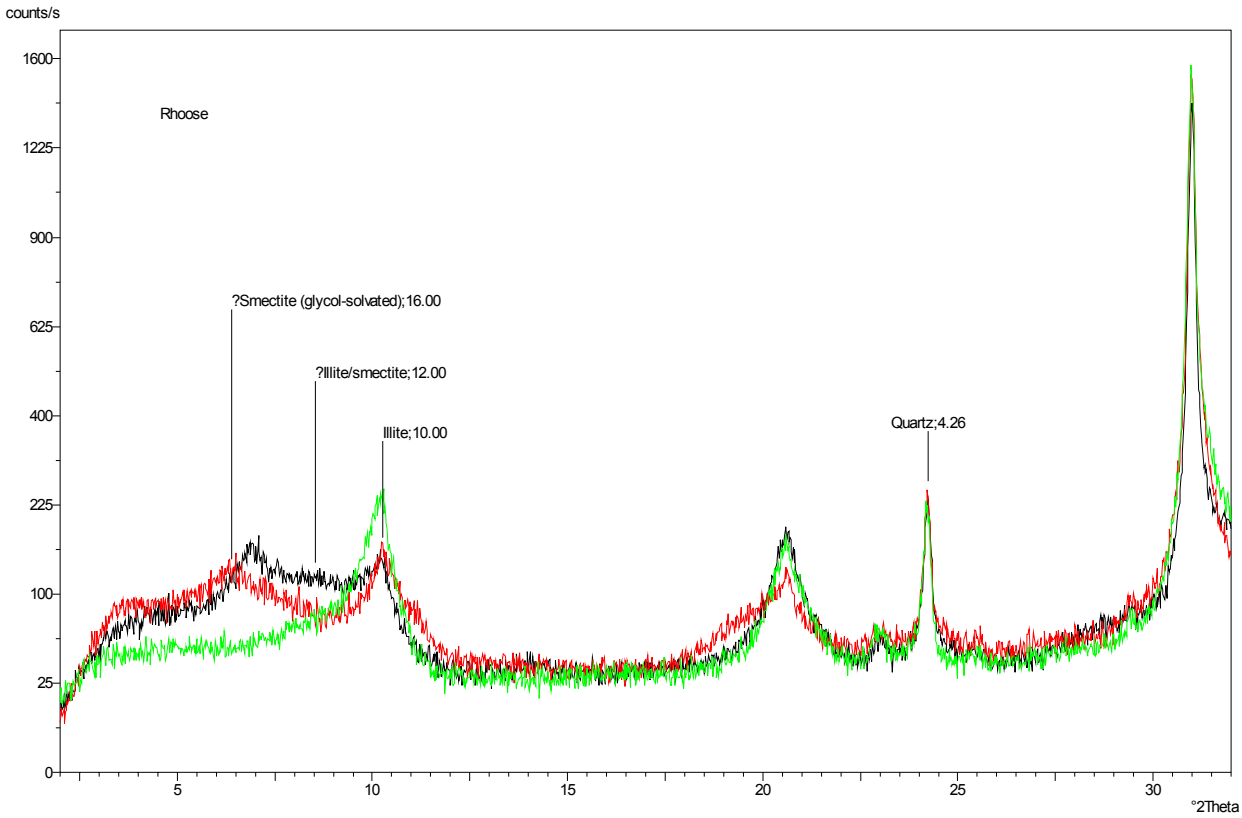
Lake View


counts/s
2500
1600
900
400
100
0
Lake View
Calcite;3.03
Quartz;3.34
Dolomite;2.89
Pyrite;2.71
?Kaolinite +/- ?chlorite;7.17
'Mica';9.98
10
20
30
40
50
°2Theta

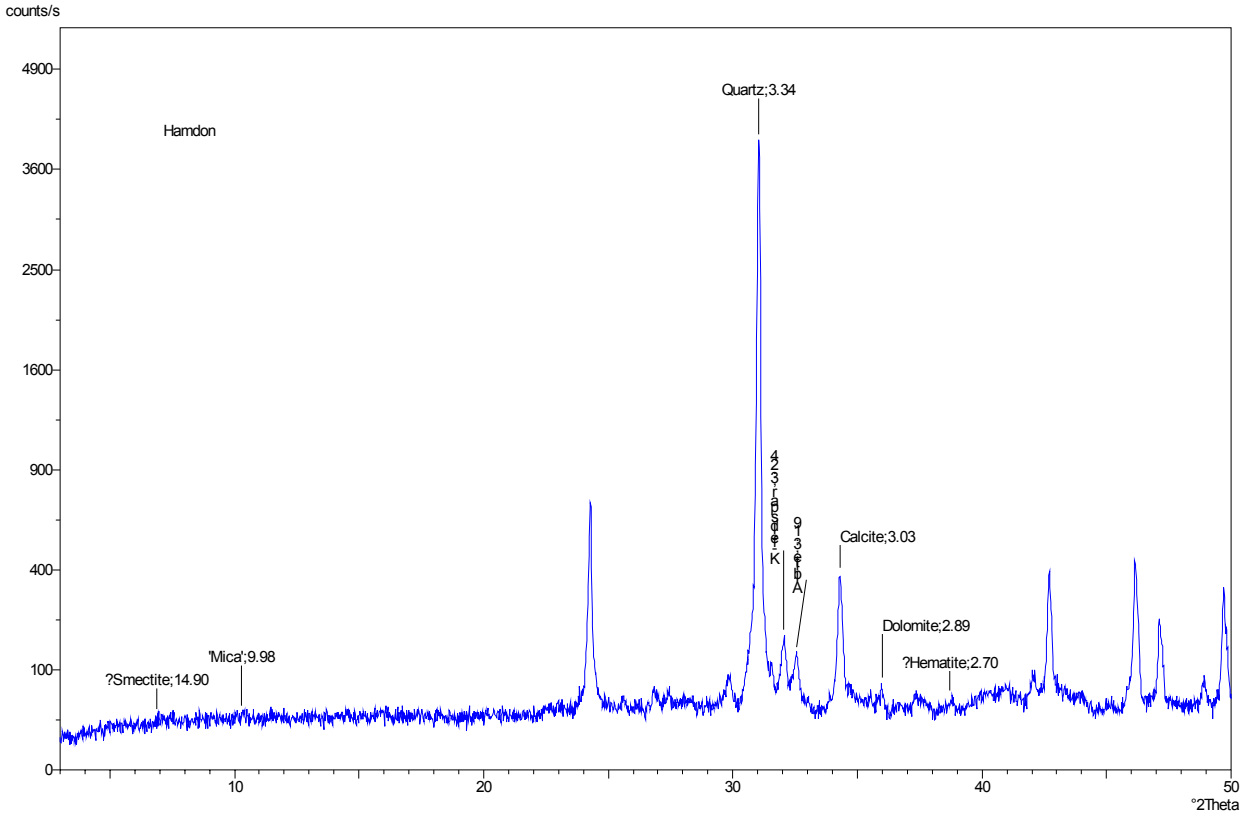

counts/s
900
625
400
225
100
25
0
Lake View
Illite;9.94
?Illite/smectite;12.00
Chlorite;14.18
Kaolinite +/- chlorite;7.14
Quartz;4.26
5
10
15
20
25
30
°2Theta

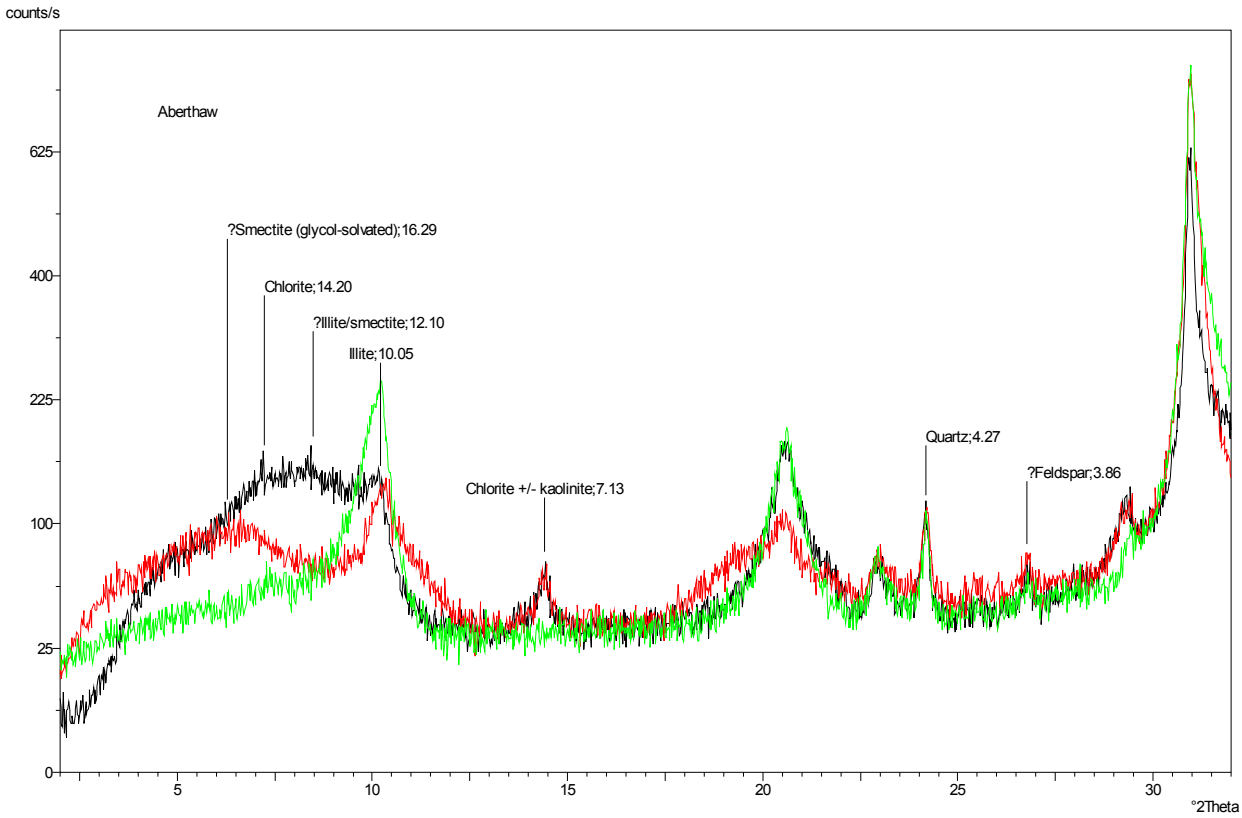
Lliswerry, Rhoose



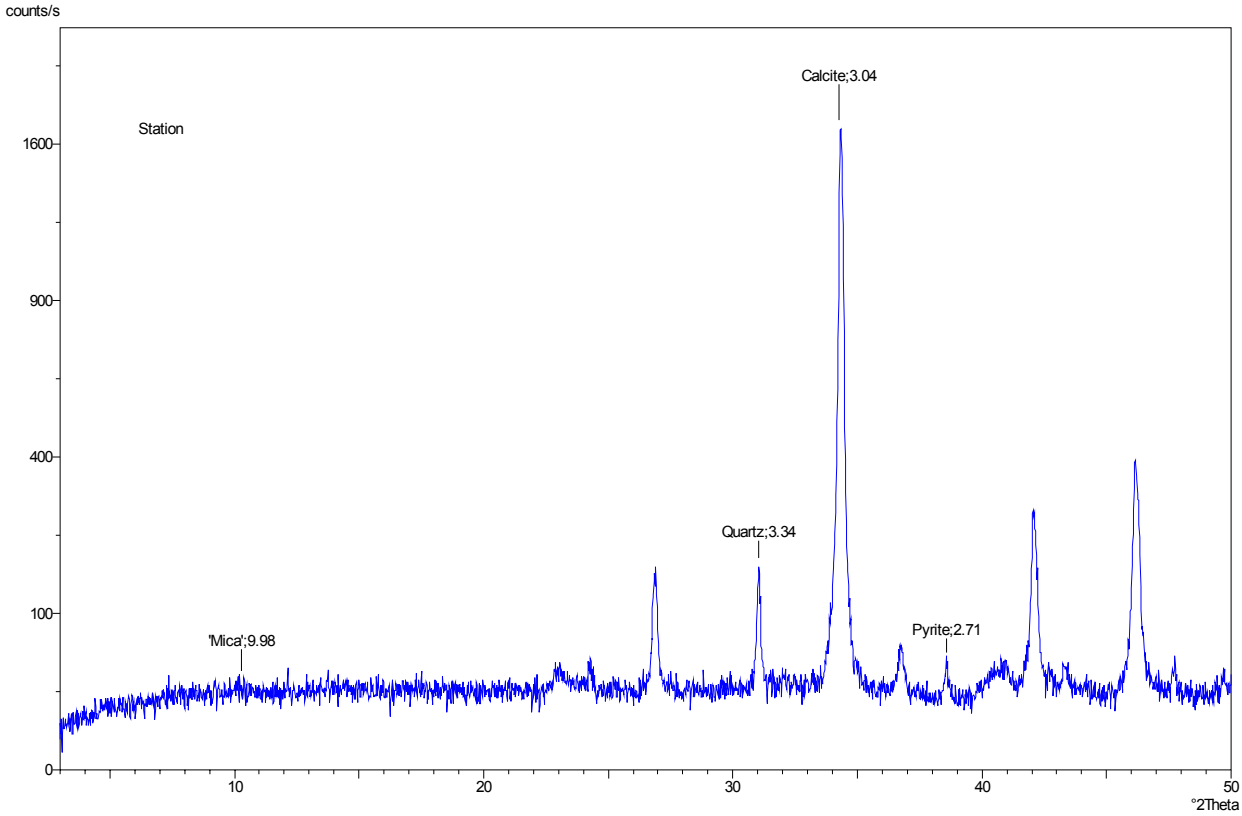


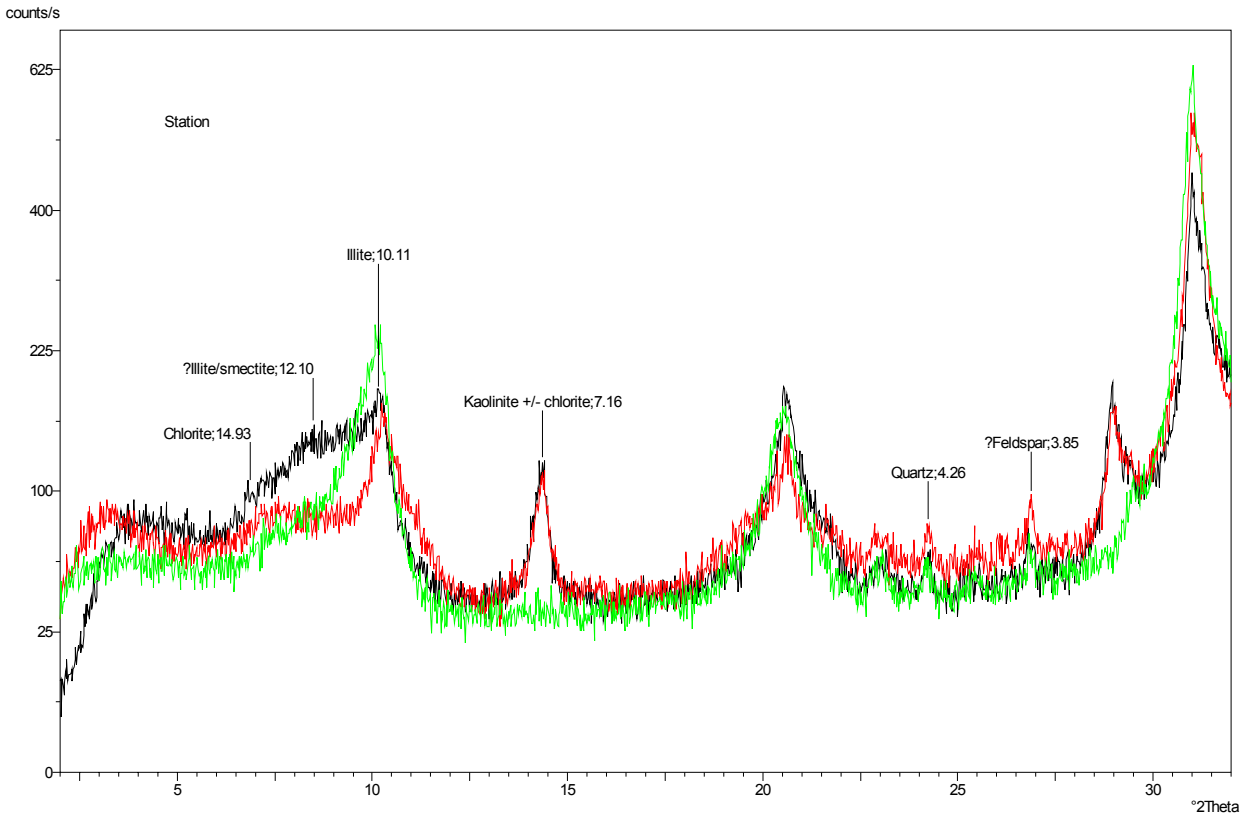
Barry, Aberthaw



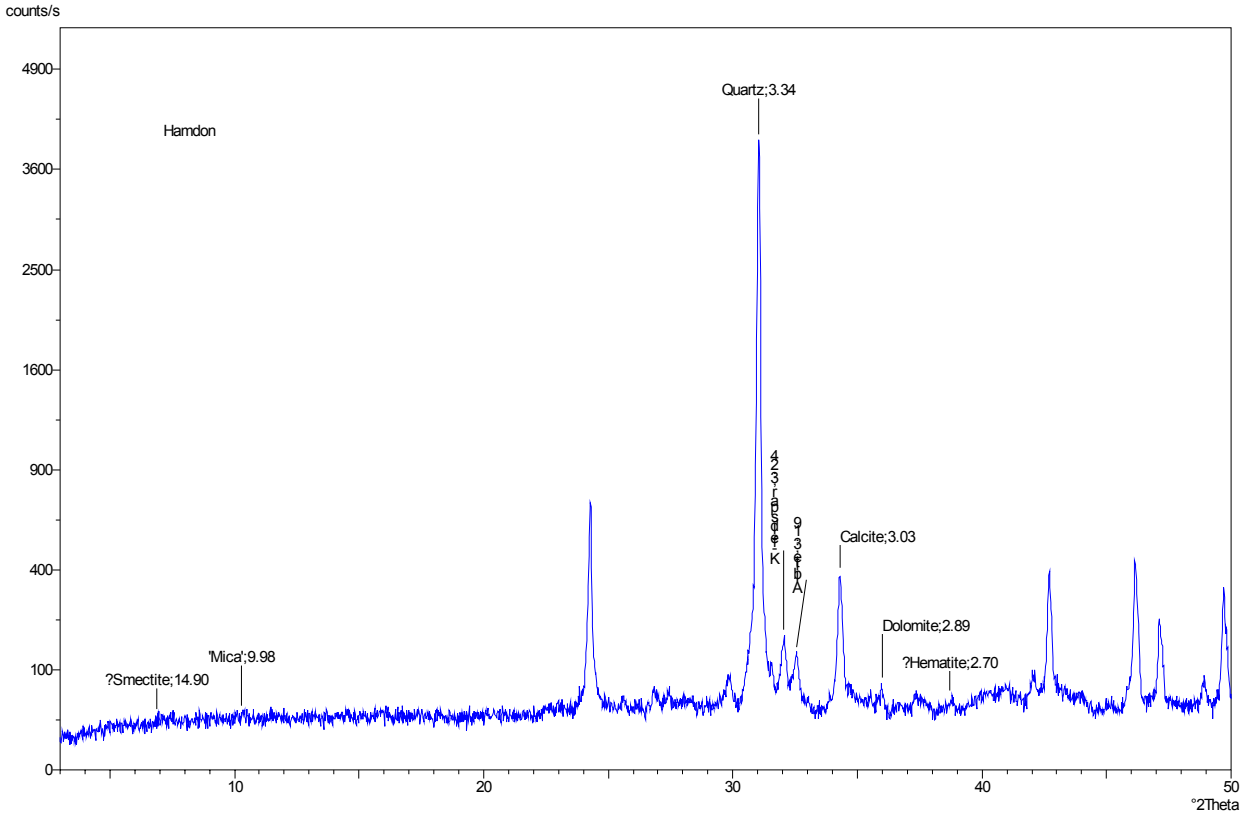


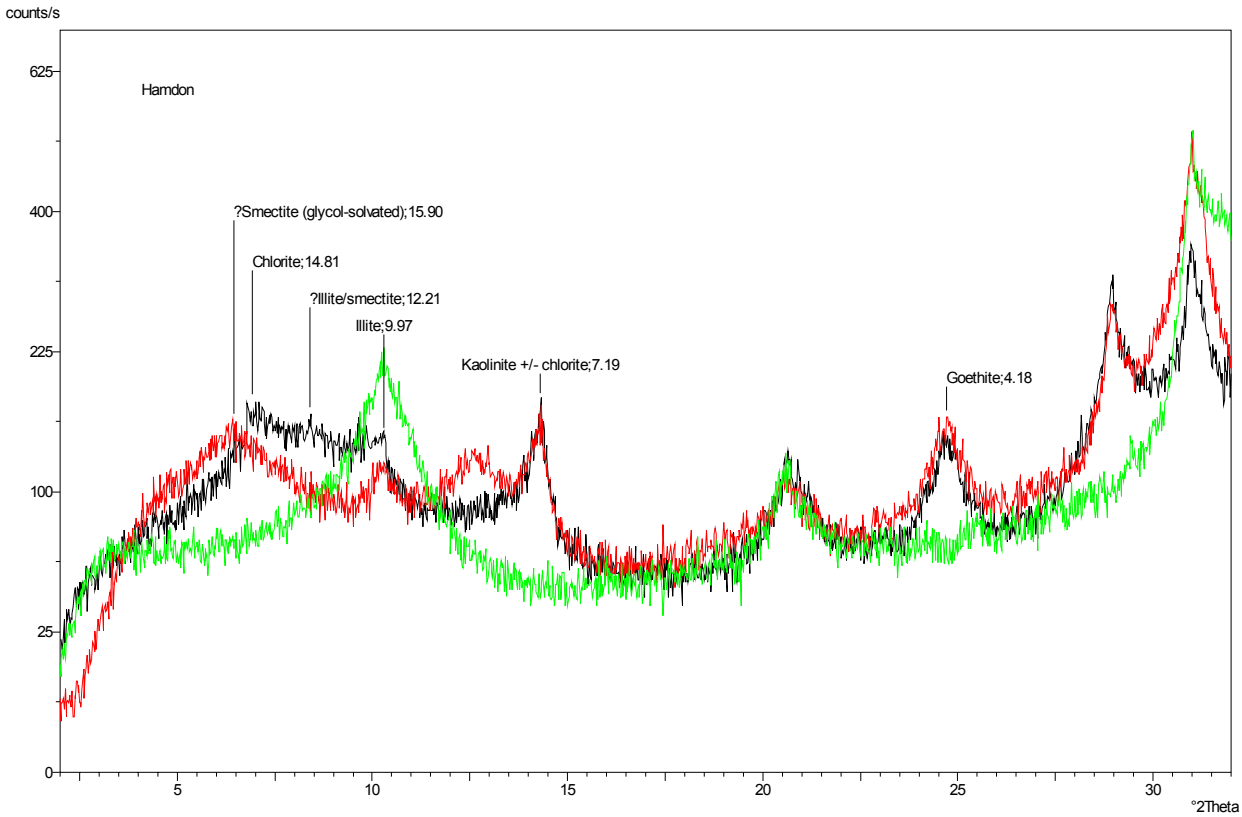
Somerton, Station



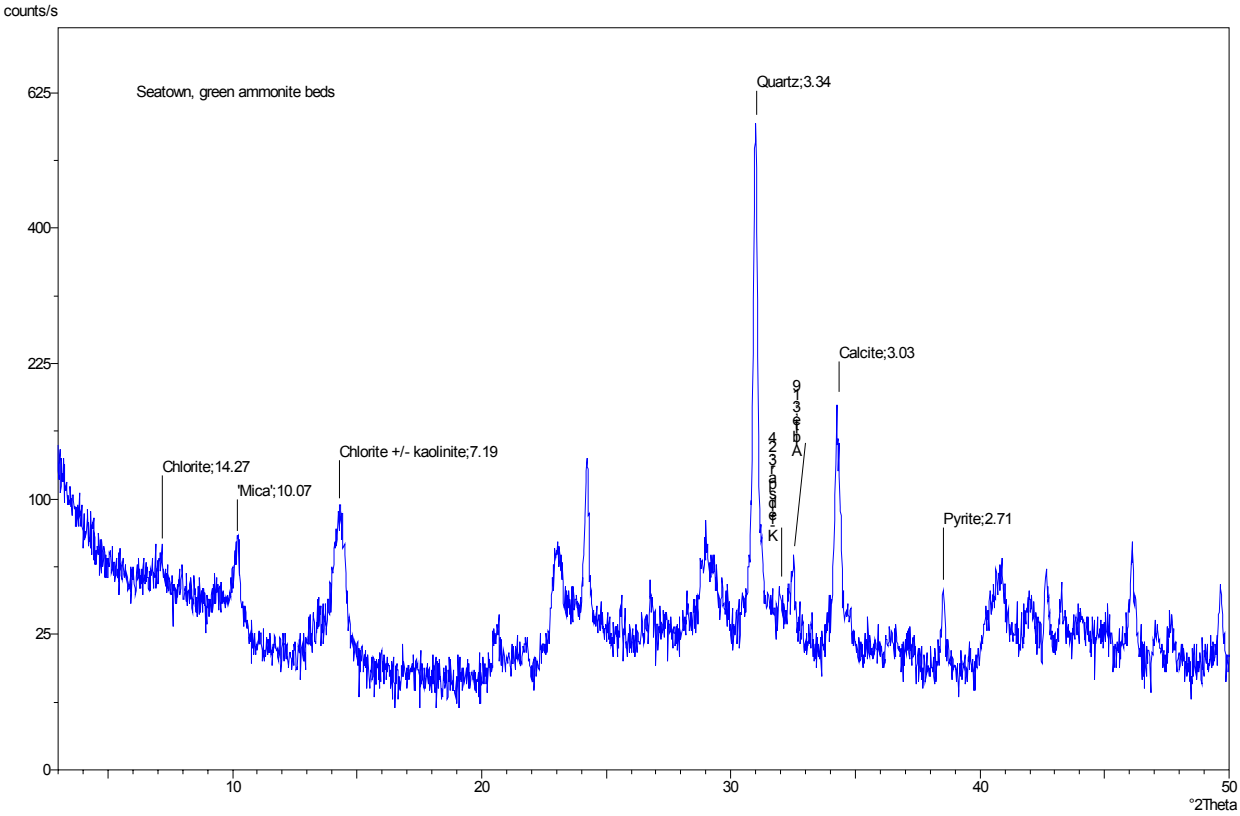


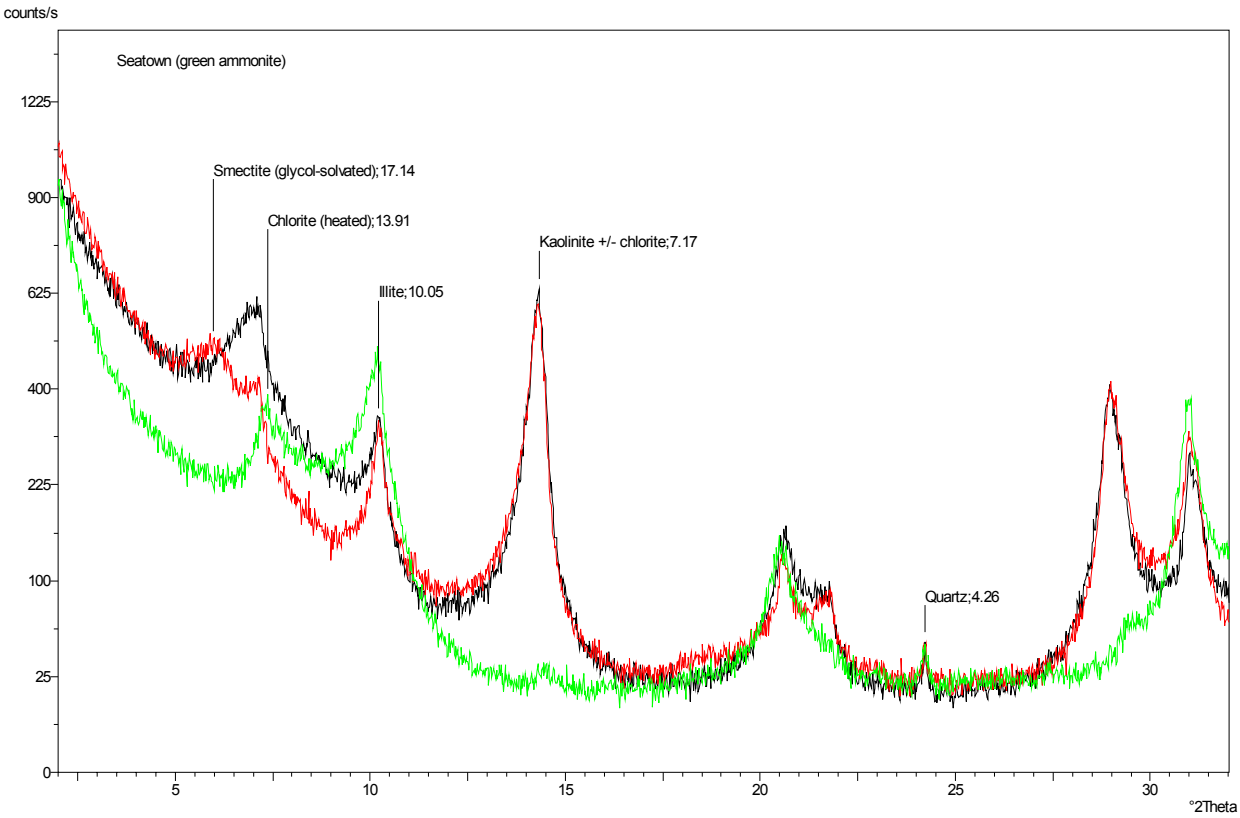
Hamdon Hill, Hamdon



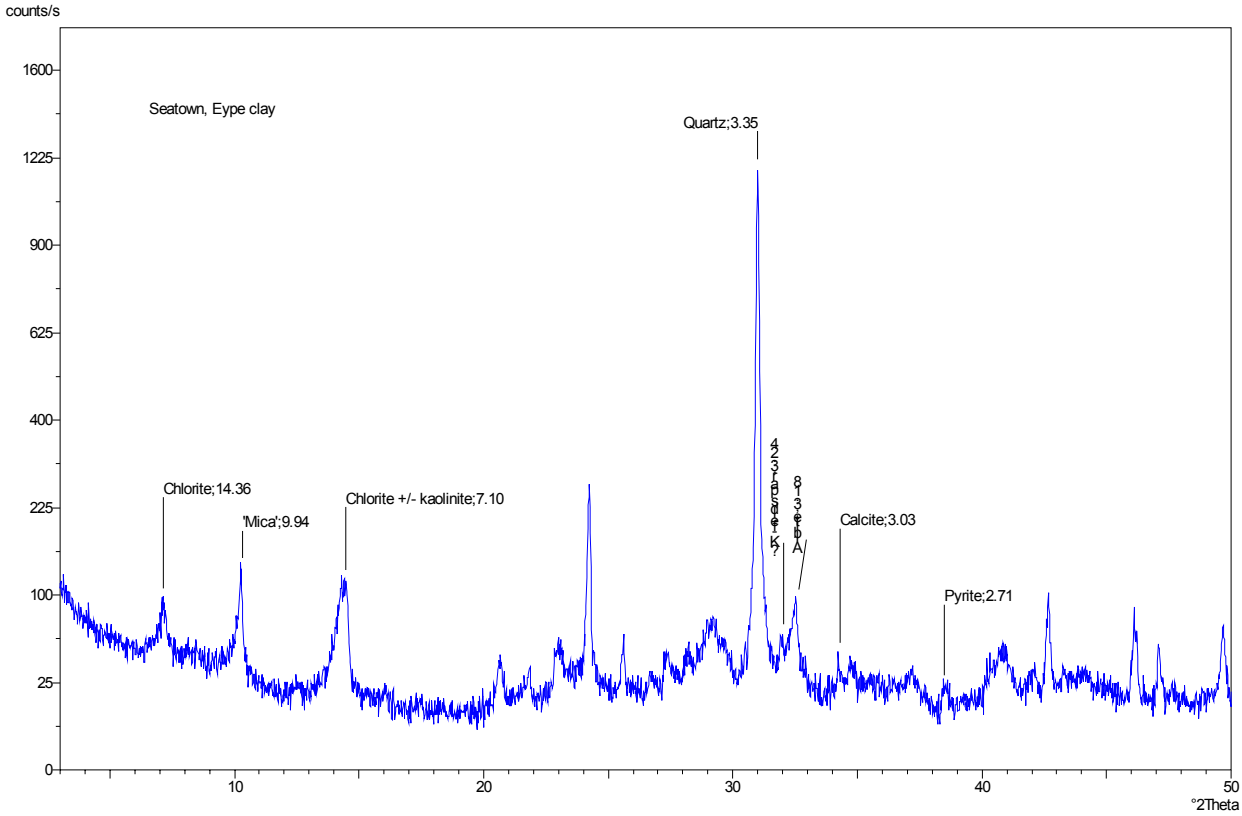


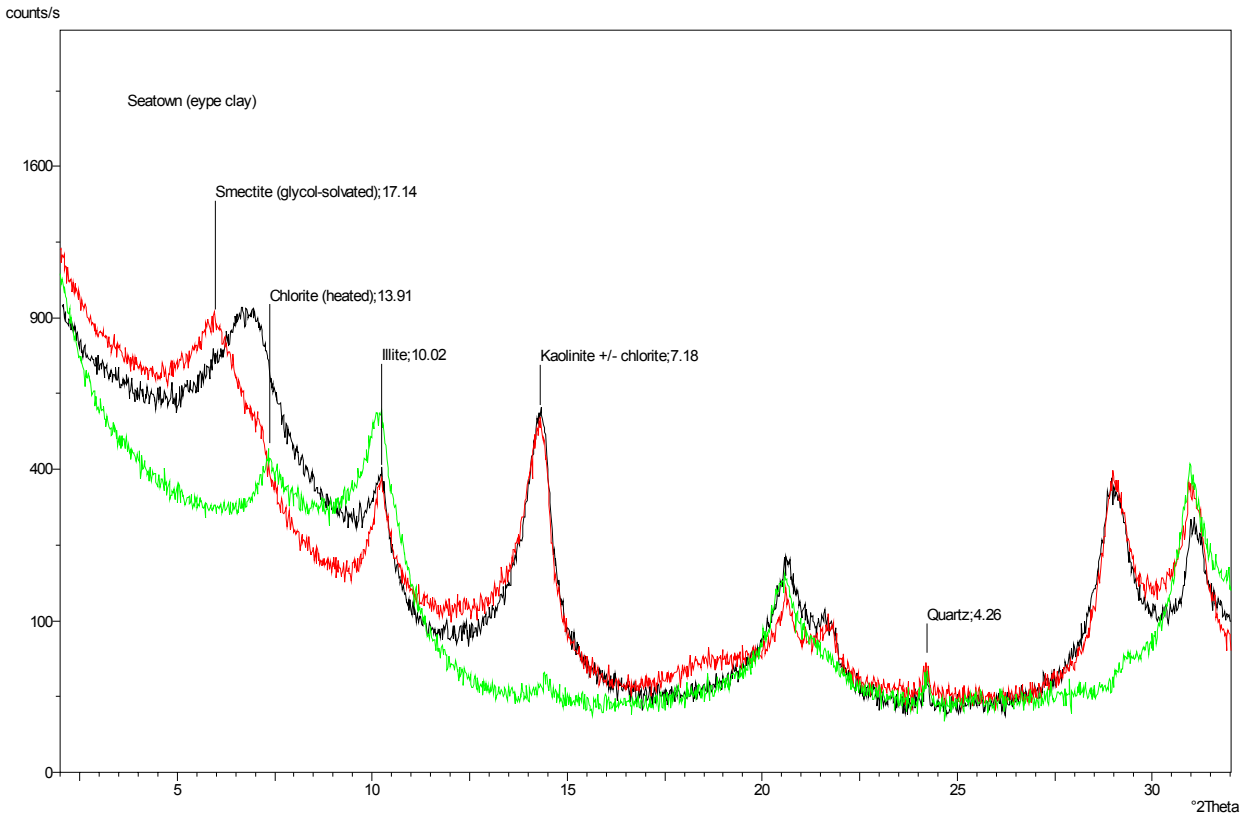
Seatown, Green Ammonite Beds



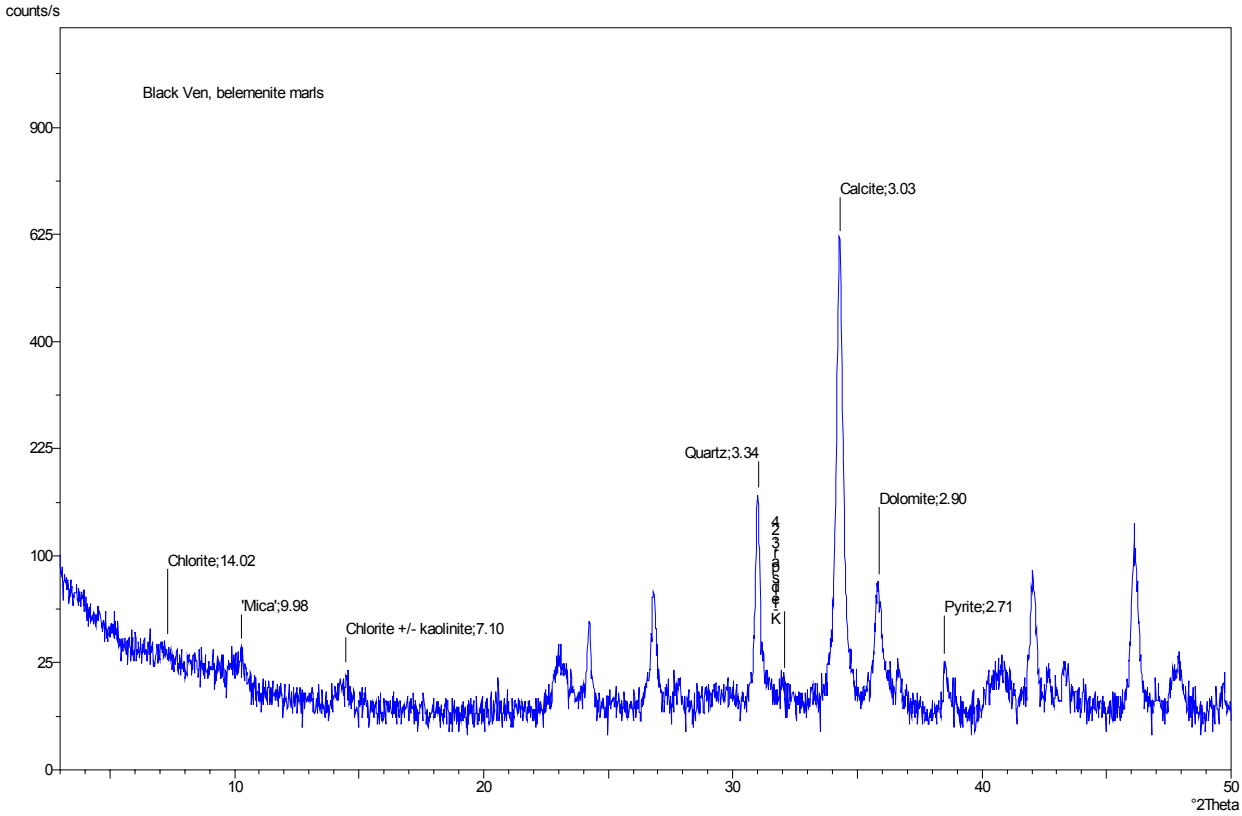


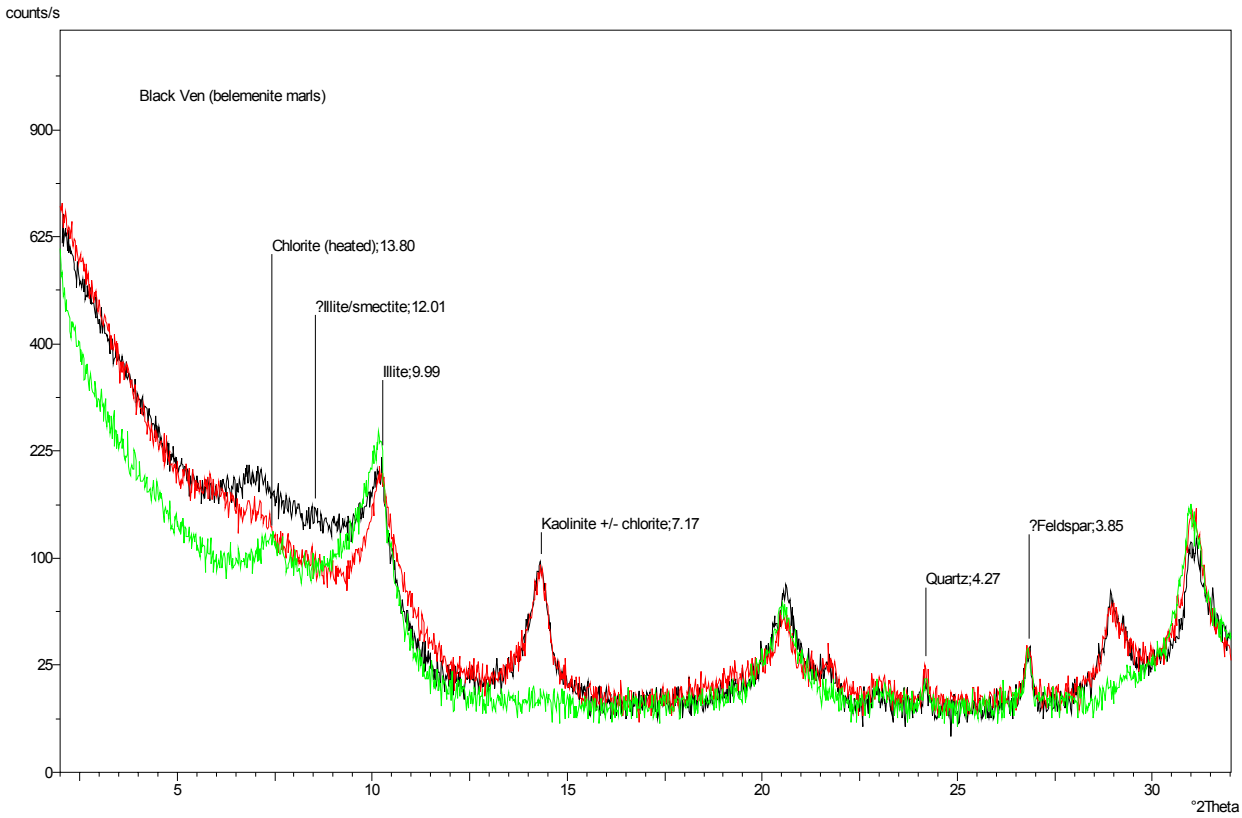
Seatown, Eype Clay



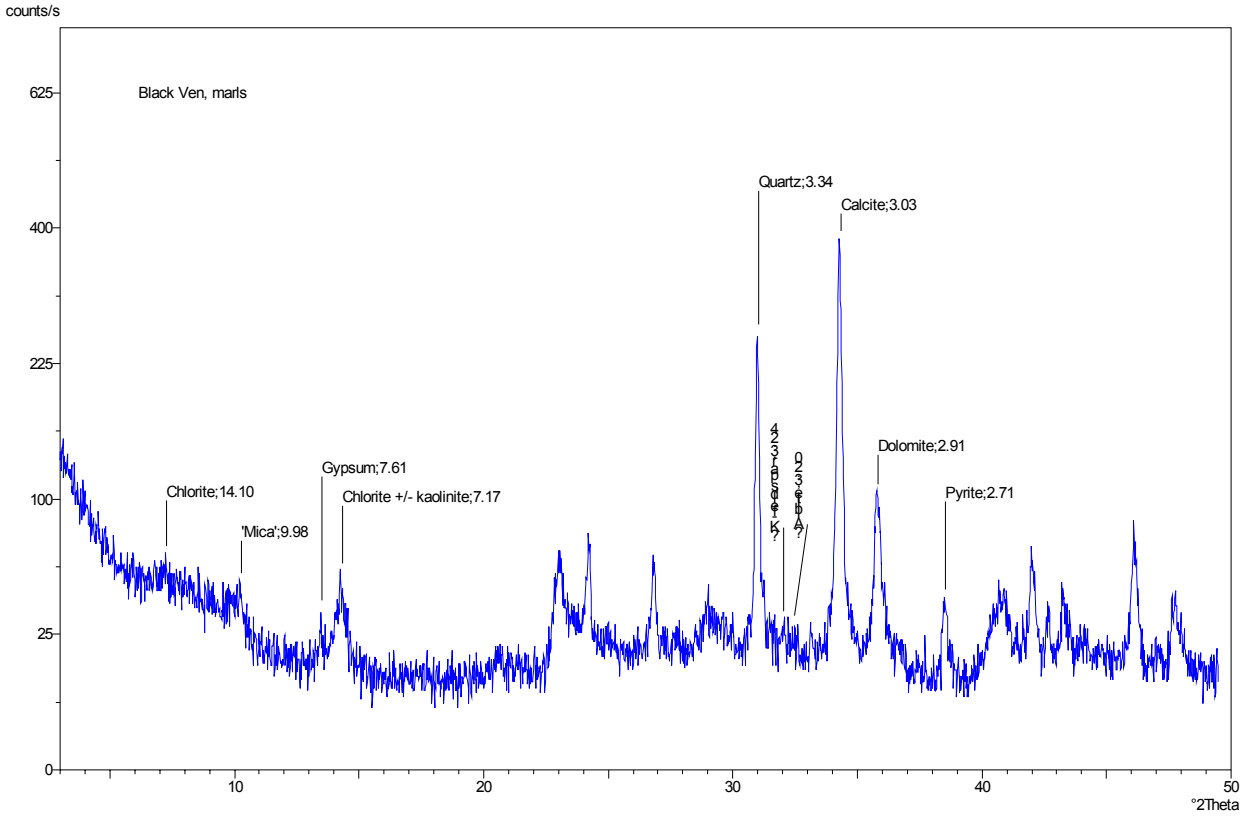


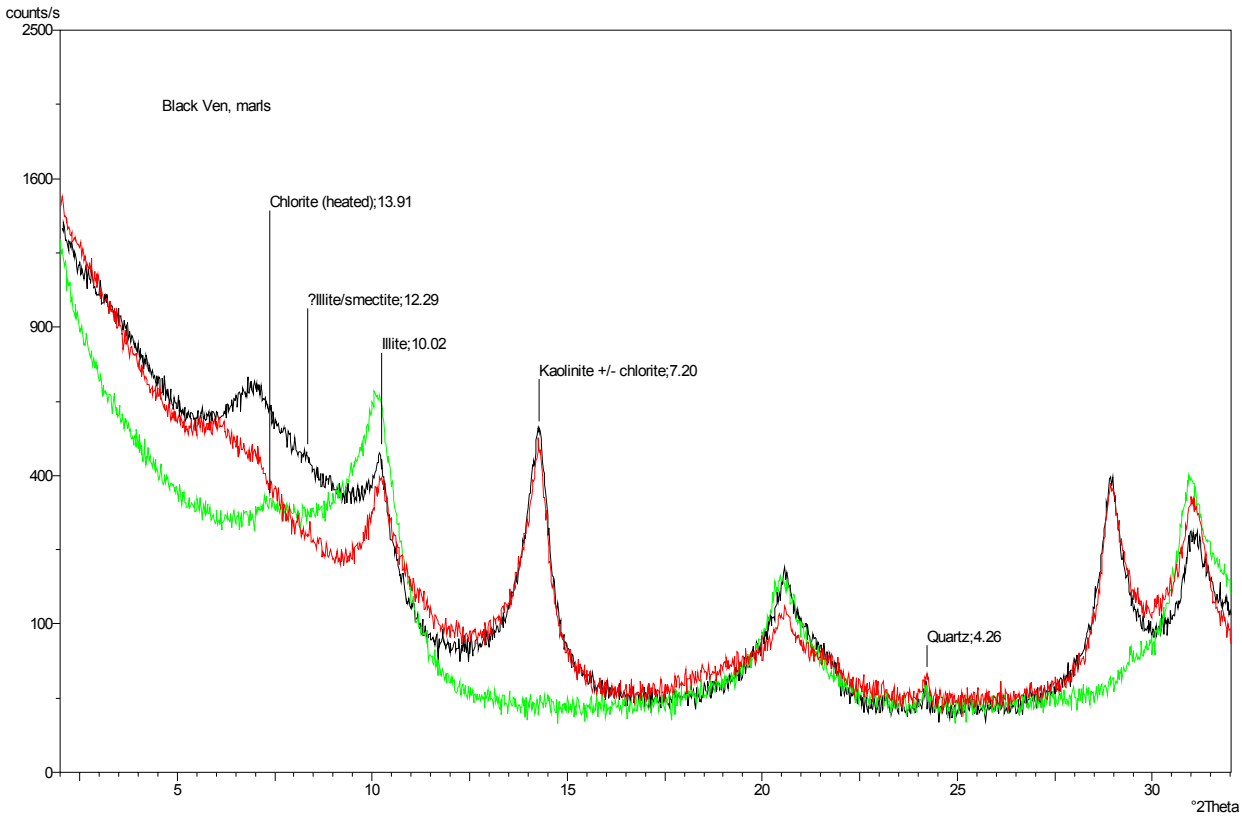
Black Ven, Belemnite Marls



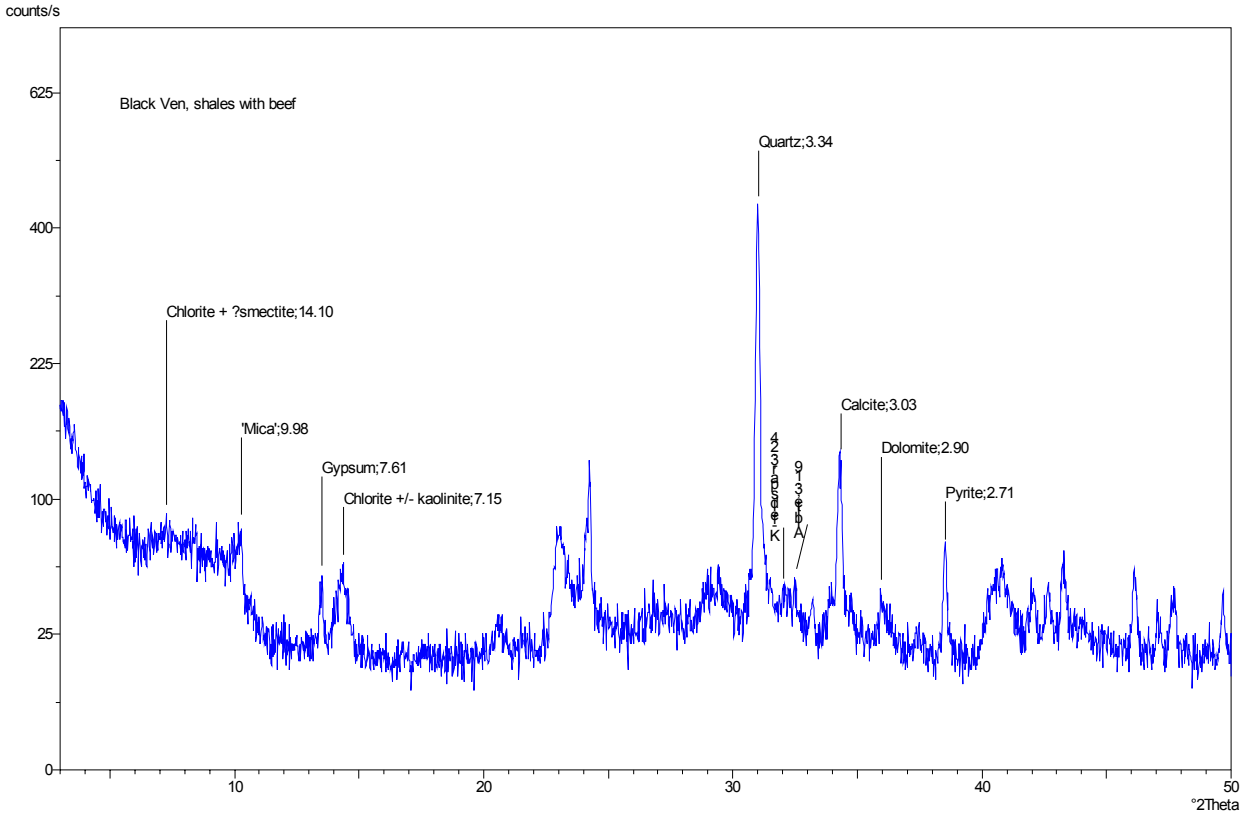


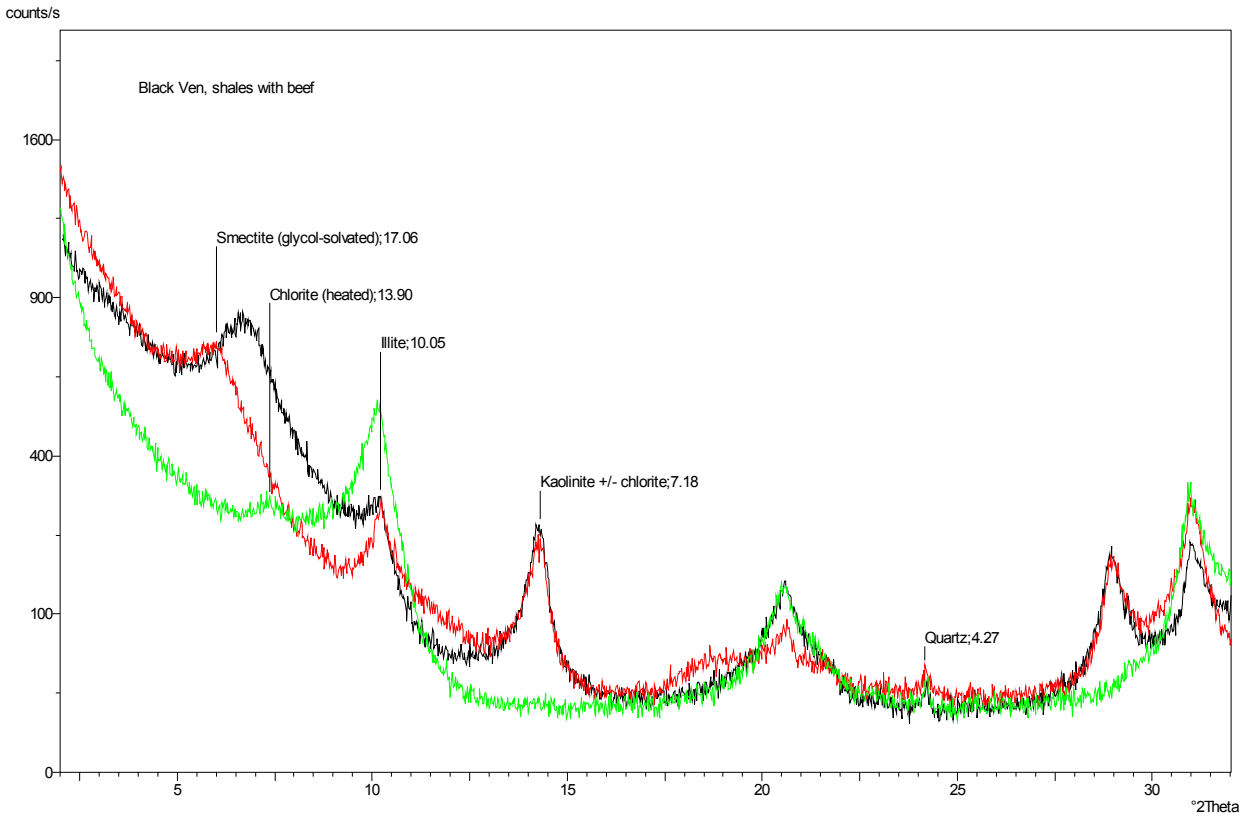
Black Ven, Marls



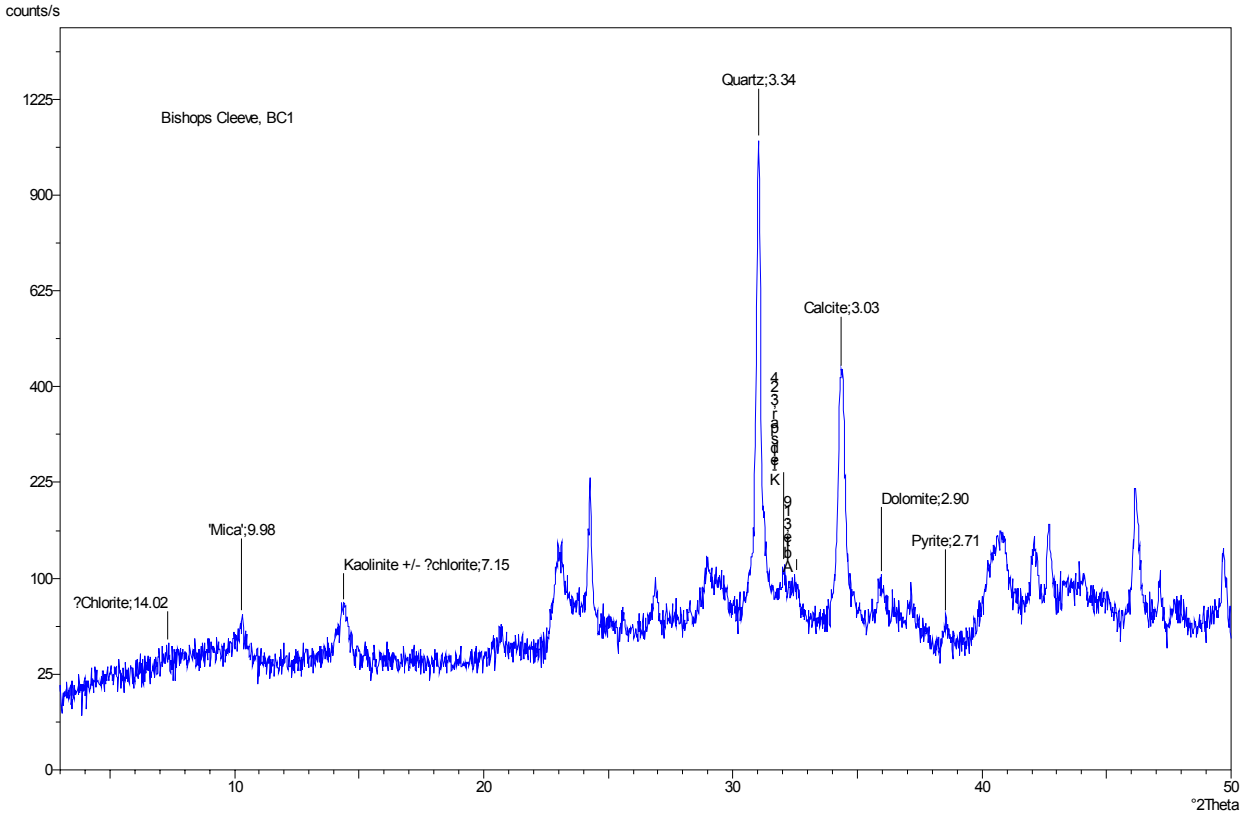


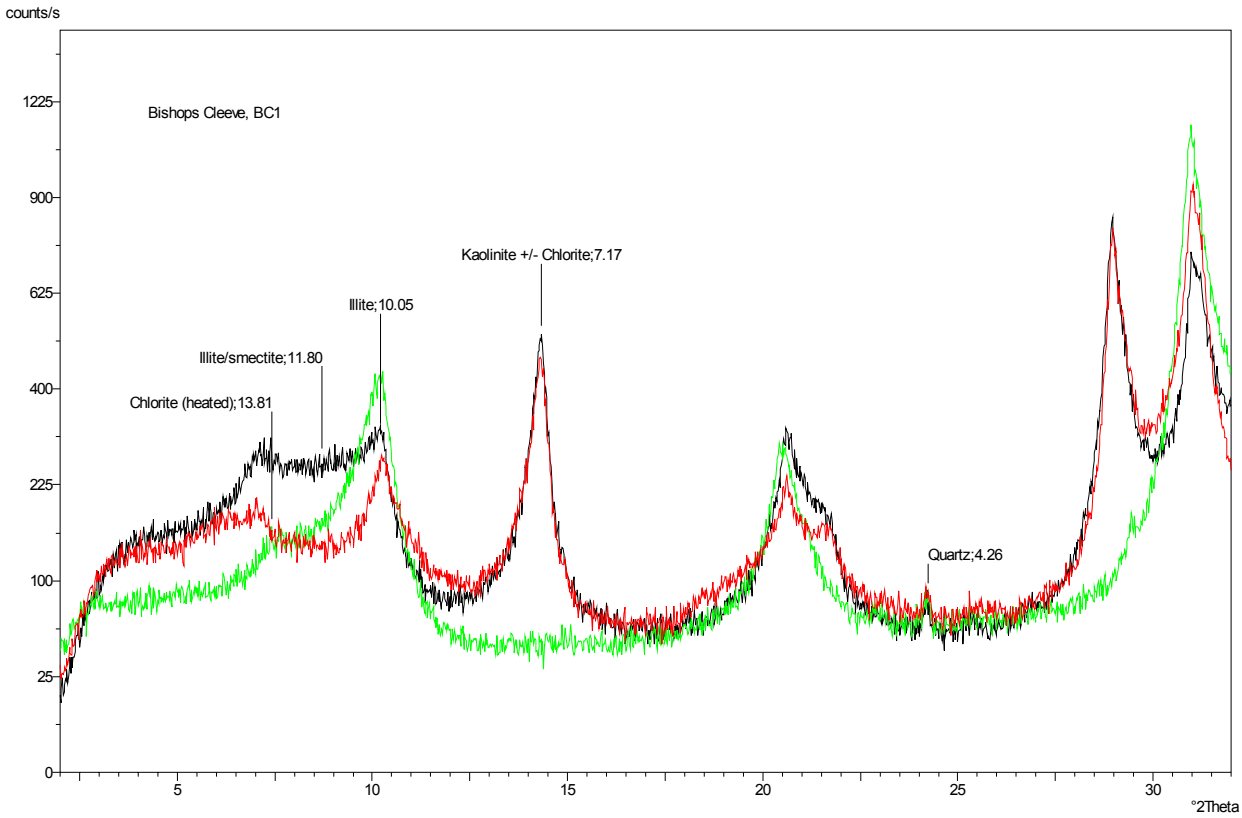
Black Ven, Shales with Beef



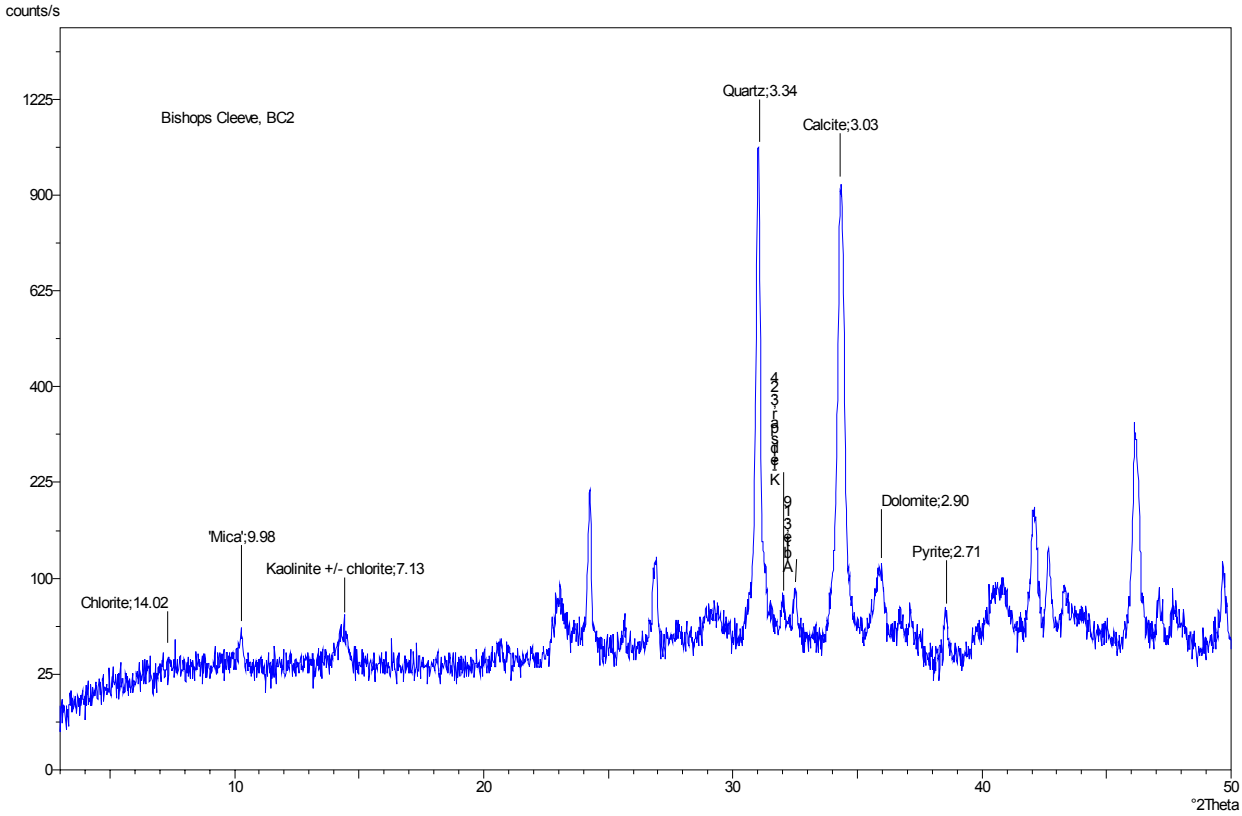


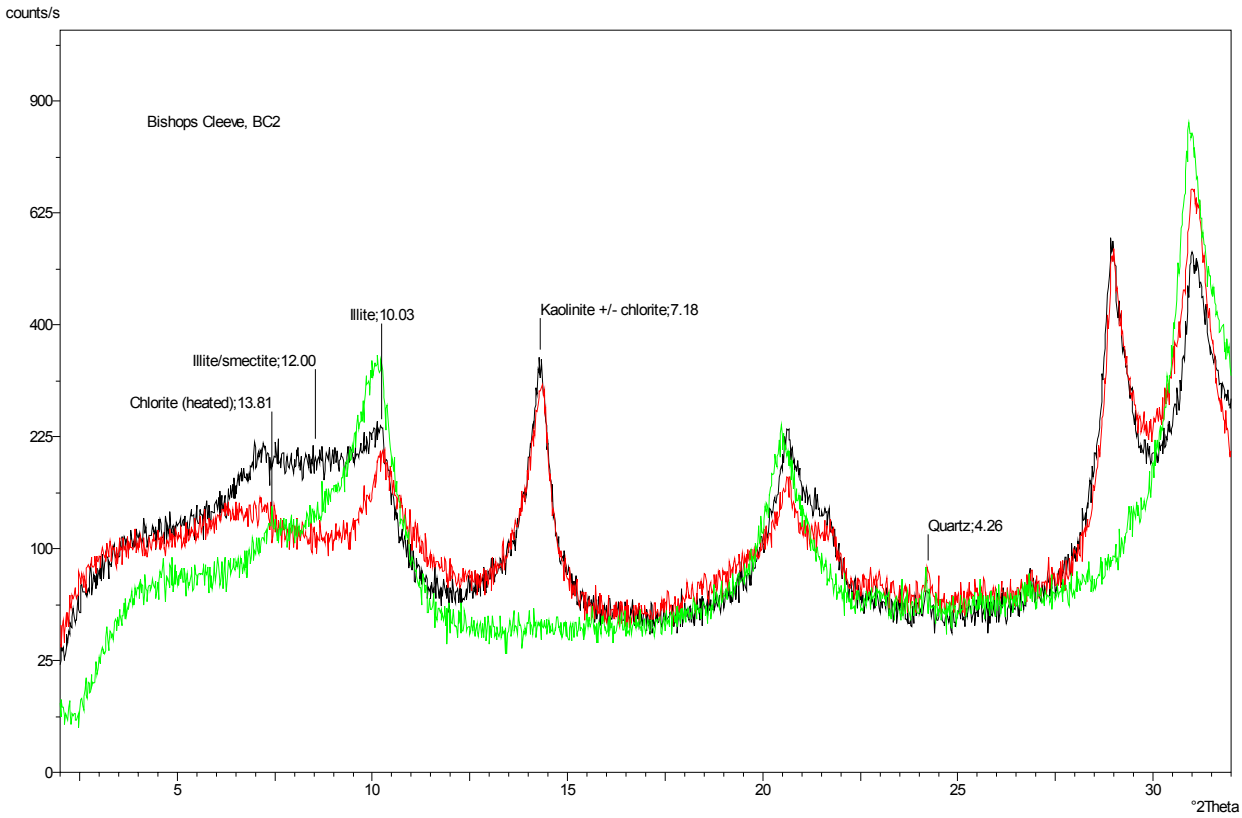
Bishops Cleeve, BC1



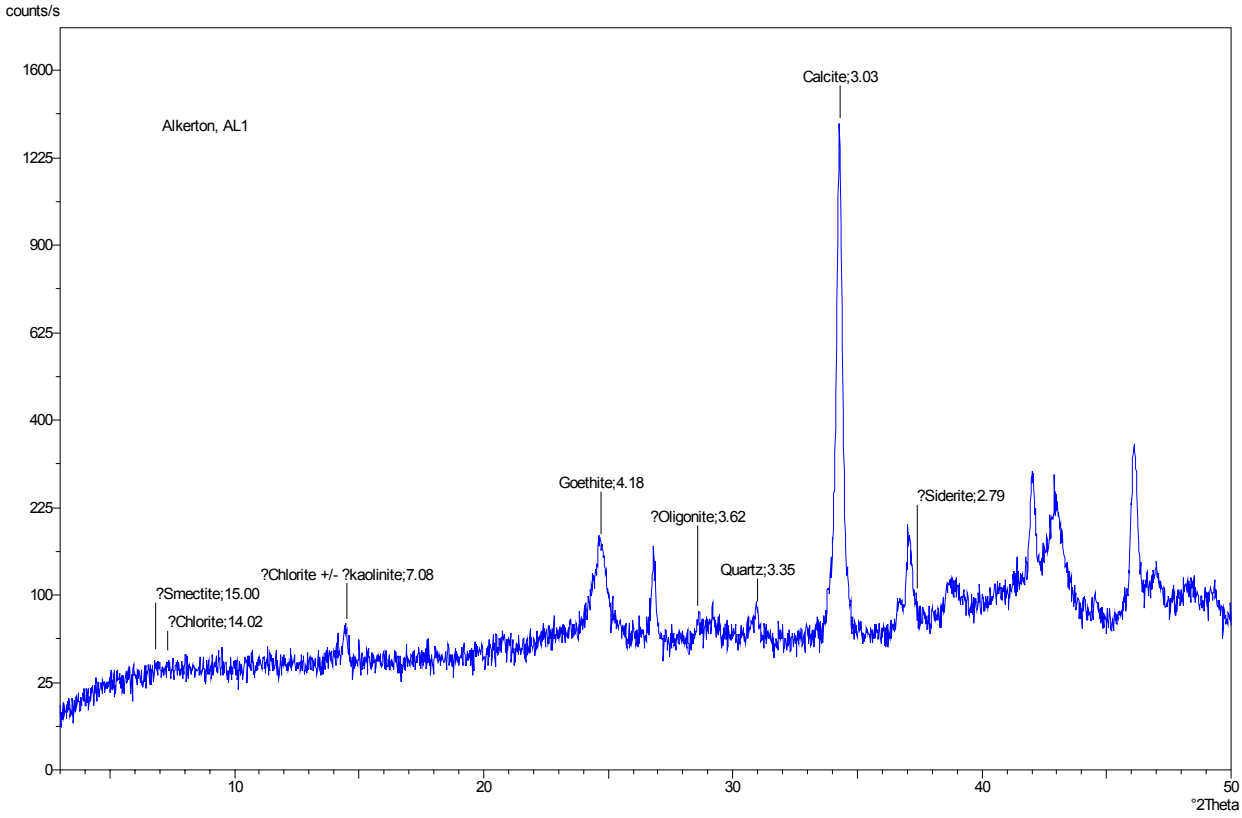


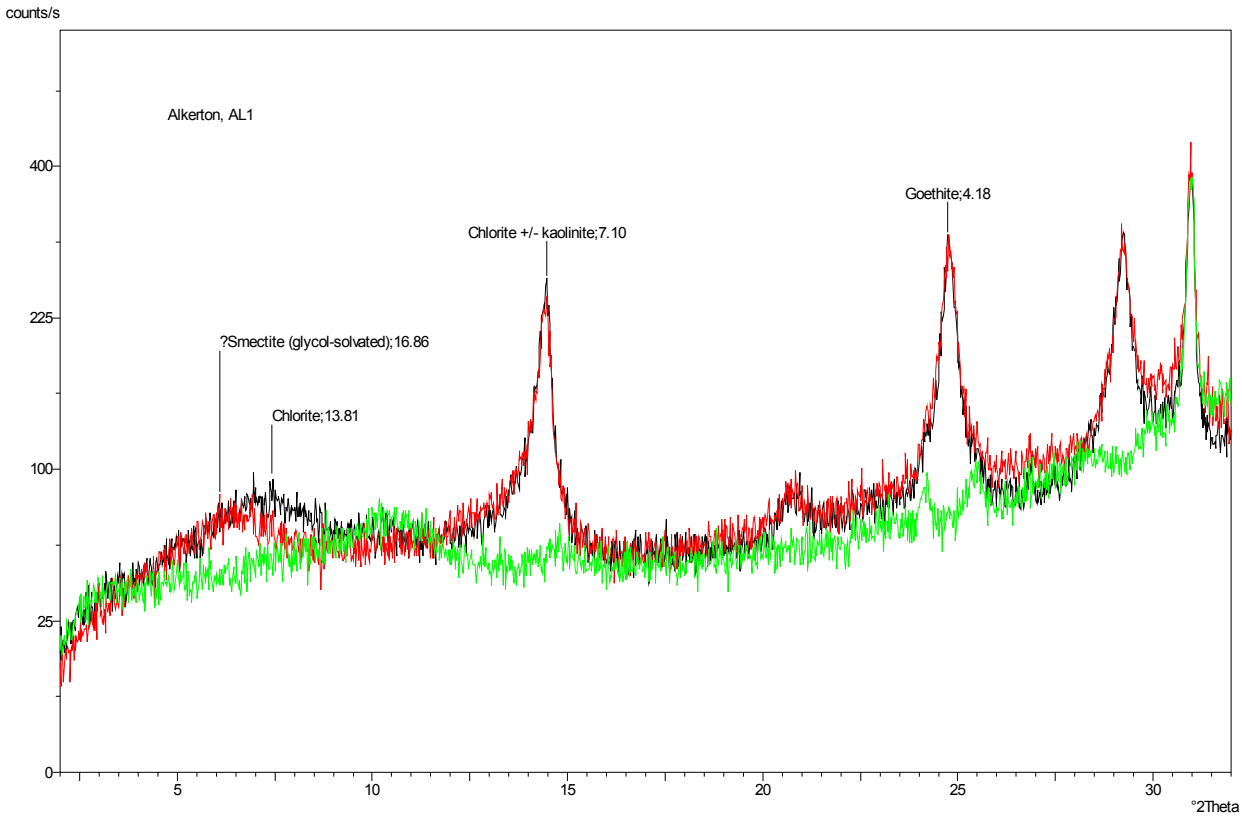
Bishops Cleeve, BC2



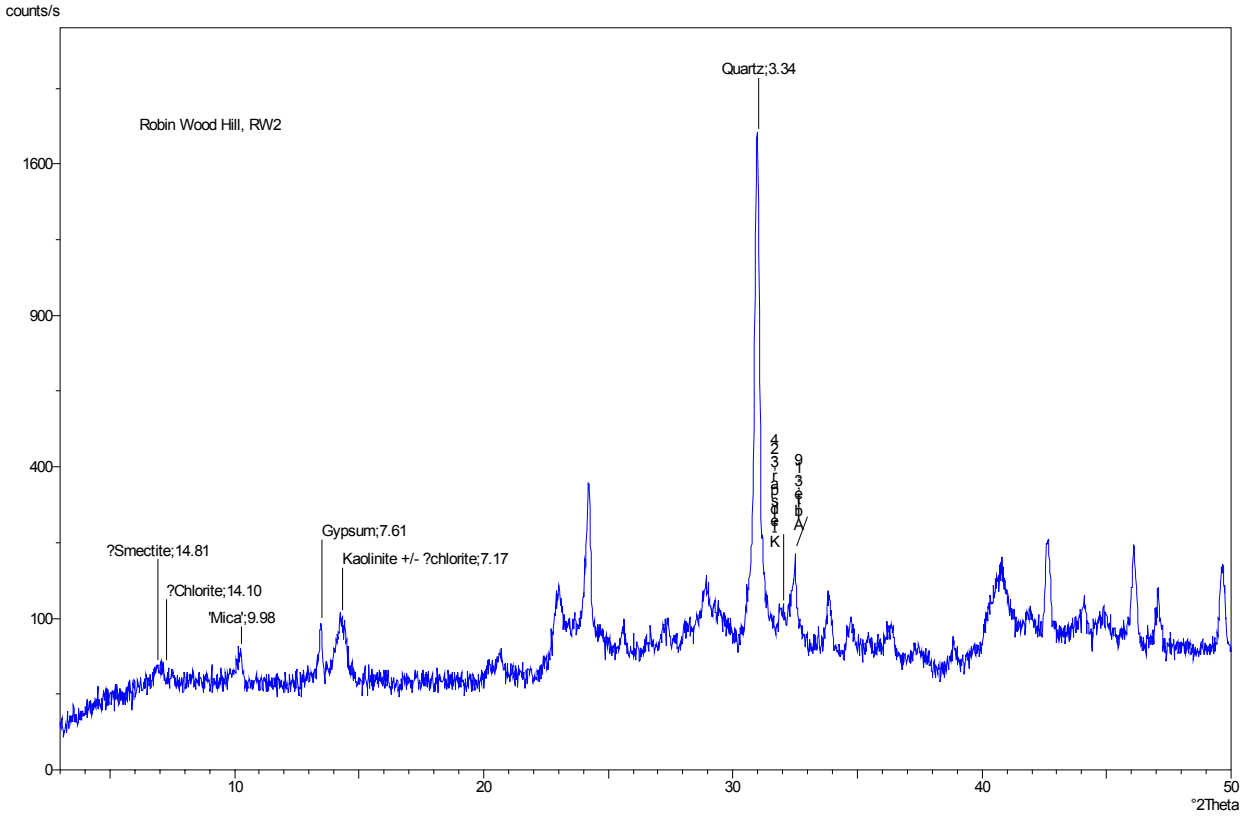


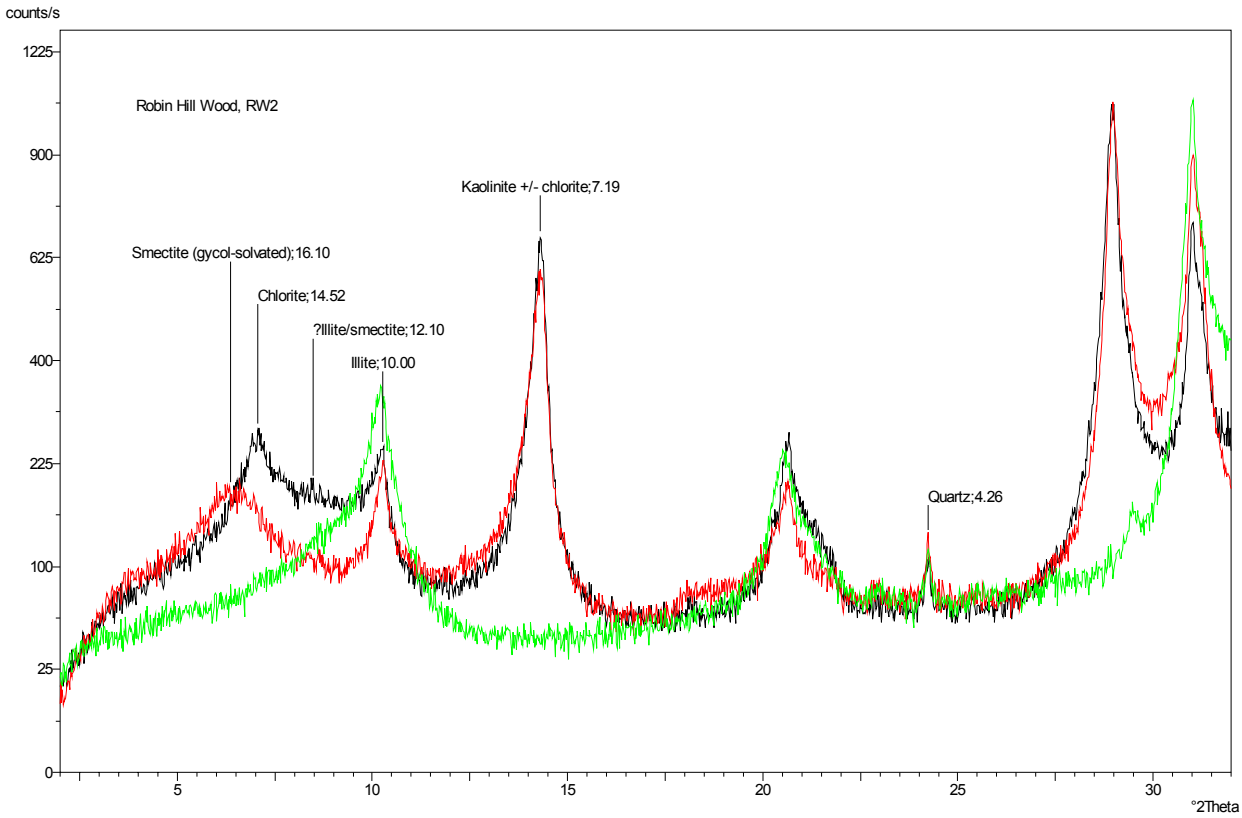
Alkerton, AL1



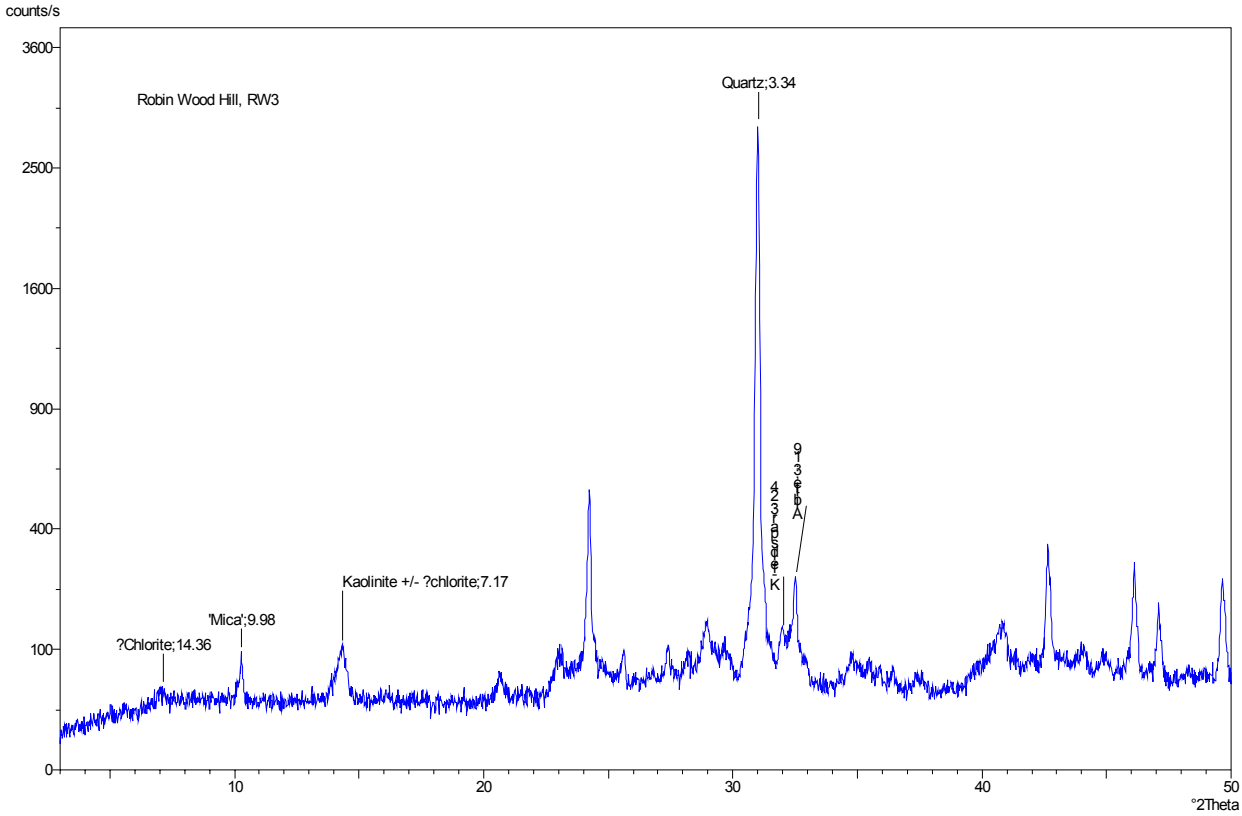


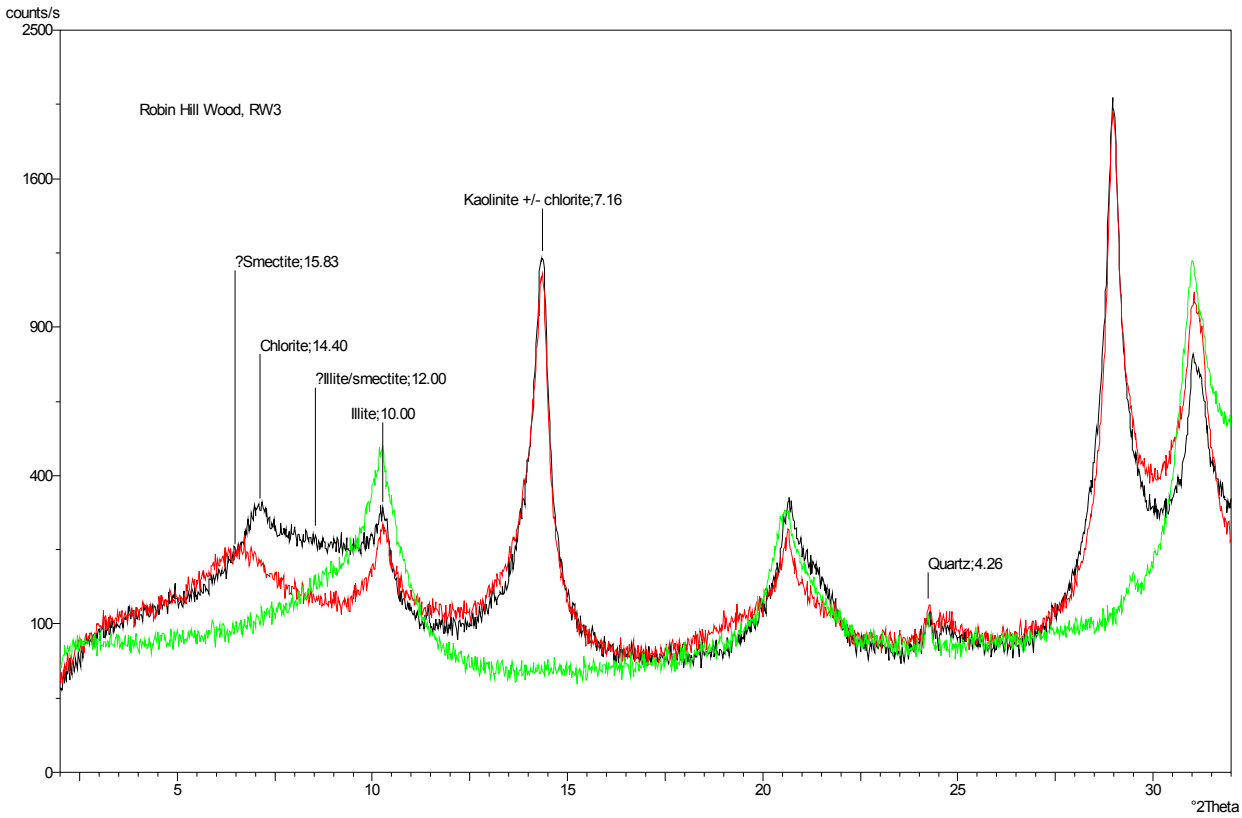
Robin Wood Hill, RW2



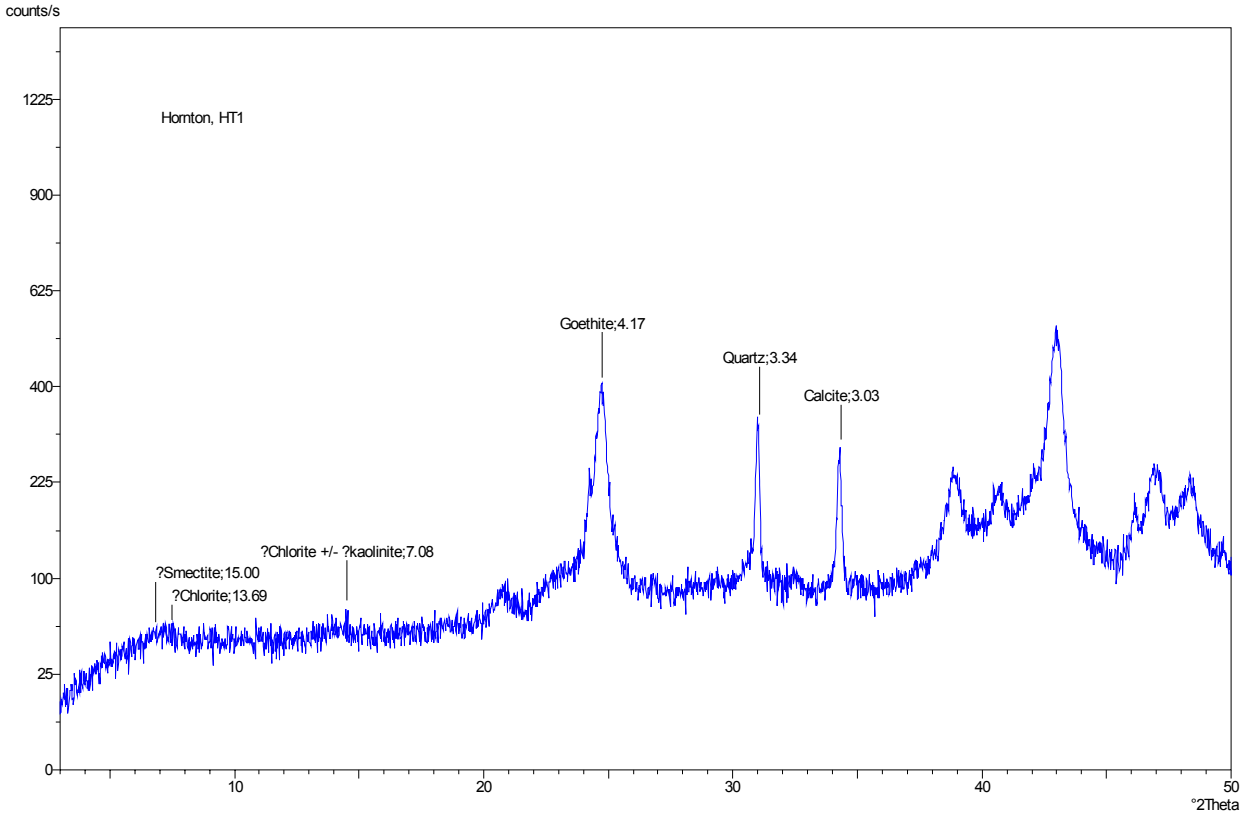


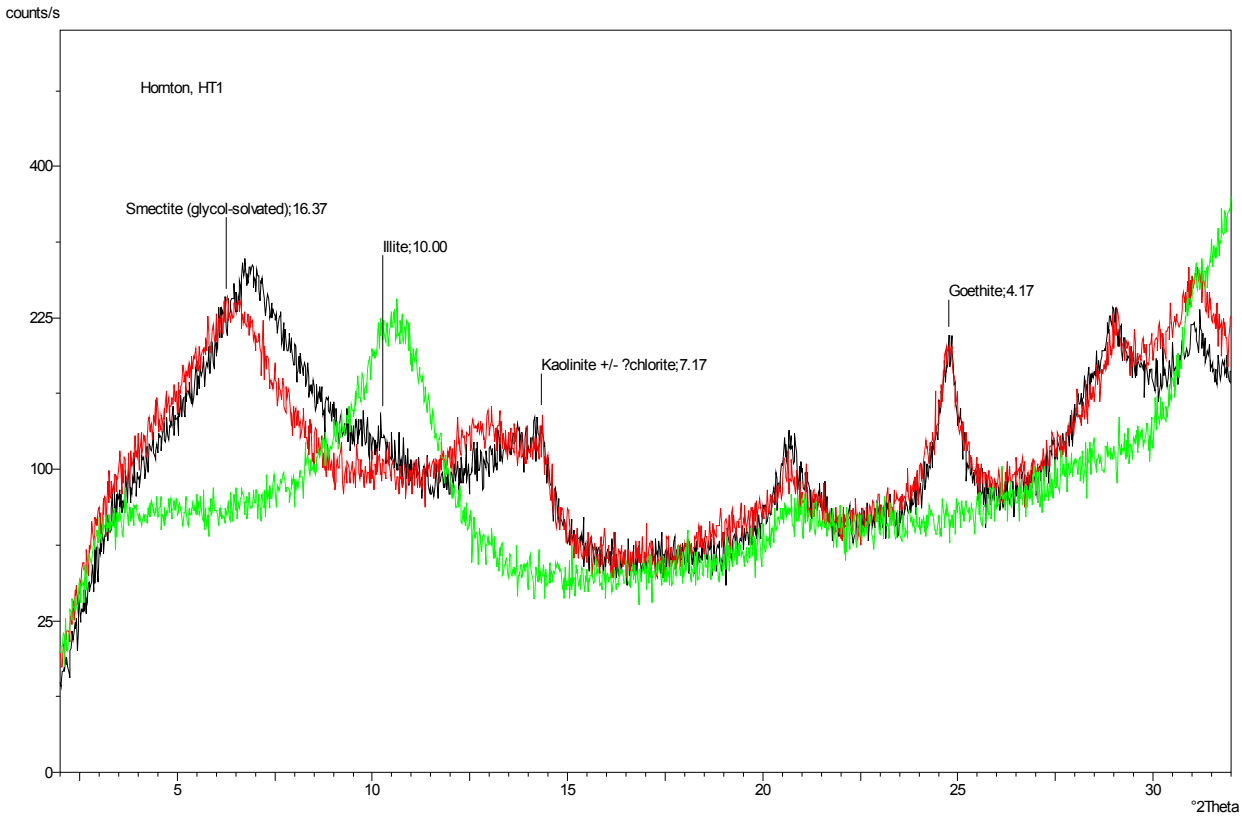
Robin Wood Hill, RW3



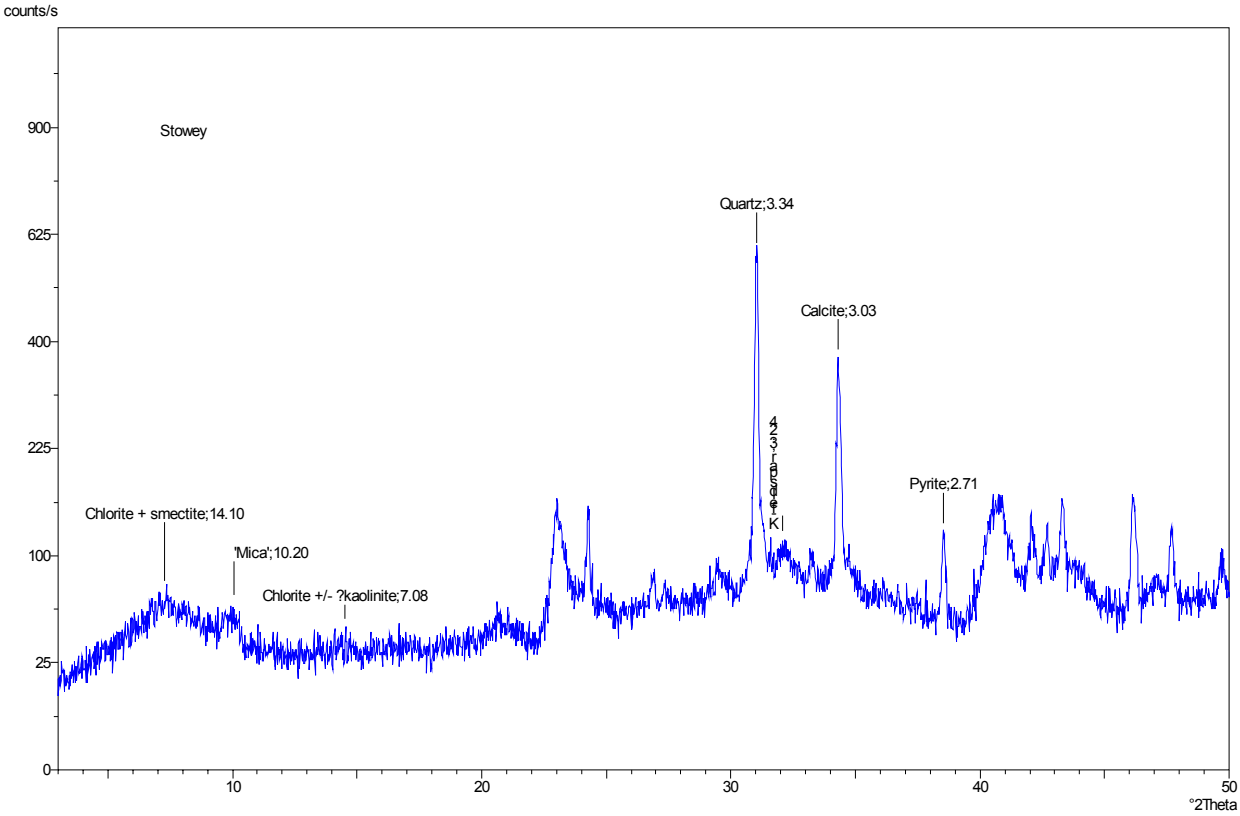


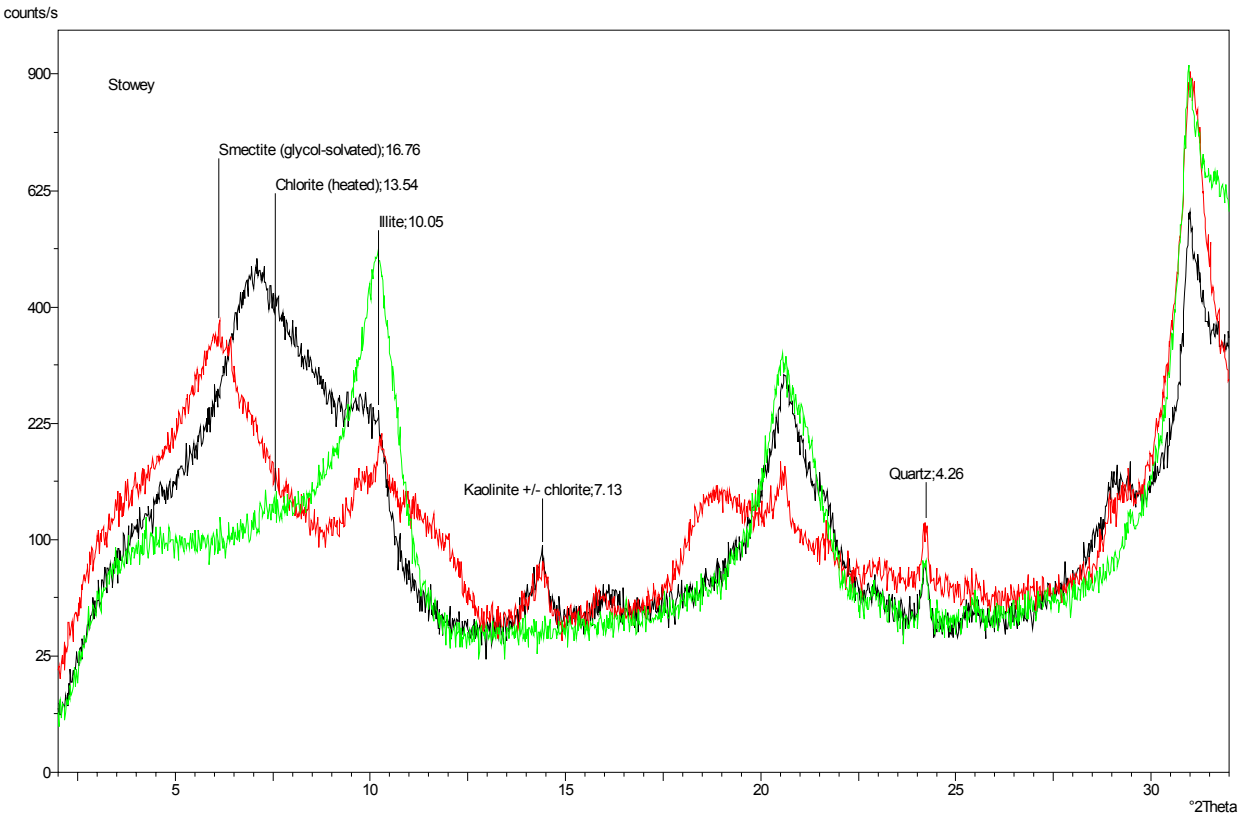
Horton, HT1


counts/s
Horton, HT1
1225
900
625
400
225
100
25
0
Goethite;4.17
Quartz;3.34
Calcite;3.03
?Chlorite +/- ?kaolinite;7.08
?Smectite;15.00
?Chlorite;13.69
10
20
30
40
50
°2Theta

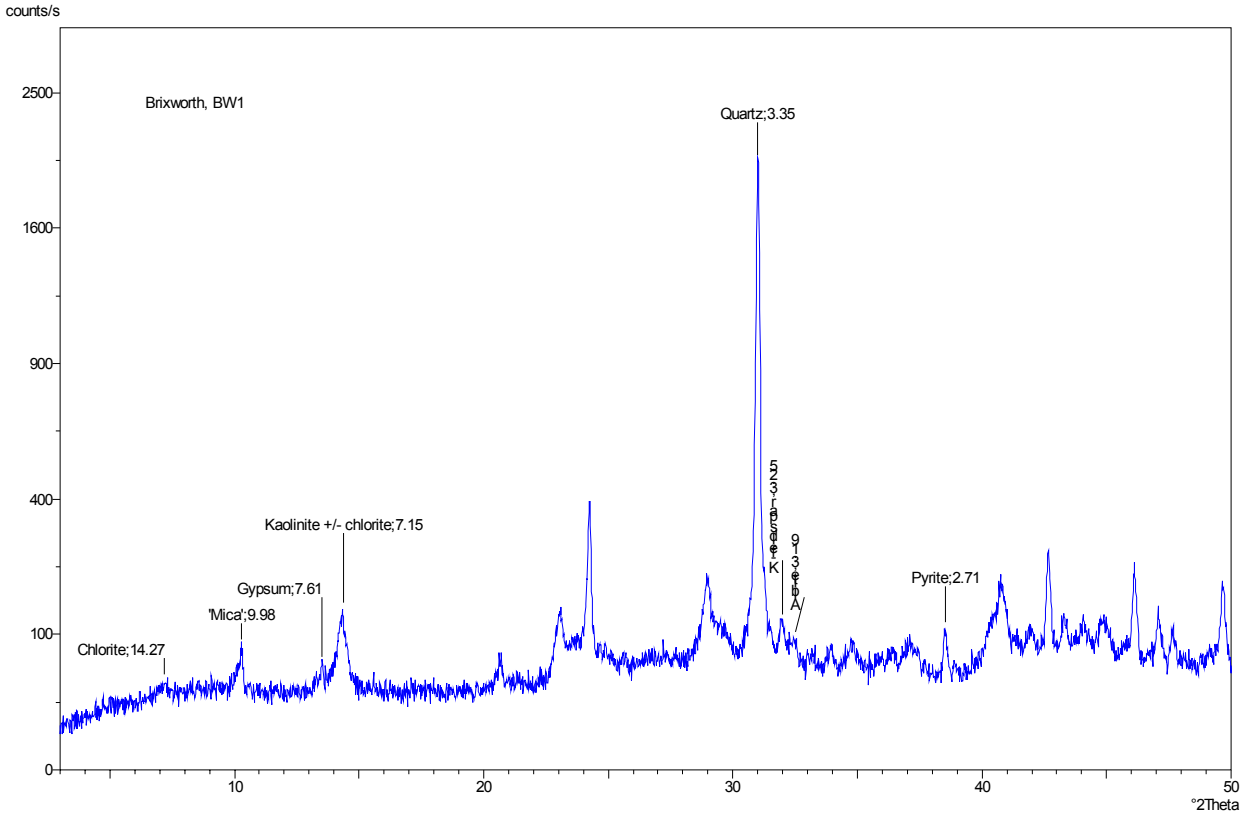

counts/s
Horton, HT1
400
225
100
25
0
Smectite (glycol-solvated);16.37
Illite;10.00
Kaolinite +/- ?chlorite;7.17
Goethite;4.17
5
10
15
20
25
30
°2Theta

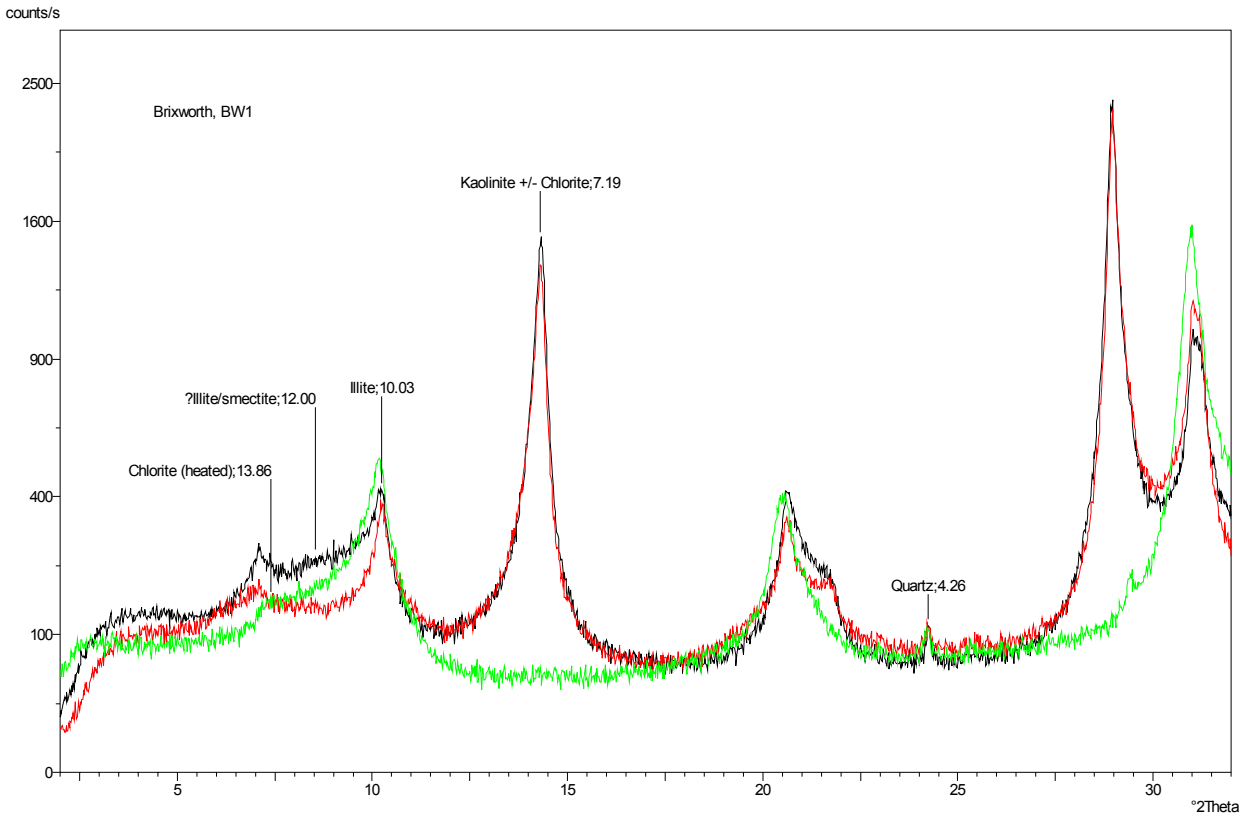
Stowey


counts/s
Stowey
Quartz;3.34
Calcite;3.03
Pyrite;2.71
Chlorite + smectite;14.10
'Mica';10.20
Chlorite +/- ?kaolinite;7.08
°2Theta

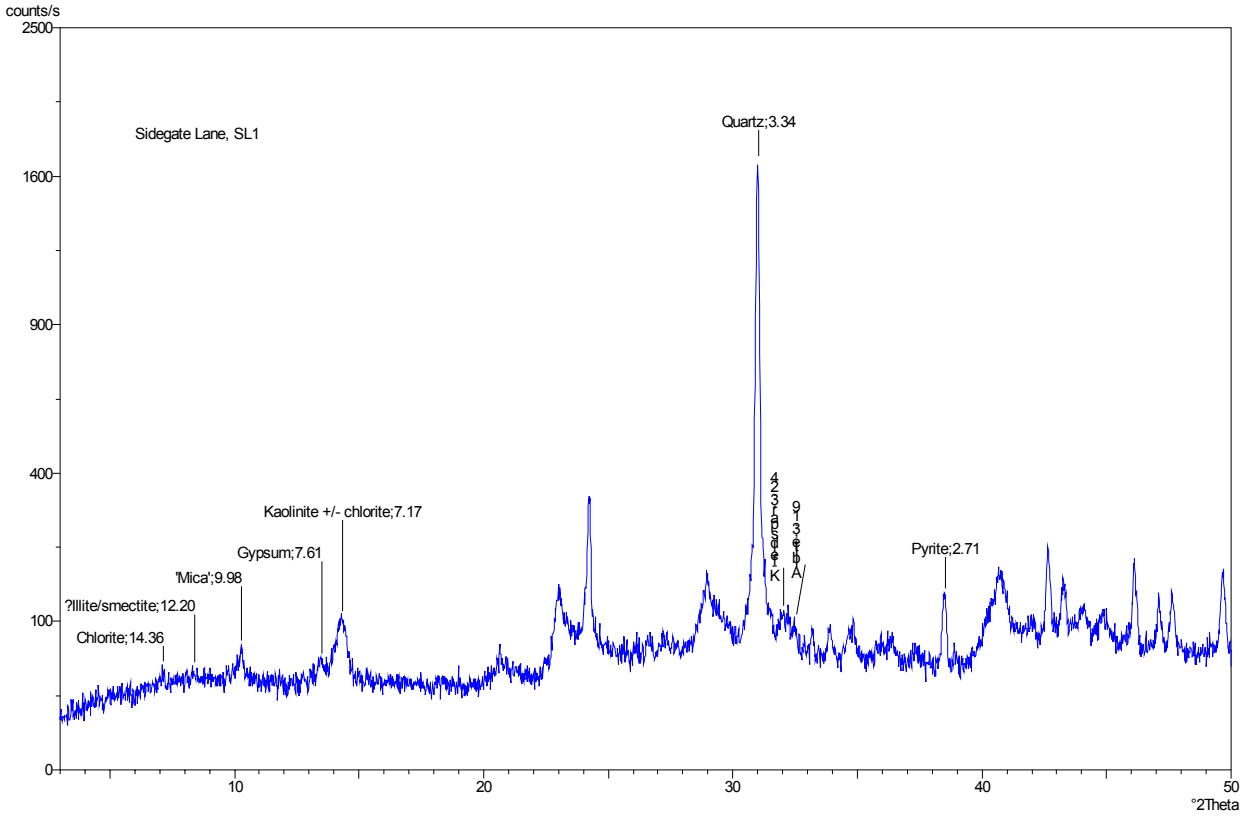

counts/s
Stowey
Smectite (glycol-solvated);16.76
Chlorite (heated);13.54
Illite;10.05
Kaolinite +/- chlorite;7.13
Quartz;4.26
°2Theta

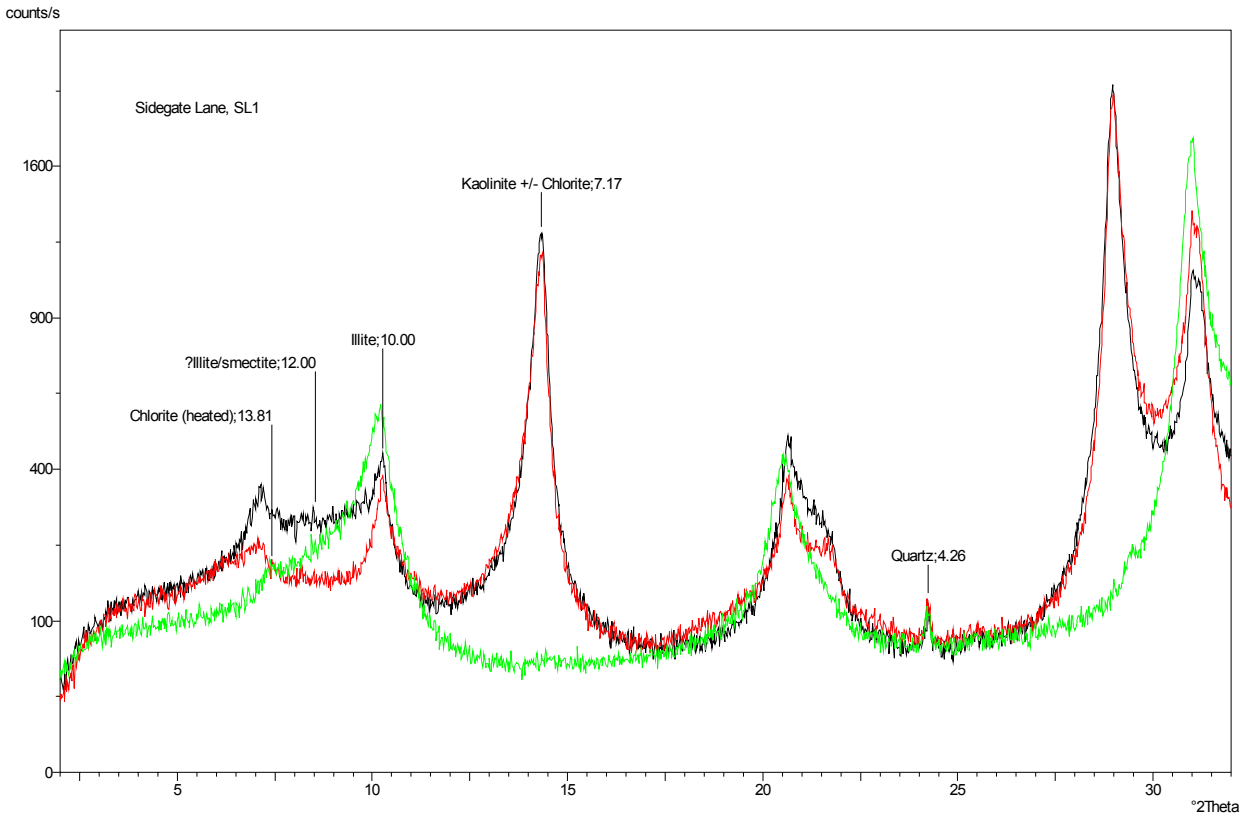
Brixworth, BW1



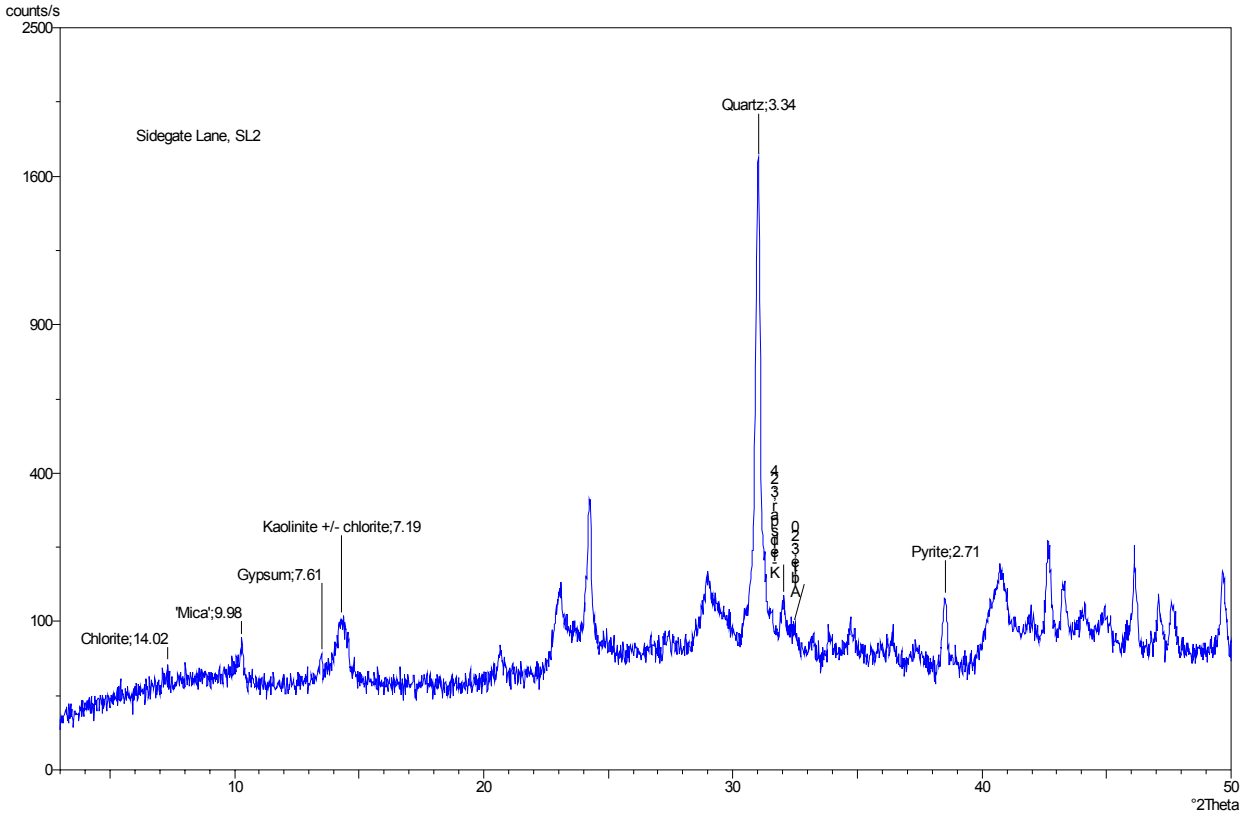


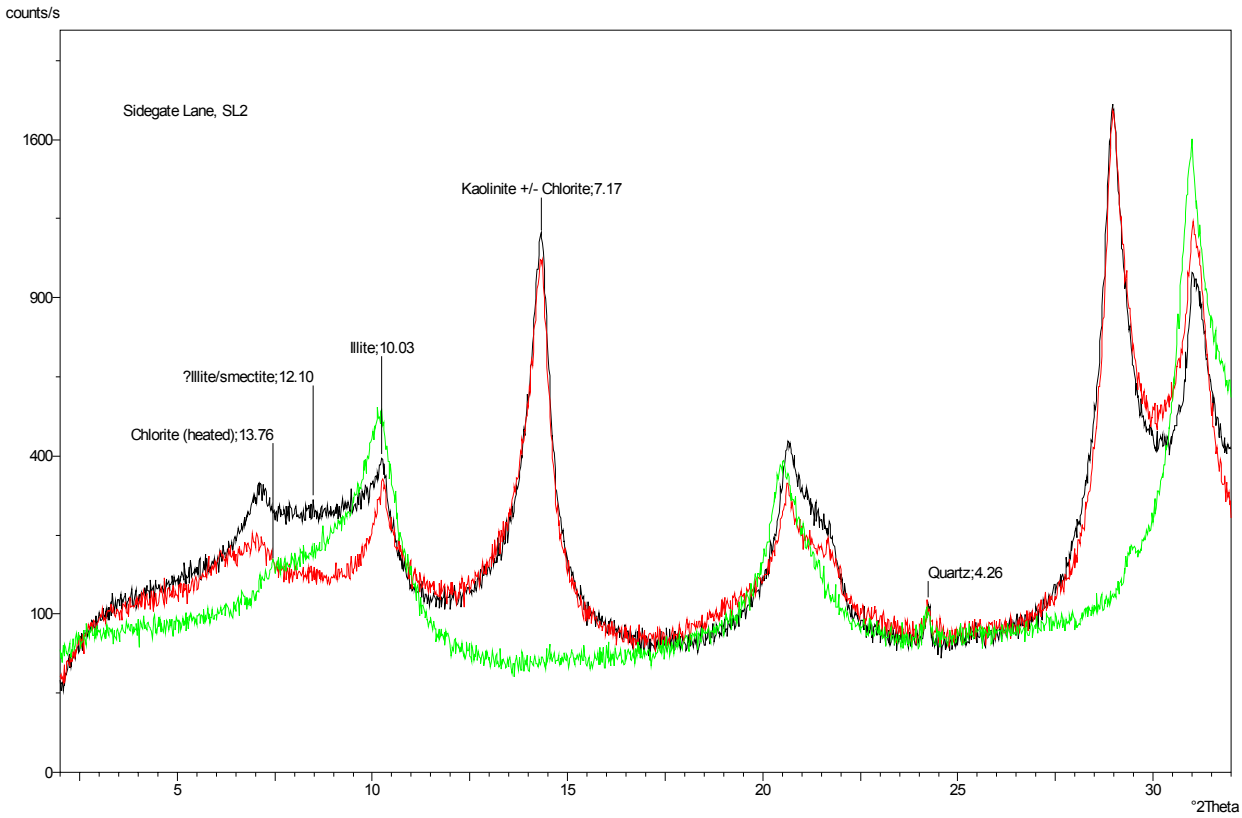
Sidegate Lane, SL1



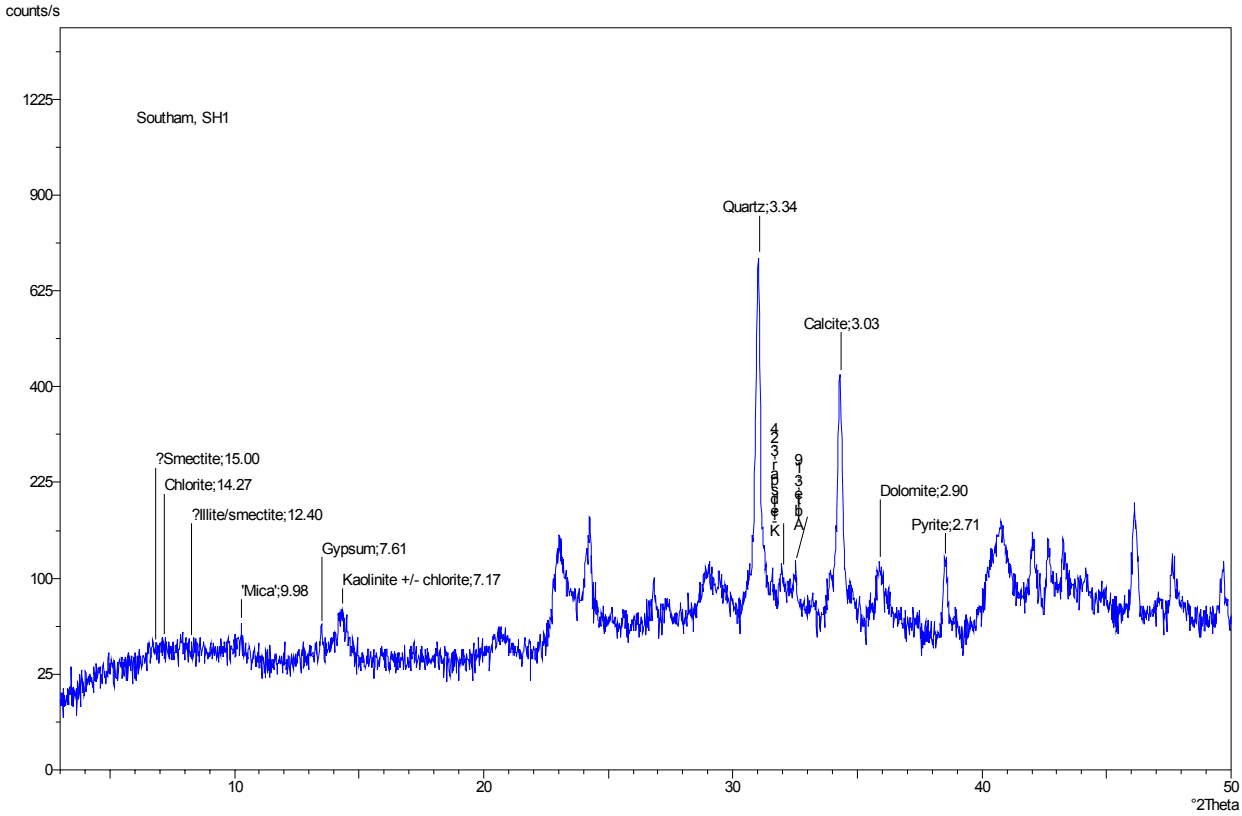


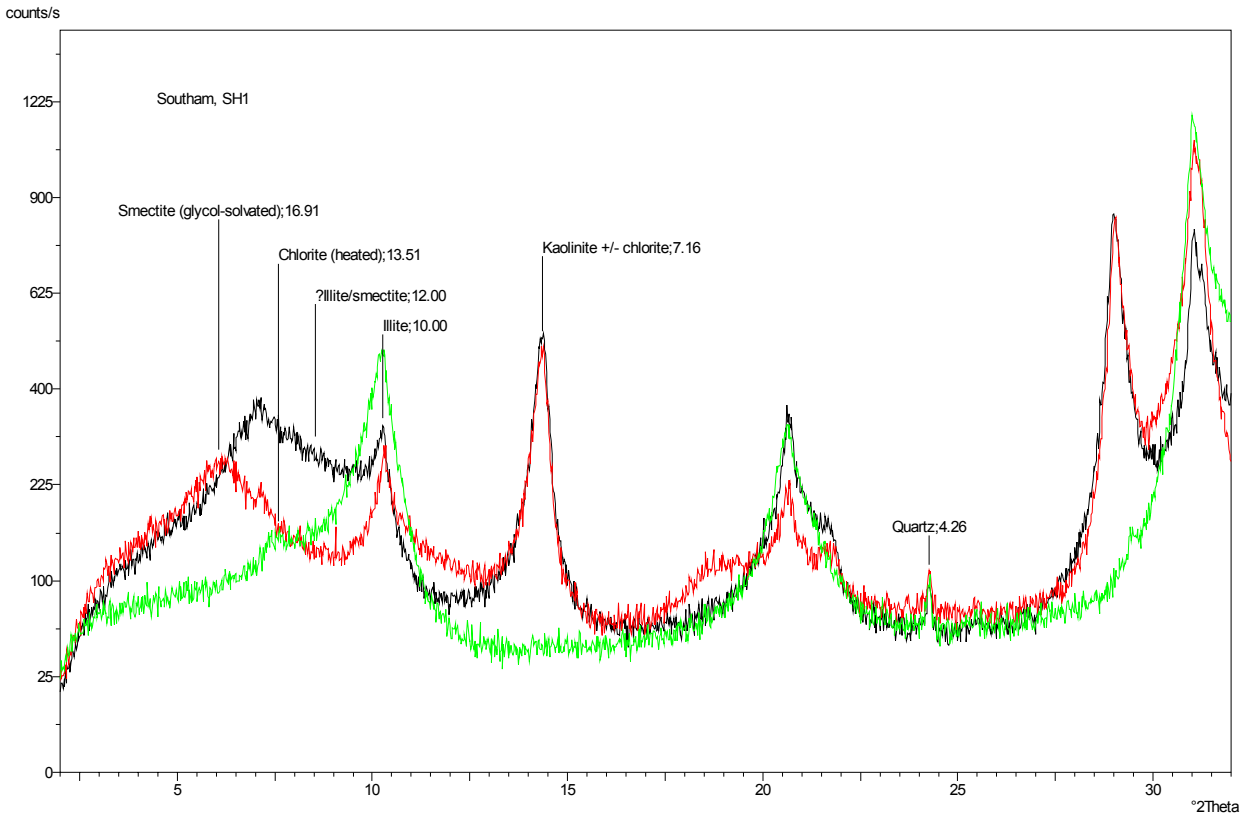
Sidegate Lane, SL2



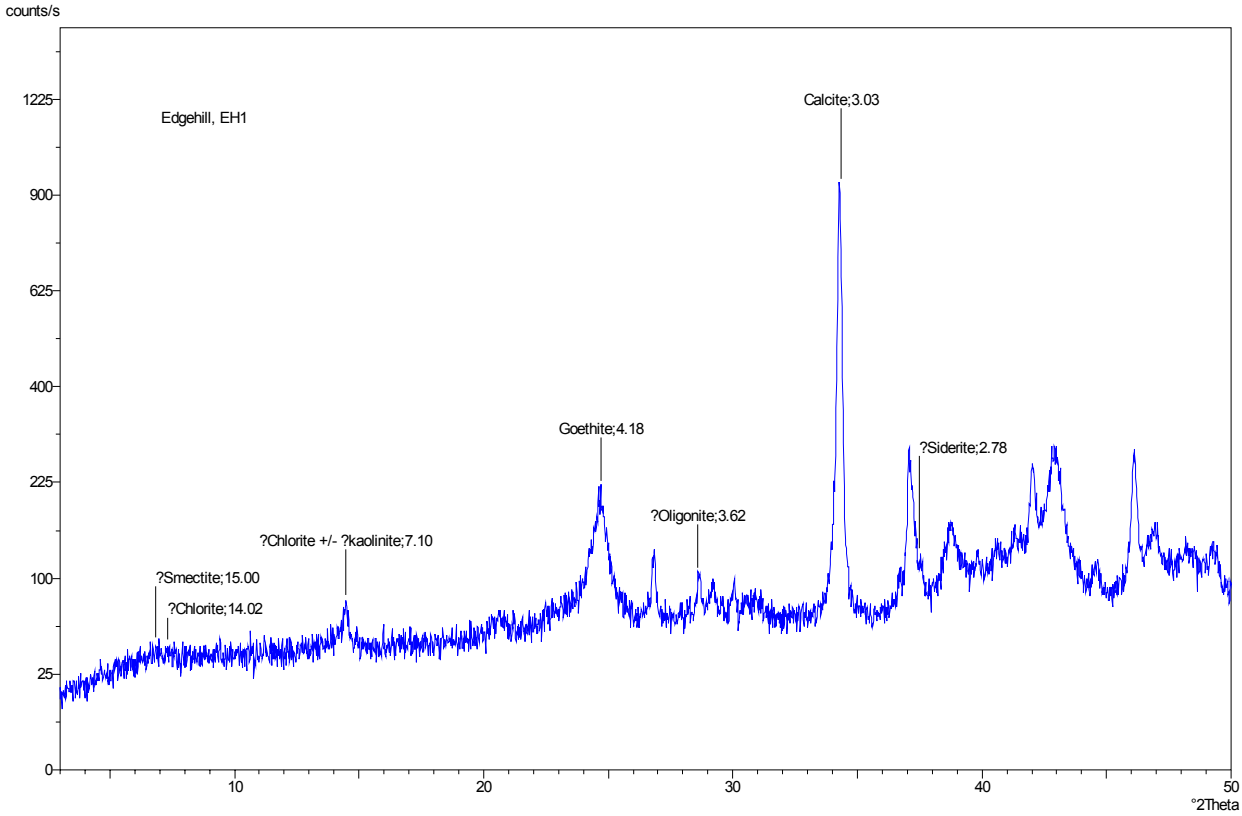


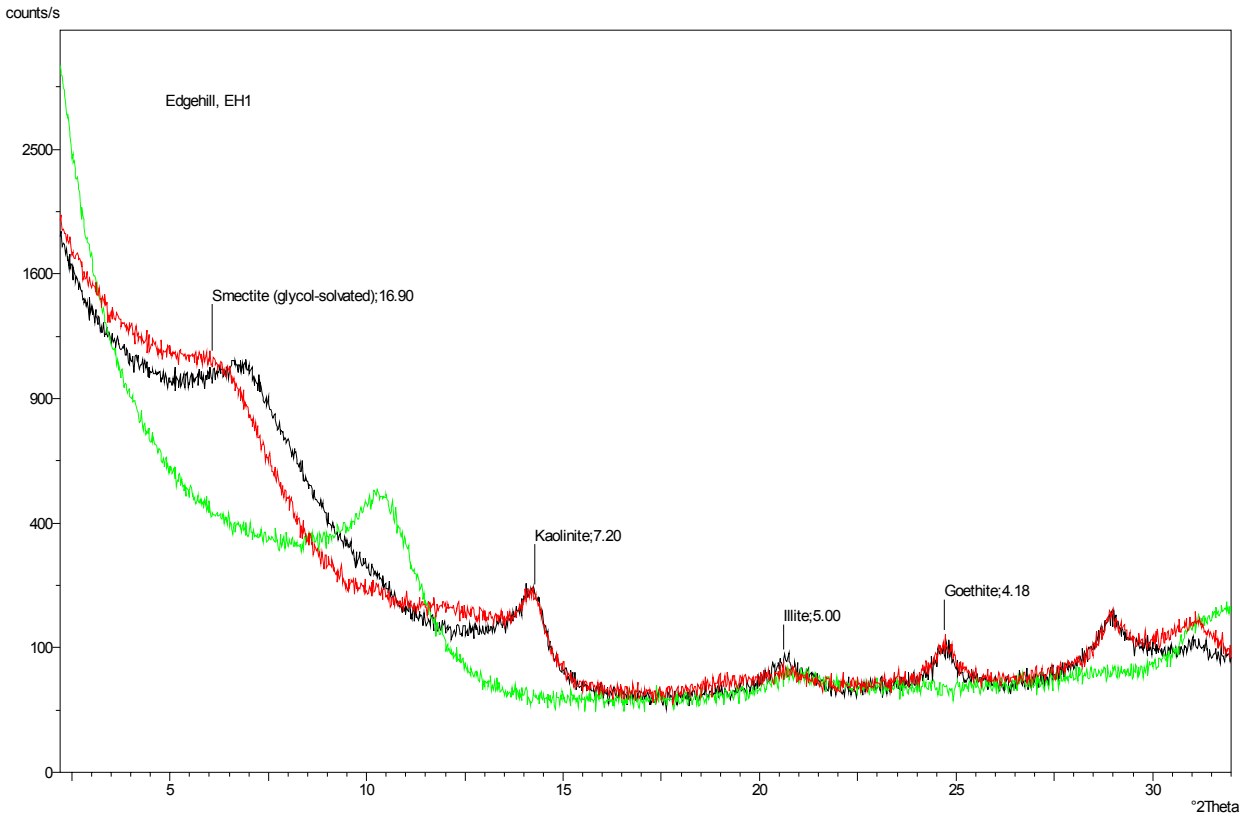
Southam, SH1


counts/s
Southam, SH1
?Smectite;15.00
Chlorite;14.27
?Illite/smectite;12.40
'Mica';9.98
Gypsum;7.61
Kaolinite +/- chlorite;7.17
Quartz;3.34
Calcite;3.03
Dolomite;2.90
Pyrite;2.71
°2Theta

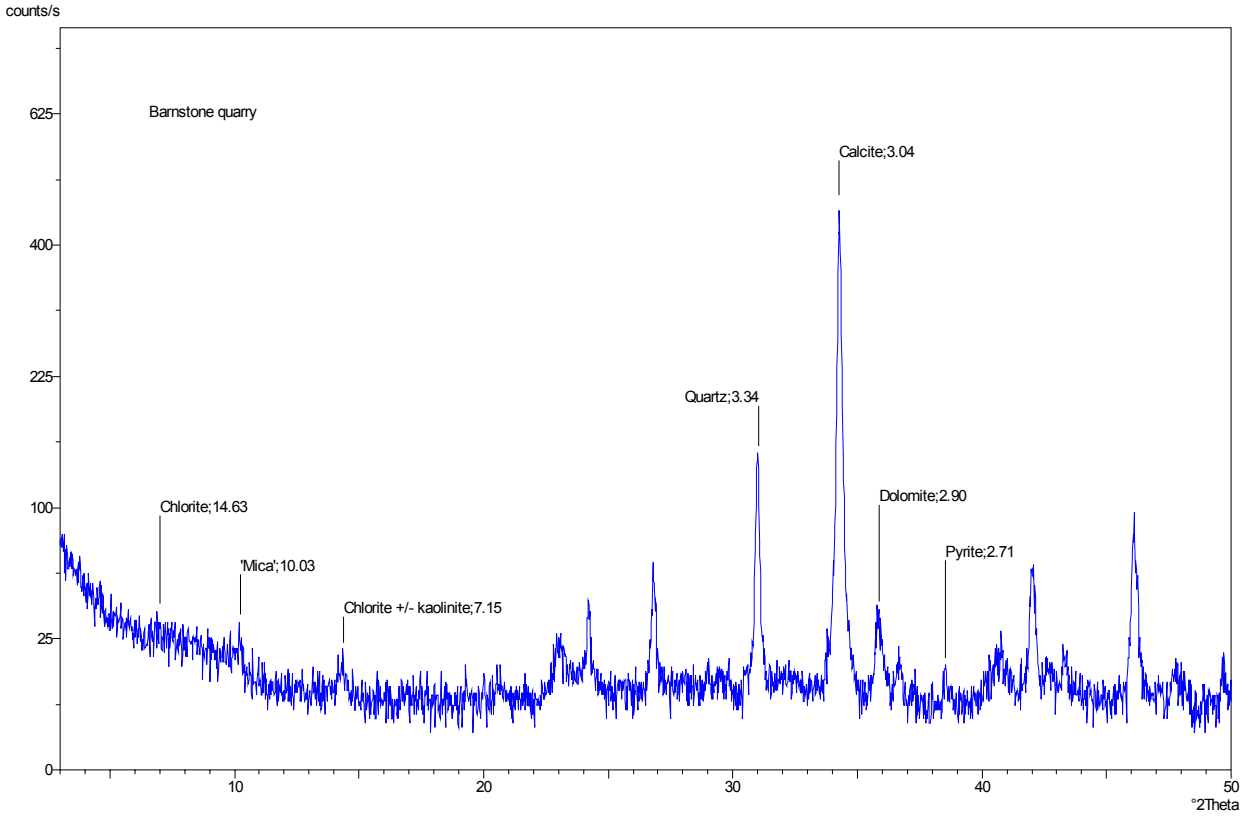

counts/s
Southam, SH1
Smectite (glycol-solvated);16.91
Chlorite (heated);13.51
?Illite/smectite;12.00
Illite;10.00
Kaolinite +/- chlorite;7.16
Quartz;4.26
°2Theta

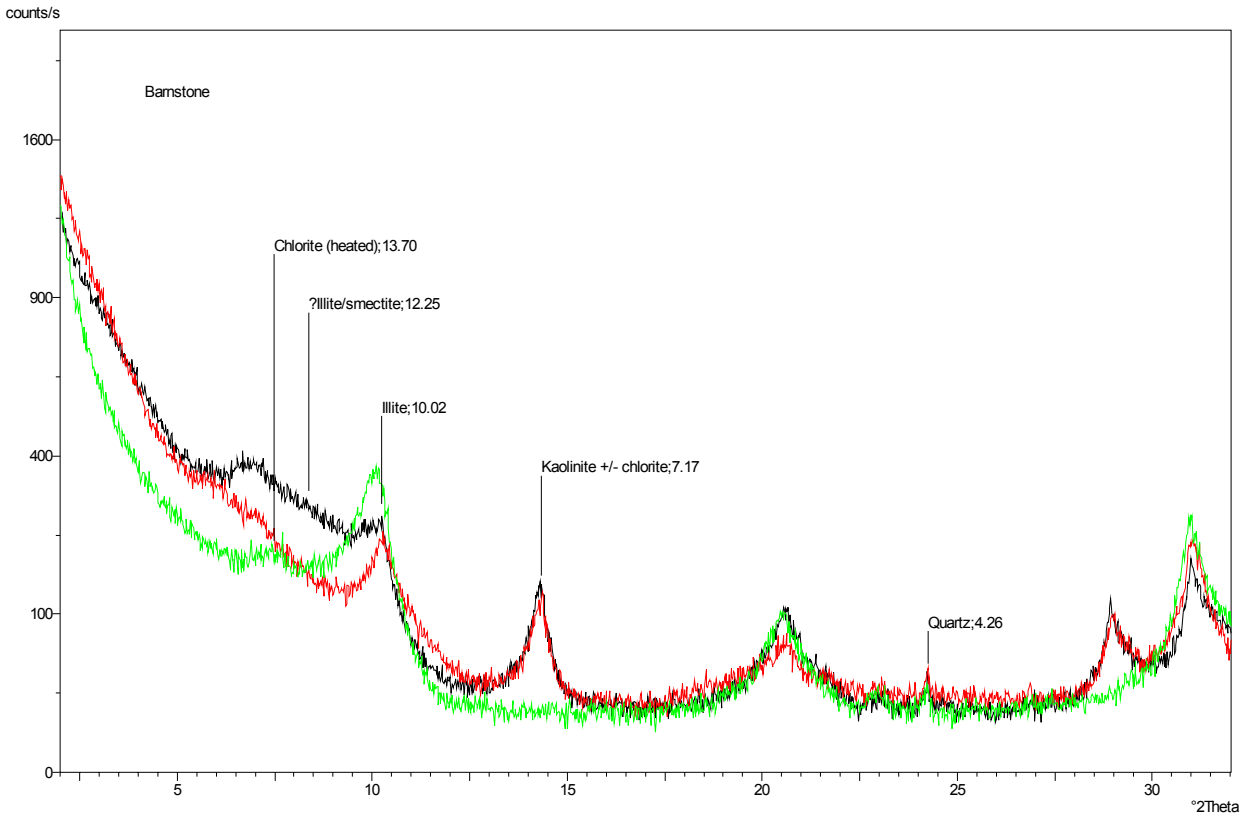
Edgehill, EH1



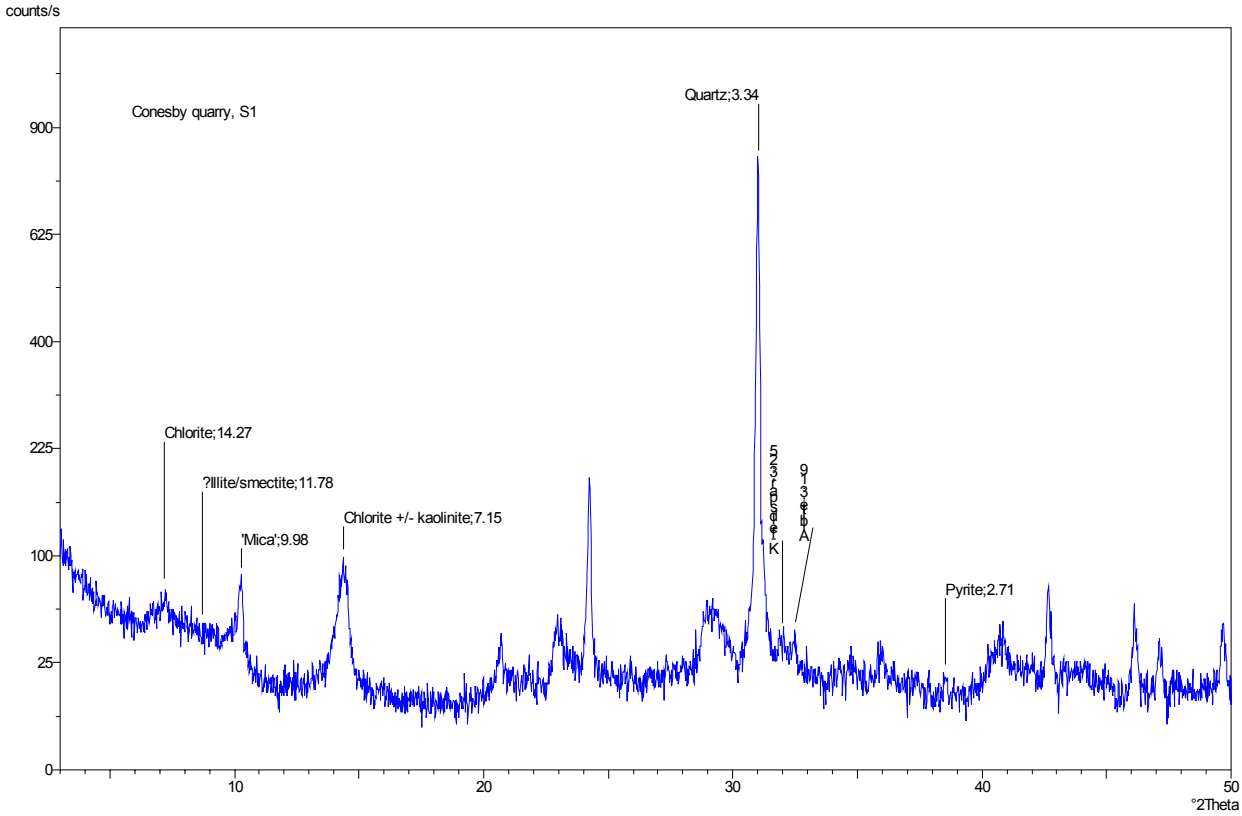


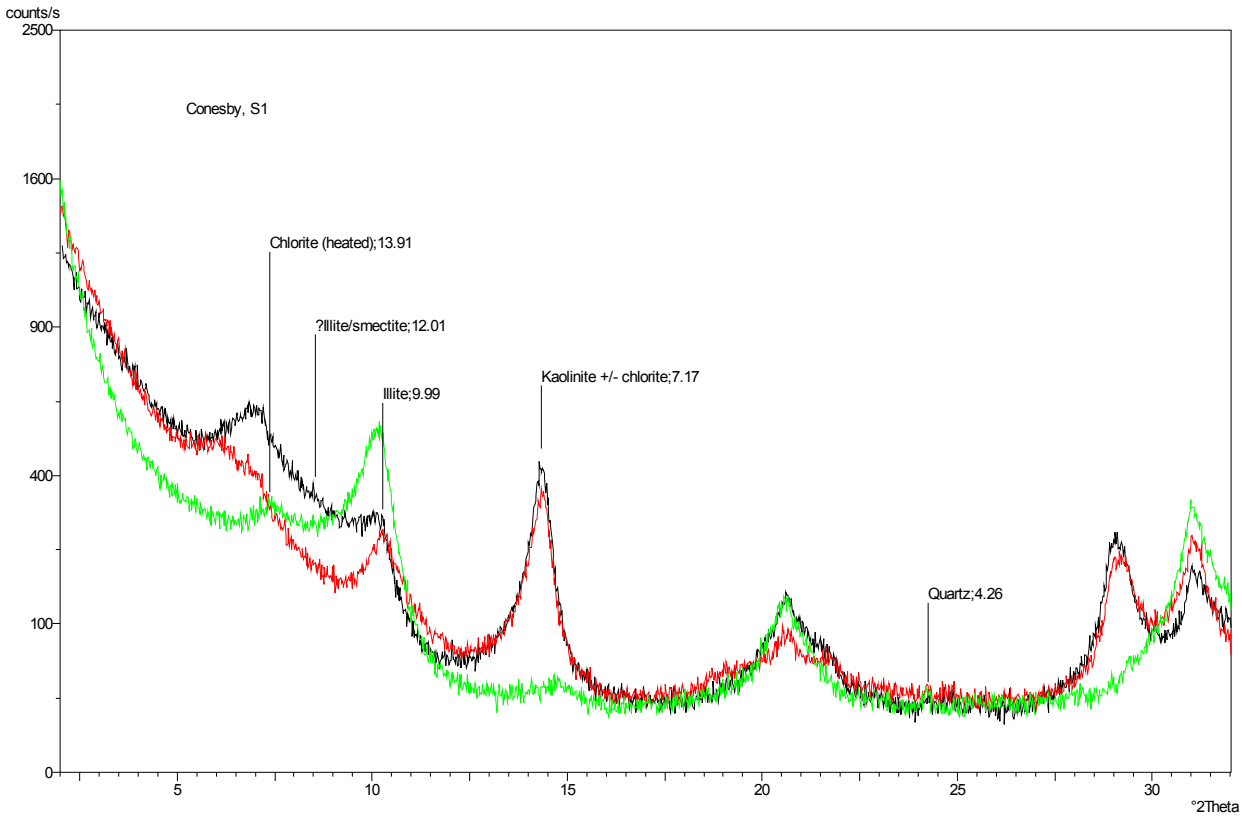
Barnstone


counts/s
Barnstone quarry
Calcite;3.04
Quartz;3.34
Dolomite;2.90
Pyrite;2.71
Chlorite;14.63
'Mica';10.03
Chlorite +/- kaolinite;7.15
°2Theta

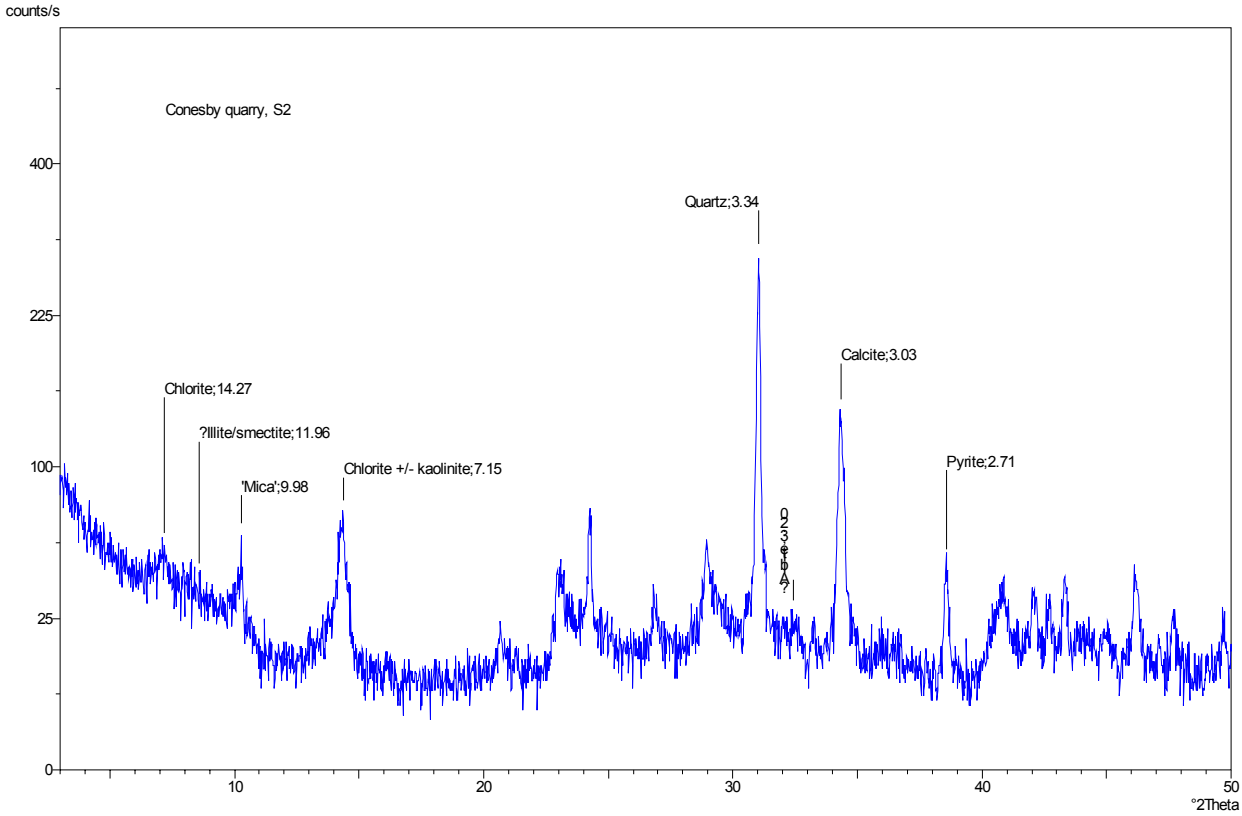

counts/s
Barnstone
Chlorite (heated);13.70
?Illite/smectite;12.25
Illite;10.02
Kaolinite +/- chlorite;7.17
Quartz;4.26
°2Theta

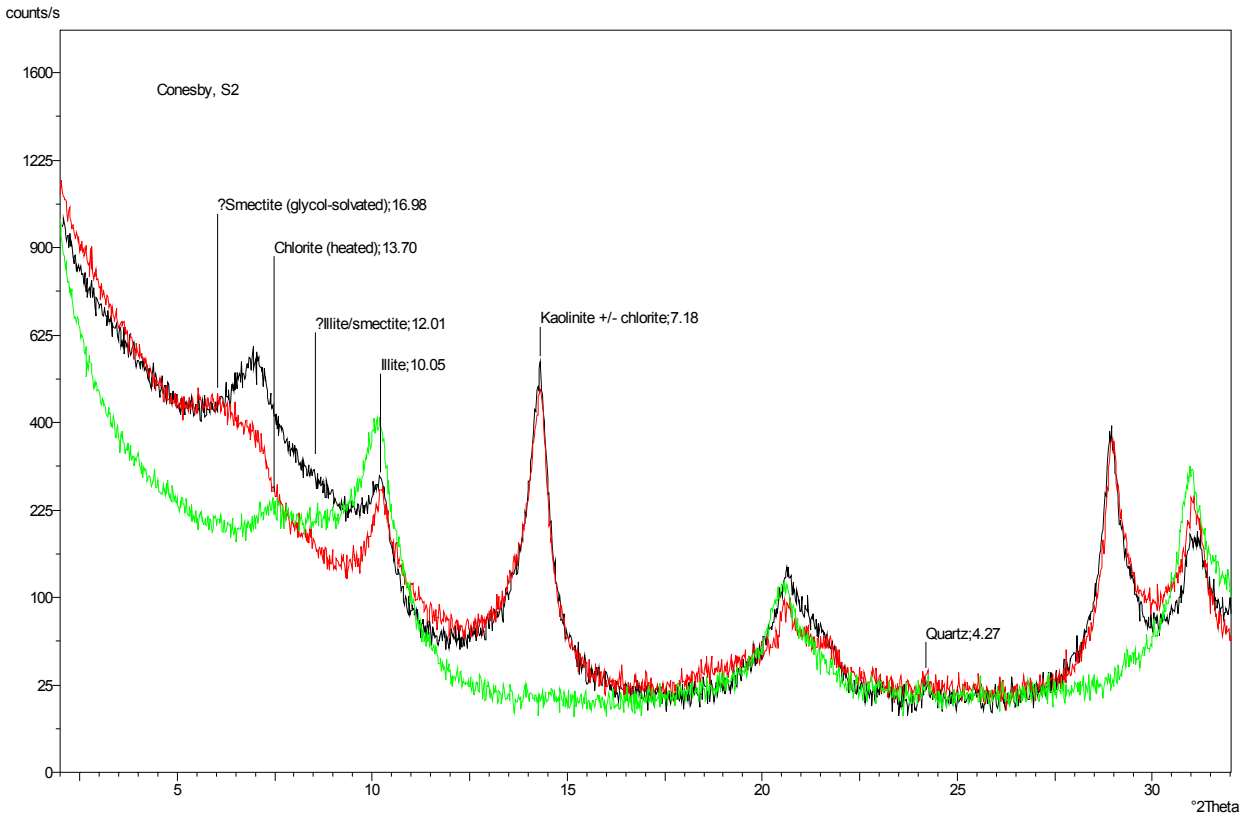
Conesby, S1


counts/s
Conesby quarry, S1
Quartz;3.34
Chlorite;14.27
?Illite/smectite;11.78
'Mica';9.98
Chlorite +/- kaolinite;7.15
Pyrite;2.71
°2Theta

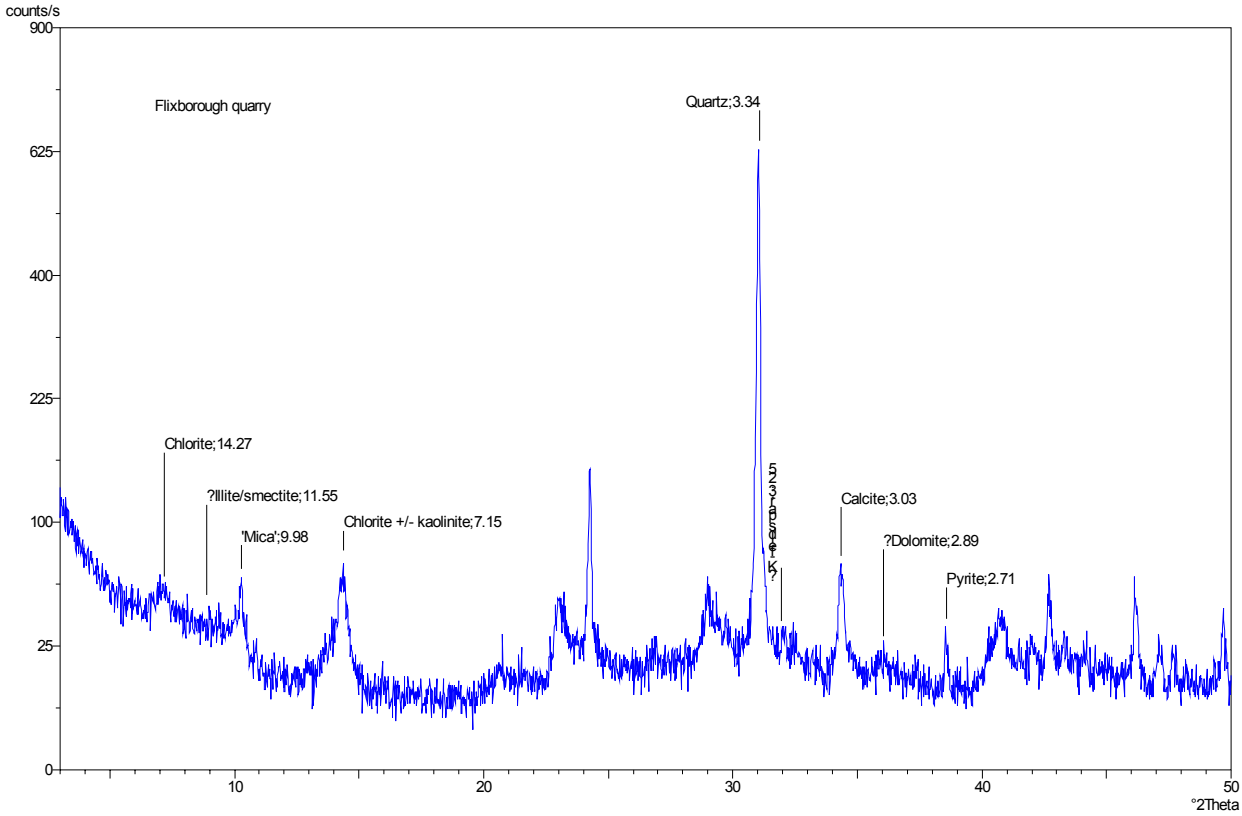

counts/s
Conesby, S1
Chlorite (heated);13.91
?Illite/smectite;12.01
Illite;9.99
Kaolinite +/- chlorite;7.17
Quartz;4.26
°2Theta

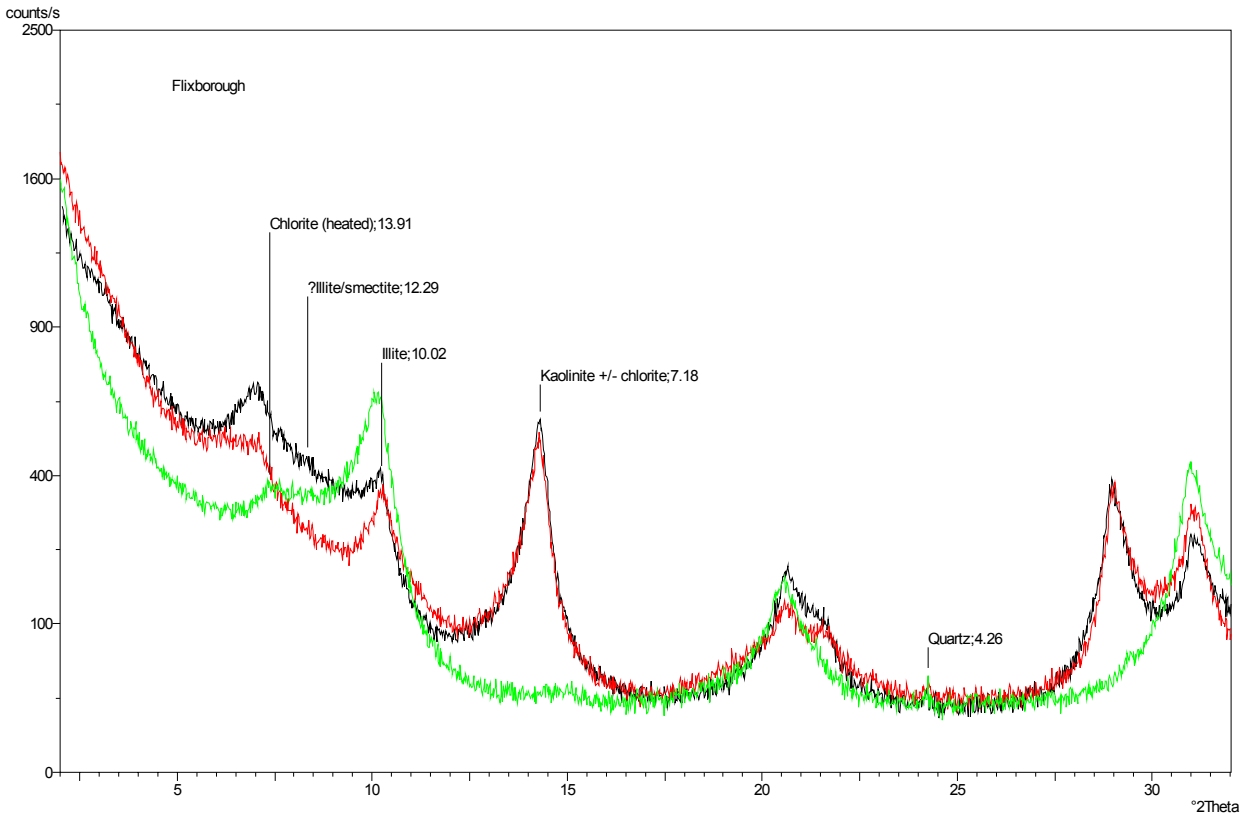
Conesby, S2


counts/s
Conesby quarry, S2
Quartz;3.34
Calcite;3.03
Chlorite;14.27
?Illite/smectite;11.96
'Mica';9.98
Chlorite +/- kaolinite;7.15
Pyrite;2.71
0 2 3 e b A ?
400
225
100
25
0
10
20
30
40
50
°2Theta

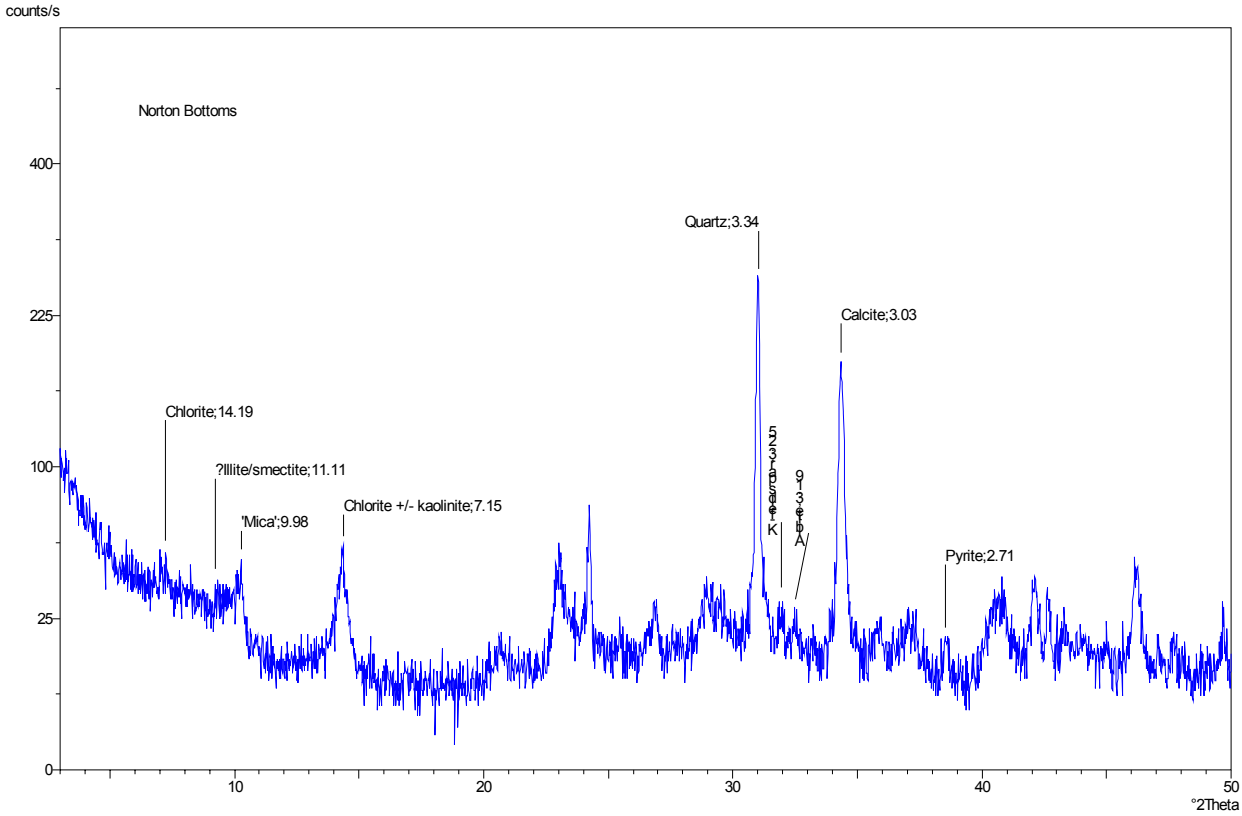

counts/s
Conesby, S2
?Smectite (glycol-solvated);16.98
Chlorite (heated);13.70
?Illite/smectite;12.01
Illite;10.05
Kaolinite +/- chlorite;7.18
Quartz;4.27
1600
1225
900
625
400
225
100
25
0
5
10
15
20
25
30
°2Theta

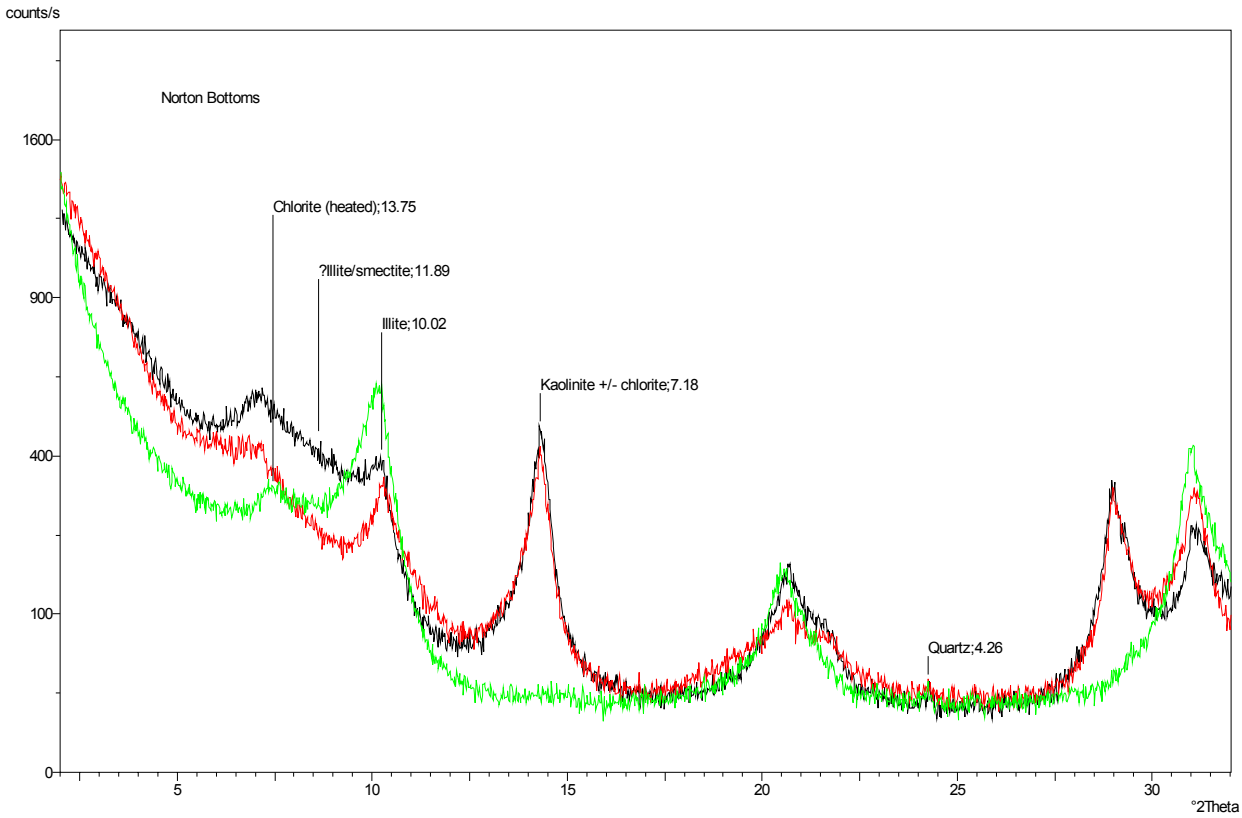
Flixborough



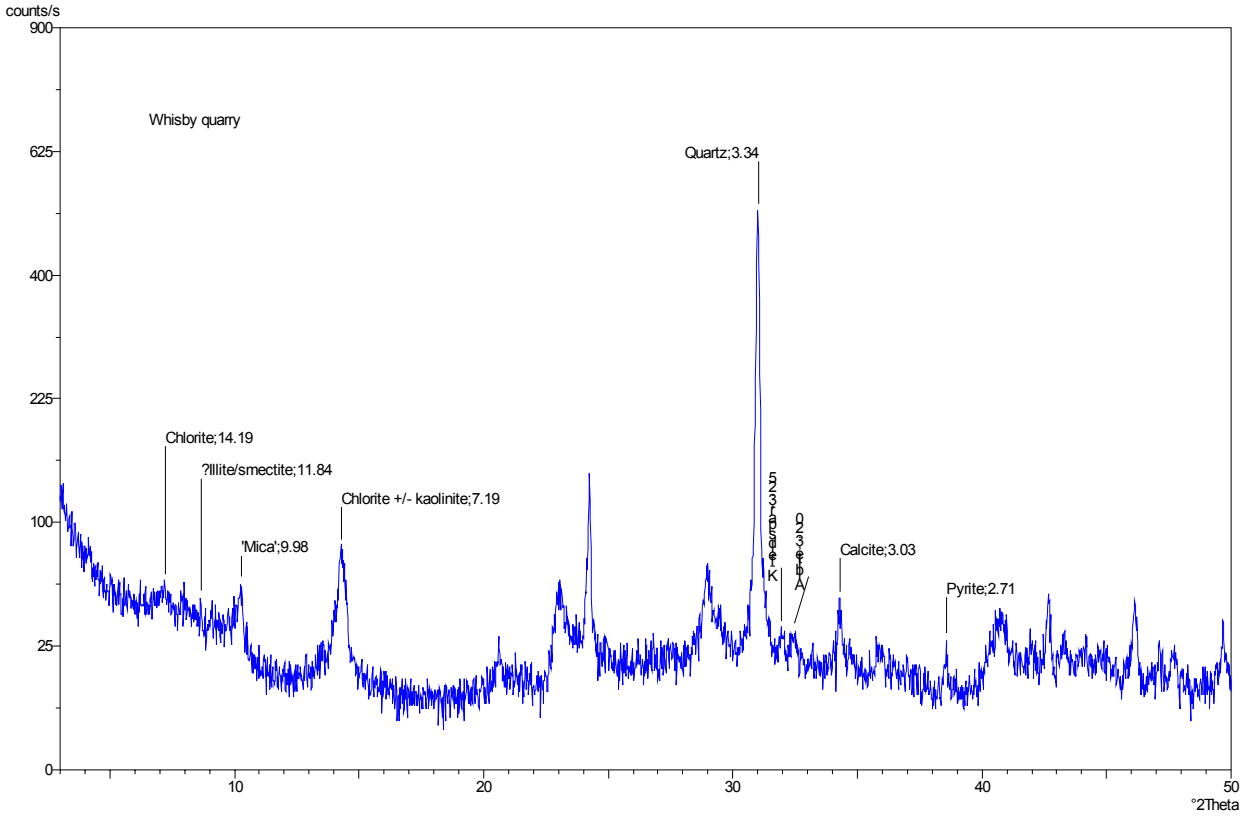


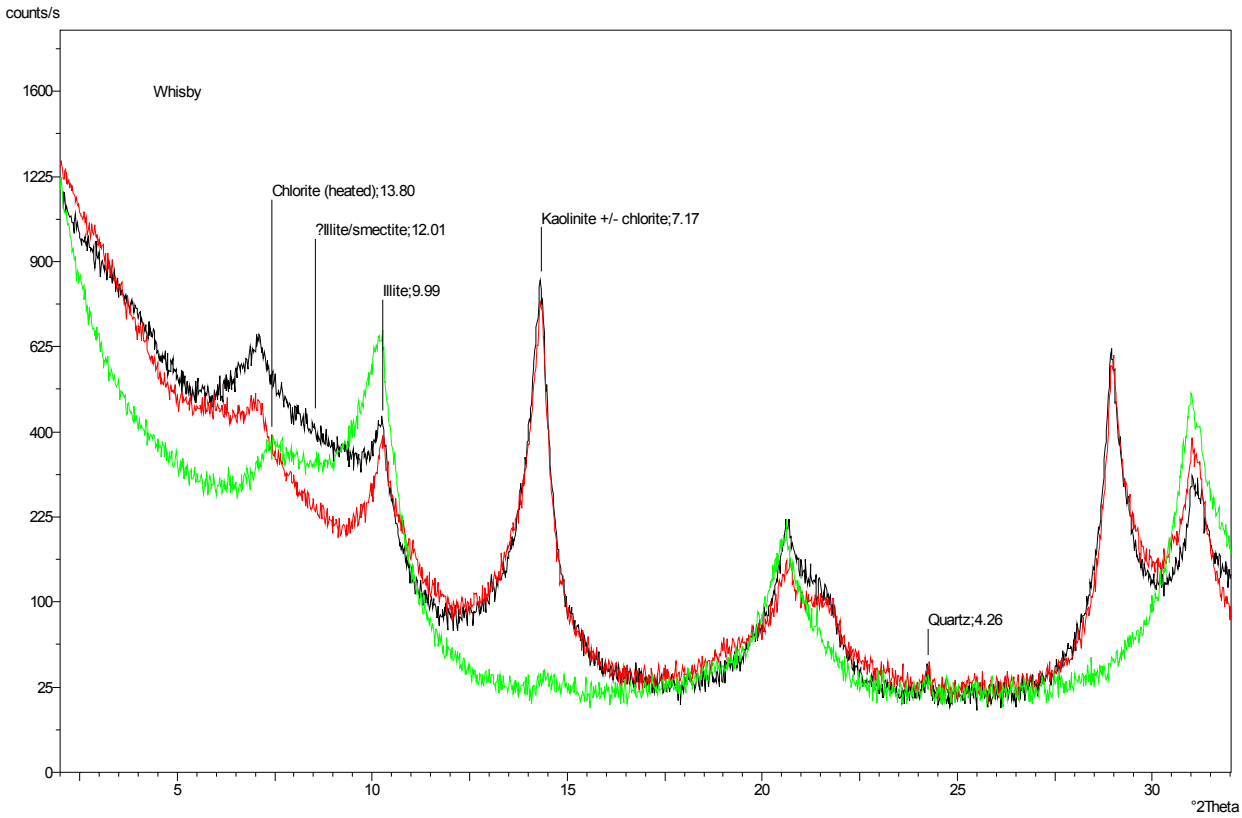
Norton Bottoms



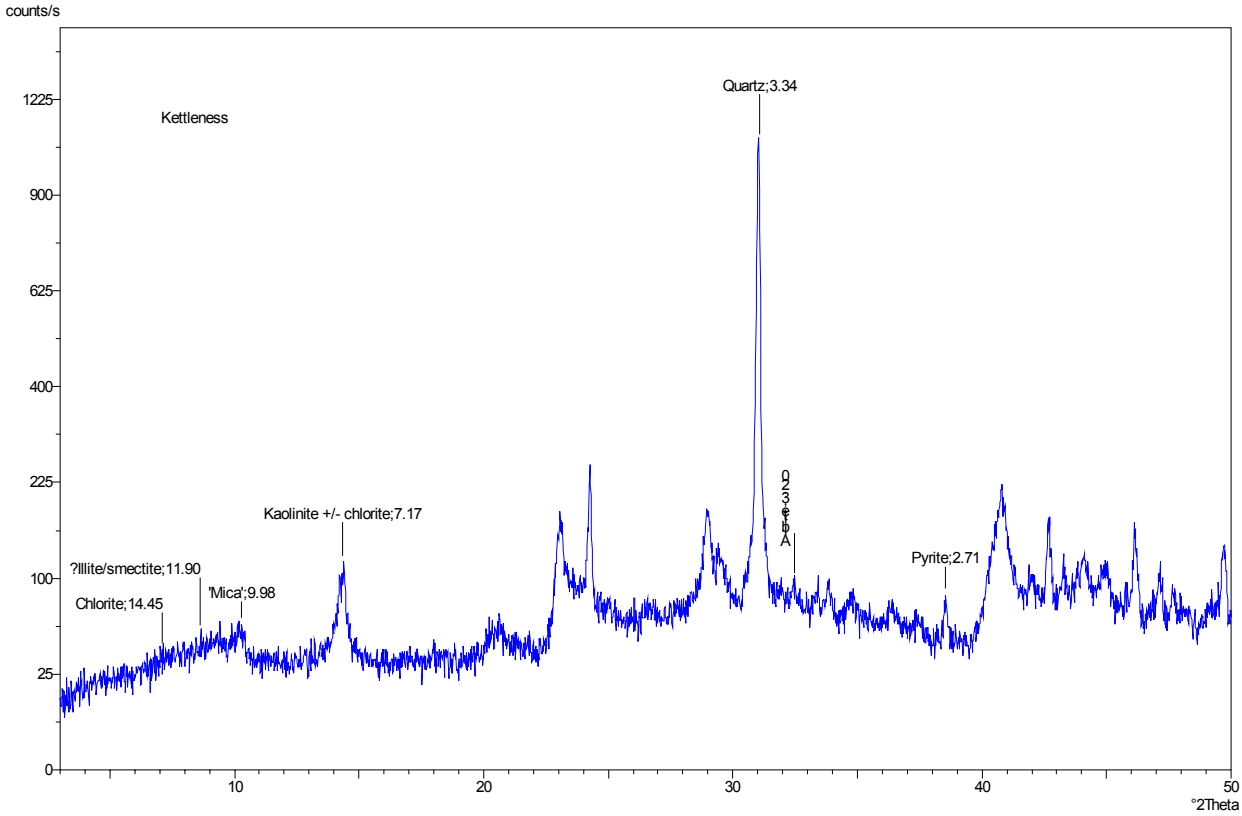


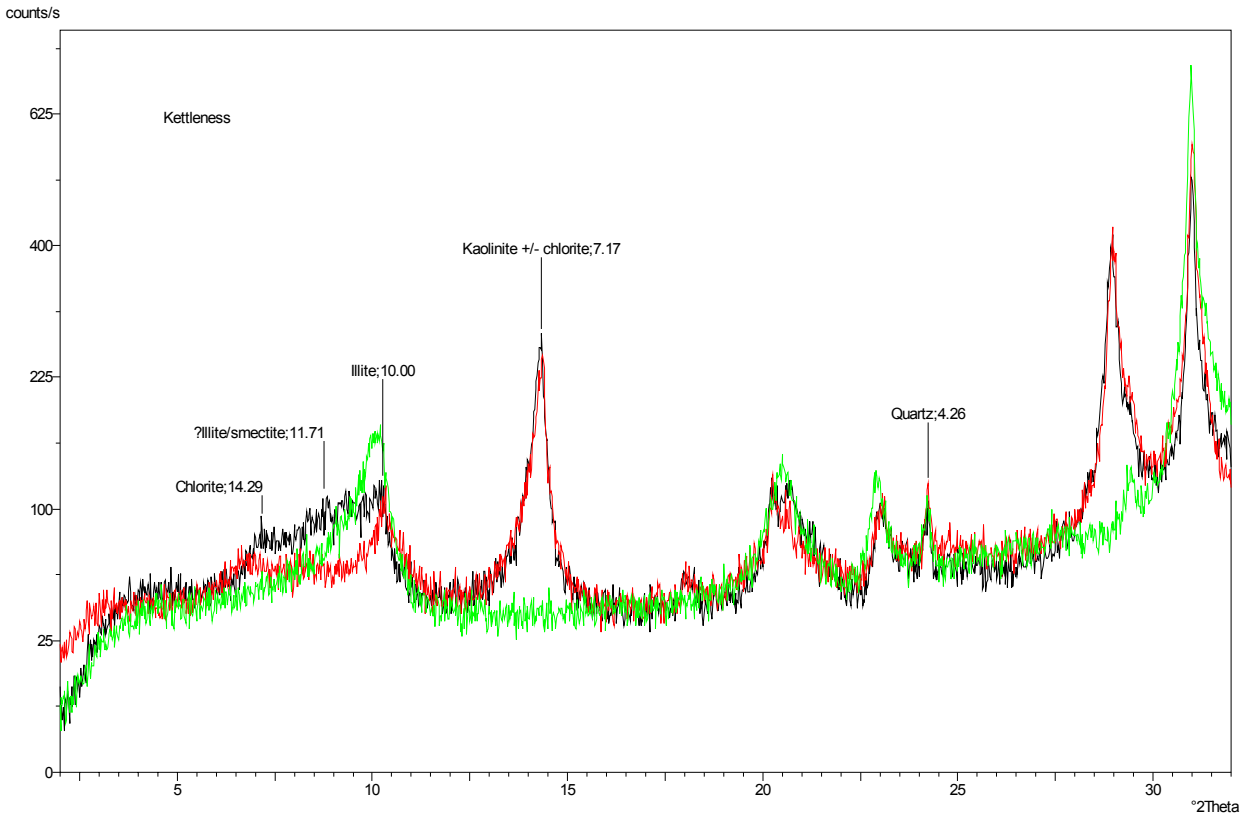
Whisby


counts/s
900
625
400
225
100
25
0
Whisby quarry
Quartz;3.34
Chlorite;14.19
?Illite/smectite;11.84
Chlorite +/- kaolinite;7.19
'Mica';9.98
Calcite;3.03
Pyrite;2.71
10
20
30
40
50
°2Theta

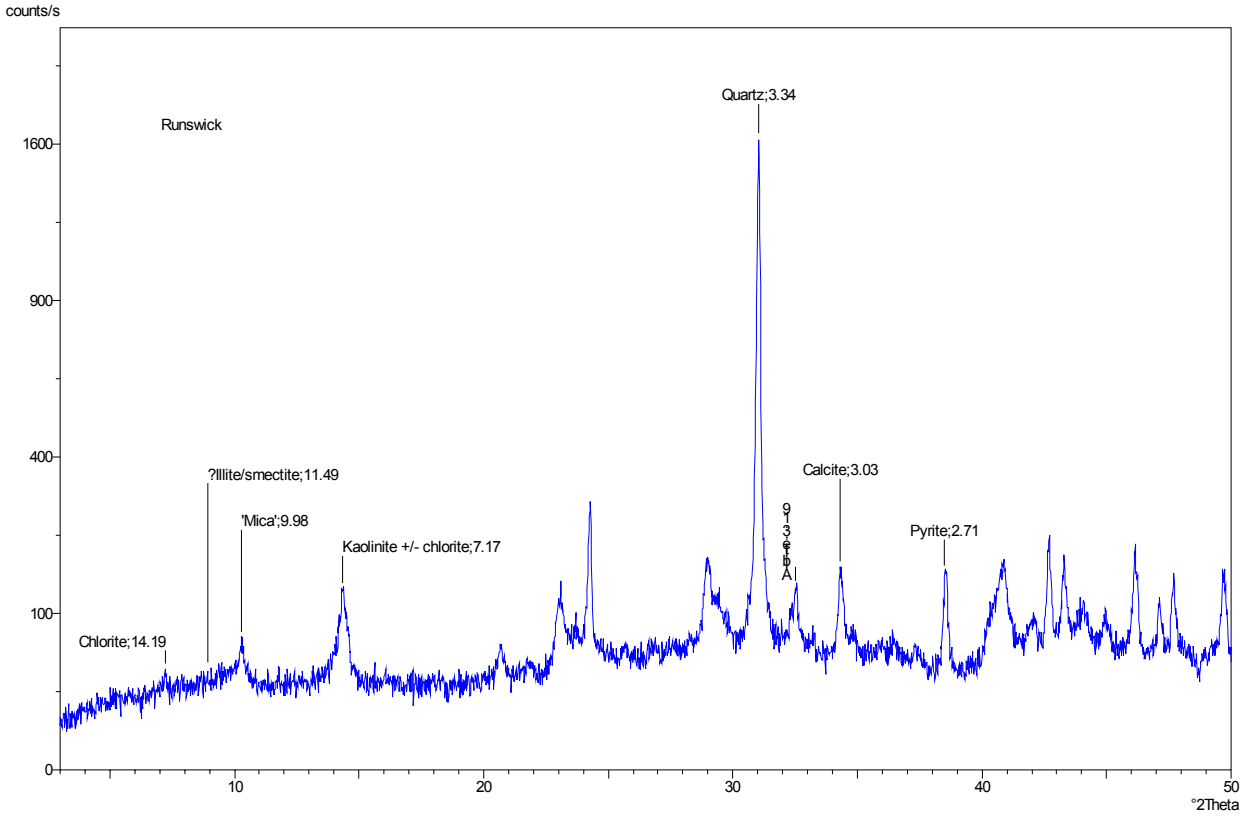

counts/s
1600
1225
900
625
400
225
100
25
0
Whisby
Chlorite (heated);13.80
?Illite/smectite;12.01
Illite;9.99
Kaolinite +/- chlorite;7.17
Quartz;4.26
5
10
15
20
25
30
°2Theta

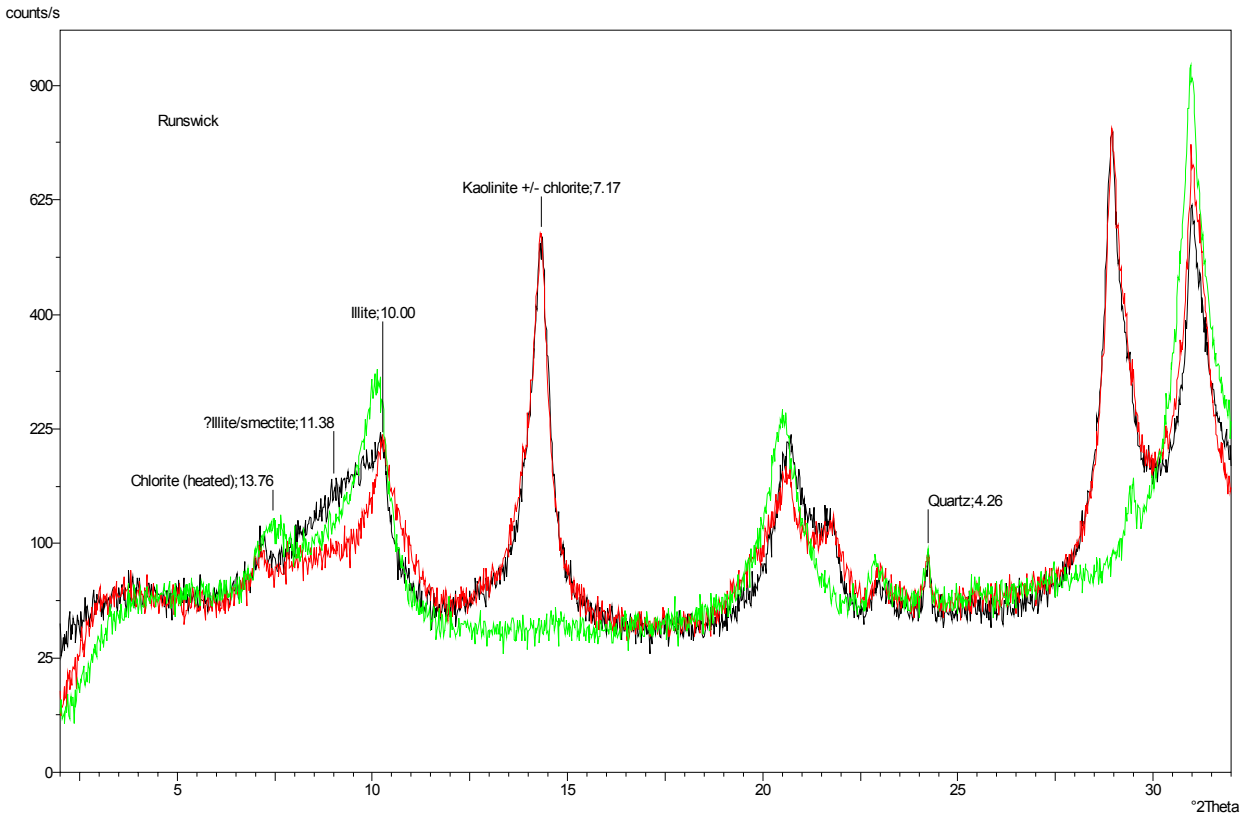
Kettleness


counts/s
Kettleness
Quartz;3.34
Kaolinite +/- chlorite;7.17
?Illite/smectite;11.90
'Mica';9.98
Chlorite;14.45
Pyrite;2.71
°2Theta

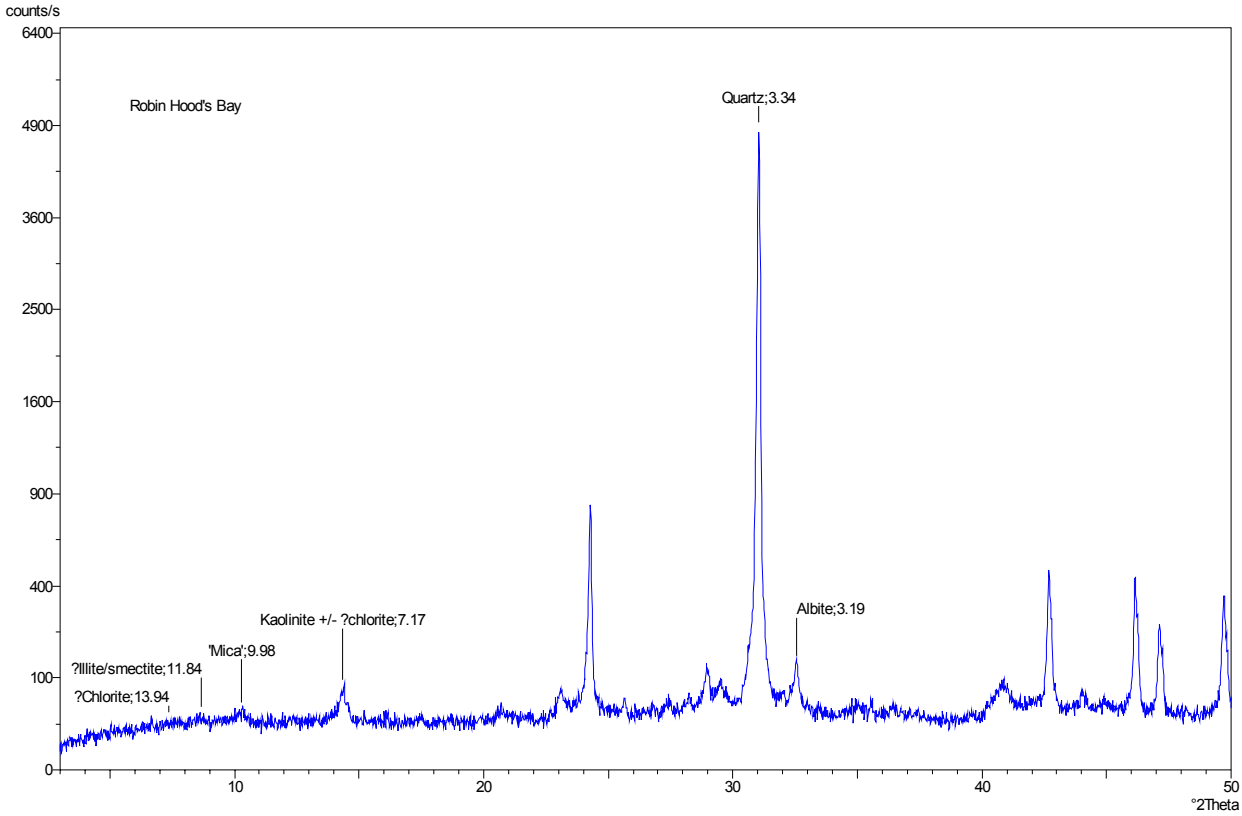

counts/s
Kettleness
Kaolinite +/- chlorite;7.17
Illite;10.00
?Illite/smectite;11.71
Chlorite;14.29
Quartz;4.26
°2Theta

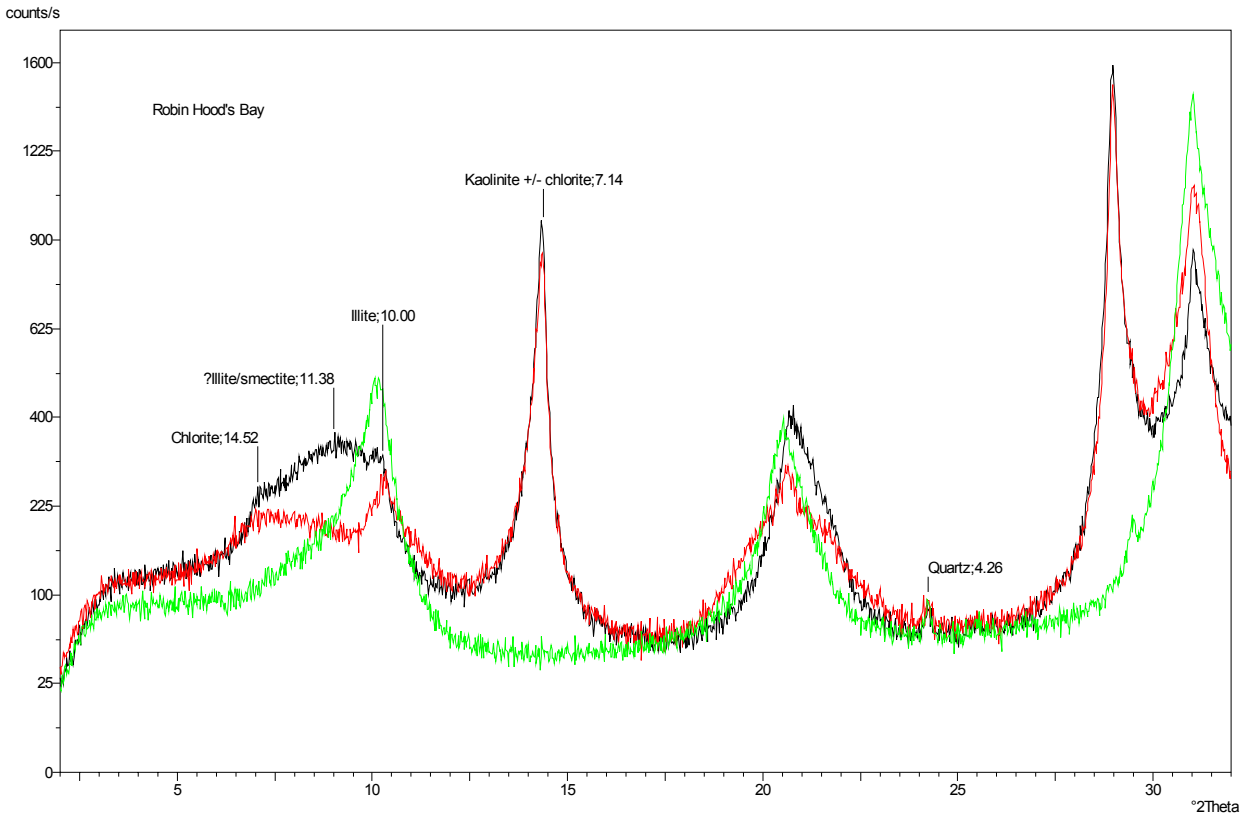
Runswick


counts/s
Runswick
Quartz;3.34
Calcite;3.03
Pyrite;2.71
?Illite/smectite;11.49
'Mica';9.98
Kaolinite +/- chlorite;7.17
Chlorite;14.19
3.36Å
1600
900
400
100
0
10
20
30
40
50
°2Theta

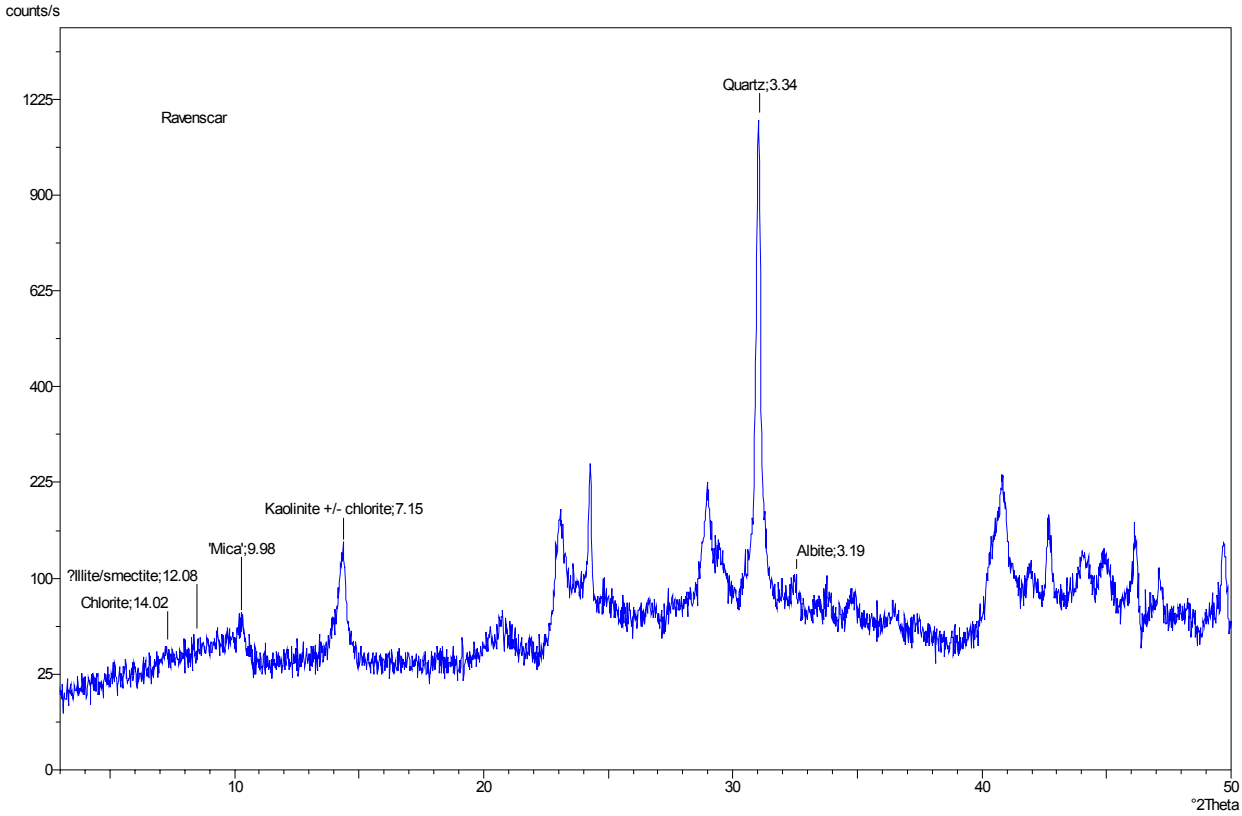

counts/s
Runswick
Kaolinite +/- chlorite;7.17
Illite;10.00
?Illite/smectite;11.38
Chlorite (heated);13.76
Quartz;4.26
900
625
400
225
100
25
0
5
10
15
20
25
30
°2Theta

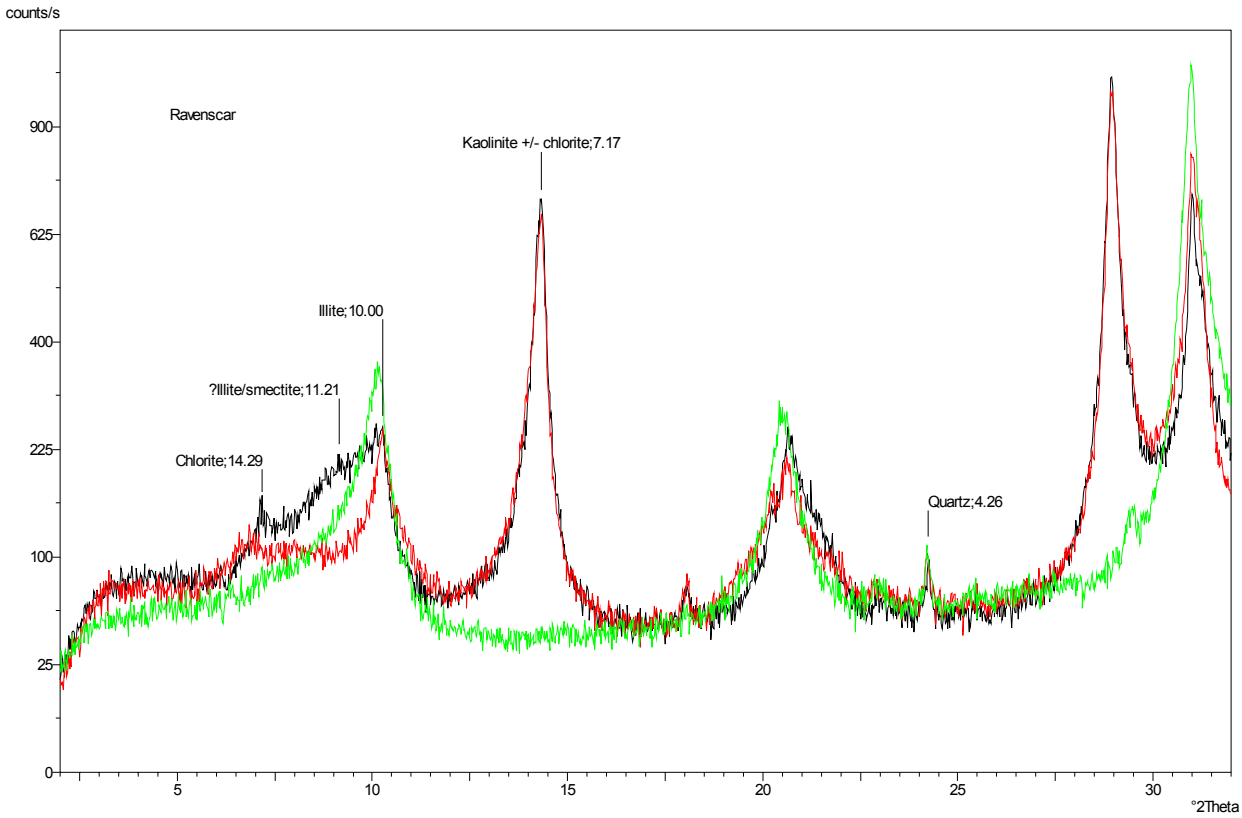
Robin Hood's Bay



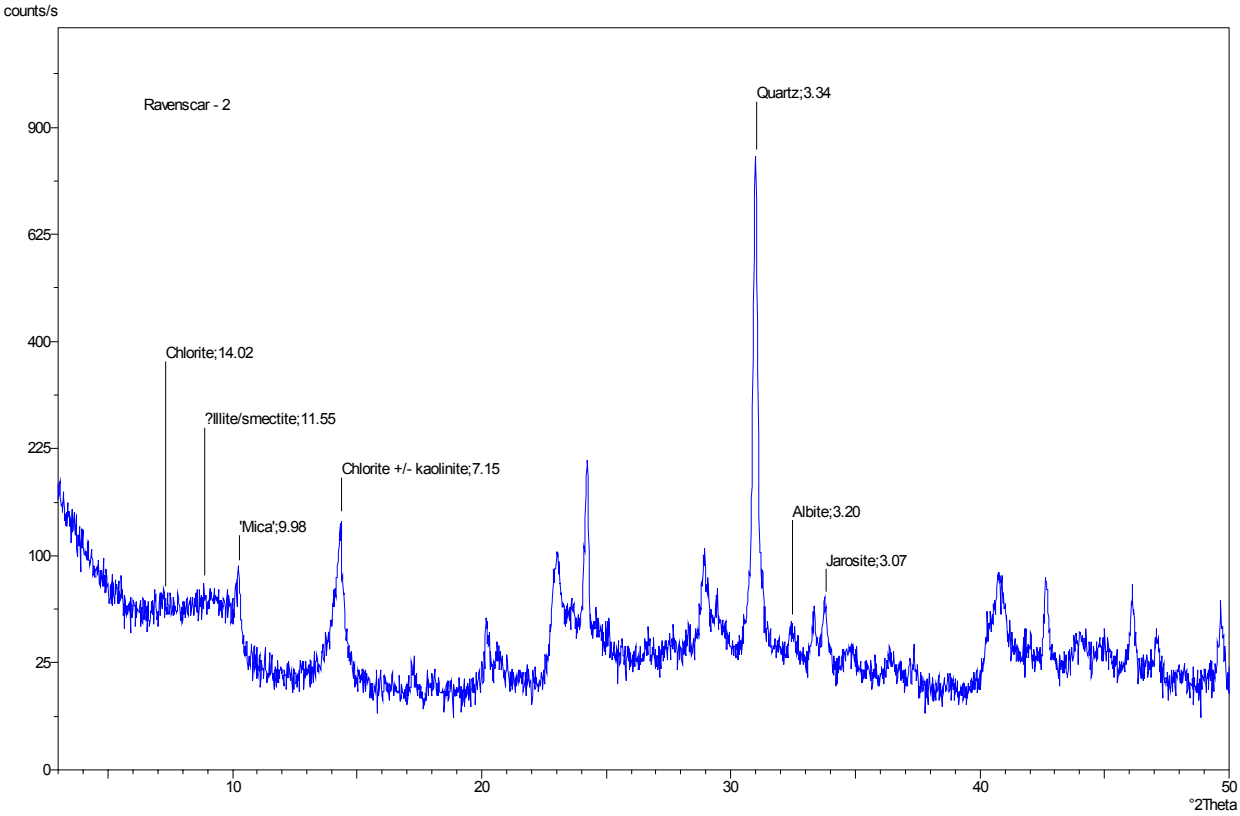


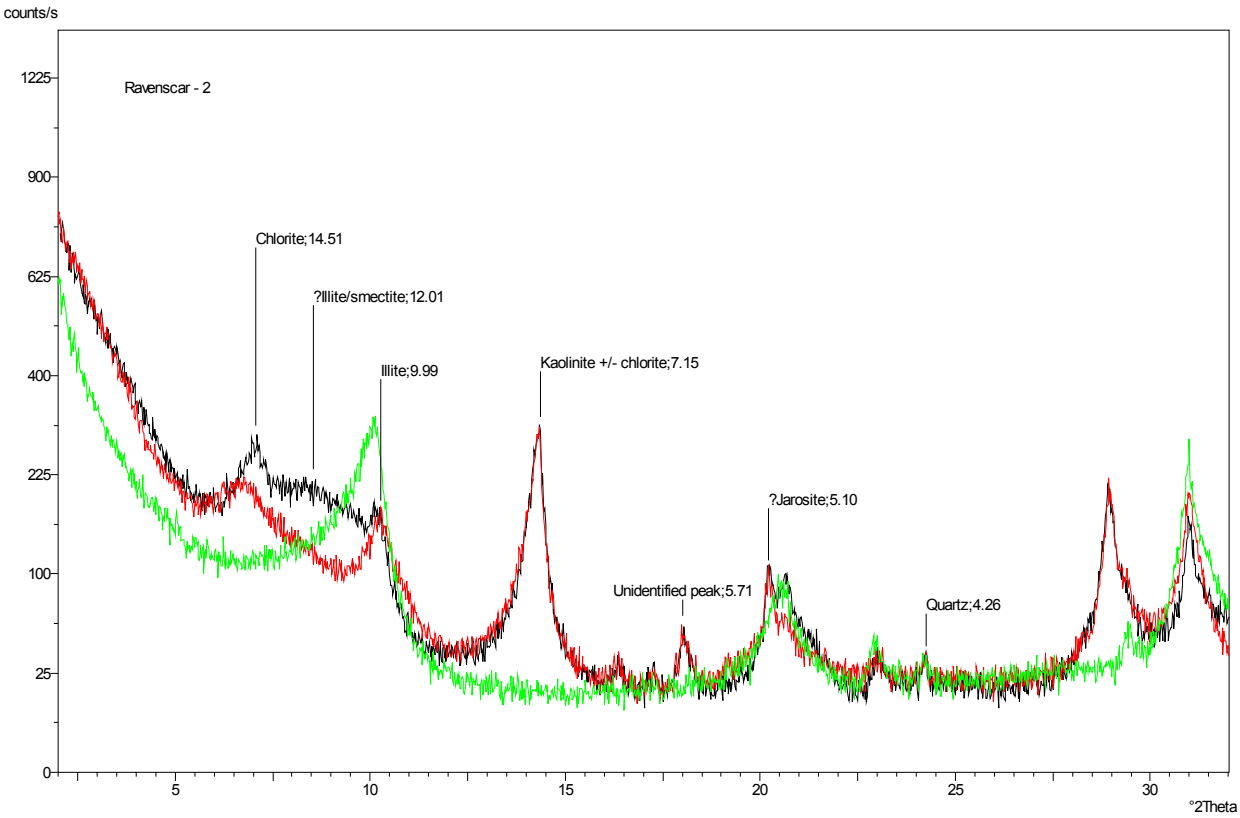
Ravenscar


counts/s
Ravenscar
Quartz;3.34
Kaolinite +/- chlorite;7.15
'Mica';9.98
?Illite/smectite;12.08
Chlorite;14.02
Albite;3.19
°2Theta


counts/s
Ravenscar
Kaolinite +/- chlorite;7.17
Illite;10.00
?Illite/smectite;11.21
Chlorite;14.29
Quartz;4.26
°2Theta

Ravenscar – 2


counts/s
Ravenscar - 2
Quartz;3.34
Chlorite;14.02
?Illite/smectite;11.55
Chlorite +/- kaolinite;7.15
'Mica';9.98
Albite;3.20
Jarosite;3.07
°2Theta


counts/s
Ravenscar - 2
Chlorite;14.51
?Illite/smectite;12.01
Illite;9.99
Kaolinite +/- chlorite;7.15
?Jarosite;5.10
Unidentified peak;5.71
Quartz;4.26
°2Theta