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Abstract

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Keywords	flint; geochemistry; prehistory; Britain; Ireland

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Sources of flint in Britain and Ireland: a quantitative assessment of geochemical characterisation using acid digestion inductively coupled plasma-mass spectrometry (ICP-MS)

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Abstract

The aim of this study is to investigate the potential of acid digestion inductively coupled plasma-mass spectrometry (ICP-MS) to determine the source of flint used for tool-making during British and Irish prehistory. To achieve this, ICP-MS was used to characterise flint geochemistry and to determine whether flint sources in Britain and Ireland can be distinguished using this method. Samples were obtained from the Northern, Southern, and Transitional Chalk provinces in England, as well as the Northern Ireland Chalk formation. This paper presents preliminary quantitative analysis of these samples and demonstrates that acid digestion ICP-MS is capable of distinguishing flint sourced from within and between the different Chalk provinces using discriminant function analysis. The implications of this research are discussed as well as directions for future study.

Keywords: flint; geochemistry; prehistory; Britain; Ireland

1. Introduction

Flint was a common material used for toolmaking throughout British and Irish prehistory. It was perhaps the most common, although its ability to survive virtually unchanged through the course of many millennia compared to tools made from organic material may skew our perception. The durability of flint has resulted in huge numbers of artefacts being recovered and excavated through archaeological investigations, demonstrating that flint was the predominant raw material choice for the majority (if not all) of worked lithic assemblages. Flint can be found in nodular or tabular form in Cretaceous chalk (primary sources), as well as in pebbles, within river gravels and on beaches (secondary sources). During prehistory, there is evidence that flint for toolmaking was obtained from a variety of locations, however, its subsequent movement has been more difficult to demonstrate. Characterisation of Upper Palaeolithic artefacts from England using LA-ICP-MS has demonstrated the extent of raw material movement, as well as the presence of flint from multiple sources at one site (Pettitt *et al.* 2012).

Previous studies in the area of flint sourcing have focused on a small geographic area (e.g. differentiation of a coastal and inland source within the north of Ireland in Griffiths and Woodman 1987), or a narrow temporal range (e.g. movement of flint during the British Final Magdalenian in Pettitt *et al.* 2012). The current work has opted for a broad study area to include the major flint-producing areas of Britain and Ireland, with no focus on a particular archaeological period. This work represents the first comparison (and subsequent differentiation) of flint obtained from the British Northern, Southern, and Transitional Chalk provinces, as well as inland and coastal samples from the Northern Ireland Chalk formation. In the past (as today), the Irish Sea was no barrier to the movement of people, objects, materials, and ideas, so it was important for this study to have as broad an approach as possible to the identification and differentiation of flint sources. In doing so, this study has created a foundation for future analyses of flint from across Britain and Ireland, which will facilitate the detection and interpretation of raw material procurement strategies and movement of people and resources.

1.1 Characterising stone and flint

The ability of chemical sourcing studies to reconstruct movements of objects in the past has led to a large number of such analyses appearing in archaeological literature. These studies utilise a wide array of methodologies to meet the requirements of the 'provenance postulate' (Weigand *et al.* 1977, 24; Neff 2001, 107-8), which states that successful characterisation is possible only if the inter-source chemical or mineralogical variation is greater than the intra-source chemical or mineralogical variation (Glascock 2002, 2).

The scientific analysis of lithic material has long been a part of archaeological investigation. Petrographic analysis has been applied to a wide range of British and Irish lithologies and is showcased most prominently in Stone Axe Studies I and II (Clough & Cummins 1979; 1988) and Stone Axe Studies III (Davis & Edmonds 2011). The research outlined in these publications determined over 30 main stone axe groups in use during the Neolithic in Britain and Ireland, and identified the sites of raw material procurement, allowing reconstruction of raw material procurement strategies and/or trade networks. Analysis of exotic material has unequivocally demonstrated that pan-European circulation of axeheads made from Alpine jadetite occurred during the Neolithic in Europe, with a distribution network that ranged across thousands of kilometres and lasted over 2000 years (Pétrequin & Pétrequin 2016, 55). Outside of Britain and Ireland, the success of geochemical sourcing is most clearly demonstrated in the identification of obsidian exchange patterns in the Near East, allowing archaeologists to gain insight into cultural interaction and infer the socio-economic complexity of prehistoric societies in that region (Pollard & Heron 2008, 91).

Repeated exploitation of particular types of raw material and/or certain locations were also important ways in which people conceptualised their place within the landscape and society, as well as the creation or maintenance of social relationships (Edmonds 1995, 18). There is a growing awareness that procurement of flint in prehistoric Britain and Ireland was not due to wholly utilitarian concerns. The utilisation of inferior-quality local material at Toome Bridge, Co. Antrim, is difficult to explain in the context of supposed large-scale transport of high-quality coastal flint throughout the Bann Valley in the north of Ireland (Kimball 2000, 53; Woodman 2009, xli). Conversely, in the Vale of Pickering coastal sources were preferentially used over the local gravel flint at some sites, despite the long distances required to obtain it (Conneller & Schadla-Hall 2003, 100). There may have been symbolic importance afforded to exotic or unusual material.

Despite the widespread availability and use of chemical analyses to characterise archaeological material, flint has been frequently identified to a particular source area on the basis of macroscopic characteristics, particularly colour or the 'quality' of the flint for toolmaking (Briggs 1986, 188; Conneller 2012, 98). This is no doubt due, in part, to the sheer number of flint artefacts recovered from excavations, for which even standard lithics recording can be a hugely time-consuming exercise, without taking into consideration the expense, time, and potential damage to the artefact that chemical analysis can incur. Geochemical analysis of flint samples from Scandinavia has demonstrated that there is no correlation between the appearance of flint and the parent chalk, chemical composition, or source location (Högberg *et al.* 2012, 234). The source of flint raw material cannot be determined using petrological analysis, as thin sections of flint do not reveal distinctive mineral structures that can be matched to raw material sources (Tingle 1998, 89).

A number of attempts have been made to chemically characterise flint using a suite of analytical approaches: atomic emission spectroscopy and atomic absorption spectroscopy of samples from British flint mines (Sieveking *et al.* 1970 and 1972), neutron activation analysis of flint from British mines (Aspinall & Feather 1972) and flint tools from the Iberian peninsula (Prudêncio *et al.* 2016), electron spin resonance of flint from the north of Ireland (Griffiths & Woodman 1987), laser ablation ICP-MS of British and European flint samples (Rockman 2003, Durst 2009, Pettitt *et al.* 2012), acid digestion ICP-MS of British and French flint samples (Rockman 2003) and samples of flint from Scandinavia (Olofsson & Rodushkin 2011), and X-Ray fluorescence of Scandinavian flint samples (Hughes *et al.* 2010, Högberg *et al.* 2011, Hughes *et al.* 2012). These studies have demonstrated that flint samples from different areas of Cretaceous chalk can be distinguished on the basis of their geochemical composition.

These analytical approaches vary in terms of the range and concentrations of elements they can detect. Acid digestion ICP-MS was selected for this analysis due to the clear advantages offered in terms of multi-element quantification (>70 elements), detection limits (<parts per trillion), and speed of analysis (Thomas 2008, 1; Georgiou & Danezis 2015, 173). ICP-MS also uses a minute amount of sample material (0.04g in this study). This method also has some drawbacks, the most pressing of which in relation to archaeological material is the wholly destructive nature of the analysis. When applied to artefacts, acid digestion ICP-MS analysis would necessitate the removal and digestion of a portion of the artefact. ICP-MS is also comparatively more expensive than other approaches, and spectral interferences can occur (however these are well defined).

1.2 Cretaceous geology of Britain and Ireland

The warm, shallow seas that covered much of Europe during the Cretaceous period were occupied by calcareous organisms whose calcium-carbonate plates formed the nanofossil ooze that blanketed the Cretaceous seabed, later becoming chalk (Rawson 2006, 387). Deposition of chalk occurred over enormous areas during the Late Cretaceous, with chalk formations stretching from Ireland to Kazakhstan (over 7,000km) (Rawson 2006, 387).

Cretaceous chalk deposits in England are divided into three distinct provinces; Northern, Southern, and Transitional (Hopson 2005, 2). The chalk of the Northern Province is harder than that in the Southern Province, indicating that it may have formed under deeper water (Toghill 2000, 150). The Northern and Southern provinces are well-defined based on differences in rock type and fossil species; the Transitional province is poorly defined by comparison and contains a mixture of Northern and Southern rock types and fossil species (Mortimore *et al.* 2001, 7). The Northern Chalk province is more closely related to the chalk found in the Boreal Realm (northern Europe, including Germany and Scandinavia), whereas the Southern Chalk province links to the chalk of the Paris Basin and onwards to the Tethyan Realm (southern Europe, Mediterranean) (Mortimore *et al.* 2001, 7). The chalk found in the north of Ireland is younger than the deposits found in Britain and has been protected from erosion and disturbance by the Tertiary lavas of the Antrim Plateau (Wilson *et al.* 2001, 345).

The diagenesis of flint has been the subject of debate however the basic process is that of silicification, whereby organic remains become saturated with silica and the carbonate elements are replaced by precipitation of silica cement (Flügel 2009, 643). With regards flint formation, the silica is of biogenic origin, originating from the mineral skeletons of radiolarians and diatoms that lived in the Cretaceous oceans (Monroe & Wicander 2001, 168). The process through which a solution of biogenic silica hardens into flint is also a matter of debate amongst geologists. The general process is considered to be the gradual replacement of the calcium carbonate of the chalk by silica, incorporating the non-carbonate materials (clay minerals, quartz, and heavy minerals) that are, in effect, contamination (Sieveking *et al.* 1970, 252). It is this preservation of the non-carbonate material within flint that provides the theoretical framework that underpins geochemical sourcing (Bush & Sieveking 1986, 134). In analysing and quantifying the trace elements contained within flint it may be possible to detect variation within and between different geographical areas.

1.3 Use of acid digestion ICP-MS

ICP-MS is a highly sensitive method and can detect a wide range of elements at low concentrations. There are two sampling methodologies that ICP-MS can use to provide geochemical signatures necessary for sourcing studies. Both of these methods provide the requisite sensitivity, however they differ significantly in terms of sample preparation and suitability for use on archaeological artefacts - laser ablation (LA-) ICP-MS and acid digestion ICP-MS.

The ultimate aim of most chemical characterisation work within archaeology is to obtain data from artefacts that is compared to results from geological or mineral sources. While acid digestion is more sensitive, LA-ICP-MS is likely to be more attractive in terms of testing items from museum collections or 'one of a kind' artefacts as it is virtually non-destructive (the scar from the laser can be viewed under magnification). However, LA-ICP-MS would still require subsampling of the artefact as it must fit into the analysis chamber – a process that may be more destructive than the actual analysis. LA-ICP-MS is also not as sensitive as acid digestion ICP-MS and cannot detect the same large range of elements.

Overall, the description of acid digestion ICP-MS as "the gold standard" of chemical analysis (Vanhaecke & Degryse 2012, xv) due to its exceptional sensitivity to a wide range of elements at very low concentrations make it a suitable candidate for the analysis of flint, particularly in the preliminary stages of investigating the geochemical variability of samples from across a large study area.

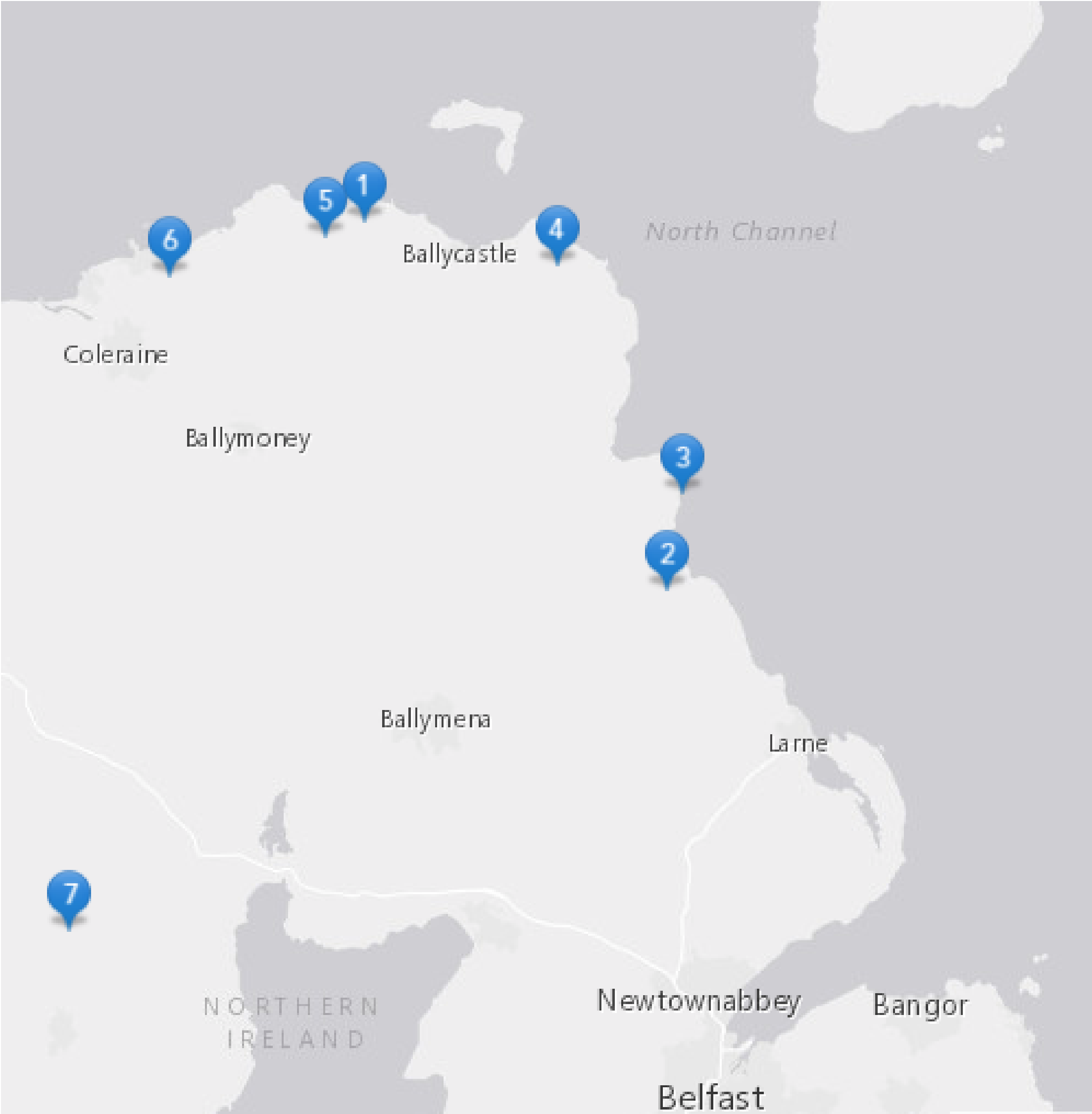
2. Collection, preparation, and analysis of samples

Sampling locations were identified through a variety of different sources: geological literature (e.g. British Geological Survey, Geological Survey of Ireland); archaeological reports detailing presence of local sources of flint (e.g. Bradley & Leivers 2009, 13; Collins 1983, 6); previous sourcing studies (Pettitt *et al*. 2012, 281; Rockman 2003, 312-20); as well as the author's (SB) own knowledge of flint outcrops in the north of Ireland. The aim was to characterise with confidence a particular geographic area where flint outcrops above ground. Due to the limited geological occurrence of primary outcrops of flint, it was decided that focusing on these areas would be most appropriate to determine whether they can be geochemically distinguished using acid digestion ICP-MS.

Secondary sources of flint are widely distributed, comingled, and have been eroded from multiple different primary sources, some of which are located underwater or may be in another country (Butler 2005, 17). Investigation of primary sources of flint enabled elemental characterisation of a discrete area, whereas analysis of secondary sources would provide multiple signatures and confuse attempts to gain a chemical 'fingerprint' of a particular area.

2.1 Sample locations

The sample locations from Northern Ireland are outlined in map 1. Map 2 shows sampling locations in the Southern and Transitional Chalk Provinces. Northern Chalk Province sampling locations are shown in map 3.



Map 1 – Sample collection locations in Northern Ireland. Key: 1 – Ballintoy, 2 – Carnlough, 3 – Cloughastucan and Garron Point, 4 – Murlough Bay, 5 – Portbraddan and White Park Bay, 6 – White Rocks, 7 – Slieve Gallion (ArcGIS Online).

Map 2 – Sample collection locations within the Transitional and Southern Chalk Provinces. Key: 1 – Grime's Graves, 2 – Isle of Wight Lane and Landpark Wood, 3 – A2 Dover, 4 – Dover Coast, 5 – Beer, 6 – A342 Pewsey, 7 – Southwick Hill, 8 – Hackpen Hill, 9 – Harrow Hill, 10 – Moon's Copse, 11 – Cissbury, 12 – Everleigh Road Pewsey (ArcGIS Online).

Map 3 – Sample collection locations within the Northern Chalk Province. Key: 1 – Rifle Butts, 2 – Sledmere/Malton, 3 – Welton-le-Wold, 4 – Malton, 5 – Arras Hill, 6 – Mill Hill, 7 – North Ormsby, 8 – Middleton (ArcGIS Online).

Table 1 – Sampling Locations in Britain and Ireland

Northern Ireland Chalk Province	
Site Location	**Samples Analysed (*subsamples*)**
Ballintoy, Antrim	1 (*3*), 2 (*3*)
Carnlough, Antrim	1 (*3*), 2 (*3*), 4 (*3*), 5 (*1*), 7 (*2*), 9 (*2*)
Cloughastucan, Antrim	1 (*2*), 2 (*3*)
Garron Point, Antrim	1 (*2*), 2 (*2*)
Murlough Bay, Antrim	1 (*1*)
Portbraddan, Antrim	1 (*1*), 2 (*2*)

White Park Bay, Antrim	1 (*3*), 2 (*2*), 3 (*1*), 4 (*1*), 5 (*1*)
White Rocks, Antrim	1 (*1*), 3 (*3*), 4 (*3*), A1 (*2*), A2 (*1*), B1 (*3*), B2 (*2*)
Slieve Gallion, Derry	1 (*3*), 2 (*5*), 4 (*1*), 6 (*2*)
Transitional Province	
Grime's Graves, Norfolk	1 (*1*)
Isle of Wight Lane, Dunstable	1 (*1*)
Landpark Wood, Bedfordshire	1 (*3*)
Southern Province	
A2, Dover, Kent	1 (*1*), 2 (*1*)
Dover coast, Kent	1 (*2*), 2 (*2*)
Beer, Devon	1 (*1*), 2 (*1*)
A 342, Pewsey	1 (*2*)
Southwick Hill, East Sussex	1 (*4*), 2 (*2*)
Hackpen Hill, Wiltshire	1 (*1*), 2 (*1*)
Harrow Hill, East Sussex	1 (*1*)
Moon's Copse, Hampshire	4 (*2*)
Cissbury, East Sussex	1 (*2*), 2 (*3*)
Everleigh Road, Pewsey	1 (*1*), 2 (*1*)
Northern Province	
Rifle Butts, Yorkshire Wolds	1 (*1*), 2 (*1*)
Sledmere/Malton, Yorkshire Wolds	1 (*1*), 2 (*1*), 3 (*1*)
Welton-le-Wold, Yorkshire Wolds	1 (*1*), 2 (*1*), 3 (*1*), 4 (*1*), 5 (*2*)
Malton, Yorkshire Wolds	2 (*2*), 3 (*1*)
Arras Hill, Lincolnshire Wolds	1 (*1*), 2 (*1*), 3 (*1*), 4 (*1*)
Mill Hill, Lincolnshire Wolds	1 (*1*), 2 (*1*)
North Ormsby, Lincolnshire Wolds	1 (*1*), 2 (*1*), 3 (*1*), 4 (*1*)
Middleton, Lincolnshire Wolds	1 (*1*), 2 (*1*)

Within each sample location, a variety of flint nodules were collected in order to obtain multiple readings from each source. The samples were sealed in clean unused plastic bags, and labelled with the name of the site, date, and GPS co-ordinates.

2.2 Sample preparation

After the collection of samples, in order to accurately identify the number of elements present, and the concentration of those elements, the sample itself must be absolutely free of contamination. Contamination can occur from a number of different sources, at any stage of analysis, therefore great care must be taken when preparing the sample.

During collection, samples of flint were not reduced in the field as they were frequently covered in soil or other potential contaminant. Any samples that had large/numerous chalky or fossiliferous inclusions were excluded from analysis. Chalky inclusions throughout the flint (either an area of chalk formed within the flint, or small 'speckled' areas of very light coloured flint) could provide erroneous results. The chalky cortex on the exterior of nodules or pebbles was also excluded from analysis. Fossil inclusions are common in flint and are composed of a quartz-like crystalline material that could potentially introduce contamination. These areas were not selected for sampling. As the samples were not reduced in the field there was no way to anticipate whether the flint would be sufficiently free of inclusions to permit analysis. A number of samples were therefore discarded at this stage when it was revealed they were unsuitable.

Sample preparation for ICP-MS is complex and time-consuming due to the care taken to avoid contamination. The sample, after being washed and dried, was reduced into much smaller fragments (less than 10mm in size). Small pieces of flint that were free from inclusions and cortex were selected for analysis. These fragments were ground into a fine powder using a Fritsch Analysette 3E mechanical ball mill. This ball mill used a hardened steel crucible and ball which vibrated to crush any sample placed within the crucible. It was necessary to use small fragments of flint as the ball mill had difficulty breaking up larger samples. The samples of flint were placed in the machine for approximately 3-3.5 minutes. The resulting powder was very fine in texture, almost flour-like. The ball mill was thoroughly cleaned before and between each sample to prevent contamination with Fisher Scientific acetone (laboratory reagent grade) (99.5+ %) – this stage increased the time spent using the ball mill but was absolutely necessary to ensure that no contamination was introduced. Potential contaminants from the ball mill include carbon and iron. Carbon was not included in the analysis and iron contamination is unlikely as some samples returned iron results of 0ppb. Each sample was a fine powder and ready for digestion and analysis.

2.3 Sample analysis

Acid digestion took place in a CEM MARS 5 microwave. The microwave vessels were rinsed with deionised water prior to use. When completely dry, the vessel caps were inspected and the plastic rupture disc was replaced. The plastic rupture disc is a failsafe measure to prevent the vessel exploding under high pressure, and ensures that digestion occurs under closed conditions. Into each vessel was placed 0.04g of each sample and 10ml concentrated nitric acid (70%). The vessel was capped and placed inside a Kevlar sleeve, then clamped inside a support module using a torque wrench.

The vessels were placed on the carousel inside the microwave. One was a control and had a fibre optic temperature sensor inserted, ensuring that it reached the sample mixture at the bottom of the vessel. Although the microwave has slots for 12 vessels, due to equipment limitations a maximum of 8 vessels could be placed within the microwave at any time. The microwave was programmed to heat the samples to 200°C, ramping to this temperature over 15 minutes. The temperature was maintained for 60 minutes, then cooled over a period of 120-180 minutes, until the temperature measured by the sensor was less than 50°C. If the vessels were opened prior to this the sudden release of pressure would lead to loss of samples and potential injury. In total the time spent cleaning vessels, weighing samples, preparing for digestion, and the necessary cool down, resulted in approximately 5 hours spent digesting 8 samples.

The samples were now prepared for introduction to the ICP-MS (instrument used was a Thermo X-Series II ICP-MS system). 100 µl of sample solution was pipetted into a 10ml test tube, topped up to 10ml with MilliQ deionised water. The test tubes were placed on the autosampler. The ICP-MS was controlled through the accompanying software, PlasmaLab. The programme will identify and quantify a range of elements: lithium, beryllium, sodium, magnesium, aluminium, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, rubidium, strontium, molybdenum, cadmium, caesium, barium, and lead.

Analysis included an external standard, SIGMA-ALDRICH 54704 multi-element standard solution 5 for ICP (in 10% nitric acid, Fischer Scientific). The elements that were present in this standard in certified quantities were: argon, aluminium, barium, beryllium, bismuth, calcium, cadmium, cobalt, chromium, caesium, copper, iron, gallium, indium, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, lead, rubidium, strontium, thallium, vanadium, and zinc. The standard solution was run at seven different concentrations: 0.5ppb (parts per billion), 1ppb, 1.5ppb, 2ppb, 2.5ppb, 4ppb and 5ppb.

2.4 Data handling and analysis

The results of the ICP-MS analysis were converted into Excel spreadsheets using PlasmaLab and provided in parts per billion (ppb). The results were analysed using canonical discriminant function analysis using SPSS (version 20). This multivariate statistical analysis determines which variables distinguish between two or more groups and enables the classification of unknown objects into those groups. The groups are established prior to analysis and unclassified samples/observations are assigned group membership based on the measured variables. Here, the established groups are the areas of flint occurrence from which the samples were collected (in Britain, Northern/Southern/Transitional, and the Northern Ireland chalk formation). The discriminant function analysis also provides classification accuracy for the dataset, which describes how well group membership can be predicted. The classification function can be used to predict group membership for samples for which group membership is unknown.

To investigate the representativeness of the results, a single piece of flint obtained from a site was analysed a number of times and the standard deviation calculated for each element to assess the homogeneity (or otherwise) of the flint. Presented below are the results from sample 2 from Slieve Gallion, Northern Ireland (table 2).

Table 2 – Elements detected in five samples of same flint nodule from Slieve Gallion, NI

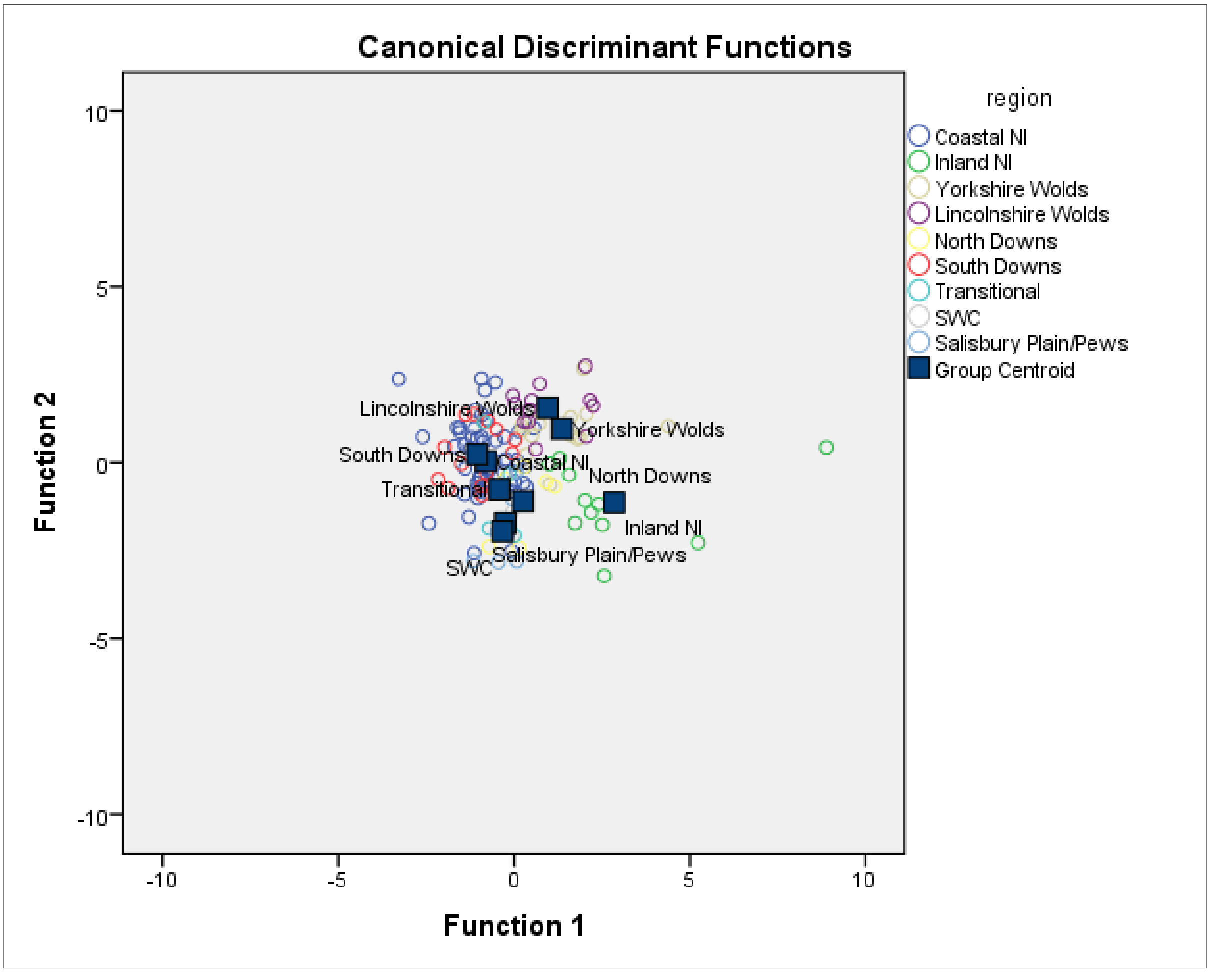
Element	Repeat 1 (ppb)	Repeat 2 (ppb)	Repeat 3 (ppb)	Repeat 4 (ppb)	Repeat 5 (ppb)	Standard Deviation
Li	0.00	0.01	0.01	0.00	0.01	0.01
Be	0.00	0.00	0.00	0.00	0.00	0.00
Na	6.12	3.77	3.95	3.51	2.71	1.27
Mg	0.58	0.69	0.61	0.55	0.18	0.20
Al	1.54	4.49	3.19	1.35	2.25	1.30
K	3.89	2.67	4.01	4.45	0.95	1.42
Ca	28.61	30.49	27.03	26.45	26.54	1.72
Cr	1.30	1.64	0.82	1.12	0.96	0.32
Mn	0.09	0.16	0.07	0.08	0.18	0.05
Fe	6.24	9.69	4.61	7.58	7.14	1.86
Co	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.03	0.13	0.07	0.02	0.02	0.05
Cu	0.09	0.09	0.15	0.08	0.06	0.03
Zn	0.29	0.25	0.25	0.25	0.13	0.06
Rb	0.00	0.01	0.00	0.00	0.00	0.00
Sr	0.03	0.07	0.03	0.04	0.02	0.02
Mo	0.12	0.12	0.08	0.09	0.00	0.05
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Cs	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.15	0.27	0.15	0.06	0.13	0.08
Pb	0.00	0.00	0.00	0.00	0.00	0.00

3. Results

The results of the ICP-MS analyses are presented here (results are presented in full as supplementary data). Due to the time-consuming nature of the acid digestion ICP-MS process, this preliminary study examined 126 samples from throughout the study area using this method. Of the 126 samples collected from the study area, 59 were from within Britain; 26 from the Northern province, 28 from the Southern province, and 5 from the Transitional province.

The sampling regions referred to in this section are: coastal NI (Northern Ireland), inland NI, Yorkshire Wolds, Lincolnshire Wolds, North Downs, South Downs, Transitional, SWC (Southwestern chalk), and Salisbury Plain/Pewsey.

3.1 Britain and Ireland



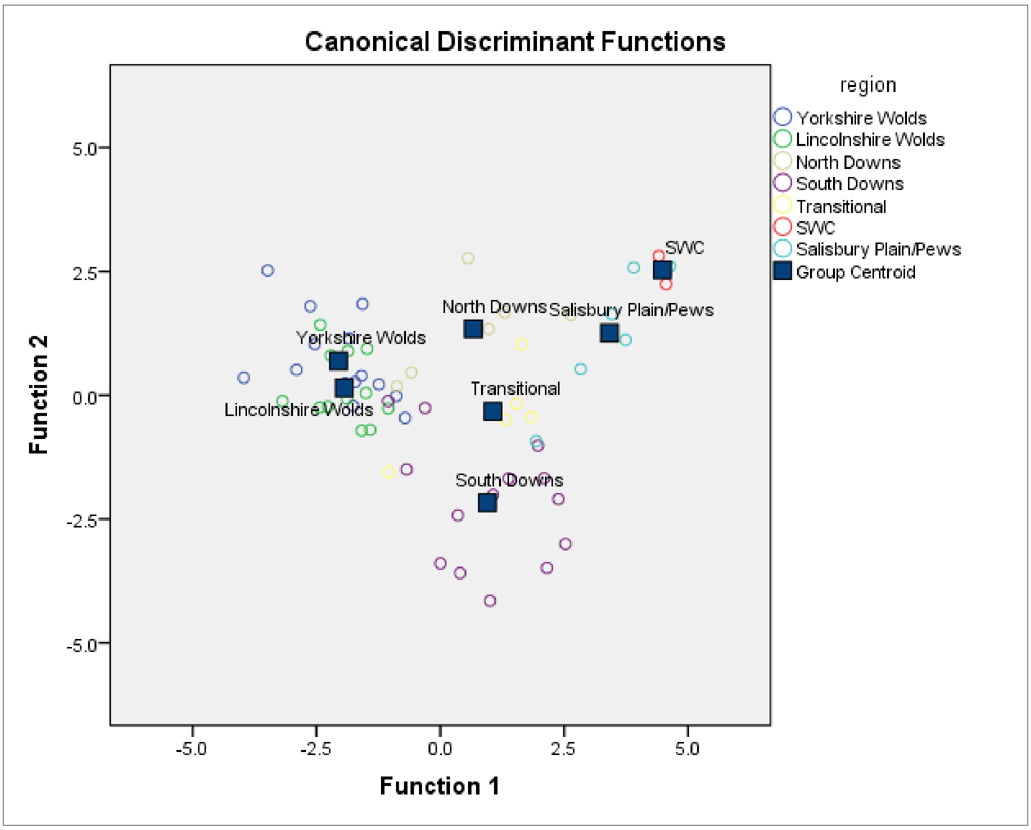
Graph 1 – Discriminant function plot of all sample locations from Britain and Ireland

Graph 1 shows the results from all sample regions within Britain and Ireland. The majority of samples are tightly clustered however it possible to see some differentiation in the samples from the Lincolnshire and Yorkshire Wolds, as well as samples from inland Northern Ireland. The classification accuracy for this dataset is quite poor, with 60.3% of original grouped cases correctly classified (table 3).

Table 3 – Classification statistics of all sample locations within Britain and Ireland

	Predicted Group Membership %								
Region	CNI	INI	YW	LW	ND	SD	T	SWC	SPP
CNI	51.8	.0	1.8	7.1	1.8	25	.0	3.6	8.9
INI	.0	72.7	.0	9.1	9.1	.0	.0	9.1	.0
YW	.0	.0	64.3	35.7	.0	.0	.0	.0	.0
LW	.0	.0	25	75	.0	.0	.0	.0	.0
ND	16.7	.0	.0	.0	66.7	.0	.0	.0	16.7
SD	21.4	.0	7.1	.0	.0	71.4	.0	.0	.0
T	60	.0	.0	.0	.0	20	20	.0	.0
SWC	.0	.0	.0	.0	.0	.0	.0	50	50
SPP	16.7	.0	.0	.0	.0	.0	.0	.0	83.3

(Sampling locations: CNI = Coastal NI, INI = Inland NI, YW = Yorkshire Wolds, LW = Lincolnshire Wolds, ND = North Downs, SD = South Downs, T = Transitional, SWC = Southwestern Chalk, SPP = Salisbury Plain/Pewsey).



Graph 2 – Discriminant function plot of all sampling locations within Britain

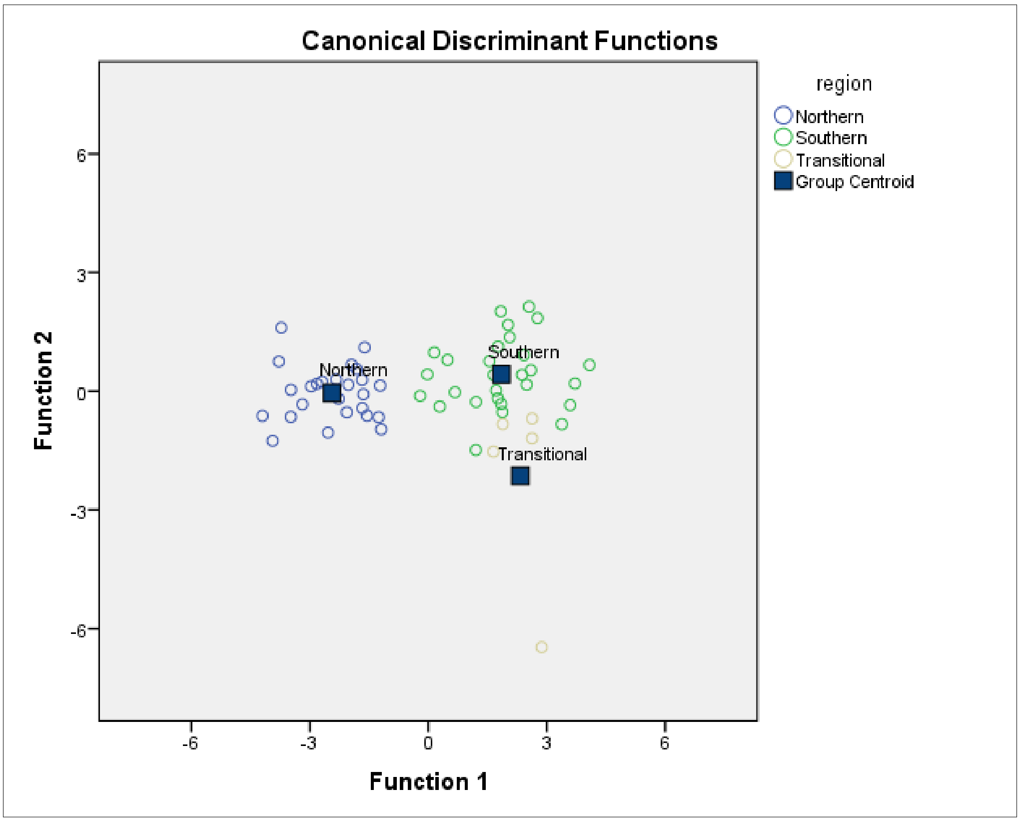
Separation of sampling locations within Britain shows that the Northern chalk province samples group quite closely (graph 2). The samples from the Transitional province are poorly differentiated from the samples from the Southern province. Overall, the classification accuracy for these groups (excluding samples from Northern Ireland) is 81.4% (table 4). When the results from Northern Ireland are removed from analysis, the classification accuracy of each sampling location improves, with the exception of the North Downs which remains at 66.7%.

Table 4 – Classification statistics of all sample locations within Britain

	Predicted Group Membership %						
Region	YW	LW	ND	SD	T	SWC	SPP
YW	85.7	14.3	.0	.0	.0	.0	.0
LW	16.7	83.3	.0	.0	.0	.0	.0
ND	16.7	.0	66.7	.0	.0	.0	16.7
SD	14.3	.0	.0	85.7	.0	.0	.0
T	.0	.0	.0	20	80	.0	.0
SWC	.0	.0	.0	.0	.0	100	.0
SPP	.0	.0	.0	16.7	.0	16.7	66.7

(Sampling locations: YW = Yorkshire Wolds, LW = Lincolnshire Wolds, ND = North Downs, SD = South Downs, T = Transitional, SWC = Southwestern Chalk, SPP = Salisbury Plain/Pewsey).

When the samples from Britain are grouped into the broader chalk province groups, the distinction between them becomes clearer, however the samples from the Southern and Transitional provinces remain poorly differentiated (graph 3).



Graph 3 – Discriminant function plot of Chalk provinces within Britain

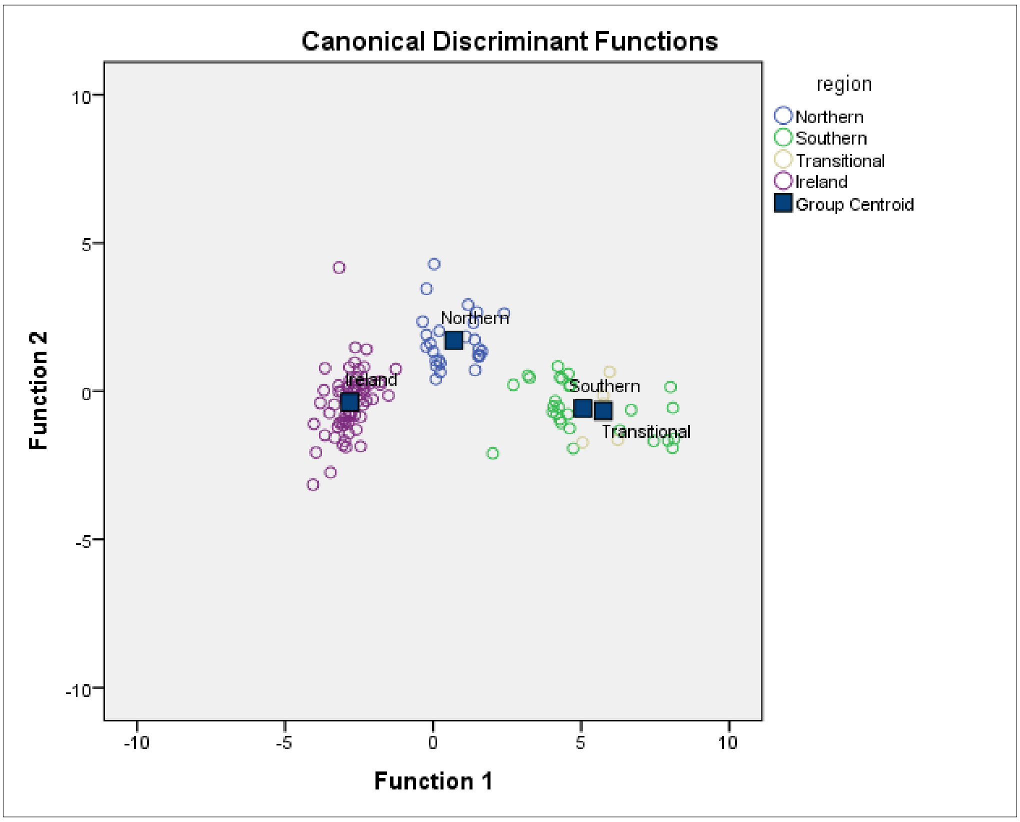
The grouping of samples from Britain into chalk provinces increases the classification accuracy to 93.2% (table 5).

Table 5 – Classification statistics of Chalk provinces within Britain

	Predicted Group Membership %		
Region	Northern	Southern	Transitional
Northern	100	.0	.0
Southern	.0	92.9	7.1
Transitional	.0	40	60

The classification accuracy for the chalk provinces shows clearly that the samples from the Northern province are quite distinct from the samples from the Southern and Transitional provinces, being classified correctly 100% of the time. There is a degree of overlap between the samples from the Transitional and Southern provinces, with Transitional province samples being misclassified as Southern more frequently than Southern province samples being misclassified as Transitional.

When the samples from Ireland are included, the grouping of samples becomes clearer, apart from the close overlay of samples from the Transitional and Southern provinces (graph 4).



Graph 4 – Discriminant function plot of samples from the Northern, Southern, Transitional, and Northern Ireland provinces

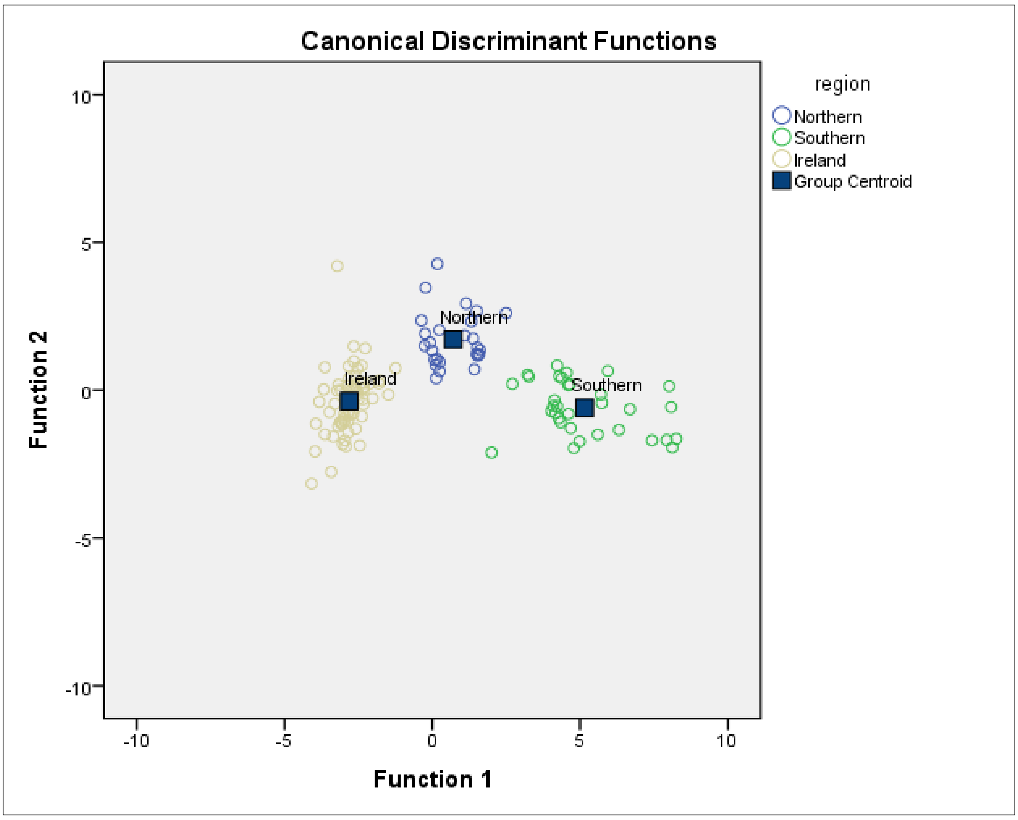
The classification accuracy for the four-group separation (graph 4) is 96% (table 6).

Table 6 – Classification statistics of Chalk provinces within Britain and Ireland

	Predicted Group Membership %			
Region	Northern	Southern	Transitional	Ireland
Northern	100	.0	.0	.0
Southern	3.6	96.4	.0	.0
Transitional	.0	80	20	.0
Ireland	.0	.0	.0	100

Table 6 shows that samples from the Northern province and from Ireland were correctly classified 100% of the time. There were again overlapping results between the Southern and Transitional provinces, with 80% of Transitional province samples misclassified as Southern. One sample from the Southern province was misclassified as coming from the Northern province.

When the samples from the Southern and Transitional provinces are combined (this grouping referred to here as just 'Southern' in graph 5), the separation of the provinces becomes clearer.



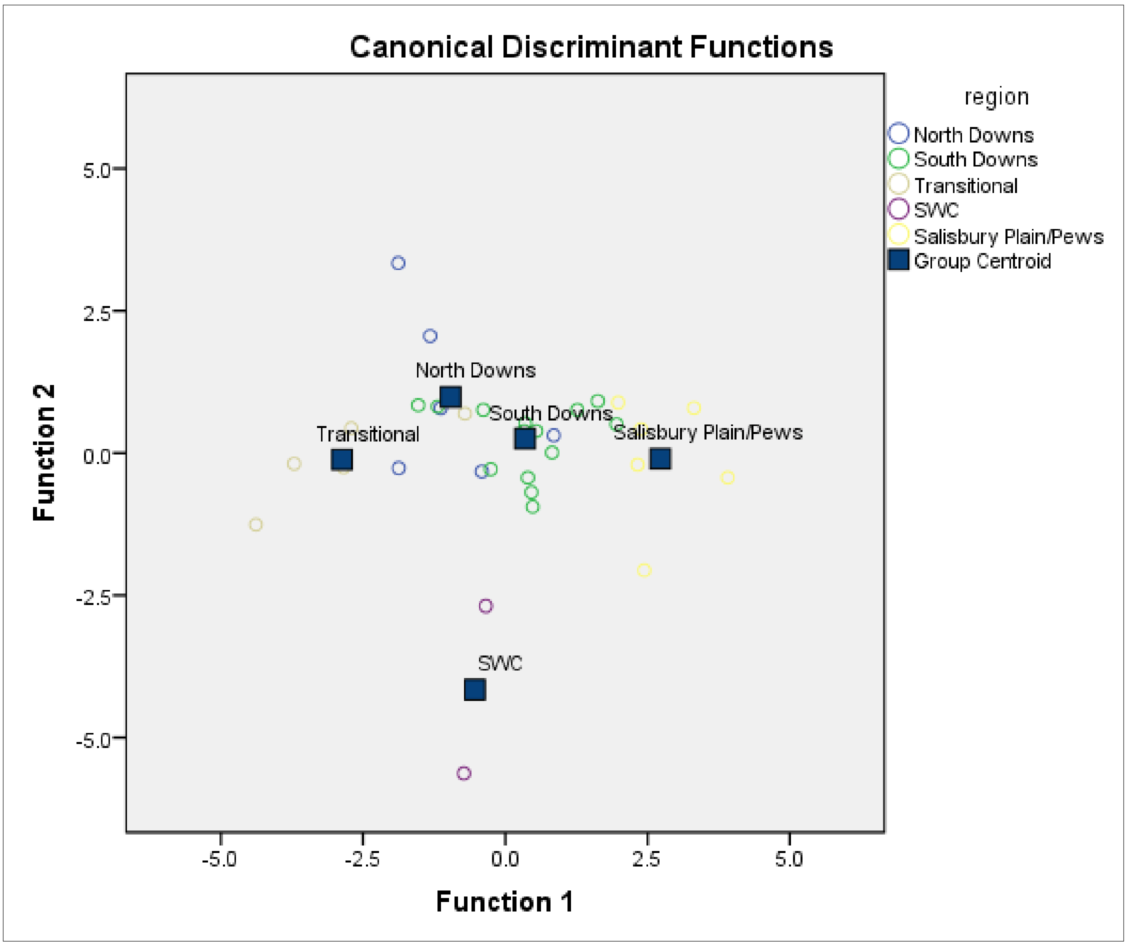
Graph 5 – Discriminant function plot of samples from the Northern, Southern, and Northern Ireland provinces

When the Southern and Transitional samples are combined and compared to the Northern and Ireland groups, the classification accuracy rises to 99.2% (table 7).

Table 7 – Classification statistics of Chalk provinces within Britain and Ireland (Southern and Transitional samples combined)

	Predicted Group Membership %		
Region	Northern	Southern	Ireland
Northern	100	.0	.0
Southern	3	97	.0
Ireland	.0	.0	100

Looking at samples from locations within the Southern province in more detail (graph 6), it appears that the flint collected from the South Downs, North Downs, Salisbury Plain/Pewsey, and Transitional areas are clearly differentiated from those collected from the Southwestern chalk at Beer (Devon). The samples from the Transitional province are poorly distinguished from results obtained from flint obtained from the North and South Downs, with results from one sample plotted amidst these two groups. With the exception of the samples from Southwestern chalk, the results from the rest of the Southern province are not clearly distinguished and overlap in a number of cases.



Graph 6 – Discriminant function plot of samples from locations within the Southern province

The classification accuracy for the sampling locations with the Southern and Transitional provinces was 87.9% (table 8).

Table 8 – Classification statistics of all sample locations within the Southern and Transitional provinces

	Predicted Group Membership %				
Region	ND	SD	T	SWC	SPP
ND	66.7	.0	16.7	.0	16.7
SD	.0	100	.0	.0	.0
T	.0	20	80	.0	.0
SWC	.0	.0	.0	100	.0
SPP	.0	16.7	.0	.0	83.3

(Sampling locations: ND = North Downs, SD = South Downs, T = Transitional, SWC = Southwestern Chalk, SPP = Salisbury Plain/Pewsey)

Within the Southern and Transitional provinces the samples from the South Downs and Southwestern chalk are correctly classified 100% of the time, with the samples from the North Downs, Transitional, and Salisbury Plain/Pewsey locations occasionally misclassified.

A minimum of three sample groups are needed within SPSS to create a discriminant function plot however classification accuracies are still produced. There are three two-group comparisons outlined here: comparison of samples from Britain and Ireland; samples from within the Northern Province; and samples from within Ireland.

Of the 126 ICP-MS samples, 60 were collected from Britain and 66 from Ireland. The classification results are outlined in table 9.

Table 9 – Classification statistics of samples from Britain and Ireland

	Predicted Group Membership %	
Region	Ireland	Britain
Ireland	71.2	28.8
Britain	21.7	78.3

The overall classification accuracy for this two-group separation is 74.6%, with slightly more samples from Ireland misclassified as British.

The Yorkshire Wolds and Lincolnshire Wolds were the two regions sampled within the Northern Province, with a total of 26 samples collected in total. Fourteen of these were from the Yorkshire Wolds and 12 from the Lincolnshire Wolds. The classification accuracy here was 88.5% (table 10).

Table 10 – Classification statistics of samples from within the Northern Province

	Predicted Group Membership %	
Region	Yorkshire Wolds	Lincolnshire Wolds
Yorkshire Wolds	92.9	7.1
Lincolnshire Wolds	16.7	83.3

Slightly more samples from the Lincolnshire Wolds were misclassified as being from the Yorkshire Wolds.

Samples from Northern Ireland were collected from two distinct areas: inland sites and coastal sites. A total of 67 samples were collected in total, 56 from coastal sites and 11 from inland sites. The classification accuracy here was 100% (table 11).

Table 11 – Classification statistics of samples from within Northern Ireland

	Predicted Group Membership %	
Region	Coastal NI	Inland NI
Coastal NI	100	.0
Inland NI	.0	100

Acid digestion ICP-MS demonstrated that the flint-producing areas within Britain and Ireland can be distinguished. The elements with statistically significant variation between these regions have been identified (table 12).

Table 12 – Elements with statistically significant variation between the different flint-producing areas of Britain and Ireland

	Element(s)
Differentiating between:	
Britain and Ireland	Magnesium, Aluminium, Molybdenum
Southern province and Transitional province	Nickel, Copper, Molybdenum
Northern province and Transitional province	Manganese
Southern province and Northern province	Molybdenum
Within Northern Ireland: Inland and Coastal	Barium, Manganese

4. Discussion

This study set out to investigate different areas of flint-bearing chalk within Britain and Ireland and determine whether they can be distinguished on the basis of the chemical composition of flint samples using acid digestion ICP-MS. It is the first study to include samples from both Britain and Ireland and demonstrates that the flint samples obtained from these areas can be distinguished on the basis of their geochemistry.

The results provide corroborative data for published literature regarding geochemical characterisation of flint (Rockman 2003; Hughes *et al.* 2010; Högberg *et al.* 2012; Pettitt *et al.* 2012) which collectively demonstrate proof of principle, that sourcing flint is possible, but with a caveat that distinguishing within and between some areas are more difficult than others. No study published to date has the geographic range of the results outlined here, or comparison of flint from Britain and Ireland. Högberg *et al.* (2012, 234) accurately summarise the challenges of geochemical sourcing of flint: "*…classification based on appearance, geography, geology and geochemistry sometimes groups the samples…but sometimes not*". It is difficult to determine to what extent one can confidently state that a flint source/outcrop is geochemically characterised when the internal variation can be so great, and when the outcrops themselves can stretch for hundreds of kilometres and contain multiple bands of flint-bearing chalk. The results presented here represent a preliminary foray into this issue in relation to British and Irish flint. The results echo those of Högberg *et al.*, "…both encouraging and sobering" (2012, 235). Comprehensively characterising the geochemical variability of the flint from Britain and Ireland will require enormous numbers of sample readings, not likely to be accomplished by isolated researchers. It will likely have to be a collaborative effort and comparability of the data gathered will be crucial to build up a suite of results.

The greatest classification accuracy (99.2%) was obtained when the samples were divided into three groups: samples from Ireland, samples from the Northern province, and samples from the Southern + Transitional province. When these groups were subdivided, the classification accuracy dropped. This may be to do with small sample sizes or the inherent chemical homogeneity of the flint. Geochemical characterisation of flint is demonstrably possible however the degree of geographic specificity required will depend on the needs of the archaeologist; in some scenarios it may be sufficient to know whether the flint in question is from Britain or Ireland, or from Northern or Southern Britain.

Accurate characterisation of archaeological artefacts has the potential to greatly increase our understanding of the processes that led to their creation, such as raw material procurement, trade and exchange. A definitive means of identifying the source of flint for tool-making has the potential to grant insights into trade/procurement of raw material, as well as movement of people through landscapes. The Stone Axe Studies I & II monographs (Clough & Cummins 1979, 1988) were (and remain) of great significance in terms of understanding the procurement, use, and movement of a variety of lithologies within and between Britain and Ireland. Analysis of flint sources on the same scale would provide hitherto unrecognised understanding of how this most common of materials was used in British and Irish prehistory.

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