REPORT

Understanding the geochemical variability of flint across spatial scales from micrometers to kilometers

Chemo-stratigraphy—the use of elemental concentrations in rocks for their characterisation and correlation—has been a staple of sedimentary geologists since the 1980s and used extensively in Europe and beyond as part of oil exploration (e.g. review of Craigie 2021). The ability to 'fingerprint' these rocks across both space and time is particularly attractive for regional mapping when other diagnostic tools such as mineralogy or fossil specimens are inconclusive. The pioneering work of Clayton (1984) was the first detailed geochemistry on flint, focusing on the modes of flint formation and geological controls. Bands of flint nodules in chalk are a readily visible macroscopic feature for large scale stratigraphy. Mortimore (2020) noted that the Seven Sisters Flint Band could be followed from Yorkshire in the northeast to Devon in the southwest, and across the English Channel in the south to the Yonne region of the eastern Paris Basin, France. Flint is not only found within well-defined stratigraphic sections (primary sources) but may be found as 'clay with flints' in southern England, the likely result of dissolution of original chalk (Gallois 2009), or in secondary surficial deposits such as tills or river gravels, e.g. in the Trent valley (Henson 1985). Additionally, there are flints that have been moved by man, for example a valuable and robust cutting tool used in the East Midlands (at Creswell Crags) since the Late Middle Palaeolithic (60–40,000 b.p.). Such flints are widely found in plough soil, in particular later material from the Neolithic and Bronze ages.

Archaeologists are particularly keen to identify sources of flint to understand both the movement of people and their material culture artefacts. Simple macroscopic observations on flint colour, alteration zones or fossil remnants have been used to assign likely flint geological sources (Bradley et al 2020). As a result of the synergy of geology and archaeology, much of the work on chemo-typing flint artefacts and making use of chemo-stratigraphy to fingerprint flint has been by geo-archaeologists. This work has been predicated on the assumption that the elemental chemistry of a flint from a site is representative of that region and that different regions will have a different signature. One of the authors with others produced a database of flint chemistries from material collected as nodules from English geological locations and grouped these into eight regions. Geostatistics (canonical discriminant analysis) were then used to produce a chemical fingerprint for each region. Subsequent analysis of archaeological flints allowed them to be assigned these regional groups, with in most cases a sensible attribution (Pettitt et al 2012). A similar England-wide study by Bradley et al (2020), including geological source material from Northern Ireland, used a related methodology. They also chose to only break down their sites into the three English regional groups of Hopson (2005): Northern, Southern and Transitional, as well as a fourth from Northern Ireland.

The UK is not the only area where chemo-typing of flint has occurred: others include material from Italy (Moroni & Petrelli 2005), Demark and Sweden (Hughes et al 2012), Belgium (Fiers et al 2019), Israel (Finkel et al 2019) and the Balkans (Moreau et al 2016). All these archaeological studies have concluded that it is possible to chemo-type flints and make some intra- and intra-regional assignments, but the results are frequently not as clear-cut as might be desired.

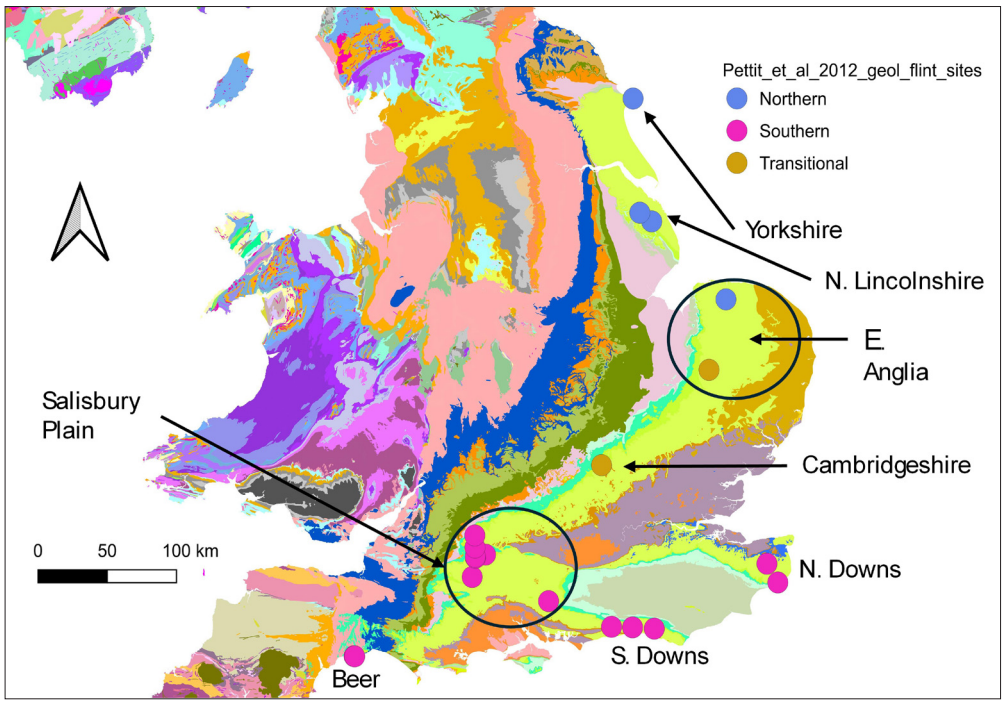

***Figure 1**. Geological flint collection sites, placed on BGS open source 625K geological base map, with site province (Northern, Southern and Transitional after Hopson, 2005) and assigned geographical region (Pettitt et al, 2012).*

Recent work by the authors on flint artefacts from Farndon Fields (Nottinghamshire), when compared to the Pettitt et al (2012) geological flint database, has suggested less than likely origins, with apparent refit fragments falling into different groupings. Coupling this to a synthesis of reservations from the previous studies has led us to question how robust is the assumption of stable regional geochemical signatures. To investigate and quantify the robustness we must (i) consider the spatial and temporal scales at which we could identify variability; (ii) how we should sample to quantify the variability; (iii) what pertinent information we already have, and (iv) where are the biggest or most significant information gaps. The purpose of the current article is to lay out this future research strategy.

Studying flint chemistry at different spatial and temporal scales

Here we will take a top down decompositional approach to discuss sampling of flints for their geochemical signatures. The different sampling levels are shown diagrammatically in Figure 2.

At the coarsest spatial scales, regional and continental, there will sometimes also be a natural temporal separation, i.e. the Eocene flint of Israel (Finkel et al 2019) and Upper Cretaceous of Belgium (Fiers et al 2019). The largest-scale areas, across 10–100 km, can be equated to the Southern, Northern and Transitional provinces of the Upper Cretaceous chalk, as defined by diagnostic lithologies and fossils (see Mortimore et al 2001). For each province standard sections have been described and potential sub-provinces identified with different depositional or faunal environments. The regions of Pettitt et al (2012) are of a similar scale to these

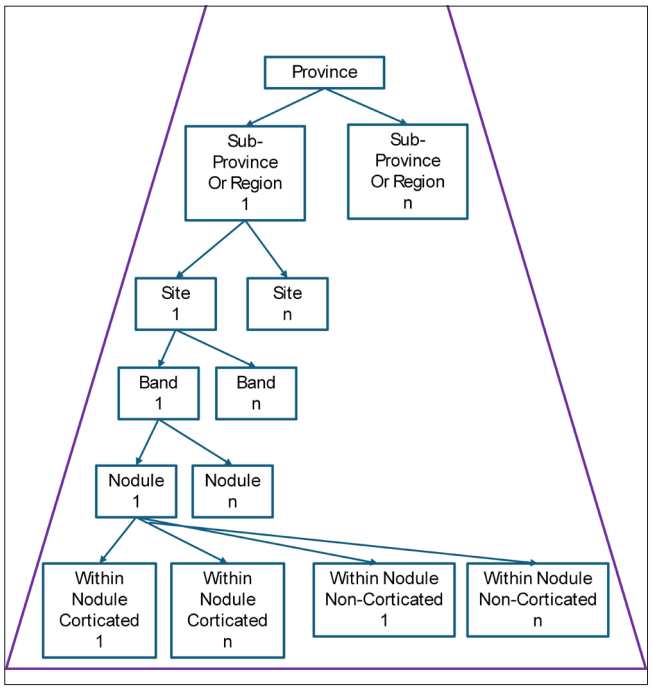

***Figure 2**. Sampling Pyramid where n is an appropriate number of replicates (1,2,3..n) to be representative of the natural variation at this sampling level.*

sub-provinces but based simply on geographical area. Within each sub-province, sampling should be from a number of sites across 1–10 km, and representative of those areas. How many sites per region to be sampled is a difficult question, but with a minimum of three it is possible to start gauging within sub-province/regional variation; three indistinguishable sites would mean that the variability has been likely captured but two similar and one dissimilar would suggest not. At this point it would perhaps be appropriate to sample more sites and perhaps sub-divide the region.

Within an individual site, temporal constraints may come into play and if a section is available rather than loose surface material, the stratigraphy of the site becomes significant and multiple flint bands may need to be sampled. Here the difference in end-interest between geochemist and archaeologist becomes apparent. The geochemist would prefer primary material from a fresh section where stratigraphy can be correlated across sites; whereas the archaeologist might prefer secondary material that past populations may have adventitiously found and used. Within each band of flint(s), individual nodules may be found over a scale of 1–100 m. These nodules may vary in size, shape and potentially degrees of alteration (such as cortication). Again, the ability to capture within-site variability should define the number of nodule samples. Three would again be a minimum but five or more better to 'average' results when comparing sites.

Once sampling and analysing individual nodules begins, a range of new considerations must be made. These must account for potential heterogeneity within the nodule caused by depositional, post-depositional and alteration processes. A detailed review of flint formation and its associated chemistry is beyond the current report. But the following generic processes are of relevance to the sampling and analytical methodologies used in chemo-typing. The bulk of the flint nodule is silica (SiO_2), its source is as described by Hesse (1989; a synthesis of the Clayton 1986 model) where silica precipitation occurs at a redox boundary between a higher oxic and lower anoxic microchemical environment. This is believed to be early in the diagenetic process and at burial depths as shallow as 5–10 m. Other elements may be contained within the matrix through the following processes: (i) direct co-precipitation of elements with the silica; if the precipitation is in an open chemical system then the proportions of the elements should remain constant, but if a 'closed' or 'partially closed' system, then the elemental proportions will change with time as the chemistry of the parent pore water changes, potentially resulting in zonation; (ii) occlusion of macro-solids such as parts of sponge spicules (SiO_2) or shell fragments ($CaCO_3$); (iii) occlusion of micro-solids (micron scale) such as clays, oxides or sulphides (pyrite), either solid when trapped in pore fluid or precipitated separately to the silica; (iv) post-solidification of the flint nodule, elements including the matrix may be added either by later fracture fills or other sorption

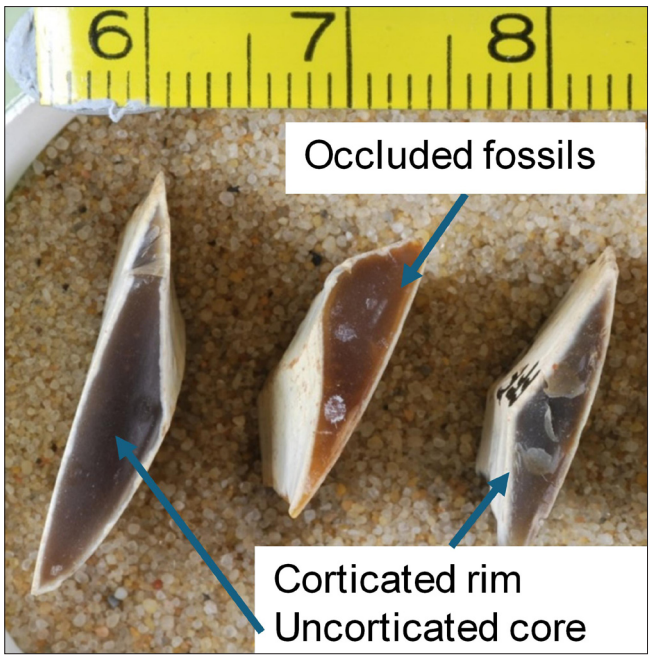

***Figure 3**. Archaeological flints with corticated rims, uncorticated cores, and occluded fossils. These also show the varying colours and opacities found.*

processes or subtracted by leaching/partial dissolution or re-crystallisation. The latter is best exemplified by cortication, also known as patination—the white layer usually found on the surface of the nodules but often more pervasively through flint artefacts found in surface soils. This is described by Rottländer (1975) as the result of small holes produced by partial dissolution.

The heterogeneity of the nodules has led some researchers to choose a sampling methodology that uses some large fraction of a geological flint nodule in an effort to average out variations across the bulk. Energy Dispersive - X-Ray Fluorescence Spectrometry (ED-XRFS) was chosen by Hughes et al (2012) as this samples a relatively large area (c. 36 mm^2) and depth of several millimetres. The advantage of the ED-XRFS is its non-destructive nature. Unfortunately, only nine elements were analysed and many of these were close to or below detection limit. Fiers et al (2019) used a micro-XRFS system over a smaller area 0.4 mm^2 accepting that it only produced semi-quantitative results. Others have preferred the more sensitive inductively coupled plasma – mass spectrometry (ICP-MS) technique. Some have milled the flint nodule to a fine powder before digesting the powder in acid to further homogenise the sample. However, this is not a preferred technique for archaeologists due to, in the case of Finkel et al (2019), destroying complete artefacts to provide grams of material, or Bradley et al (2020), chipping off a small fragment selected to avoid visual inclusions that eventual provided 0.04 g of powder. In both cases the samples could potentially have been contaminated by the tungsten carbide and steel mills respectively; this could potentially be quite significant considering the naturally low concentrations of most elements in flint.

The preferred technique of the authors (Pettitt et al 2012; Pettitt et al 2015 and also Moroni and Petrelli 2005; Moreau et al 2016) has been solid sampling using laser ablation – ICP-MS. This combines the sensitivity of the mass spectrometer with direct non-contact solid sampling of the flint avoiding the risk of contamination. The small spot or rastered area (typically 0.1 mm^2) allows the avoidance of macroscopic and semi-microscopic inclusions but with the disadvantage of the risk of unrepresentative sampling (Fig. 3). However, the rapid nature of the analysis, less than a minute per ablation spot, allows multiple measurements to be taken.

Initial results and discussion

Starting at the bottom of the sampling pyramid, the within-nodule or for archaeological material within-object, the most obvious potential source of variability is associated with cortication, i.e. the milky grey-white surface rim and the often dark glassy core. Groups of analyses on nine archaeological flints where it was possible to analyse both corticated and uncorticated materials showed three apparent geochemical relationships (Fig. 4) exemplified by (a) sodium concentrations, where both types of material showed good agreement; (b) aluminium where corticated concentrations were higher suggesting leaching of material, and (c) iron where an apparent random relationship suggests that this element is very

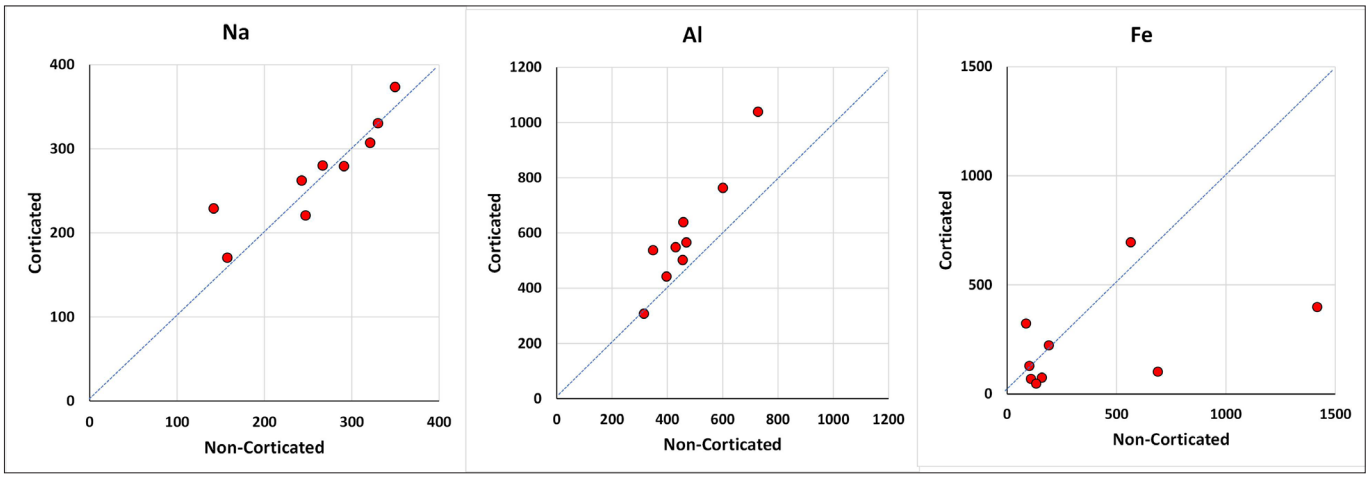

***Figure 4**. Comparison of the chemistry of corticated and un-corticated area of archaeological flints*

inhomogeneously distributed possibly due to micro-inclusions. Each data point was typically the median of nine individual measurements. These results suggest that a greater understanding of the geochemical distribution of the elements within a flint is required. We propose to look at this by detailed sampling of geological flints from the original geological sample archive of Pettitt et al (2012) where they can be sectioned to provide easy access to sampling corticated and uncorticated areas and elementally 'mapping' the flint to identify any zoning of elements associated with both original deposition and alteration processes. This should provide us with a list of elements that can be sampled without consideration of alteration or zoning but also allow us to define within-flint sampling strategies for those elements that are subject to alteration etc.

Access to the Pettitt archive will also allow us to re-sample different flints (i) from the same site to further consider the within-site variation in the light of any modified sampling strategies, and (ii) investigate if the chemistry can be related to considerable differences in colouration and opacity of flints from different sites/regions that may in itself suggest different degrees of within-flint variability.

Beyond these investigations into within-flint and within-site variation, when matching archaeological flints to the Pettitt geological flint database (Fig. 5) some archaeological material clearly does not match the geographical groups. This may mean that the database is lacking key sites. One of the authors (DG) has identified at least one potential site in Norfolk that should be carefully sampled for addition to the database.

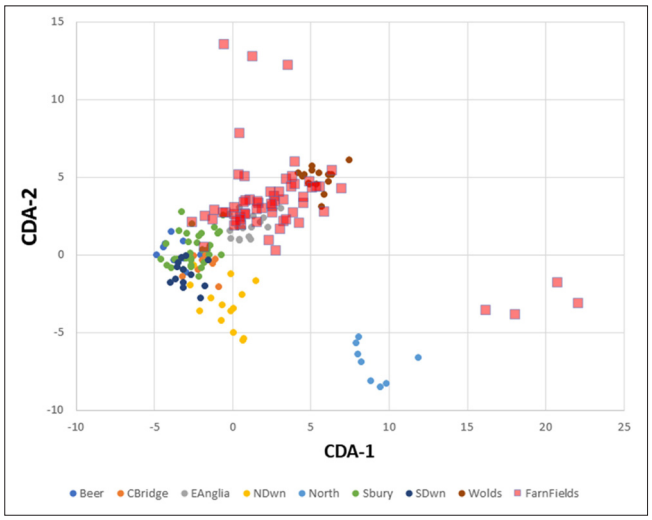

***Figure 5**. Canonical Discriminant Analysis of Farndon Fields archaeological flints versus geological flint database samples, showing some samples may be assigned to regional geological groups but some fall clearly outside known groups.*

Acknowledgements

The overarching project 'Ice Age Insights' was supported by a National Lottery Heritage Fund grant and the LA-ICP-MS work specifically by a small grant from the Council for British Archaeology – East Midlands.

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