Trace element analysis of Belgium flint mine products.

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In order to identify the sources of the raw material of flint artifacts, G. de G. SIEVEKING et al. (1972) proposed and tested a method of trace element analysis on flint. They analysed eight elements: Phosphorus, Aluminium, Magnesium, Iron, Calcium, Potassium, Sodium and Lithium on 179 flint samples from seven flint mine or axe factory sites in England and from three flint mining areas on the Continent.

By discriminant analysis, a technique of multivariate statistical analysis, they were able to differentiate sufficiently flint originating from the ten investigated sites on basis of the results of analysis of the eight trace elements. They expressed the hope that their investigation would lead to further study of these problems, suggesting the rich flint workshops and mines in Northern France and Belgium.

The wish to identify the source of flint found in some recently excavated setlements prompted us to try this method of identification. But soon a more thorough verification of validity and applicability of the method appeared necessary.

Similar methods of preparation, dissolving and analysis of the same eight elements were applied on the flint samples as used by G. de G. SIEVEKING et al.

Patina and cortex are removed from the flint sample and small flakes are knocked off from a flint nodule on some ten different spots or more. These flakes are heated with aqua regia for two minutes and the thoroughly washed with distilled water, dried with filter paper and heated in a covered nickel curcible before quenching in distilled water. The clean, dried and friable flint fragments are then ground in an automatic agate mortar to a fine powder.

A weighed portion of about 0.5 g of this powder is dissolved by evaporating in a mixture of 2 ml distilled water, 2 ml conc. HNO_3, 0.5 ml conc. H_2SO_4 and 20 ml conc. HF on a hot plate. The residue is heated with 2 ml distilled water and 2 ml conc. HCl just to dissolve it and then transfereed and diluted with distilled water to 50 ml in a graduated flask. This homogenized solution is filtered and kept ready for analysis in polyethylene flasks of 100 ml.

Absorption spectrophotometry is used to determine Phosphorus by its blue reduced heteropolymolybdic acid, and also Aluminium by its yellow 8-oxychinolate complex, extracted in chloroform at a pH of 5.5 after reduction of the iron by thioglycolic acid. Iron, Magnesium, Calcium, Sodium and Potassium are determined by atomic absorption spectrophotometry using the appropriate flames and wavelengths. Lithium is determined by flame emission spectrophotometry.

A blank including all the dissolving steps was prepared and the analytical results proved a background value, not negligible in the case of small contents of Sodium, Magnesium and Aluminium in the flint.

To ascertain the reproducibility of the method, analysis was made of 11 separate portions drawn from the same powdered and homogenized sample. The coefficient of variation proved to be less than 5% for the elements Calcium, Sodium, Potassium, Phosphorus and Aluminium. If one deviating result was not ta-

ken into account Magnesium was also in this range. But Iron showed a coefficient of variation of 7.3% and Lithium of 14.3%, the latter due to the very low concentrations near the detection limit.

To have an idea of the homogeneity of a normal flint nodule as taken in the field, samples were taken for analysis from nine different spots of one nodule of 3.4 kg and fifteen of another nodule of 2.8 kg. The coefficients of variation were reasonably low (max. 20%) for both nodules in the case of Sodium, Magnesium, Aluminium and Potassium, but amounted tot 58% for Lithium and 69% for Phosphorus in the first nodule and tot 55% for Iron and 88% for Calcium in the second nodule. In the latter nodule, the six higher Calcium contents (about three times as high as the Calcium contents for the nine other spots) were situated all together in the same part of the nodule giving separate coefficients of variation of 43% for the six higher Calcium contents and only 8% for the nine lower Calcium contents. The higher coefficients of variation for iron proved to be due to one result outside the normal range and the coefficient of variation goes from 55% for fifteen results to 27% for fourteen results if this result was excluded.

Possibly bigger samples could counterbalance these local heterogeneities, but preparation and grinding of more pure flint powder is a time and labour consuming task.

The coefficient of variation of trace element contents in a series of nodules in the same flint layer (over about 50 m, see sample listing further down) were in fact of the same order as in the nodule itself, e.g. from 6% (Potassium) to 84% (Phosphorus) for ten flint nodules in the *Craie d'Obourg* at Harmignies, and from 11% (Potassium and Iron) to 57% (Sodium) for ten flint nodules in the *Craie de Spiennes* at Harmignies.

It was our intention tot make an intensive sampling of the exploited flint layers in the prehistoric flint mines. Unfortunately it soon became clear that in Belgium only a few mine shafts were open where flint could be sampled. In order to document the horizontal and vertical variations of the parametes, we turned to nearby quarry exposures of the flint bearing formations. Finally artifacts from prehistoric sites in the vicinity of the mines were sampled in the asumption that they could have been made on flint of the mined formation.*

1. Samples from quarry exposures.
    1.1. Harmignies, C.B.R., has an exposure with the *Craie de Spiennes*, the *Craie de Nouvelles* (without flint) and at the base the *Craie d'Obourg* (Cp3a). The Obourg chalk provided 23 samples: 10 from layer 1 (Fig. 1), the others from vertical profiles of the different layers at point I and k. The Spiennes chalk provided 25 samples: 10 from layer 2, and at least 2 from each of the other layers, exept layers 4 and 5.
    1.2. Obourg, Ciments d'Obourg, provided 6 samples from two flint layers and 1 isolated sample, all from the *Craie d'Obourg*.
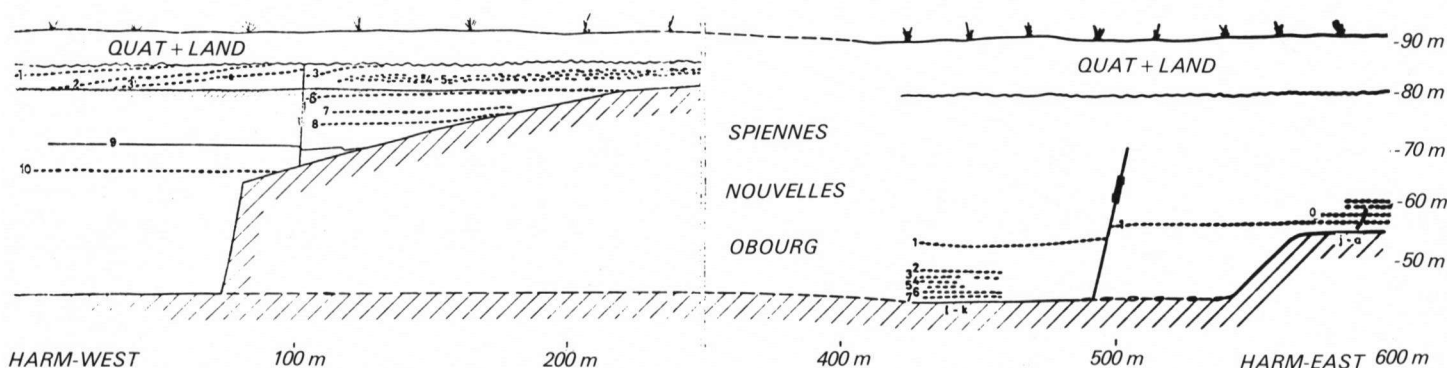   1.3. Maisières, Carrière, provided 5 samples from a flint layer in the *Craie de Maisières* (Tr2b).
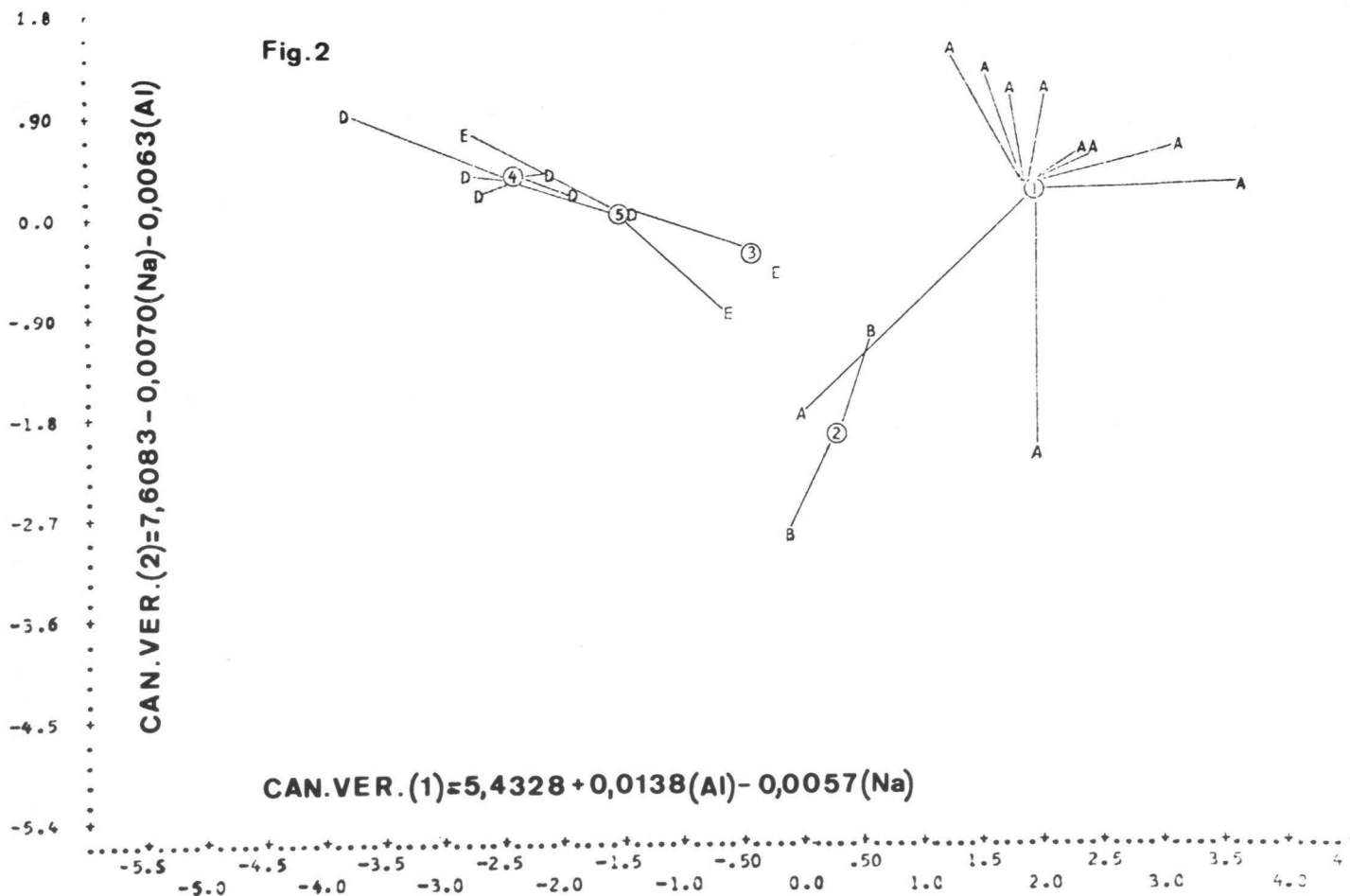2. Samples from flint mines.
    2.1. Spiennes, Camp à Cayaux, mine of the Service National des Fouilles, where the mined flint is situated in the *Craie de Spiennes* (Cp4a), provided 3 samples of the same layer.
    2.2. Spiennes, Petit Spiennes, mine nr. 1 of the Société de

Fig. 1

Fig.2

$$\text{CAN.VER.}(2)=7{,}6083-0{,}0070(\text{Na})-0{,}0063(\text{Al})$$

$$\text{CAN.VER.}(1)=5{,}4328+0{,}0138(\text{Al})-0{,}0057(\text{Na})$$

Fig. 3

$$\text{CAN. VER.} = 5{,}5920-0{,}0243\,(\text{P})$$

Fig. 4

$$\text{CAN.VER.} = 1{,}31770-0{,}00053\,(\text{Ca})$$

recherche préhistorique en Hainaut, where the mined flint is also in the Cp4a, provided 1 sample from a depth of 6,5 m, 3 from 7 m and 3 from 8 m.

2.3. Orp or Jandrain-Jandrenouille, puits Doguet, provided 2 samples from a mine in the Cp3.

2.4. Ryckholt Sint Geertruid, Groot Atelier, where the flint is situated in the *Gulpensch Krijt* (Cp4 or VII^w), provided 4 samples of the mined layer and 5 more of deeper layers which were only mined on a small scale.

3. Samples from prehistoric sites.

3.1. Vlijtingen: 3 flakes from excavations of a Danubian settlement.

3.2. Dommartin: 1 flake from the surface of a Danubian settlement. Avennes: 3 flakes from excavations of a flint mine (Michelsberg ?) in the Cp3.

3.3. Thieusies: 6 flakes from excavations of a Michelsberg settlement.

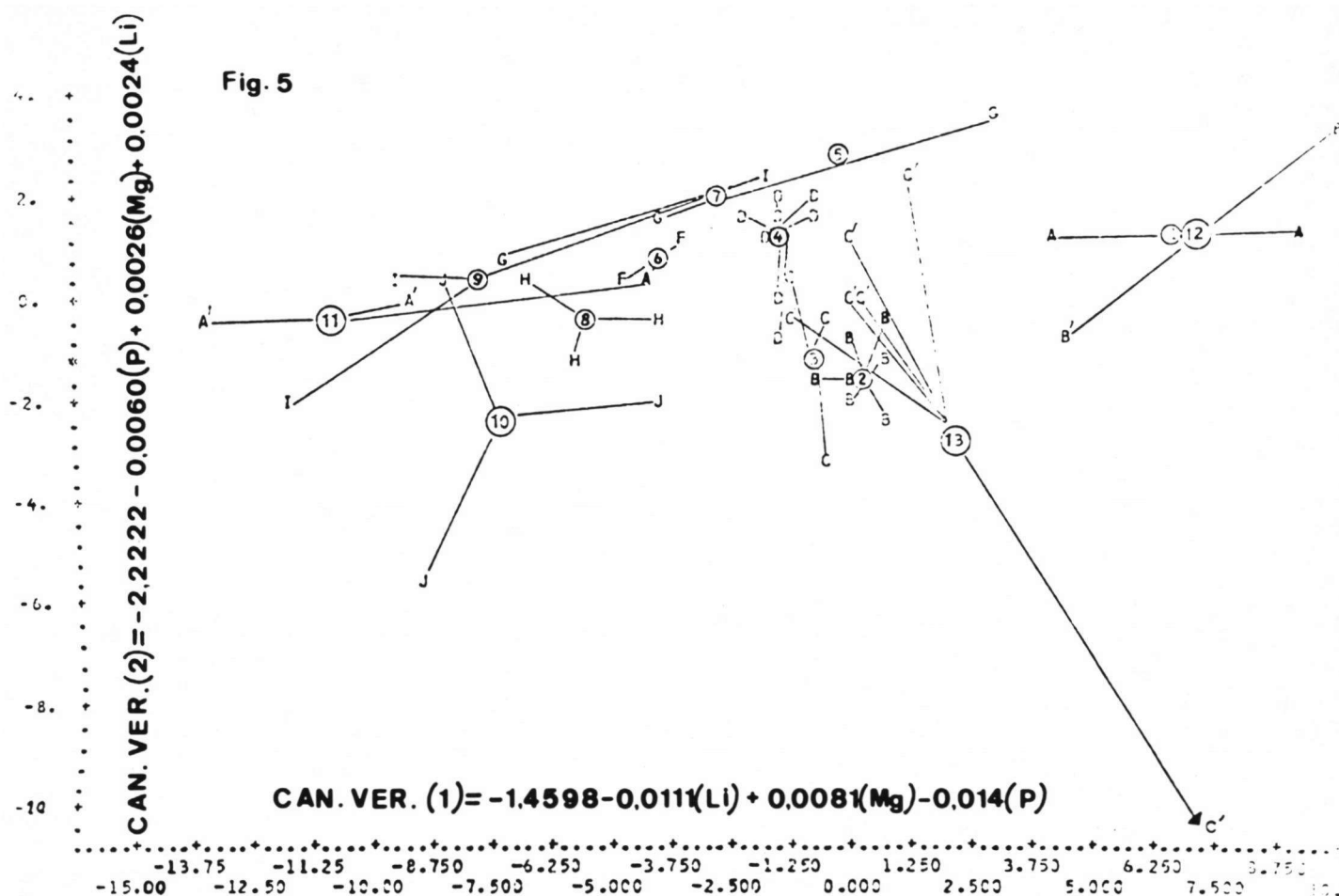Petit Spiennes: 3 flakes from excavations of a Michelsberg settlement.

Neufville: idem.

Spiennes, Camp à Cayaux: 2 flakes from the surface near mine shafts.

Blicqny: 4 flakes from excavations of a Danubian settlement.

Maisières: 3 flakes from excavations of an Upper Perigordian settlement.

In the biomedical computer programs BMDP edited by W.J. DIXON, University of California 1975, we found a multivariate

Fig. 5

$$\text{CAN. VER. (1)} = -1.4598 - 0.0111(\text{Li}) + 0.0081(\text{Mg}) - 0.014(\text{P})$$

Y-axis: CAN. VER. (2) = -2.2222 - 0.0060(P) + 0.0026(Mg) + 0.0024(Li)

statistical analysis method for discriminant analysis. In this method the cases are divided in groups and the program makes a stepwise selection of those variables that maximize group differences, eliminating the variables whose contribution is negligible. A geometrical interpretation of discriminant analysis is given by plotting each case as a point in a histogram with one or more axes with the canonical variables, functions of the selected variables which give the maximum spread of the groups. Also other groups of cases may be entered and plotted in relation to the first defined canonical variables to find out to which group they may belong.

Discriminant analysis allows to distinguish the two upper flint layers 1 and 2 (= A and B) from the three layers underneath, 3, 4 and 5 (= C, D and E) of the *Craie d'Obourg* at Harmignies on the basis of the Aluminium content and the Sodium content, but no good distinction is seen among the separate layers in these two groups (Fig. 2). In the same way the 2nd (B) and the 3rd (C) layer, which are mutually separated if one sample is disregarded are well discriminated from the six other layers (A and D-H) of the *Craie de Spiennes* at Harmignies, using the Phosphorous content as the selected variable (Fig. 3).
The two flint layers and the isolated flint at Obourg are distinguished by their Sodium, Calcium and Lithium contents.
If we try now to discriminate the flint layers in the *Craie d'Obourg* (B) from those in the *Craie de Spiennes* (A) the Calcium content is selected as the only differentiating parameter but nearly half of the samples in each group are overlapping. By adding the samples of the *Craie d'Obourg* at Obourg (C) and of the *Craie de Maisières* (D), the Calcium content continues to be the differentiating parameter, but the samples of the *Craie d'Obourg* at Obourg are separated from the same at Harmignies (B) by those of the *Craie de Spiennes* at Harmignies (A), and the samples of the *Craie de Maisières* (D) overlap the other (Fig. 4).
If we apply discriminant analysis to the samples of the three flint mine areas Spiennes (10 sampes) (B and C), Orp (2 samples) (A) and Ryckholt (9 samples) (D), they are discriminated on the basis of their Phosporus, Magnesium and Lithium contents (Fig. 5). We have applied the same method to the 20 samples of Spiennes

and the 20 samples of Ryckholt, published by G. de G. SIEVEKING et al. and they are distinguished on the basis of the same three elements with in addition Aluminium. But on the other hand there appears also a difference between our samples of Spiennes and those of G. de G. SIEVEKING et al. on the basis of the Sodium and the Lithium contents, and between our samples of Ryckholt and those of G. de G. SIEVEKING et al. on the basis of the Sodium and Iron contents. The Lithium difference is probably due to a decimal error and the Sodium and Iron differences might be explained by a difference in analytical standards as occurs in similar trace analytical work between different laboratories.

Looking at a distinction between the nine groups of flint artifacts, Sodium appears to be the only discriminating element. Only the two samples of Spiennes Camp à Cayaux may well be distinguished from the others and the six samples of Thieusies show also some convergence. The other sample groups have no discriminating elements. We may now make the best discrimination of the nine groups based on the selected variables Magnesium, Lithium ans Phosphorus and allow the samples of the nine groups of artifacts to be plotted in the histogram with the same canonical variables (Fig. 5). We see that five of the six samples of Thieusies (C') are lying near the samples of the flint mines of Petit Spiennes (B) and of Spiennes Camp à Cayaux (C), but the two samples found at the surface at Spiennes camp à Cayaux (B') are near the two mine samples of Orp (A), and all the other artifacts (5-11) are situated at the other side of the samples of the mines.

As is also concluded from the results of other trace element determinations in flint by neutron activation analysis (C.C. BAKELS, 1974, 1978), a difference may be seen in trace element contents, if one considers a limited number of mined layers in different areas, but if one compares different sampling places in the same area, no good distinction can be made from trace element constituents.
In short we arrive at the conclusion with regard to our area that this method does not offer a satisfying answer as to the distinction and identification of flint.

* *The results of trace elements of these 108 samples together with the results to ascertain reproducibility and homogeneity may be obtained on request.*

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