

Sourcing flint from Sweden and Denmark A pilot study employing non-destructive energy dispersive X-ray fluorescence spectrometry

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This article presents the results of a pilot study exploring the feasibility of using non-destructive energy dispersive X-ray fluorescence (EDXRF) spectrometry for the chemical sourcing of flint from three geographical areas: eastern Denmark and southwestern Sweden (Stevns Klint, Møns Klint, Södra Sallerup), south and southwestern Sweden (Klagshamn, Östra Torp, Smygehuk) and southeastern Sweden (Hanaskog). The EDXRF results showed that the flint samples from Stevns Klint are all chemically alike on the basis of Si/Ca/Fe and Ca/Fe ratio data, even though they possess markedly different visual qualities and are of different geological ages. The samples from Södra Sallerup, Sweden, and Stevns Klint, Denmark, are chemically similar. Since the chalk slabs at Södra Sallerup were re-deposited by glacial ice, the results of the chemical analysis may indicate that they originated from the same formation that emerges at Stevns Klint. The samples from Klagshamn, Östra Torp and Smygehuk are visually alike and bear the same chemical signature; all three originate from the same geological formation of Danian age but are from different localities. The Common Kristianstad Flint (Hanaskog) is distinctive in appearance and the results of the EDXRF instrumental analysis yielded a corresponding unique Ca/Fe chemical signature. In summary, the pilot study successfully revealed distinctions among the flint samples.

Keywords: flint, chemical sourcing, energy dispersive X-ray fluorescence (EDXRF) analysis, south Sweden, Denmark

Archaeologists have long been in need of reliable and replicable means to identify the specific sources of the raw materials used to manufacture archaeological artefacts. In Scandinavian archaeology, Carl Johan Becker (1952) made one of the first efforts to establish reliable criteria for differentiating Scandinavian flint types so that the origins of the raw material sources for the Neolithic flint axe hoards in northern Sweden could be identified. Becker relied on appearance and physical

qualities to narrow down the origin of the flint to the Senonian deposits of eastern Zealand or southwestern Scania (Becker 1952:69; Knutsson 1988:51). In a recent study of Late Neolithic daggers, Jan Apel (2001) drew on Becker's results to advance far-reaching conclusions about manufacturing centres 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).

The terms “flint” and “chert” are often used interchangeably and there is a lack of consensus among archaeologists as to what to call fine-grained, knappable siliceous rocks. Some regard flint as a type of chert, others consider flint to be one type of rock and chert another (Luedtke 1992). In this article we follow the Scandinavian practice and refer to all chert varieties as flint.

There are two ways to identify the primary source of a piece of flint: 1) based on optical, or macroscopic, properties of the material, and 2) via instrumental analyses of chemical composition. Although many Scandinavian archaeologists have addressed questions concerned with the origins of flint as a raw material, most conclusions have been based on macroscopic properties, which tend to be described subjectively and can be altered significantly by post-depositional knapping and/or patination. A recent study of Scandinavian flint (Högberg & Olausson 2007) illustrates the variety and complexity of this material and demonstrates the difficulties involved in arriving at a wholly satisfactory macroscopic classification based on morphology alone.

This article presents the results of a pilot study which explores the feasibility of using non-destructive energy dispersive X-ray fluorescence spectrometry (EDXRF) for the chemical sourcing of flint from southern Sweden and eastern Denmark. At the outset, it is necessary to clarify what we mean by “source”, a term that has been used in a variety of ways in archaeology (for a discussion, see Hughes 1998). From the standpoint of instrumentally-based analyses, the term source usually refers to a distinct entity – a basalt, andesite, obsidian, chert or flint – defined on the basis of unique combinations and concentrations of chemical constituents (Hughes 1986:49) that may be differentially bounded in space. In obsidian sourcing research, sources are defined geochemically, by their chemical composition rather than by their spatial extent (Hughes 1998:104). In western North America, for example, some chemically discrete obsidian sources occur over a very small geographical area, perhaps only a few kilometres, while artefact-quality obsidian formed in ash-flow tuff sheets in adjacent geographical areas may occur widely over an area of perhaps 10 000 square kilometres (Hughes & Smith 1993). Scandinavian flint chemical types occur over even larger areas. Consequently, we use the term “source” interchangeably with “chemical type” to underscore chemical coherence, not spatial distribution.

Optical Methods

Optical methods, appealing to the observable physical properties of specimens, are of course the fastest and least costly way to assign a flint artefact to a source. Becker’s (1952) classification relied on visual qualities, as does the system proposed recently by Högberg and Olausson (2007). Although it is generally possible to distinguish among Scandinavian flint types using variables such as colour, cortex morphology, translucency and homogeneity, it is clear that there is some overlap and ambiguity involved in any optical classification system (Bettinger et al. 1984). The classification proposed by Högberg and Olausson (2007) is based principally on the appearance of primary flint augmented by observations made at the various primary sources visited in the course of the study. However, the appearance of flint can be seriously altered by post-depositional weathering and patination (Luedtke 1992). In some cases the appearance of the cortex or the transition between the cortex and the flint are the main diagnostic feature. When this is absent it may be impossible to distinguish visually between two types (Fig. 1). Högberg and Olausson (2007) also show that the same type of flint can sometimes occur at a number of separate locations.

In an earlier attempt to identify flint on the basis of appearance, Lis Ekelund Nielsen (1993) was able to distinguish reliably between three varieties of flint used for the manufacture of Neolithic axes on Jutland by employing a combination of visual characteristics (mostly colour, texture and fossils), thin sections and examination at 25–50× magnifications under a stereomicroscope to support her classification. Kinnunen et al. (1985) and Tralau (1974) have attempted to identify flint sources on the basis of their fossil content, but because not all types of Scandinavian flints contain recognizable fossils, this method is of limited value.

Instrumental Methods

Although various geochemical analyses of chalk flint have been carried out in England and the Netherlands (de Bruin et al. 1972; Sieveking et al. 1972; Craddock et al. 1983; Bush & Sieveking 1986; Gardiner 1990; McDonnell et al. 1997), no systematic work has been done to characterize the geochemical composition of Scandinavian flint sources. A chemical analysis of specimens of Senonian flint from Stevns Klint, Denmark showed that it consisted of 98.44% SiO₂ (Micheelsen 1966:308). In order to identify flint artefacts found at

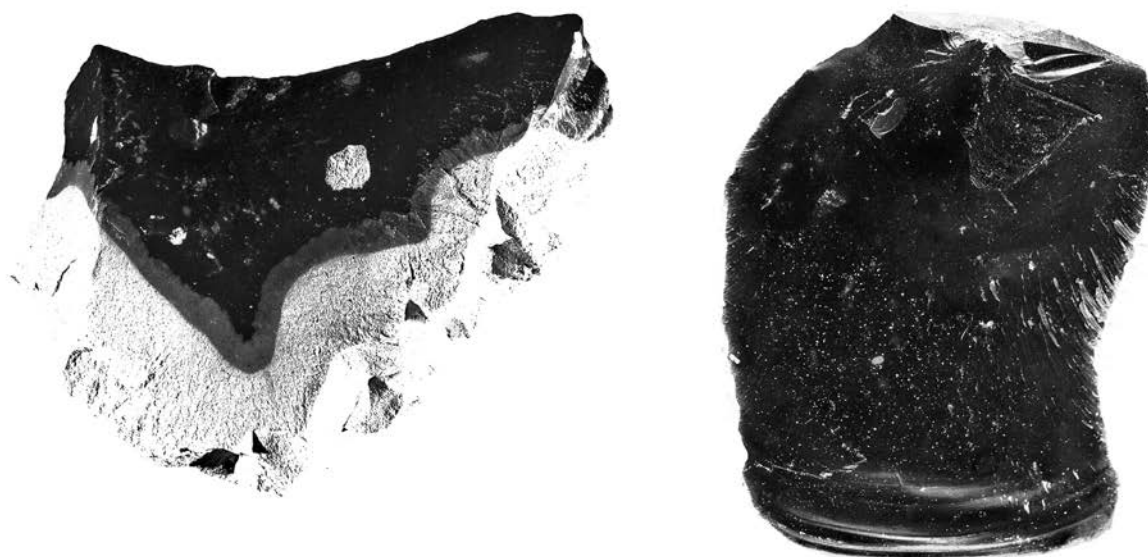


Figure 1. An example illustrating the difficulty of visually distinguishing among different types of flint. The Grey Band Danian Flint (Högberg & Olausson 2007:104ff) to the left can be found on northern Jutland in Denmark and in southwestern Scania in Sweden. It has a characteristic grey band at the transition between the flint matrix and the cortex. If this flint is knapped so that the cortex and grey band are removed, it becomes difficult to distinguish it on visual qualities alone from the Scandinavian Senonian Flint (to the right), for example (Högberg & Olausson 2007:88ff). Scandinavian Senonian Flint can be found in northern Jutland and on Zealand in Denmark and in southwestern Scania in Sweden.

Finnish Stone Age and Bronze Age sites as being made either of “eastern” (i.e. Russian) or “western” (i.e. Danish or Swedish) flint, Matiskainen et al. (1989) used atomic absorption spectrometry to analyse 71 samples for 20 chemical elements, and succeeded in distinguishing between these two broad source categories on the basis of five elements. Subsequently, Costopoulos (2003) tested new elemental composition data on the same samples using an electron microprobe and an energy dispersive spectrometer and arrived at a similar conclusion.

As with optical characterization, there are problems associated with instrumental methods. The instrumentation required to carry out the analyses is expensive and the work requires specialist knowledge. Costs can be high and the analysis generally requires close cooperation between the archaeologist and the analyst. Bush (1976:48) lists the following prerequisites for successful identification of a chert source by trace element analysis, but these strictures also apply to the use of other (major, minor and rare earth) elements:

1. The material from each source must not vary widely in its trace element composition.
2. The trace elements used should be ones that

will be uniformly distributed through the chert and not likely to be concentrated in occasional rare mineral grains.

3. The “fingerprint” of each source, i.e. its composition in terms of trace elements, must be sufficiently distinct to allow for differentiation between sources.

While the actual elements used to construct source-specific chemical signatures (*sensu* Hughes 1998:104) may vary from region to region depending on the compositions of the materials studied, the combinations of elements must be sufficiently clear-cut to distinguish among the possible outcrops/sources in any particular area (cf. Malyk-Selivanova et al. 1998:679).

The Flint Problem

Because of the way they are formed, flints in chalk and limestone can be assumed to fulfil the three requirements listed by Bush (1976). Since flint is composed mainly of SiO_2 , one approach has been to measure the trace elements whose origins are non-carbonate materials (e.g. clay minerals and heavy minerals) which

were incorporated in the flint as it was being formed by the replacement of calcium carbonate with silica (Tite 1972:308). The impurities present in a specific flint are a reflection of many factors, including the types of rock present in adjacent land masses, weathering processes affecting these rocks, the nature of the processes transporting sediments into bodies of water, the chemical conditions in the deposition basin, and the distance between the basin where the flint was forming and dry land (Luedtke 1992:36). 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 served 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 (Sieveking et al. 1972:156; Bush 1976:48; Craddock et al. 1983:138; Bush & Sieveking 1986:134; McDonnell et al. 1997). 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 & Sieveking 1986:134; Luedtke 1992:55).

Through the entire Late Cretaceous-Danian time interval the land masses surrounding the Danish Basin 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 (Surluk & Håkansson 1999). Because of this, Scandinavian flints contain low concentrations of trace elements, which place 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. Traditional analytical methods such as X-ray fluorescence, PIXE or NAA have previously yielded variable results when employed for flint sourcing (Craddock et al. 1983:138).

Primary and Secondary Flint Sources in Scandinavia

Flint can be found in primary deposits in Denmark and in southern Sweden, where there are numerous outcrops of Danian, Maastrichtian and Campanian age. These sources were exploited *in situ* by prehistoric

people to varying degrees, either through mining efforts or by taking advantage of flint layers eroding out of cliff faces. The primary sources were then augmented by secondary ones located in glacial moraines and on beaches, where ice movements had excavated flint from primary sources and redeposited it, creating a complex mixture of different flint types over large parts of the region. Provenance determinations in Scandinavia are therefore greatly complicated by the geological conditions, which have made large quantities of secondary flint available to prehistoric populations on beaches and in glacial till (Högberg & Olausson 2007). The instrumental sourcing methods in use today can tell us the primary source of the flint we are investigating, but they do not enable us to distinguish between primary and secondary sources. Once the primary sources have been successfully defined, there may be further difficulties connected with linking a piece of flint (or a flint artefact) from a secondary context with one of the primary sources.

For the geochemical fingerprinting of flint to be useful in sourcing archaeological artefacts, it must be assumed that the flint composition remain unaltered by exposure to soil, weathering, or other processes for the long periods of time for which the flint remains were exposed at the surface (Bush 1976:48; Rapp 1985:355; McDonnell et al. 1997:372). Luedtke (1992:57) and Thacker & Ellwood (2002:476) caution against using cortical or weathered surfaces of samples for geochemical sourcing, since flint is susceptible to a number of post-depositional processes which can alter their internal chemistry. Only a few systematic studies have been carried out to test this assumption, however. In one such study, de Bruin et al. (1972) used non-destructive NAA to measure elements in flint from several north European sources and found when comparing the results for nodules in the Rijckholt mine in the Netherlands with those for flint flakes from the workshop outside the mine that the Rijckholt mine and workshop specimens were not chemically identical. Their conclusion was that the chemical composition of the flakes had been altered by the depositional environment (de Bruin et al. 1972:63). However, Bush (1976:48) writes that chalk cherts (flints) are dense and of low permeability, which reduces the possibility of trace elements being removed by leaching or of material being added from the groundwater.

The conclusion to be drawn is that geochemical analyses of flints from secondary contexts may be complicated and the prospects of identifying the primary source for any given artefact may be problematic.

Table 1. Source, description, type of flint according to Högberg and Olausson (2007) and samples included in the study.

Source	Description	Type of flint	Sample
Östra Torp	An abandoned modern limestone quarry.	Matte Danian Flint, Östra Torp Variety	Ten flint nodules collected from a quarry dump.
Klagshamn	An abandoned modern limestone quarry.	Matte Danian Flint, Östra Torp Variety	Ten flint nodules collected from a quarry dump.
Stevns Klint	A Maastrichtian chalk and Danian limestone cliff by the sea.	Matte Danian Flint, Östra Torp Variety and Scandinavian Senonian Flint	Ten flint nodules from each of two layers of Danian age and ten nodules from one layer of Senonian age, all collected in situ.
Smygehuk	An outcrop on a beach.	Matte Danian Flint, Östra Torp Variety	Ten flint nodules collected from the outcrop.
Södra Sallerup	Large chalk slabs containing flint which were scooped up by glacial ice and re-deposited at the site. Systematic mining of flint started here in the Early Neolithic, and chalk quarrying has continued until quite recently.	Scandinavian Senonian Flint	Ten flint nodules collected in situ from dumps at the modern quarry.
Møns Klint	A Maastrichtian chalk cliff by the sea.	Scandinavian Senonian Flint	Twenty nodules from each of two flint layers.
Hanaskog	An abandoned modern limestone quarry.	Common Kristianstad Flint	Nine nodules collected from quarry dumps.

Nevertheless, the first order of business is to generate a chemical “fingerprint”, or chemical profile, for each known primary source. Once that step is completed, one may find that the geochemical signature of a secondary flint occurrence matches that of one of the primary sources (prompting one to conclude that the flint came from that source), or that it may not match any of the known sources.

However, even assuming we are able to achieve a successful characterization of the primary sources, geochemical analysis alone cannot tell us whether the flint was collected or mined directly from the outcrop in question or whether it was derived from a nodule in a secondary geological deposit that was “mined” by a glacier (Williams-Thorpe et al. 1999:210). A possible method for making this distinction has been described by Shockey (1995), who used polarization to distinguish between quarry area specimens and stream-rolled rocks representing the same material.

Geochemical Analysis of Scandinavian Flints

In an attempt to find a reliable method for chemically characterizing Scandinavian flint sources, Högberg and Olausson initiated a study of flint from ten geological contexts. A total of 119 nodules were collected from the ten localities in southern Sweden and Denmark (Table 1, Fig. 2) and samples from these nodules were submitted for geochemical analysis.

Several methods were tested: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) of solutions, ICP-MS of solutions and Energy Dispersive X-ray Fluorescence (EDXRF). LA-ICP-MS can provide compositional data on 50–60 elements, while the other techniques typically provide compositional data on 30 elements or less (Speakman et al. 2002). Laser ablation ICP-MS has lower detection limits for many elements than do the other instrumental techniques (Gratuze et al. 2001; Speakman et al. 2002), and this method has been used successfully on English chalk flint (Rockman pers. comm. 2002). EDXRF typically measures fewer elements than ICP techniques, and with a lower precision, but it can rapidly generate data for a large number of elements without sacrificing any portion of the sample for analysis (Giauque et al. 1993).

Only the last of these methods proved effective for the present samples. Before we describe the successful results we achieved using EDXRF, we will briefly describe the difficulties we encountered with the others.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

A total of 360 flake samples taken from the 119 flint nodules were submitted to the Research Reactor



Figure 2. Map of south Scandinavia showing the sources of flint mentioned in the text. The distance between Klagshamn and Hanaskog is approximately 125 km.

Center at the University of Missouri-Columbia for LA-ICP-MS. Laser ablation ICP-MS requires little sample preparation other than resizing to fit inside the sample chamber. The samples were washed in deionized water and left to dry. Each sample was then crushed into coarse fragments, and relatively flat interior fragments with little or no cortex were selected for analysis.

The results showed that the samples had a high silica concentration, which unfortunately resulted in

dilution of the other elements. The conclusion was that this method, as employed under existing analytical conditions, was unsuitable for characterizing Scandinavian flint types (Speakman et al. 2002; Speakman pers. comm. 2004).

Samples from the same nodules were subsequently analysed by Inductively Coupled Plasma-Mass Spectroscopy and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-MS and ICP-OES) of solutions at the Analytical Unit of the University of

Greenwich. Sample preparation for this method involved crushing the flakes and then milling them to a fine powder. 0.5000 g of each powder was then dissolved in acid and heated to near dryness. This procedure was repeated twice, and finally the powder was dissolved in nitric acid. This approach resulted in the removal of Si from the flint and dissolving of the remaining flint (Wray 2005).

The results indicated that the samples were quite homogeneous within each respective layer or locality, while the layers and localities were distinct from each other (Wray pers. comm. 2006). Further sampling and more detailed analyses would be necessary, however, before definitive geochemical compositions could be established for the sources using these methods.

Energy Dispersive X-ray Fluorescence Analysis (EDXRF)

Because of the obvious importance of artefact conservation in archaeology, neither ICP-MS nor ICP-OES, being destructive methods, is ideally suited for use in artefact provenance studies. Although X-ray fluorescence analysis has been applied with great success to the study of volcanic rocks such as obsidian (e.g. Jack 1976; Reeves & Ward 1976; Stross et al. 1976; Nelson 1984, 1985; Hughes 1986; Asaro et al. 1994; Shackley 2005; Iovino et al. 2008; Hughes & Lucas 2009), it has not to our knowledge been as widely used on sedimentary rocks such as chalk flint. EDXRF has certain other advantages in addition to being a completely non-destructive method. 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 low atomic number major elements (e.g. Al, Si, K, Ca, and Fe) allows measurements of these to be used in combination to identify contrasts among certain Scandinavian flint types.

Instrumentation and Results

To determine whether or not non-destructive EDXRF would be useful for the characterization of Scandinavian flints, a sample of five flakes detached from different nodules recovered from each of ten collection localities (including three separate layers at Stevns Klint and two at Møns Klint) was analysed (see Table 1 and Fig. 2 for locations). The instrumental analysis was performed by Hughes using a QuanX-EC™ (Thermo Electron Corporation) EDXRF 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. The X-ray tube was operated at various voltage and current settings to optimize the excitation of the elements selected for analysis.

Sample pretreatment for the whole rock EDXRF analyses was limited to cleaning with distilled water to remove any noticeable surface contaminants. Special care was taken to avoid directing the X-ray beam onto obvious patinated surfaces (see above) or calcareous or fossil inclusions. The only other requirement was that each sample should be relatively flat, > c. 2–3 mm thick and >15–20 mm in diameter. Although no analyses were performed here on flint artefacts, the same size parameters should apply to archaeological specimens as to geological samples.

Initial analyses were conducted for the trace elements rubidium (Rb $K\alpha$), strontium (Sr $K\alpha$), yttrium (Y $K\alpha$), zirconium (Zr $K\alpha$) and niobium (Nb $K\alpha$), but it quickly became apparent that these data could not be employed because the peak/background counts were far lower than the element-specific detection limits of EDXRF. A second set of experiments included analyses for Al, Si, K, Ca, Ti, Mn and Fe (using the $K\alpha$ emission line for each element) but, as with the above trace elements, the extremely low number of X-ray emission counts/second generated for Al, K, Ti and Mn indicated that these elements similarly would not yield reliable data. Subsequent experiments focused on Si, Ca and Fe, as these generated much higher count rates (counts/second over the background). The analyses for Si, Ca, and Fe were conducted at 30 deadtime-corrected seconds in order to generate background-subtracted integrated net count rate (counts/second) data. Overlapping $K\alpha$ and $K\beta$ line contributions from adjacent elements were stripped, and the tube current was scaled automatically to the physical size of each specimen. Although these experiments employed integrated count rate data, the typical 2σ quantitative analysis measurement precision for SiO_2 , Ca and Fe was 1–2% relative.

A ternary diagram plot for the 50 specimens examined by EDXRF in this pilot study is shown in Figure 3. As expected in the light of the data published by Micheelsen (1966), all the samples contained relatively high amounts of SiO_2 , but the variations in Ca and Fe composition allowed the flints to be partitioned into two general groups, one consisting of the samples from Smygehuk, Östra Torp and Klagshamn and the other of those from Møns Klint, Stevns Klint

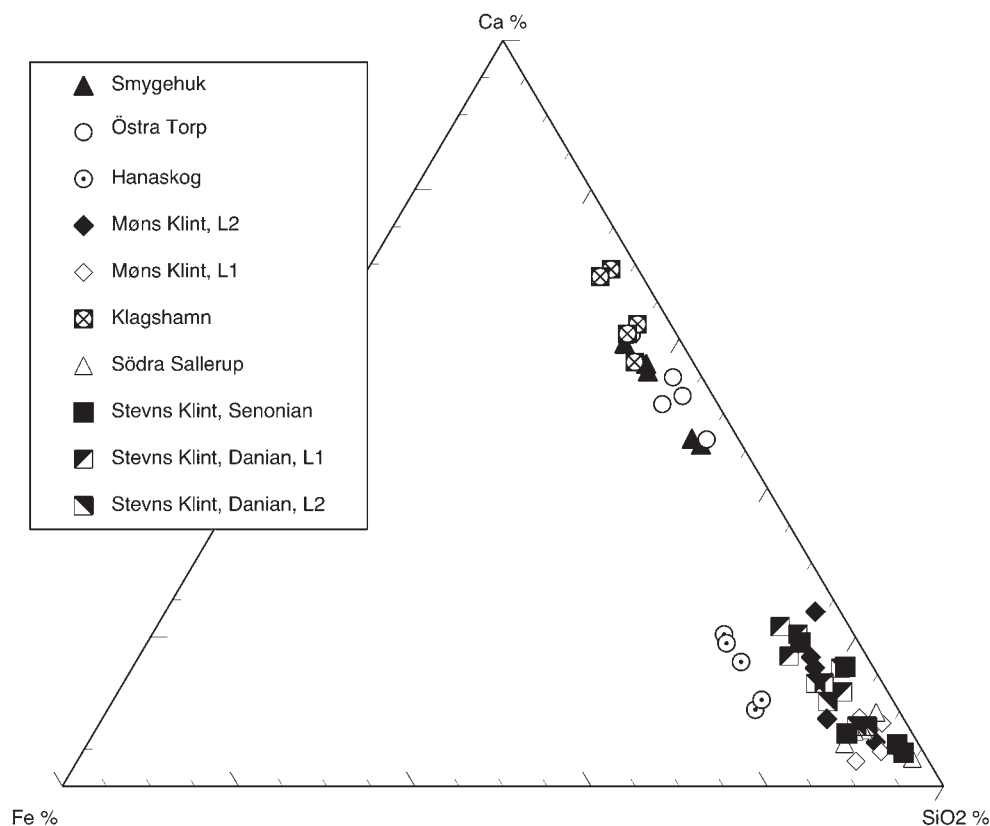


Figure 3. Ternary diagram plot for the Scandinavian flint samples.

and Södra Sallerup. The samples from Hanaskog plotted close to the latter group, although this source was found to contain a higher proportion of Fe.

A bivariate plot of Ca vs. Fe (Fig. 4) provides a somewhat clearer picture of these chemical relations by removing the high Si from the picture. The same two-part separation as was documented in Figure 3 also appears in Figure 4, but with some refinement. In this case a relatively high Ca group (made up of Smygehuk, Östra Torp and Klagshamn) and a group with relatively low Ca and Fe (consisting of Møns Klint, Stevns Klint and Södra Sallerup) are apparent, while Hanaskog is clearly distinguished from both of these other two groups on the basis of its relatively higher Fe.

The reader will have immediately noticed that these provisional chemical groupings are to a certain extent geographically discrete. The Smygehuk, Östra Torp and Klagshamn localities are all in southwestern Scania, Sweden, Hanaskog is in northeastern Scania, Sweden, and Møns Klint, Stevns Klint and Södra Sallerup are in eastern Denmark and southwestern Scania (see Fig. 2). It is notable that, although Klagshamn and Södra Sallerup are located only about

20 km from one another, the Ca/Fe ratio data show that flints from these sources represent quite different chemical types.

Discussion

Luedtke (1992) observed that chemical variation in chert formations is often correlated with variability in their visual characteristics. In general, the more extreme the visible differences within a chert type, the more extreme the chemical variability (Luedtke 1992:54). The results indicate, however, that this generalization cannot be reliably applied to the flints we have analysed.

When we compare the chemical signatures based on the EDXRF analyses with the geological contexts, spatial locations and visual qualities of the flint samples, interesting results appear. The samples from Stevns Klint are all chemically alike in terms of their Si/Ca/Fe and Ca/Fe ratio data, yet they possess markedly different visual qualities and are of different geological ages. The samples are of both Maastrichtian and Danian ages and are classified visually as representing Scandinavian Senonian Flint or the Östra Torp Variety of

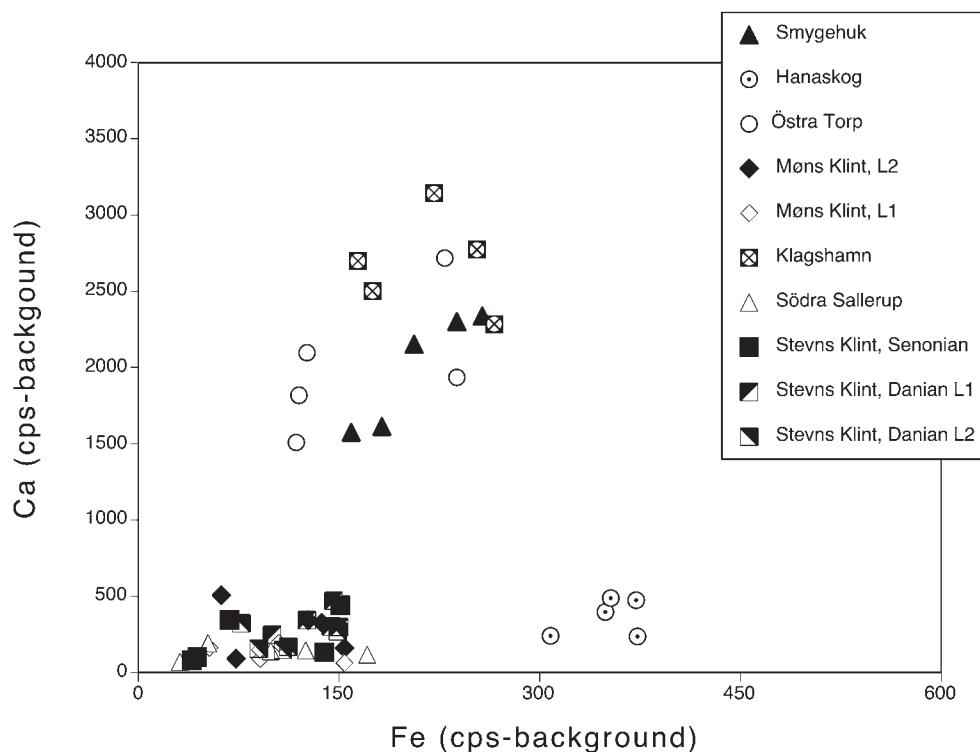


Figure 4. Bivariate plot of Ca/Fe composition for the Scandinavian flint samples.

Matte Danian Flint.

We note, too, that the samples from Södra Sallerup and those from Stevns Klint are chemically similar, although the two localities are about 50 km apart. We know that the chalk slabs at Södra Sallerup are not *in situ*. Bertil Ringberg (1980:57ff) has suggested that they were removed from the floor of the Baltic Sea to the south and re-deposited in their present location by glacial ice. It is therefore entirely possible that the chalk and its flint at Södra Sallerup comes from the same formation as that which emerges at Stevns Klint, in which case the origin of the slabs must lie southwest of Södra Sallerup. Our chemical data are consonant with this conclusion.

The samples from Klagshamn, Östra Torp and Smygehuk are visually alike and bear the same chemical signature. All three originate from the same geological formation of Danian age but are from different localities. The Common Kristianstad Flint (Hanaskog) is distinctive in appearance and the results of our EDXRF instrumental analysis yielded a corresponding unique Ca/Fe chemical signature.

Future work notwithstanding, these pilot study results reveal distinctions among three geographical

areas: eastern Denmark with southwestern Sweden (Stevns Klint, Møns Klint, Södra Sallerup), southwestern Sweden (Klagshamn, Östra Torp, Smygehuk) and southeastern Sweden (Hanaskog).

While we are gratified by these initial research results, we caution that they are only preliminary. More samples need to be analysed from these localities to ensure that the groupings remain discrete, and additional samples need to be tested from localities *not* included in this study to determine the degree to which Si/Ca/Fe signatures remain useful for identifying flints in this part of the world in general. Further work will also be undertaken to convert the integrated intensity data to concentration estimates in order to facilitate comparisons with research conducted at other laboratories.

It should be pointed out that these results are applicable to fresh, unpatinated surfaces. Since patination may alter the surface chemistry (Shepherd 1972; Luedtke 1992; Högberg & Olausson 2007), it is important to investigate whether EDXRF analysis is accurate for patinated flint as well. This will be the subject of further studies. Our ultimate objective is to apply these chemical distinctions to the analysis

of prehistoric artefacts of different ages to establish whether or not there was change and/or continuity through time in material acquisition and conveyance patterns in different parts of Scandinavia.

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