

The archaeological and geochemical implications of trace element distributions in some English, Dutch and Belgian Flints

M.R. Cowell

Introduction

The possibility of tracing the raw material sources of archaeological flints by elemental analysis has, in recent years, been investigated by a number of groups of workers. Characterising the composition of source material has usually been carried out, for reasons of economy, by analysing a relatively small number of samples, typically 10-20. To examine the distribution at mine sites in more detail and to determine the likely chemical location of some trace elements in flint, two sources were more extensively sampled.

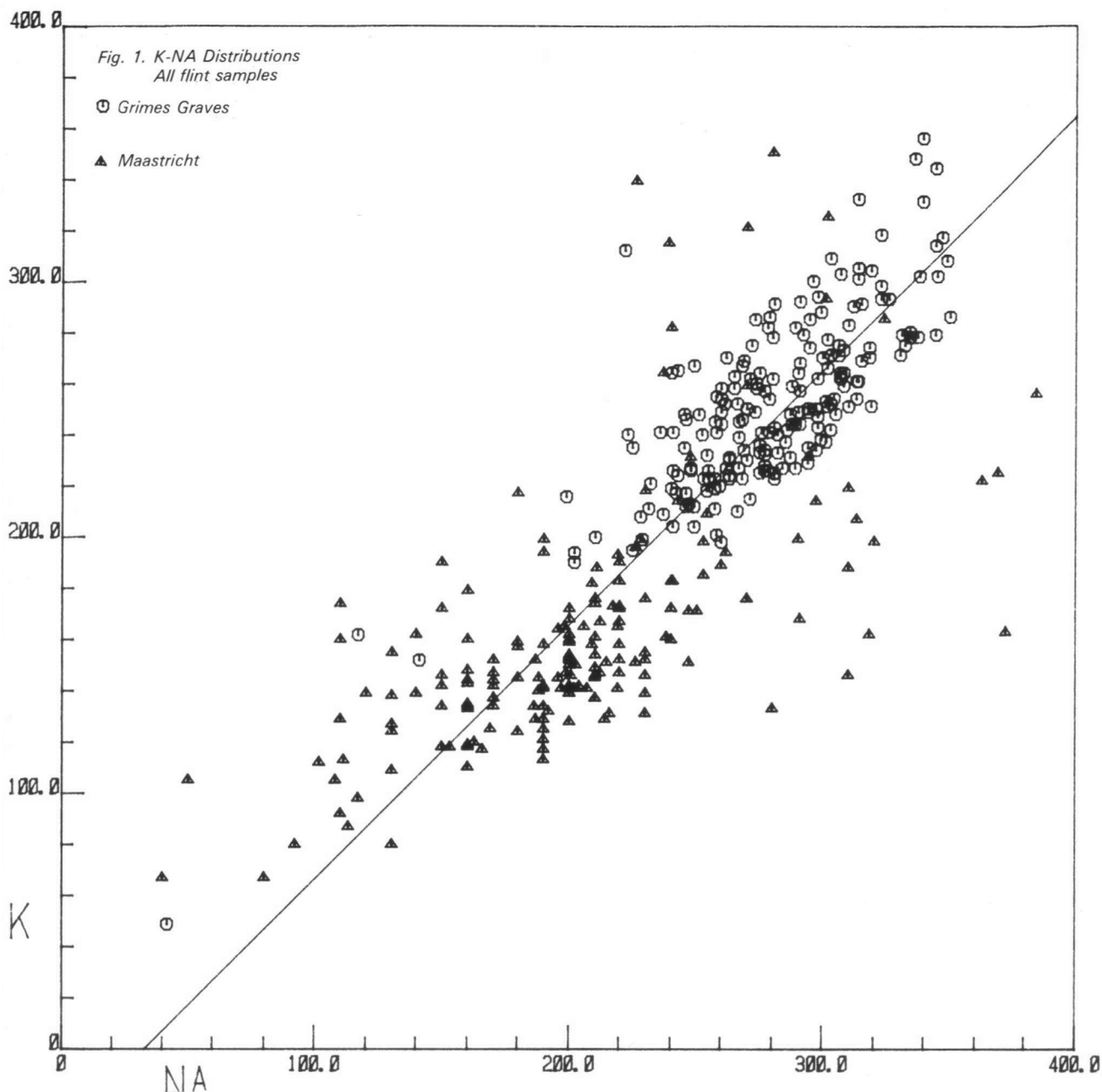
Material and chemical analysis

The sources chosen for more detailed examination were the mine site complex of Grimes Graves, Norfolk, England and the Ryckholt mine and exposures of flint in the area around Maastricht. The 197 Grimes Graves samples analysed were all collected from the 'floorstone' layer in the upper *Terebratulina lata* zone exposed at the base of shafts and also at a nearby quarry. The 197 samples analysed from the Maastricht area were all collected from the Lanaye Chalk from exposures more widely separated than at Grimes Graves. Most are representative of layer 13 or 14 within the zone but those from Ryckholt are from layer 10. The location of exposures and numbers of samples analysed was as follows: St. Pietersberg layer 13 (34 samples), and layer 14 (48), Groeve Noord 13/14 (49), Romontbos 13/14 (9), Vredesburght 13/14 (39) and Ryckholt 10 (18). The analytical techniques used were atomic absorption and colorimetry as described in SIEVEKING et al (1972). The following elements were determined in all samples: Al, Fe, Mg, Ca, K, Na, Li, P.

Statistical analysis

Both sets of log transformed data were analysed by multivariate analysis of variance (MANOVA) and linear discriminant analysis. The Grimes Graves data from the archaeological site, arranged into 5 groups, gave an F ratio on equality of means of  $F = 1.75$  [ $F(0.01) = 1.71$ ]. This is just significant at probability  $p = 0.01$  and gives grounds for suspecting a slight disparity amongst the group means. However the groups as a whole overlap considerably. Comparison of the largest Grimes Graves group, Greenwell's pit (103 samples), with that of the Taplin's quarry data (3 km from the archaeological site) gave an F ratio on equality of means of  $F = 3.0$  which is definitely significant at  $p < 0.01$  ( $F = 2.65$ ). There are thus definite grounds for suspecting changes in trace element distributions over a 3 km scale as well as possible minor changes across the site itself although these latter are probably insufficient to cause significant misclassification of archaeological data. To test this the previous flint mine data for all major British sites was used as training groups and the new Grimes Graves geological data treated as unknowns. Only 3 unknowns were classified to a mine site other than Grimes Graves. It is therefore clear that the original 20 samples used to characterise the Grimes Graves source material are sufficiently representative to correctly classify samples drawn from anywhere within the site. The results from the analysis of the Maastricht area data which are summarised below were rather more definitive.

Manova Tests on Maastricht area samples		
Data	Equality of means	Expected at $p = 0.01$
All Six Groups	$F = 14.5$	$F = 1.6$
Ryckholt Excluded	$F = 9.2$	$F = 1.7$
St. Pietersberg 13 and 14	$F = 6.1$	$F = 2.8$



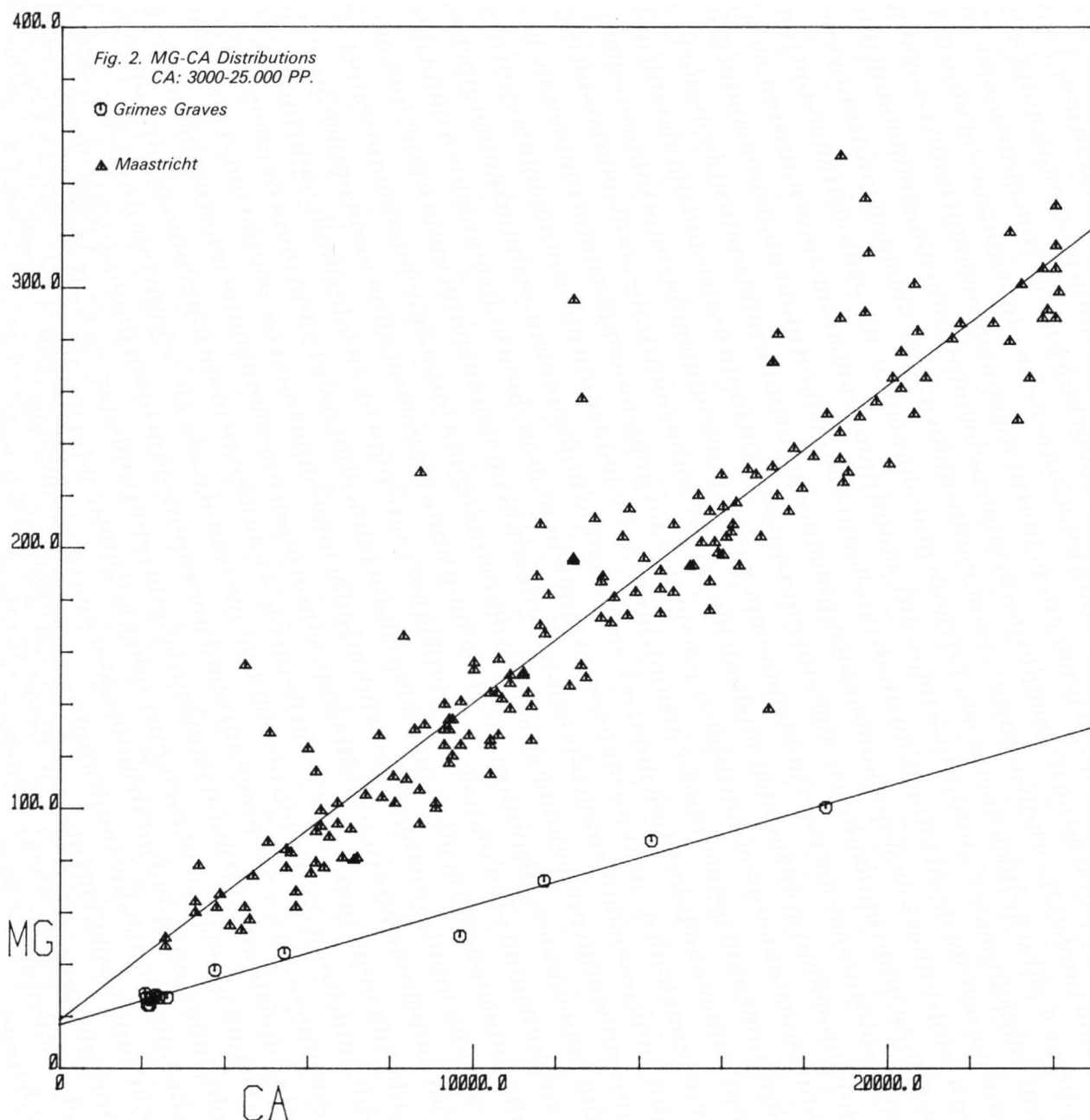
The high F ratio obtained when considering all six groups strongly suggests that they are not drawn from a common population. Examination of the distributions on the first discriminant axes showed that Ryckholt probably has the largest disparity. Exclusion of the Ryckholt data from the next test lowered the F ratio but there is still a significant inequality in the means. Comparison of the samples from the two layers at St. Pietersberg also showed a significant difference in their means. There is therefore little doubt that chemical differences exist between the flint layers sampled at St. Pietersberg and that the flint collected from layer 10 at Ryckholt can be clearly discriminated from the other groups of samples from the Maastricht area.

A linear discriminant analysis was carried out using the St. Pietersberg data as training groups and classifying the remaining samples as unknowns. The St. Pietersberg samples were 80% correctly classified and 30% of the unknowns were classified with St. Pietersberg layer 14 at  $p > 0.5$ . No unknowns were classified to layer 13 with this constraint and no Ryckholt samples were classified to either layer.

#### Trace elements in flint

The 8 elements determined in all samples (i.e. Al, Mg, Fe, K, Na, Li, P, and Ca) represent the majority of the minor components above about 10ppm concentration. A number of features concerning their relative distributions are discussed below:

- 1) **Sodium-Potassium** - The sodium and potassium contents of all samples are similar in magnitude and are very highly correlated. The distribution of the Grimes Graves and Maastricht data (Fig. 1), show very similar behaviour in spite of the sources being so widely separated. The functional relationship between the two variables is expressed by the line (not a regression since there are measurement errors in both variables) with slope 1.03 and intercept at 39ppm sodium. This intercept is significantly different from zero which suggests that there is a reasonably constant residual amount of sodium but that the main bulk of both elements are equally present in some common source within the flint. This could be a clay mineral although clay minerals with equal amounts of sodium and potassium are not common.
- 2) **Calcium-Magnesium** - At high concentrations (Ca > 2000 ppm) these elements are strongly correlated but the functional relationship between them is different for the two sites (Fig. 2). The Maastricht area samples have slope 0.0122 (equivalent to a 1.2% replacement of magnesium for calcium in calcite) and Grimes Graves have a slope of 0.0046 (equivalent to a 0.45% replacement of magnesium for calcium). At lower concentrations of calcium (less than 500 ppm) the majority of points cluster below this linear relationship which suggests that some of the magnesium and calcium is derived from a source other than calcite which is



richer in magnesium. A silicate mineral seems the most likely alternative.

**3) Potassium-Aluminium** - The data for these elements exhibit high correlation when analysed by site groups (Fig. 3). Functional relationships were determined for three groups: The Grimes Graves data suggests a source with a Al/K ratio of about 2.9 (oxide ratio of 4.6) and the Noord and Vredesburg combined data suggest a source with Al/K of about 7.1 (oxide ratio of 11.1). Both of these could be accounted for by a combination of silicate minerals, e.g. feldspars, illite and smectites. Most of the other samples lie close to the intersection of these two relationships except for the bulk of the combined St. Pietersberg data which have an Al/K ratio of only 0.33. Indeed the samples with potassium greater than 200ppm have an almost constant aluminium content of 300ppm suggesting that there is then no formal relationship between them. The reasons for this are not clear, but massive intrusive potassium by sample contamination via ground water of during analysis seems unlikely since the relationship between potassium and sodium exhibited by other samples also holds for these.

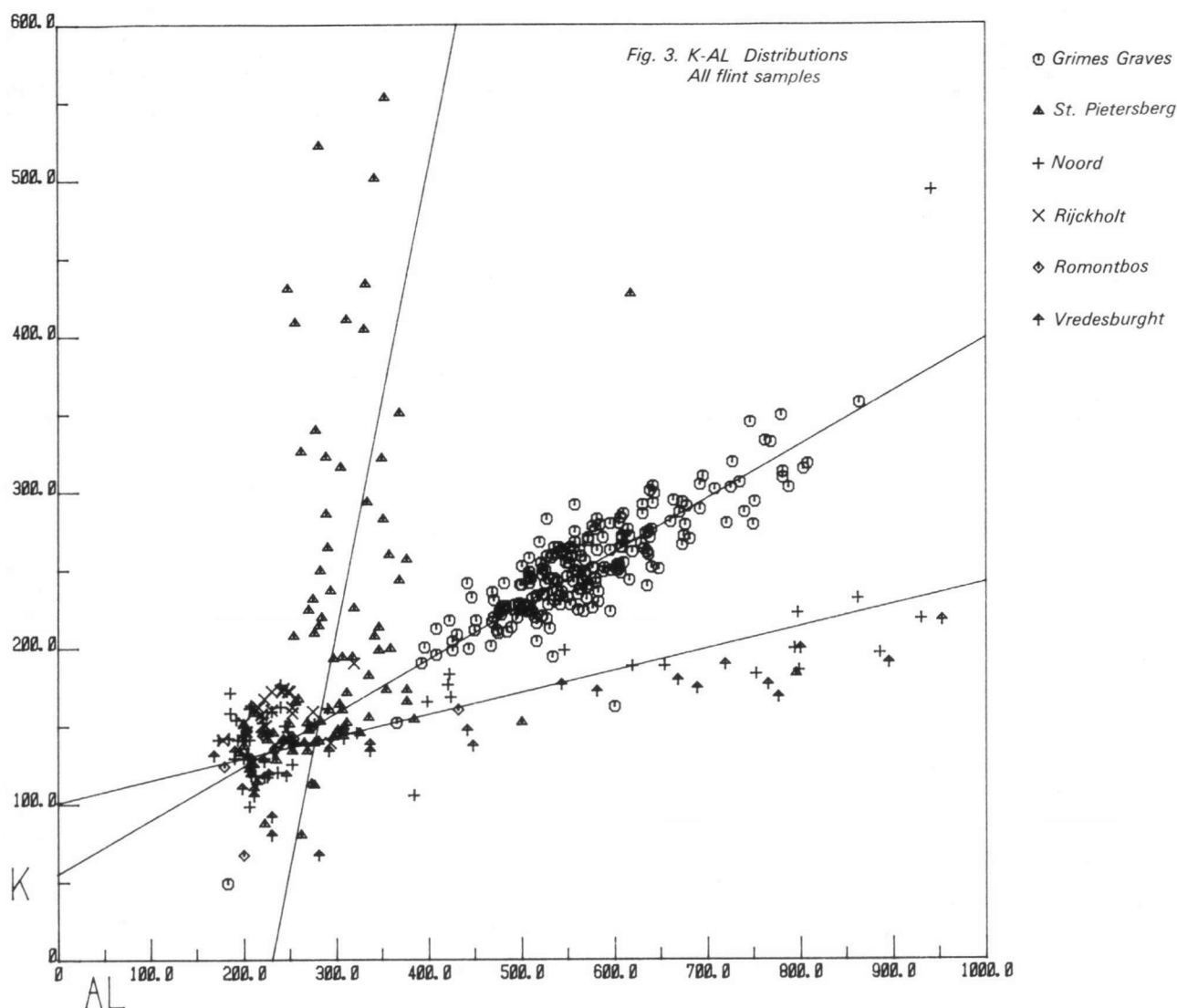
#### 4) Distribution of trace elements in flint

The trace elements determined may reside in any of 4 major phases in the flint:

- In the water held in the micropores between the quartz crystals, possibly the remains of original saline interstitial waters. (FOLK and WEAVER, 1952).
- In the unreplaced relics of calcite
- As discrete non-carbonate, non-silica minerals, such as clay minerals (SIEVEKING et al, 1972)
- Adsorbed onto the surface of the quartz microcrystals (MICHEELSON, 1966).

To obtain some information about how the trace elements are distributed through these phases, 3 samples of crushed flint (<63µm) from Grimes Graves, Noord and St. Pietersberg, respectively, were extracted successively with distilled water, dilute hydrochloric acid and finally dissolved in hydrofluoric and perchloric acids. The first extraction was designed to predominantly sample phase (a), the second, phase (b) and the third phases (c) and (d). Scrupulous precautions were taken to avoid contamination, particularly of sodium. The results are given in the following table. Concentrations are in ppm and since each extract is of equal volume direct comparisons can be made. The results can be summarised as follows:

- The first aqueous extracts contain mainly Na, K, Mg, Ca. The magnesium and calcium are probably derived from dissolved calcite. The Na/K ratio is about 7-10: 1 whereas the flint as a whole contains about equal amounts of these elements. If some pore waters are extracted in this experiment, then this



	Grimes Graves			Noord			St. Pietersberg		
	H <sub>2</sub> O	HC1	REM.	H <sub>2</sub> O	HC1	REM.	H <sub>2</sub> O	HC1	REM.
Al	<0.1	0.6	16.2	<0.1	0.4	6.3	0.1	0.8	8.1
Mg	<0.01	0.05	0.6	0.13	6.5	0.95	0.07	2.5	0.69
K	0.06	0.34	5.9	0.03	0.32	4.0	0.03	0.34	4.3
Na	0.61	0.7	7.3	0.2	0.9	5.7	0.27	0.78	5.2
Li	<0.001	0.006	0.15	<0.001	<0.001	0.11	<0.001	<0.001	0.11
Ca	0.7	5	5.4	4	530	26	4	245	16

strongly suggests that they are richer in sodium which is consistent with them being derived from trapped interstitial water. The evidence provided by the distribution in Fig. 1 suggests, however, that sodium may well reside in more than one of the above phases.

- (b) The treatment with dilute hydrochloric acid, during which effervescence was observed, suggesting breakdown of carbonates, are characterised by the extraction of most of the calcium and magnesium. The ratios of Mg/Ca are similar to those observed in Fig. 2. Further potassium and sodium are also extracted at this stage. This may be due to further fragmentation of sample grains, releasing more pore water from calcite and quartz, or slight breakdown of silicate minerals.
- (c) The final stage of analysis shows that the majority of the aluminium and lithium is unaffected by previous treatments and may therefore be principally derived from phases (c) and (d), i.e. clay minerals or adsorbed ions.

### Conclusions

Minor changes in composition are detectable over the Grimes Graves site but these are insignificant when compared with the inter-site variations. The analytical evidence strongly supports the stratigraphical evidence that the samples collected at Rijckholt are not from the same flint layers exposed at the other sites sampled around Maastricht. Those samples from layer 13/14 of the Lanaye Chalk show a greater similarity to layer 14 at St. Pietersberg than layer 13, suggesting continuation of the former. The percentage so classified is small but this might be expected since the sites are several kilometres apart.

The distribution of trace elements in the samples examined here supports a replacement mechanism for the origin of flint with trapped interstitial saline water, unreplaced calcite and detrital clay minerals being included in the silica matrix.

### REFERENCES

- FOLK & WEAVER, 1952 - 'A study of the Texture and Composition of Chert', *Am. J. Sci.*, 250, 498-510.  
 MICHEELSON, H., 1966 - 'The Structure of the Dark Flint from Stevns, Denmark', *Medd. Fra. Dansk Geol.*, 16, 285-368.  
 SIEVEKING et al., 1972 - 'Prehistoric Flint Mines and their Identification as Sources of Raw material', *Archeometry*, 14, 151-176.

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M.R. Cowell  
 British Museum; London.