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Chapter Eight

The Use of Non-Destructive Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis for Sourcing Flint in Northern Europe: Progress to Date and Prospects for the Future

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Abstract

The article summarizes the results of work since 2010 to develop non-destructive energy dispersive X-ray fluorescence analysis (EDXRF) as a non-destructive method for determining the provenience of flint in northern Europe. Some 40 localities from Sweden, Denmark, Germany, Poland, and Ukraine have been sampled and analyzed. Trace elements have not proven particularly effective in drawing distinctions between and among flint and chert because they often occur below, or near, detection limits. However CaO and Fe compositions usually generated the highest count rates and total counts using EDXRF and their concentrations allowed satisfactory partitioning of some of the flints we analyzed.
The Use of Non-Destructive EDXRF for Sourcing Flint

EDXRF can help us to discriminate among various outcrops of flint used for tool production during prehistory. Future work involves investigating correlations between flint chemistry and visual appearance, as well as investigating source-critical aspects of post-depositional effects on tool surfaces.

**Keywords:** Non-destructive energy dispersive X-ray analysis, flint, provenience analysis, geochemistry

**Introduction**

Archaeologists need reliable and replicable means to identify the specific sources of the raw materials used to manufacture archaeological artifacts. Regarding flint, Carl Johan Becker (1952) was one of the first to seek reliable criteria for differentiating sources of Scandinavian flint. Based on appearance and physical qualities he narrowed down the origin of the flint in the caches from Bjurselet to the Senonian deposits in eastern Zealand or southwestern Scania (Becker 1952, 69; Knutsson 1988, 51; Olausson et al. 2012). In his study of Late Neolithic daggers, Jan Apel (2001) drew on Becker’s results to advance far-reaching conclusions about manufacturing centers and exchange systems. Other studies have focused on the availability and use of different flint sources and outcrops on a local or regional level (Högberg 2001, 2002; Knarrström 2001; Carlsson 2004).

Although many archaeologists have addressed questions concerned with the origins of Scandinavian flint as a raw material, most conclusions have been based on macroscopic properties. However, these properties are by necessity described subjectively and can be altered significantly by knapping and/or post-depositional weathering. Högberg and Olausson’s study of Scandinavian flint (2007) illustrated the variety and complexity of this material and demonstrated the difficulties involved in arriving at a wholly satisfactory macroscopic classification based on morphology alone. In the present article we describe our attempts to use chemical compositions as a complement to visual appearance for differentiating flint types.

**Geological prerequisites for chemical characterization of north European flint**

Since flint is composed mainly of SiO₂, instrumental analysis usually concentrates on measuring the elements whose origins are non-carbonate materials (e.g. clay minerals and heavy minerals) incorporated in the flint
as it was being formed by the replacement of calcium carbonate with silica (Tite 1972, 308). The flints in the north European Maastrichtian chalk and the Danian limestone were formed by the replacement of calcium carbonate in a molecule-to-molecule process, resulting in the preservation of the non-carbonate material that existed in the chalk/limestone. It is this non-carbonate material that serves as the prime source of trace elements in the flint. The chalk in any particular horizon is generally uniform in composition, but there are nonetheless significant chemical variations with time between horizons, so that one horizon should be discernable from another (Bush 1976, 48; Bush and Sieveking 1986, 134; Craddock et al. 1983, 138; McDonnell et al. 1997; Sieveking et al. 1972, 156). Parts of a formation that were closer to the source of sediments, were covered by shallower water, or were deposited in water with somewhat different pH or oxidizing/reducing conditions may nevertheless differ in some ways from the rest of the formation, although they may be similar in other ways (Bush and Sieveking 1986, 134; Luedtke 1992, 55).

Through the entire Late Cretaceous-Danian time interval the land masses surrounding the Danish Basin in present-day southern Scandinavia were flat and low-lying and the climate was arid. As a result, very little terrigenous material reached the shallow epicontinental sea in northwestern Europe (Surlyk and Håkansson 1999). Because of this, Scandinavian flints contain low concentrations of trace elements, placing high demands on analytical methods. Ideally, these must be capable of detecting a large suite of elements, even when these elements occur at very low concentrations.

Non-destructive energy dispersive X-ray fluorescence analysis (EDXRF)

In sourcing work, the first order of business is to generate a chemical “fingerprint”, or chemical profile, for primary flint sources available to prehistoric peoples. The method we have used is non-destructive energy dispersive X-ray fluorescence analysis (EDXRF). The fact that the method is non-destructive makes it particularly attractive for provenience studies of archaeological artifacts. Its precision for trace and rare earth element measurement is not as good as that of ICP-MS or ICP-OES, but its sensitivity to certain major elements (e.g. Al, Si, K, Ca and Fe) means we can use measurements of these elements in combination to identify contrasts among flint types (Hughes et al. 2010, 21; Hughes et al. 2012, 780). Collaboration between archaeologists Anders Högborg and Deborah Olausson and geochemist Richard E. Hughes beginning in 2010 (Hughes
et al. 2010; Hughes et al. 2012; Höberg et al. 2012; Höberg et al. 2013; Höberg et al. 2014; Höberg et al. 2016) has resulted in the chemical characterization of samples from some 40 flint localities in Sweden (including the islands of Öland and Gotland), Denmark, Poland, Ukraine, and northern Germany including the island of Heligoland in the North Sea (Fig. 8.1). In addition, we have returned to the archaeological collections at Bjurselet, investigated by Becker in 1952, and tested the efficacy of the method for determining the provenience of flint used for archaeological artifacts (Olausson et al. 2012).

Instrumental analysis of geological specimens was conducted by Hughes using a QuanX-ECi™ (Thermo Electron Corporation) energy dispersive x-ray fluorescence spectrometer equipped with a silver (Ag) x-ray tube, a 50 kV x-ray generator, a digital pulse processor with automated energy calibration, and a Peltier cooled solid state detector with 145 eV resolution (FWHM) at 5.9 keV. Previous research (Hughes et al. 2010: 21) showed that X-ray intensities above background for certain trace elements were too low to yield reliable composition estimates. Therefore analyses here focused on major and selected minor elements. Of the nine elements analyzed (Al, Si, S, Cl, K, Ca, Ti, Mn and Fe) using the Kα emission line for each, Si, Ca and Fe typically generated the highest count rates (counts per second over background) and total counts, so these elements were employed to characterize differences among flint sources. The analyses for SiO₂, CaO and Fe (and other reported elements) were conducted in vacuum under three different sets of operating conditions to optimize excitation of major and minor elements of interest. Background-subtracted integrated net count rate (counts per second) data were converted to composition estimates (ppm and wt% composition) using a special fundamental parameters algorithm incorporating international rock standards, after overlapping Kα and Kβ line contributions from adjacent elements were stripped and matrix correction algorithms applied. The X-ray tube current was scaled automatically to the physical size of each specimen.

**Our most important results to date**

The published tables and plots showing trace element compositions for the approximately 40 primary flint localities or types of secondary flint we have sampled represent the most important result of our work to date (Hughes et al. 2010; Hughes et al. 2012; Höberg et al. 2012; Höberg et al. 2013; Höberg et al. 2014; Höberg et al. 2016). Analysis with EDXRF has revealed patterns in CaO and Fe compositions enabling us to suggest
chemical types which can be used for comparisons with specimens of unknown provenience (Table 8.1; Fig. 8.1 and 8.2).

![Fig. 8.1. Map showing the sampling location for the 18 chemical types presented in Table 8.1. Note that this map does not show all of the 40 localities we have sampled.](image)

Because there rarely is a one-to-one relationship between chemical composition and flint source, the non-destructive EDXRF method does not provide us with an infallible tool for provenience analysis. For example, we are unable to establish an exact correlation between visual appearance and properties, location of outcrop, and chemical composition. However, comparisons of unknown samples with the identified chemical types does allow us to eliminate certain flint types as possible sources. Some of the
chemical types we identify are based on few samples from a particular locality (Table 8.1). Therefore, further sampling and analysis is needed to clarify the homogeneity of all locations but especially those with few samples.

**Congruence or divergence between chemical type and visual appearance**

When comparing Ca and Fe compositions in our pilot study we found clear clustering of samples from Møns Klint, Södra Sallerup, Stevns Klint Senonian flint and Stevns Klint Danian flint. We labeled this cluster the Stevns Klint chemical type (Fig. 8.2c). Samples from Smygehuk, Östra Torp, and Klagshamn were also clustered; we called this cluster the Östra Torp chemical type. Finally, the five samples from Hanaskog also formed a cluster we named Hanaskog chemical type (Hughes et al. 2010). In the pilot study we limited ourselves to localities in southwestern Sweden and eastern Denmark, but when we expanded our sampling to include the rest of Denmark and Sweden (Högberg et al. 2012; Hughes et al. 2012), we discovered that the picture was no longer as clear-cut. Specifically, we found that the geographical distribution of newly identified examples belonging to previously identified chemical types was wider than implied by our original names. However we retain the terminology to avoid confusion. Let us look more closely at what we have found regarding the relationship between chemical type and visual appearance.

Flint from Danian and Senonian layers at Stevns Klint (Fig. 8.2a) is of different ages and different appearance (Högberg and Olausson 2007, 36 f.). Therefore we were surprised to discover that Senonian and Danian flint could not be distinguished on the basis of CaO and Fe content (Hughes et al. 2010, 22). However, they could be differentiated by Cl data (Hughes et al. 2012, 791).

In some instances, flint types whose macroscopic appearance was quite different proved to share similar chemical signatures. For instance, the Śródborze flint sample from Poland shares a similar chemistry with Scandinavian Senonian flint from Møn or Södra Sallerup although its appearance is different (Högberg et al. 2013, 259). Likewise, the chemical signature of Brown Bryozoan Flint is similar to that of Scandinavian Senonian, even though visually these types are very different (Högberg et al. 2012, 233). While these particular flints are easily distinguishable from each other on the basis of macroscopic appearance, the systematic application of thin-section petrography to all the geological samples might further enhance our ability to distinguish among sources (see discussion in de Kruyck and Timmer 2014).
In some cases the chemical analyses enabled us to distinguish between types of flint whose appearance was similar. For instance, Black Heligoland flint is visually similar to Rügen flint from Jasmund (Fig. 8.2b, 2d) but the chemical signatures are not the same (Högberg et al. 2014, 63). Another example is flint from Mielnik in Poland. It resembles Scandinavian Senonian flint from Møn or Södra Sallerup but has a different chemical signature (Högberg et al. 2013, 259). In some cases CaO and Fe compositions are not sufficient for making distinctions and other elements must be consulted. For instance, we found that Speckled Senonian flint from Ellidshøj and black Heligoland flint are chemically similar regarding CaO and Fe composition but can be distinguished on the basis of Al₂O₃ (Högberg et al. 2014, 63).

The ideal situation for archaeologists, of course, would be one in which differences in appearance mirror differences in chemical composition and in geological source. Differences in chemical composition corresponded to differences in appearance in regard to the two visual types of flint we sampled from Gotland (Fig. 8.2e) (Högberg et al. 2016). Likewise the distinctive Ordovician flint from Öland and flint from Kinnekulle show dramatic differences in CaO/Fe in comparison with all the other kinds of flint we have analyzed. The same is true of Black Kristianstad flint and Ball flint (Högberg et al. 2012, 232, 237). In the case of the distinctive red Heligoland flint the uniqueness of the appearance is reflected in a unique chemical signature with higher levels of Fe than any other kind of flint we have sampled (Högberg et al. 2014, 63). The visual types labeled Common Kristianstad Flint and Black Kristianstad flint also differ in chemical composition (Hughes et al. 2012, 790). Finally, the visual type we labeled grey flint from Gotland has a chemical composition unlike any other we have analyzed so far (Högberg et al. 2016).

**Congruence or divergence between chemical type and outcrop location**

Ideally we would wish for a situation with absolute congruence between chemical type and a specific outcrop location. Unfortunately, this has not proven to be the case. We concluded in 2012, after our expanded sample analyses that – just as in obsidian analysis (Hughes 1998) – chemical type does not always correspond to geographic proximity (Högberg et al. 2012, 234; Hughes et al. 2012, 793). Subsequent analysis since that time has reinforced this conclusion.
In our pilot study (Hughes et al. 2010) we discovered that samples from Stevns Klint in Denmark and Södra Sallerup in Sweden, sites that are about 50 km apart, were chemically similar. The chalk slabs at Södra Sallerup are not in situ outcrops but rather are thought to have been transported by glacial movement (Högberg and Olausson 2007, 52).
Therefore, we reasoned, the flint at Södra Sallerup might originate from the same geological formation as we see at Stevns Klint (Hughes et al. 2010). However, the expanded survey we conducted in 2012 showed that Scandinavian Senonian flints which are visually similar and have the same chemical composition are not limited to eastern Denmark or southwestern Sweden but are much more widely spread over Denmark (Högberg et al. 2012, Fig. 8.5). And the analyses of flint samples from Poland and the Ukraine revealed that flint types with similar appearance and similar CaO and Fe compositions can come from places as far apart as southern Scandinavia and western Ukraine (Högberg et al. 2013, 259). Finally, we found a slight chemical overlap between what we labeled white/brown flint from Gotland and flint from southwestern Scandinavia (Högberg et al. 2016).

Analyzing archaeological artifacts; patination

In our analysis of flint artifacts from Bjurselet (Fig. 8.3) we found that EDXRF allowed us to eliminate many known flint outcrops as possible candidates for the raw material source. However, as we mentioned above, the Stevns Klint chemical type is represented by many geological localities, so the method is not sufficient to choose among them. Although EDXRF data alone were not sufficient for pinpointing the exact place of origin for the flint at Bjurselet, the results confirmed conclusions based on other kinds of evidence (Olausson et al. 2012).

As the element compositions in our tables are in most cases based on unweathered geological samples culled from primary deposits, we need to eliminate possible chemical disturbances due to weathering and patination on non-fresh surfaces (problems which often plague archaeological artifacts) before we can make direct comparisons (e.g. Gauthier and Burke 2011). Encouragingly, values for the Bjurselet artifacts proved to be closely comparable to those of the geological samples for the Stevns Klint chemical type except for somewhat elevated values for iron content for the artifacts (Olausson et al. 2012, Fig. 21). We interpreted this as a possible effect of Fe enrichment due to patination. In other words, values were not so different from the geological samples that we could not identify the flint as belonging to the Stevns Klint chemical type, but they were sufficiently dissimilar to enable us to identify patination effects. We have found indications that a patinated surface shows SiO₂ depletion and elevated Al₂O₃, K₂O, Cl and Ti (Högberg et al. 2012, 229 f.; Hughes et al. 2012, 787), suggesting that these elements might be indicative of patination. However more systematic work on this question needs to be done.
Fig. 8.3. In 1827, a cache containing six Neolithic flint axes arranged in a star pattern around a slate axe and a slate whetstone was discovered on a terrace of the Bjurselet River in northern Sweden. Five years later, in 1832, a cache containing 70 flint axes was uncovered in the same area. All artifacts were described by Becker as being made of south Scandinavian flint whose nearest source lies some 1500 kilometers distant (Becker 1952, 35). This led Mats Malmer (1962, 506) to characterize these finds as among the most unique and most difficult to explain of the north-European stone age. We considered these objects appropriate for testing EDXRF analysis on archaeological artifacts. The photograph shows three views of one of the axes, analyzed in three different spots. The yellowish tinge is due to patination, which shows chemically as slightly elevated Fe values compared to geological samples (Olausson et al. 2012). Photo by Tammara Norton.
Future work

We see at least three directions for future work. The first involves further sampling of geological localities to address the question of chemical homogeneity. We were surprised by the results from Stevns Klint, Denmark, where layers of different geological ages bore similar chemical signatures, questioning the assumption that different horizons should have different chemical signatures. Many of the localities we have sampled are represented by fewer than five samples (Table 8.1). Until we have supported our results with further samples we are hesitant about making predictions about the homogeneity of flint layers at these sources.

A second path relates to the question of the chemical effects of patination and weathering on archaeological artifacts. Even when the effects of these processes are not visible to the naked eye (Luedtke 1992; Levi Sala 1996) we must be aware of the possible chemical alterations they cause. Our initial work documented the effect of patination on the underlying chemistry of an artifact (Högberg et al. 2012, 230; Hughes et al. 2012, 787; Olausson et al. 2012), but more systematic experimental and analytical work is needed to pinpoint other possible sources of error.

A third direction involves comparing analytical methods. As Killick (2015) observes, different methods used for chemical provenience analysis of the same source may yield slightly different results. To test this we have initiated a small-scale comparative analysis using ICP-MS in collaboration with Mar Rey y Sole from University of Barcelona and the Department of Geology, Lund University. In contrast to non-destructive EDXRF, ICP-MS is a bulk technique which requires crushing a small sample of the material. The purpose is to compare results from this method with our EDXRF results. The ICP-MS work includes both comparative analysis of previously analyzed flint types (Hughes et al. 2012) and an analysis of patination effects.

Conclusion

The EDXRF studies described here were executed to evaluate the utility of a non-destructive technique to characterize flint. Archaeology’s explicit conservation ethic means that we need methods which are non-invasive and non-destructive. When using EDXRF, Ca and Fe proved to be the elements which usually generated the highest count rates and total counts and their concentrations allowed satisfactory partitioning of many of the flints we analyzed. Of importance for archaeologists, EDXRF is fast and therefore inexpensive.
In our work to date we have sampled some 40 primary localities and secondary sources of flint in Sweden, Denmark, Poland, Germany and the Ukraine. However, many of the localities are represented by a very limited number of samples, which means we cannot address the question of homogeneity for these sources until more samples are analyzed. More work to tease out the correlations between flint chemistry and visual appearance, as well as the effects of source-critical aspects of post-depositional effects on tool surfaces, is necessary before we can fully embrace EDXRF as a tool for provenience analysis of prehistoric flint artifacts. The results of our research show that it is possible to chemically distinguish different flint types from each other and we have to date indications of several distinct chemical flint types for north European flint. Although there are many difficulties involved in provenience analysis, EDXRF can be added to our arsenal of tools for discriminating among various outcrops for flint used for tool production during prehistory.

Table 8.1. The 18 chemical types defined on the basis of CaO and Fe composition. Some of the types are represented by a single sample, others, such as Stevns Klint chemical type, are defined by a cluster of samples with similar CaO and Fe content.

<table>
<thead>
<tr>
<th>Chemical type</th>
<th>Number in Fig. 8.1</th>
<th>Number of samples</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stevns Klint</td>
<td>1</td>
<td>&gt;40</td>
<td>Hughes et al. 2010, Högb erg et al. 2012</td>
</tr>
<tr>
<td>Östra Torp</td>
<td>2</td>
<td>15</td>
<td>Hughes et al. 2010</td>
</tr>
<tr>
<td>Hanaskog</td>
<td>3</td>
<td>5</td>
<td>Hughes et al. 2010</td>
</tr>
<tr>
<td>Ball flint from Bornholm</td>
<td>5</td>
<td>2</td>
<td>Högb erg et al. 2012</td>
</tr>
<tr>
<td>Jasmund</td>
<td>6</td>
<td>2</td>
<td>Högb erg et al. 2012</td>
</tr>
<tr>
<td>Helligkilde</td>
<td>7</td>
<td>1</td>
<td>Högb erg et al. 2012</td>
</tr>
<tr>
<td>Hisingen</td>
<td>8</td>
<td>2</td>
<td>Högb erg et al. 2012</td>
</tr>
<tr>
<td>Klintholm</td>
<td>9</td>
<td>5</td>
<td>Högb erg et al. 2012</td>
</tr>
<tr>
<td>Mønsted</td>
<td>10</td>
<td>2</td>
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<tr>
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<tr>
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<td>Hanaskog high Fe variety</td>
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</tr>
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<td>Ożarów</td>
<td>18</td>
<td>1</td>
<td>Högb erg et al. 2013</td>
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References


