Delft University of Technology

Distinguishing Spiennes and Lanaye Flints Using Portable ED-XRF to Trace Neolithic Exchange Networks in the Rhine-Meuse Delta

Van Den Dikkenberg, Lasse; Braekmans, Dennis

DOI
10.1002/xrs.3483

Publication date
2025

Document Version
Final published version

Published in
X-Ray Spectrometry

Citation (APA)
Van Den Dikkenberg, L., & Braekmans, D. (2025). Distinguishing Spiennes and Lanaye Flints Using Portable ED-XRF to Trace Neolithic Exchange Networks in the Rhine-Meuse Delta. *X-Ray Spectrometry*, *54*(5), 478-487. https://doi.org/10.1002/xrs.3483

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright
Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy
Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

This work is downloaded from Delft University of Technology.
For technical reasons the number of authors shown on this cover page is limited to a maximum of 10.

Check for updates

X-Ray Spectrometry

WILEY

X-RAY SPECTROMETRY

RESEARCH ARTICLE OPEN ACCESS

Distinguishing Spiennes and Lanaye Flints Using Portable ED-XRF to Trace Neolithic Exchange Networks in the Rhine-Meuse Delta

Lasse Van Den Dikkenberg[1] | Dennis Braekmans[1,2,3]

[1]Material Culture Studies, Department of Archaeological Science, Faculty of Archaeology, Leiden University, Leiden, the Netherlands | [2]Section Geology, Earth and Environmental Sciences, KU Leuven, Heverlee, Belgium | [3]Materials Science and Engineering, Faculty of Mechanical Engineering, TU Delft, Delft, the Netherlands

Correspondence: Lasse Van Den Dikkenberg (l.van.den.dikkenberg@arch.leidenuniv.nl)

Received: 19 July 2024 | **Revised:** 17 February 2025 | **Accepted:** 25 February 2025

Funding: This work was supported by an NWO grant for the project Putting Life into Late Neolithic Houses: Investigating domestic craft and subsistence activities through experiments and material analysis (grant number: AIB.19.020).

Keywords: Flint procurement | Neolithic | portable ED-XRF | Rijckholt | Spiennes

ABSTRACT

Flint, or chert, sources in the Rhine-Meuse delta are generally distinguished based on macroscopic characteristics such as fossil inclusions, colour variations, and translucency. Previous studies on chemical characterisations of flint sources proved challenging due to the variation and overlap between different sources. Energy Dispersive X-ray Fluorescence (ED-XRF) analysis, therefore, cannot, in our view, be used as an alternative to these traditional sourcing methods. Nevertheless, in this paper, we demonstrate that X-ray spectrometry can be used as a viable method when used in tandem with traditional methodologies. Macroscopically, Spiennes and Lanaye flints, notably Rijckholt flint, cannot be distinguished based on variations in colour, texture, and microfossil content. In the present study, we used a non-destructive portable ED-XRF to distinguish Spiennes, Rijckholt, and eluvial Lanaye flints. While it proved impossible to distinguish between different Lanaye sources, it is possible to distinguish between Spiennes and Lanaye flints based on the higher phosphorus concentrations in Spiennes flint. The archaeological implications have been studied using material derived from four Neolithic Vlaardingen Culture (3400–2500 BC) sites in the Rhine-Meuse delta. We demonstrated that Spiennes and Lanaye flints were present at all sites. Proximity to either of these sources was not a decisive factor in procurement strategies. Flint was exchanged both via the Meuse (leading to the Lanaye flint sources) and the Scheldt (leading to Spiennes). The four selected Vlaardingen Culture sites are located at the intersection between these exchange routes. This favourable location provided good access to high-quality exotic flint at these sites.

1 | Introduction

This study focuses on the flint from the Vlaardingen Culture (3400–2500 BC), a Neolithic group located in the Rhine-Meuse delta of the western Netherlands. Flint in this period is known to come from a wide range of sources such as Cap Blanc Nez in western France, Rijckholt in the Netherlands, Hesbaye and Spiennes in Belgium, and Lousberg near Aachen in Germany ([1–3], 82; [3], 170; [4]). Often, flint from these sources can be macroscopically attributed to these different sources based on variations in the cortex, translucency, texture, inclusions, microfossil content, and so forth. ([5], 112–118). But a major unresolved issue is the fact that Spiennes and Lanaye flints are difficult to distinguish ([5], 125). It is known that both mining areas were active in this period ([6, 7], 244). On several Vlaardingen Culture sites, flint has been identified as Spiennes

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2025 The Author(s). *X-Ray Spectrometry* published by John Wiley & Sons Ltd.

https://doi.org/10.1002/xrs.3483

or Rijckholt flint. For none of the sites where Spiennes flint was found could it be demonstrated with certainty that this was indeed Spiennes flint and not Rijckholt flint ([1], 344). The identification of flints as Rijckholt flint is often uncertain. Usually, the attributions are kept broad, identifying the flint, for example, as “Lanaye” flint or “Spiennes/Rijckholt” flint ([1], 344; [8, 9], 81; [10], 148; [4], 170). The present study aims to compare and attribute flint artefacts that were macroscopically identified as Spiennes or Lanaye flint to one of these sources using portable ED-XRF analysis. Lanaye flints in this study will encompass both Rijckholt and Lanaye flint from eluvial deposits. It was not expected that a distinction between Rijckholt and other Lanaye flints was possible as the flints come from the same geological formations ([11], 190). Nevertheless, for the reconstruction of past exchange networks, it is important to be able to distinguish between Spiennes and Lanaye flint. The flint mines from Spiennes and Rijckholt are located 150 km apart. Furthermore, from the western Netherlands, these areas are reached through different routes. The flint mines from Spiennes are reached via the Scheldt, while the mines at Rijckholt, as well as the other eluvial deposits of Lanaye flint, are reached via the Meuse (see Figure 1).

In discussing the differences between the Vlaardingen Culture and the Stein group (the latter being located in the Limburg area, who are thought to be responsible for the exploitation of the flint mines in Rijckholt) Louwe Kooijmans and Verhart pointed out that flint from the Limburg area is scarce on Vlaardingen Culture sites. They consider the scarcity of this flint, mostly Rijckholt, Valkenburg, and Lousberg flint, to be a key characteristic of the Vlaardingen Culture. It supposedly distinguishes Vlaardingen Culture sites from Stein sites, where these flint types commonly occur ([13], 60–62; [14], 220–221). While for Lousberg and Valkenburg flint the scarcity on Vlaardingen Culture sites indeed seems obvious, this is not clear for Rijckholt flint due to the similarities of this type with Spiennes flint. If we are able to chemically distinguish between Spiennes and Rijckholt flint, we will be able to better assess the supposed scarcity of Rijckholt flint on Vlaardingen Culture sites, which would be a key outcome of this study.

On multiple occasions, optical differentiation cannot, or at least conclusively distinguish between different types. Therefore, this study wants to (1) assess how chemical analysis can be used to distinguish flint types, (2) identify the presence of different flint sources in the Vlaardingen Culture exchange systems, and (3) in doing so, assess the supposed scarcity of Rijckholt flint on Vlaardingen Culture sites. Previous studies have demonstrated the difficulties surrounding the chemical identification of flint sources due to their relative homogeneity. It is noted that different sources can have nearly identical chemical signatures ([15, 16], 103). It therefore seems less valid to use chemical analysis as a general and robust alternative for optical identifications ([17], 87) although other studies [18] illustrated how chemical analysis could be used in tandem with, instead of as an alternative to, optical identifications of flint. This study therefore explores the conditions in which a non-destructive portable ED-XRF approach can contribute to flint provenance studies in the Rhine-Meuse basin and neighbouring regions. The merit of portable ED-XRF lies not only in the possibility of analysing

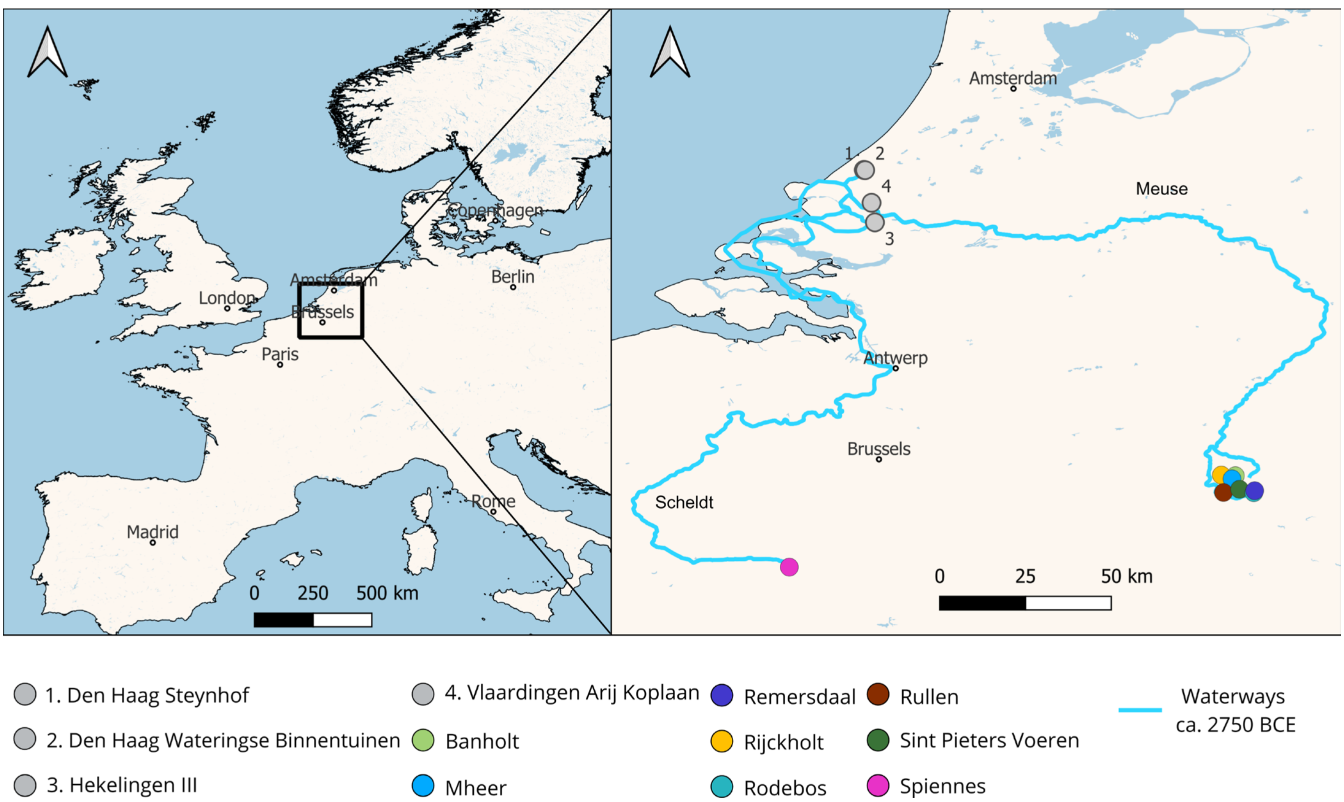

FIGURE 1 | Flint sources and archaeological sites mentioned in this study. Waterways between sources and sites for the Netherlands are reconstructed based on the palaeographic map of the Netherlands ca. 2750 BC (waterways based on [12], basemap: EuroGeographics 2024, map made in QGIS). [Colour figure can be viewed at wileyonlinelibrary.com]

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

larger assemblages but also in its non-destructive character for heritage materials.

1.1 | Lanaye and Spiennes Flint

Spiennes and Lanaye flint are notoriously difficult to distinguish macroscopically, and it has rightfully been suggested by De Grooth that it is hazardous to distinguish archaeological flints based on optical characteristics [6]. Although some eluvial Lanaye flints such as Rullen flint can often be identified based on specific post-genetic alterations in the flint ([6], 123) these flints originate from different geological layers: the Lanaye member of the Gulpen formation (Maastrichtian) for Rijckholt and other Lanaye flints, and the Spiennes Chalk formation of the Campanian for Spiennes flint ([19], 371; [20], 128). Based on the geological and archaeological reference collection at Leiden University, we also observed that generally these flints share many optical characteristics. As a group, these flints can be characterised as very dark grey to light grey coloured flint. The colour often varies within nodules, with occasionally concentric laminations and darker, more fine-grained zones under the cortex. All flints are characterised by high frequencies of similar (small) light inclusions (see Figures S1 and S2). De Grooth observed that translucency is somewhat higher in Spiennes flint than in Lanaye flint. Furthermore, slight differences in colour can be observed, and it seems that Spiennes flints lacked several secondary characteristics such as the 'bleached aspect' which is observed as a dusty surface and brownish wisps that can be observed on eluvial Lanaye flints. Nevertheless, these differences are differences of degree, not of kind ([6], 123–5). The 'dusty' aspect mentioned by De Grooth in relation to eluvial Lanaye flints also seems to be present in the Spiennes flint from the reference collection ([6], 117; also see Figure S2H).

1.2 | Compositional Studies of Flint

Several studies have analysed the composition of flint from Spiennes and Rijckholt [11, 17–19, 21–25]. Unfortunately, it needs to be noted that not all publications include the primary elemental data (e.g., [11, 17]) Therefore, comparing the results or compositional patterns from these publications cannot be used to directly or relatively distinguish between these types ([21], 42; [11]). Unfortunately, the study in which the largest sample of Spiennes and Rijckholt flint was analysed—Sieveking et al.—did not attempt to make a distinction between these groups but analysed these samples for demonstration purposes only [25]. The interpretations in the publication focused rather on the distinction of flint types from Britain ([25], 154). The most successful attempt yet to chemically distinguish between Rijckholt and Spiennes flint was presented in a thesis by Geerts [18]. This is the only retrievable study that utilised trace elements which could be used to distinguish between Spiennes and Rijckholt flint. Geerts noted that phosphorus (P) and strontium (Sr) were the main elements that could potentially be used to distinguish between these types of flint ([18], 43). Unfortunately, this study also included patinated flint, while it did not include eluvial Lanaye flint. P and Sr are elements that are not systematically reported in other chemical studies. Geerts also included some flint samples from the ENCI quarry in Maastricht and from an unknown quarry in Eben-Emael ([18], 29–30). The publication of McDonnell et al. included Rijckholt flint as well as other Lanaye flints from other deposits in Dutch Limburg and northern Belgium [19], although this study did not include flint from Spiennes.

Based on the publication of Sieveking et al., it can be concluded that trace elements Al, K, Na, Li, and Ca in Spiennes and Rijckholt flints display consistent values ([25], 169–170). The average values for Fe, Mg, and P may vary greatly depending on the flint source (see Table 1). The study by Geerts similarly reported that P values in Spiennes flint can be significantly higher than those in Rijckholt flint. In this publication, Mg was not included in the results. It has to be noted that the Fe values in this publication were significantly higher than those reported by Sieveking et al. and those reported by McDonnell et al. [19, 25]. In the study by Geerts, patinated pieces were also included, and it was suggested that the high Fe values can likely be attributed to patina ([18], 42). The notion that patinated pieces display higher Fe values is also confirmed by other studies ([16], 106). Nevertheless, it was demonstrated that P values were not significantly affected by patina ([18], 42). The effects of patination on Mg values are not clear.

Based on reported flint compositional data from McDonnell et al. [19], Geerts [18], and Sieveking et al. [25], it can be observed that Spiennes and Rijckholt flint form distinct groups; notably, the P values seem to be suitable for distinguishing between these flint types. In addition to Spiennes, Rijckholt, Banholt, Mheer, Rullen, and St. Pieters Voeren, these also include flint from Maastricht found in the ENCI quarry and one sample from an unknown quarry in Eben-Emael in Belgium ([18], 13). Because of the extreme variation in iron (Fe) values (in Spiennes occasionally > 40.000 ppm), caused most likely by patination, it seems that Fe values cannot be used to distinguish between Rijckholt and Spiennes flint.

Phosphorus (P) seems to be more suited for discriminating between these flint types. According to Geerts, strontium can also be successfully used as a discriminator with lower Sr values in Rijckholt than Spiennes ([18], 42–3). Unfortunately, the other

TABLE 1 | Average Fe, Mg, and *p* values (ppm) and standard deviations (st.dev.) for Spiennes and Rijckholt flint based on the twenty samples reported by Sieveking et al. [25].

	Fe	Fe	Mg	Mg	P	P
	ppm average	st.dev.	ppm average	st.dev.	ppm average	st.dev.
Rijckholt	205	91.9	122	87.6	210	82.3
Spiennes	104	57.0	50	22.5	590	240.2

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

publications do not include published strontium data to validate this observation. Nevertheless, the publication also includes Lanaye flint from the ENCI quarry and from Eben-Emaul. Here, the strontium values are comparable to those of Spiennes flint, suggesting it thus seems that strontium values are less reliable for distinguishing Lanaye flint from Spiennes flint ([18], 56–7).

2 | Materials and Methodology

In this paper, a chemical characterisation approach has been chosen [26], focusing on a variety of flint (geological) reference materials and archaeological objects. Chemical sourcing of lithics can take place using a wide range of techniques such as Inductively Coupled Plasma Emission Spectroscopy (ICP-OES), Atomic Emission Spectroscopy (AES), X-Ray Spectrometry (XRF), Electron Microprobe Analysis (EMPA), Neutron Activation Analysis (NAA), and Inductively-coupled Plasma Mass Spectrometry (ICP-MS) analysis [27–29]. NAA was previously carried out by Aspinal and Feather, and by De Bruin et al., on Rijckholt and Spiennes flint, as well as on several other flint types ([21, 23], 55–56). The method can be non-destructive, but as it is expensive and requires access to a nuclear reactor, it is not suitable for studying larger assemblages [28]. Other methods such as solution ICP-MS and AES provide high-resolution data, but here destructive sampling is required [25, 27, 29]. Recent developments in analytical equipment have seen the successful application of LA-ICP-MS, requiring a micro-, virtually non-destructive, approach for sourcing purposes [26, 30]. For our archaeological samples, destructive analysis could not be performed because we intended to sample all archaeological artefacts within the selected assemblages, which belonged to the Rijckholt/Lanaye/Spiennes group. The most cost-effective method for analysing larger sample groups—thus gaining a critical mass of data—is ED-XRF analysis, which has been successfully applied earlier [15, 16, 31, 32]. Because of the higher precision and accuracy provided by ICP-MS, we did use the method as quality control for a selection of two reference samples.

Following the methodology proposed by Bradley et al. [27], we used a discriminant analysis [33] to validate the statistical significance of compositional variations in the reference samples. This discriminant analysis was conducted in the Past 4 software [34]. It is visualised in a canonical score plot, and the statistical variation was tested in the confusion matrix (Table 4). In line with previous studies (e.g., [24]) we employed bivariate scatterplots to plot and provide a clear visualisation regarding the composition of our archaeological data along with our reference samples. A specific focus was laid on the elements that carry the most significance for characterisation and provenance.

2.1 | Geological Reference Material

To validate and expand the compositional patterns observed in literature, a total of eighty samples are compositionally analysed. To document and evaluate variability between sources, we measured ten geological samples from different nodules of Spiennes flint and ten geological samples of Rijckholt flint from the *Lithoteque* in the Material Culture Studies laboratory of the Faculty of Archaeology at Leiden University (also see Figures S1 and S2). In addition, the dataset includes sixty samples from six eluvial deposits of Lanaye flint (ten samples each) as well. This concerns flint from Rullen (BE), Banholt (NL), Sint Pieters Voeren (BE), Mheer (NL), Remersdaal (BE) and Rodebos (BE). These are the major eluvial Lanaye deposits that were exploited during the Neolithic ([6], 112). It is not known for all of these deposits whether they were exploited during the period of study (3400–2500 BC). It is known that the flint deposits of Banholt, Rijckholt, Rullen, and Spiennes were certainly exploited at this time ([35], 135; [7, 36], 85; [37]). For the other deposits, systematic excavations were not carried out, and the exact dates for the exploitations are unknown [38].

2.2 | Archaeological Samples

In addition to the geological reference material, archaeological flint materials ($n = 108$) are also selected from four Vlaardingen Culture sites as a case study for evaluation and validation (also see Figure S3). Den Haag Steynhof and Den Haag Wateringse Binnentuinen are the two most recent large scale excavations of Vlaardingen Culture sites in the western Netherlands [39, 40]. Vlaardingen Arij Koplaan is the type site for the Vlaardingen Culture and the largest levee site in the Western Netherlands [41]. Hekelingen III is the second largest levee site in the western Netherlands, and it is regarded as one of the key sites for this period [42–44].

From Vlaardingen Arij Koplaan, the raw materials are derived from three trenches: trench 11, trench 15, and trench 17, which were studied and macroscopically attributed to sources. For trench 11, only the tools were studied during previous research by Van Gijn ($n = 270$), as due to time constraints, it was not possible to study the entire assemblage ($n = 2259$) from this trench [45, 46]. A large group consisted of flint, which was classified as "Spiennes/Rijckholt flint" (see Table 2). The flint in this group varied from very dark grey to light grey or brownish flint (see Figure S4b). The flint is mottled, fine grained, with high frequencies of sponge needle fossils. Furthermore, darker and larger light inclusions (often coarser grained than the texture of the flint) also occur.

The group was identified as Spiennes/Rijckholt flint based on the descriptions in the literature and based on a visual comparison with the reference collection at Leiden University (Grooth 2013, 123–125). For Hekelingen III, the raw materials were studied from the selection that was previously studied by Van Gijn [43].

For the sites Den Haag Steynhof ($n = 2335$) and Den Haag Wateringse Binnentuinen ($n = 3384$) all flint that was macroscopically identified as Lanaye, Rijckholt, or Spiennes flint was initially selected (for Den Haag Steynhof $n = 26$, for Den Haag Wateringse Binnetuinen $n = 5$), as it was noted in the databases that the attributions were tentative. The identifications for these sites were made by Houkes [4, 10]. In line with the study by Hughes et al. [15] we decided to exclude patinated (and possibly patinated) flint, as patination can affect the chemical composition of flint artefacts. It is unknown whether burning affects the chemical composition of lithic artefacts. Therefore, we decided

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

TABLE 2 | Flint types in Hekelingen III and Vlaardingen Arij Koplaan.

	Terrace flint	Meuse-egg	Cap Blanc Nez and French indet.	Obourg/zeven wegen	Hesbaye	Lousberg	Spiennes/Lanaye	Indet/other
Vlaardingen WP11	0	0	9	0	65	0	29	167
Vlaardingen WP15	11	4	19	0	103	0	50	261
Vlaardingen WP17	4	3	4	1	23	0	10	63
Hekelingen III	0	0	33	0	94	1	46	168

TABLE 3 | Archaeological samples analysed per site.

Archaeological site	Samples analysed
Den Haag Wateringse Binnentuinen	3
Den Haag Steynhof	10
Hekelingen III	26
Vlaardingen Arij Koplaan trench 11	19
Vlaardingen Arij Koplaan trench 15	42
Vlaardingen Arij Koplaan trench 17	8
Total	**108**

to also exclude all burned (and possibly burned) archaeological artefacts from the study (see Table S1 for the data on all archaeological samples).

Furthermore, a few samples were excluded because the irregular or small shape of the artefacts did not allow for proper scanning, as an ~8 mm diameter flat surface to measure the samples is essential for replicable results. In Table 3 the sample assemblage is listed for each of the four sites.

The reliability of portable Energy Dispersive X-ray fluorescence analysis for distinguishing Spiennes and Lanaye flint, including also archaeological samples, will thus be explored. Our data thus includes four groups: reference material from Spiennes, reference material from Rijckholt, reference material from eluvial Lanaye sources, and lastly, archaeological artefacts of an unknown origin. The latter will be selected from the group that was macroscopically identified as Spiennes/Rijckholt flint.

2.3 | Portable Energy Dispersive X-Ray Fluorescence Analysis

Non-destructive portable ED-XRF analysis is employed to assess the variability and provenance of these flint artifacts. Analysis was conducted using a Bruker Tracer 5g handheld unit (resolution of < 140 eV @ 250,000 cps at Mn Kα) housed at the Laboratory for Material Culture Studies at the Faculty of Archaeology (Leiden University). The ED-XRF unit is equipped with a large area silicon drift detector (SDD) utilising a 1 μm graphene detector window. Measurements were run in air using a ~8 mm beam collimator for 30 s at 50 kv, 17.7 μA and with a 25 μm Ti, 300 μm Al filter in place, followed by a measurement of the exact same location under 15 kV and 22.2 μA conditions for 60 s with no filter in place to optimise for lighter element detection.

Main elements of focus for flints are Al, Si, P, S, K, Ca, Ti, Fe, Cu, Rb, Sr, Y, Zr, and Nb. For all samples, at least three measurements were taken in three different locations. The locations were randomly selected, focusing on the main matrix of the flint, avoiding major inclusions and cortex. The samples were scanned without prior sample preparation.

Net peak areas were calculated from these spectra using proprietary Bruker ARTAX software and a Bayesian deconvolution approach to obtain a semi-quantitative dataset. Data was normalised to the rhodium peak to correct for eventual variation (Table S1). In order to allow relative comparisons to other datasets for the relevant elements, these peak areas were quantified as well using a Bruker factory calibration for (sedimentary) rock materials. Ten geological reference samples of both Rijckholt and Spiennes (30 g pulverised for homogenisation) were additionally analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [47], using a lithium metaborate/tetraborate fusion approach for whole rock chemistry, as a control in addition to certified reference materials GSP-1 and NIST-2710a for both accuracy and precision evaluation of the portable ED-XRF (Table S2).

3 | Results and Discussion

From the geological reference collection of Leiden University, ten flint samples were compositionally measured per locality of Banholt (NL), Mheer (NL), Remersdaal (BE), Rijckholt (NL), Rodebos (BE), Rullen (BE), Sint Pieters Voeren (BE), and Spiennes (BE).

In the literature, it was suggested that Fe, Mg, P, and Sr could potentially be used to discriminate between these different types ([18, 19], 380; [25], 169–170). Of these, Fe is deemed unreliable for archaeological samples, and Mg yielded low values in the

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

ICP-MS analyses, often below the detection level of the portable ED-XRF (see Supporting Information). Our reference samples did show a clear difference in P and Sr (cf. Figure 2).

The phosphorus values presented here were significantly higher in Spiennes flint than in any of the Lanaye flints, supporting previously made observations and suggestions [18, 25]. Phosphorus thus seems to be a robust indicator for distinguishing Spiennes and multiple Lanaye flints (see Figure 2a). To test this specific visual indicator, a Mann–Whitney U significance test for non-parametric data was carried out specifically between the sites of Banholt and Spiennes, and between Rijckholt and Spiennes for the elements Sr and P. For P a significant difference was established ($p < 0.05$, $p = 0.00018$); for Sr there was no difference ($p > 0.05$, $p = 0.52$). Between Rijckholt and Spiennes both P and Sr are significantly different ($p < 0.05$).

In addition to phosphorus, Geerts also noted that strontium was a key factor for distinguishing Spiennes and Rijckholt flint ([18], 43). In our data, strontium intensities were generally higher in Spiennes flint than in Rijckholt flint (see Figure 2b). Banholt can potentially also be distinguished as a separate group, based on the relatively high strontium values in this group. It thus seems that a combination of phosphorus and by

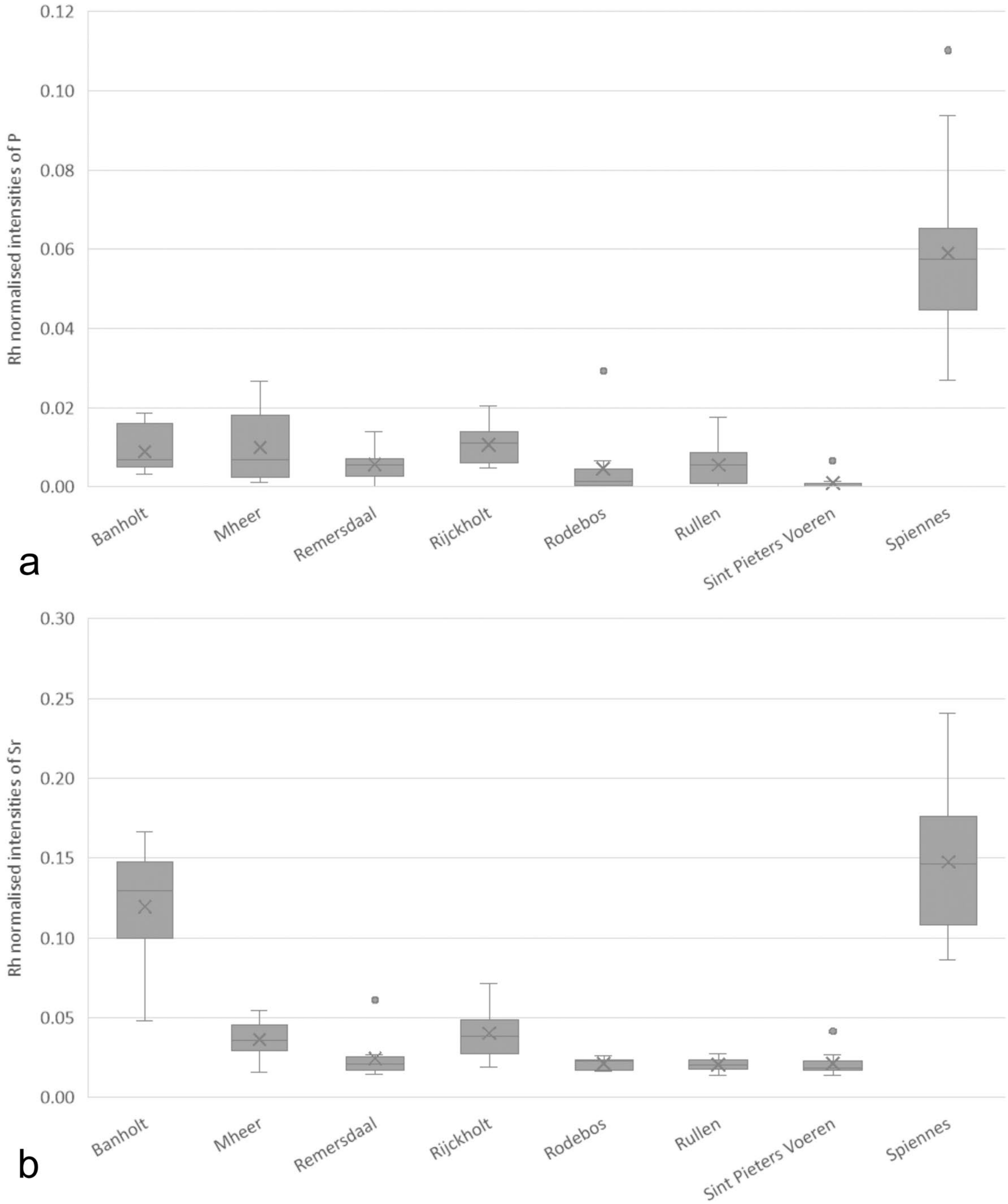

FIGURE 2 | Boxplots with average Rh normalised intensities for different flints from the reference collection; a = P intensities; b = Sr intensities ($n = 10$ samples per site).

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

extension strontium values can be used to distinguish Spiennes and Lanaye flints.

A discriminant analysis was applied to test group attributions based on the observed differences between sources. In this analysis, all significant elements are included. It can be observed that Spiennes flint and, to a lesser extent, Banholt flint can successfully be attributed to distinct groups. To a lesser extent, Rijckholt flint also had a diverting chemical signature. The flints of Mheer, Remersdaal, Rodebos, Rullen, and Sint Pieters Voeren overlapped, rendering a distinction based on the chemical composition of these flints impossible (see Figure 3 and Table 4, and Table S3).

To evaluate the discriminant analysis, a confusion matrix was constructed on the basis of this data which indicates that Spiennes flint within the reference sample is consistently classified correctly (see Table 4). Precision in the predicted group memberships is lower among the different Lanaye-type flints. This confirms the earlier observations by De Bruin et al. that these different Lanaye flints, due to their similar geological origin, have similar chemical signatures ([23], 190). The analysis confirmed that P and Sr values were the main indicators for distinguishing Spiennes and Lanaye flint.

3.1 | Archaeological Implications

The possibility to have an integrated, non-destructive, and fast approach at identifying the variability in flint does not only facilitate source attribution under certain conditions, but also

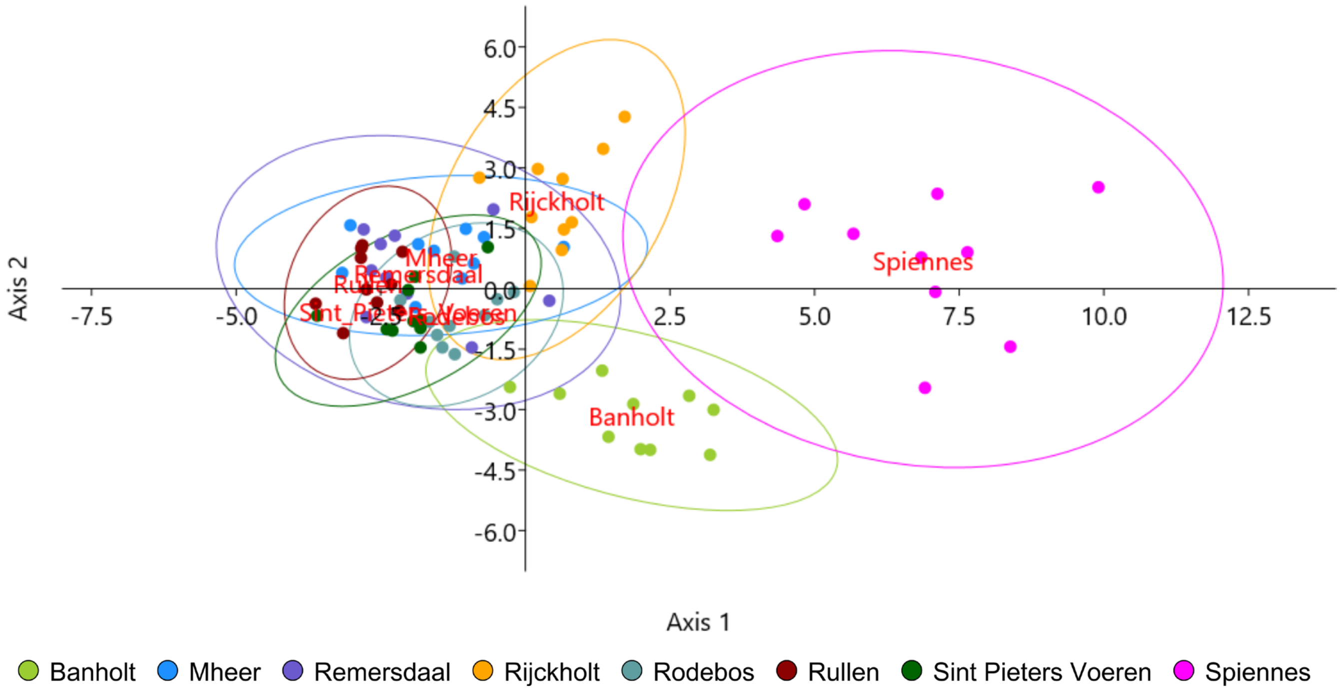

FIGURE 3 | Canonical score plot based on discriminant analysis of the reference sample (average per sample of the Rh normalised intensities for the elements Al, Si, P, S, K, Ca, Ti, Fe, Cu, Rb, Sr, Y, Zr, Nb) indicating the different groups with 95% confidence ellipses. [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4 | Confusion matrix based on the discriminant analysis of the reference sample. Predicted group membership %.

	Banholt	Mheer	Remersdaal	Rijckholt	Rode Bos	Rullen	Sint Pieters Voeren	Spiennes
Baholt	80	0	0	0	20	0	0	0
Mheer	0	70	10	0	0	10	10	0
Remersdaal	0	10	50	10	20	0	10	0
Rijckholt	0	10	10	80	0	0	0	0
Rode Bos	0	0	0	0	80	10	10	0
Rullen	0	10	0	0	10	60	20	0
Sint Pieters Voeren	0	10	0	0	10	10	70	0
Spiennes	0	0	0	0	0	0	0	100

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

generates information on the selection and use of these materials for the archaeological contexts under study.

It is clear from the compositional data that the only relevant markers for source attribution are P and, to a lesser extent, Sr. With a framework established, the implications for studying these Neolithic sites need to be elucidated. The average P and Sr values of the different selected archaeological samples were plotted in the scatterplot in Figure 4, as these elements are—on the basis of the reference dataset—hold significant potential for potential provenance determinations. Based on these geological samples, we can conclude that high phosphorus values of > 1000 ppm are characteristic of Spiennes flint, while low phosphorus values of < 500 ppm only occur in Rijckholt and other Lanaye flints. Elevated strontium values are indicative of Spiennes or Banholt flint, but variability and overlap still exist here.

It could be concluded that most archaeological samples could be grouped with either the Lanaye group or the Spiennes group. It is clear that for all archaeological sites samples fell within the Lanaye group, as well as the Spiennes group. It seems that the Lanaye group is generally dominant, but the groups are clearly not mutually exclusive. Furthermore, several samples, notably attested at the site of Vlaardingen Arij Koplaan, have elevated Sr values and low P values. It seems likely that these samples should actually be classified as Banholt flint.

Occasionally, when a distinction cannot be made macroscopically, an attribution is assumed based on proximity to either the mines in Rijckholt or Spiennes ([48], 82). It seems that this is incorrect, as proximity was not a decisive factor when it came to flint procurement. Both flint types can be present in one assemblage. The probable attribution of some of the samples to the deposits in Banholt indicates that this source remained in use until the Middle- or Late Neolithic.

The common occurrence of Rijckholt/Lanaye flint, in addition to Spiennes flint, on these sites challenges the notion previously held that flint from the Limburg area is virtually absent in the western Netherlands during the Vlaardingen Culture period. While the notion, voiced by Louwe Kooijmans and Verhart, that Lousberg flint (from the mines near Aachen) is largely absent in the western Netherlands holds true, this does not apply to the wider Limburg area ([13], 60–62; [14], 220–221). Exchange networks were not only directed towards the south, following the Scheldt river, but also to the east, following the Meuse towards the Rijckholt area.

4 | Conclusion

In this study, we demonstrated that portable ED-XRF analysis can be successfully applied in provenance studies of flint artefacts in certain instances. However, chemical compositions cannot be used as an alternative for optical identifications, as there is overlap between certain groups and flint types. Nevertheless, detailed questions, which cannot be solved macroscopically, can be solved by including this type of compositional ED-XRF analysis. In this case study, we demonstrated that Spiennes and Lanaye flints differ significantly in their chemical compositions and thus can be discriminated systematically from each other. It could be

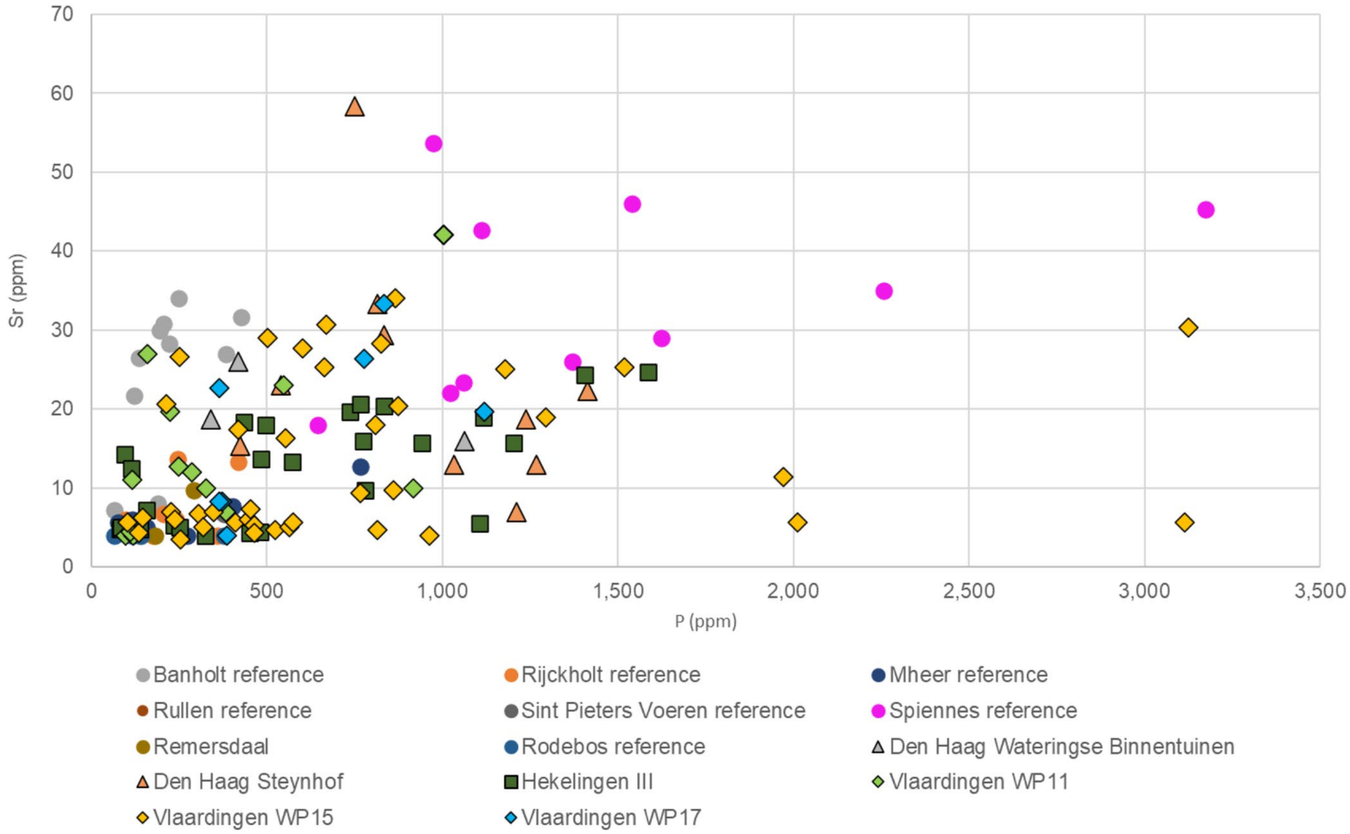

FIGURE 4 | Scatterplot with P and Sr values (ppm) of all reference and archaeological samples. [Colour figure can be viewed at wileyonlinelibrary.com]

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

demonstrated that on all four archaeological sites, both Spiennes and Lanaye flints were present. The analysis suggests that Banholt flint was also imported to this region in this period. The study indicated that Spiennes and Lanaye flints are not necessarily mutually exclusive. Contrary to what was hitherto assumed, Rijckholt/Lanaye flints were common on Vlaardingen Culture sites. Furthermore, proximity to either Spiennes or the Lanaye deposits in Limburg cannot be used as an argument to attribute these flints to either of these sources. The archaeological sites were all located closer to the Lanaye flint sources in Limburg than to the flint mines in Spiennes. If we assume water-based transport, the distance from Vlaardingen to Rijckholt is 282 km, while the distance to Spiennes is 369 km. Based on proximity to the mines, these samples would thus be misinterpreted as Lanaye flints. It is clear that the mining products of both the flint mines in Spiennes and those in Rijckholt reached these Vlaardingen Culture sites. Both the Meuse and the Scheldt were instrumental in the exchange trajectories of flint between these mining centres and the Vlaardingen Culture communities in the Rhine-Meuse delta. These networks were complementary, indicating that stable exchange networks were in place throughout the Vlaardingen Culture period. Sites such as Vlaardingen, Arij Koplaan, and Hekelingen III were conveniently located at the crossroads between these two exchange routes. Perhaps the high frequencies of exotic flint in these sites can be explained by their location at this intersection between these major exchange routes Table 3.

Methodologically, this study highlights the potential and restrictions of the use of portable ED-XRF as a suitable aid in provenance studies of flint. Due to the portable nature, the technique also allows for quick scans during archaeological fieldwork. Furthermore, flint mines in Europe usually consist of protected heritage sites; Spiennes is a UNESCO World Heritage site, and the mines in Rijckholt are a national archaeological monument. With pXRF, geological samples can now be analysed in situ using non-destructive methods.

Acknowledgements

We want to thank Annelou van Gijn, PI of the Putting Life into Late Neolithic Houses project, for her support. We would like to thank Rob Houkes and Annemieke Verbaas for their help during the macroscopic analysis and Eric Mulder for providing technical support. We would also like to thank the depot and curatorial staff of the Rijksmuseum van Oudheden and the municipal depots of Vlaardingen and The Hague for providing access to the archaeological materials. We would also like to thank the anonymous referees for their comments and improvements to the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

All data are available in the main text and the S5 of the manuscript.

References

1. L. W. S. W. Amkreutz, *Persistent Traditions A Long-Term Perspective on Communities in the Process of Neolithisation in the Lower Rhine Area (5500–2500 cal BC)* (Sidestone Pres, 2013).

2. A. L. Van Gijn, "Het gebruik van vuursteen in de Vlaardingen-tijd," *Westerheem (Special 2010: Vlaardingen-cultuur)* 2 (2010): 81–89.

3. R. Houkes, A. Verbaas, and M. Mullaart, "Vuursteen *De Wateringse Binnentuinen, Gemeente Den Haag: Een vlaardingennederzetting in het Wateringse Veld*," in *Haagse Oudheidkundige Publicaties*, vol. 20, ed. P. J. A. Stokkel and E. E. B. Bulten (Afdeling Archeologie & Natuur- en Milieueducatie Dienst Stadsbeheer Den Haag, 2017), 163–204.

4. L. B. M. Verhart, "Het vuursteen uit de opgraving Hekelingen III, Leiden Unpublished thesis Leiden University." 1983.

5. M. E. T. De Grooth, "Distinguishing Upper Cretaceous Flint Types Exploited During the Neolithic in the Region Between Maastricht, Tongeren, Liège and Aachen," in *Vergangene Zeiten. Liber amicorum. Gedenkschrift für Jürgen Hoika*, ed. J. Meurers-Balke and W. Schön (Archäologische Berichte 22, 2013), 107–130.

6. H. Collet, P. Lavachery, and W. Michel, "Raw Material Exploitation Strategies on the Flint Mining Site of Spiennes (Hainaut, Belgium)," *Journal of Lithic Studies* 3 (2016): 127–162, https://doi.org/10.2218/jls.3i2.1821.

7. M. E. T. De Grooth, "Mines in the Marl. The Flint Extraction at Rijckholt," in *The Prehistory of The Netherlands*, ed. L. P. Louwe Kooijmans, P. W. Van Den Broeke, H. Fokkens, and A. L. Van Gijn (Amsterdam University Press, 2005), 281–306.

8. L. Van den Dikkenberg, "How to Finish Your Neolithic Axe? Experimental Archaeology and Optical Microscopy, a Study of Grinding and Polishing Traces on Flint Axes From Vlaardingen Culture (3400–2500 BCE) Settlements," *Journal of Archaeological Science: Reports* 53 (2024): 104395, https://doi.org/10.1016/j.jasrep.2024.104395.

9. T. A. Goossens, "Opgraving Hellevoetsluis-Ossenhoek," in *Een nederzetting van de Vlaardingen-groep op een kwelderrug in de gemeente Hellevoetsluis* (Archol, 2009), 87.

10. R. Houkes, "Vuursteen, Steynhof (Anne Frankpark), Gemeente Den Haag, Een Vlaardingennederzetting in het Wateringse Veld," in *Steynhof (Anne Frankpark) Gemeente Den Haag Een Vlaardingennederzetting in het Wateringse Veld, Haagse Oudheidkundige Publicaties*, vol. 23, ed. R. J. Van Zoolingen and E. E. B. Bulten (Afdeling Archeologie & Natuur en Milieueducatie Dienst Stadsbeheer gemeente Den Haag, 2021), 141–172.

11. M. De Bruin, P. J. M. Korthoven, R. P. W. Duin, F. C. A. Groen, and C. C. Bakels, "Pattern Recognition as a Statistical Method for Analyzing the Confidence Level in the Identification of Objects," *Journal of Radioanalytical Chemistry* 15 (1973): 181–191, https://doi.org/10.1007/BF02516570.

12. P. Vos, M. Van Der Meulen, H. J. T. Weerts, and J. Bazelmans, *Atlas of the Holocene Netherlands, Landscape and Habitation Since the Last Ice Age* (Amsterdam University Press, 2020).

13. L. P. Louwe Kooijmans, "Tussen SOM en TRB, enige gedachten over het laat-Neolithicum in Nederland en België," *Bulletin van de Koninklijke Musea voor Kunst en Geschiedenis* 54 (1983): 55–67.

14. L. B. M. Verhart, "De zuidelijke tegenhangers van de Vlaardingen-cultuur: een schamel spoor van scherven," *Westerheem* 2 (2010): 207–222.

15. R. E. Hughes, A. Högberg, and D. Olauson, "Sourcing Flint From Sweden and Denmark; a Pilot Study Employing Non—Destructive Energy Disperse X—Ray Fluorescense Spectometry," *Journal of Nordic Archaeological Science* 17 (2010): 15–25.

16. D. Olausson, A. Högberg, and R. Hughes, "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," in *The Exploitation of Raw Materials in Prehistory: Sourcing, Processing and Distribution*, ed. T. Pereira, X. Terradas, and N. Bichoed (Cambridge Scholars Publishing, 2017), 98–112.

17. C. Stockmans, H. Bosmans, and P. Vermeersch, "Trace Element Analysis of Belgium Flint Mine Products," *Star* 6 (1981): 85–88.

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

18. D. Geerts, "*De karakterisatie van vuursteen uit Spiennes (BE) en Rijckholt-St. Geertruid (NL)* Leuven Unpublished BA thesis KU Leuven." 2013.

19. R. D. McDonnell, H. Kars, and J. J. Ben, "Petrography and Geochemistry of Flint From Neolithic Sources in Southern Limburg (The Netherlands) and Northern Belgium," in *Monografica Arte y Arqueologia*, ed. A. Ramos-Millán and M. A. Bustillo (Granada Universidad de Granada, 1997), 371–384.

20. F. Robaszynski, A. V. Dhondt, and J. W. M. Jagt, "Cretaceous Lithostratigraphic Units (Belgium)," *Geologica Belgica* 4, no. 1–2 (2001): 121–134.

21. A. Aspinall and S. W. Feather, "Neutron Activation Analysis of Prehistoric Flint Mine Products," *Archaeometry* 14 (1972): 41–53, https://doi.org/10.1111/j.1475-4754.1972.tb00049.x.

22. C. C. Bakels, M. Bruin, R. P. W. De Duin, and P. J. M. Kerkhoven, "Neutronenactiveringsanalyse van vuursteen ten behoeve van prehistorisch onderzoek," in *Tweede internationale symposium over vuursteen, 24–27 mei 1979, Maastricht*, ed. F. H. G. Engelen (Heerlen van Hooren drukkerij, 1975), 41–42.

23. M. D. De Bruin, P. J. M. Korthoven, C. C. Bakels, and F. C. A. Groen, "The Use of Non-destructive Activation Analysis and Pattern Recognition in the Study of Flint Artefacts," *Archaeometry* 14 (1972): 55–63.

24. L. Moreau, M. Brandl, P. Filzmoser, et al., "Geochemical Sourcing of Flint Artifacts From Western Belgium and the German Rhineland: Testing Hypotheses on Gravettian Period Mobility and Raw Material Conomy," *Geoarchaeology* 31 (2016): 229–243, https://doi.org/10.1002/gea.21564.

25. G. D. G. Sieveking, P. Bush, J. Ferguson, P. T. Craddock, M. J. Hughes, and M. R. Cowell, "Prehistoric Flint Mines and Their Identification as Sources of Raw Material," *Archaeometry* 14 (1972): 151–176.

26. A. L. Burke, "Chert, Silex, and Obsidian Sourcing," in *The Encyclopedia of Archaeological Sciences*, ed. S. L. López Varela (John Wiley and Sons Ltd., 2018), https://doi.org/10.1002/9781119188230.saseas0088.

27. S. Bradley, V. Cummings, and M. J. Baker, "Sources of Flint in Britain and Ireland: A Quantitative Assessment of Geochemical Characterisation Using Acid Digestion Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)," *Journal of Archaeological Science: Reports* 31 (2020): 102281, https://doi.org/10.1016/j.jasrep.2020.102281.

28. M. Edmonds, "Lithic Exploitation and Use," in *Handbook of Archaeological Sciences*, ed. D. R. Brothwell and A. M. Pollard (John Wiley and Sons Ltd., 2001), 461–470.

29. G. D. G. Sieveking, P. T. Craddock, M. J. Hughes, P. Bush, and J. Ferguson, "Characterization of Prehistoric Flint Mine Products," *Nature* 228, no. 5268 (1970): 251–254, https://doi.org/10.1038/228251a0.

30. P. Chatzimpaloglou, "A Geoarchaeological Methodology for Sourcing Chert Artefacts in the Mediterranean Region: A Case Study From Neolithic Skorba on Malta," *Geoarchaeology* 35, no. 6 (2020): 1–24, https://doi.org/10.1002/gea.21813.

31. G. Gauthier and A. L. Burke, "The Effects of Surface Weathering on the Geochemical Analysis of Archaeological Lithic Samples Using Non-destructive Polarized Energy Dispersive XRF," *Geoarchaeology* 26, no. 2 (2011): 269–291, https://doi.org/10.1002/gea.20346.

32. J. M. Mehta, G. McCall, T. Marks, and J. Enloe, "Geochemical Source Evaluation of Archaeological Chert From the Carson Mounds Site in Northwestern Mississippi Using Portable X-Ray Fluorescence (pXRF)," *Journal of Archaeological Science: Reports* 11 (2017): 381–389, https://doi.org/10.1016/j.jasrep.2016.12.014.

33. R. A. Johnson and D. W. Wichern, *Applied Multivariate Statistical Analysis* (Prentice Hall, 1988).

34. Ø. Hammer, D. A. T. Harper, and P. D. Ryan, "PAST: Paleontological Statistics Software Package for Education and Data Analysis," *Palaeontologia Electronica* 4, no. 1 (2001): 9, http://palaeo-electronica.org/2001_1/past/issue1_01.htm.

35. F. T. S. Brounen and H. Peeters, "Vroegneolithische vuursteenwinning en bewerkinginde Banholtergrubbe (Banholt, gem. Margraten)," *Archeologie* 10 (2001): 133–150.

36. M. E. T. De Grooth, R. Lauwerier, and M. E. Ter Schegget, "New C-14 Dates From the Neolithic Flint Mines at Rijckholt-St. Geertruid, the Netherlands," in *Proceedings of the 2nd International Conference of the UISPP Commission on Flint Mining in Pre- and Protohistoric Times*, vol. 2260, ed. M. Capote, S. Consuegra, P. Díaz-del-Río, and X. Terradas (Haagse Oudheidkundige Publicaties, 2011), 77–89.

37. P. Vermeersch, J. Chow, G. Creemers, I. Masson-Loots, A. J. Groenendijk, and M. Bie, "Neolithische vuursteenontginning op de site van Rullen. (Voeren, prov. Limburg), Een lijn door het landschap—Archeologie en het VTN-project 1997–1998, Deel II, 313–328." 2005.

38. F. Bostyn, H. Collet, J.-P. Collin, and F. Giligny, "Flint Mining in Northern France and Belgium: A Review," in *Between History and Archaeology, Papers in Honour of Jacek Lech*, ed. D. H. Werra and M. Woźny (Oxford Archaeopress Archeology, 2018), 25–36.

39. P. J. A. Stokkel and E. E. B. Bulten, "Synthese," in *De Wateringse Binnentuinen, Gemeente Den Haag: een Vlaardingennederzetting in het Wateringse Veld. Afdeling Archeologie & Natuur- en Milieueducatie Dienst Stadsbeheer Den Haag*, ed. P. J. A. Stokkel and E. E. B. Bulten (Haagse Oudheidkundige Publicaties, 2017), 283–305.

40. R. J. Van Zoolingen and E. E. B. Bulten, "Synthese," in *Steynhof (Anne Frankpark) Gemeente Den Haag een Vlaardingennederzetting in het Wateringse Veld*, vol. 23, ed. R. J. Van Zoolingen and E. E. B. Bulten (Afdeling Archeologie & Natuur en Milieueducatie Dienst Stadsbeheer gemeente Den Haag, 2021), 291–309.

41. J. F. Van Regteren Altena, J. A. Bakker, A. T. Clason, W. Glasbergen, W. Van Groenman- Waateringe, and L. J. Pons, "The Vlaardingen culture I," *Helinium* 2 (1962): 3–35.

42. L. P. Louwe Kooijmans, "Neolithic Settlement and Subsistence in the Wetlands of the Rhine-Meuse Delta of The Netherlands," in *European Wetlands in Prehistory*, ed. J. M. Coles and A. J. Lawson (Clarendon Press, 1987), 227–251.

43. A. L. Van Gijn, *The Wear and Tear of Flint. Principles of Functional Analysis Applied to Dutch Neolithic Assemblages*, vol. 22 (Leiden University, 1990).

44. A. L. Van Gijn and J. A. Bakker, "Megalith Builders and Sturgeon Fishers. Middle Neolithic B: Funnel Beaker Culture and Vlaardingen Group," in *The Prehistory of The Netherlands*, ed. L. P. Louwe Kooijmans, P. W. Van Den Broeke, H. Fokkens, and A. L. Van Gijn (Amsterdam University Press, 2005), 281–306.

45. A. L. Van Gijn, "Preliminary Report of the Microwear Analysis of the Flint of Vlaardingen 11, Leidschendam 4 and Voorschoten 17, Unpublished Report, IPP Amsterdam." 1984.

46. B. L. Van Beek, *Steentijd te Vlaardingen, Leidschendam en Voorschoten. De vondstverspreiding in laat-neolithische nederzettingen in het hollandse kustgebied* (Universiteit van Amsterdam, 1990).

47. H. P. Longerich, G. A. Jenner, B. J. Fryer, and S. E. Jackson, "Inductively Coupled Plasma-Mass Spectrometric Analysis of Geological Samples. A Critical Evaluation Based on Case Studies," *Chemical Geology* 83 (1990): 105–118, https://doi.org/10.1016/0009-2541(90)90143-U.

48. E. Drenth, "Vuursteen," in *Prehistorische sporen op een plateau langs de Schelde. Een archeologische opgraving aan de Heurnestraat te Eine (gemeente Oudenaarde)*, ed. P. L. M. Hazen (ADC Rapport 4764, ADC ArcheoProjecten Amersfoort, 2018), 78–86.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

10974539, 2025, 5, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/xrs.3483, Wiley Online Library on [27/08/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License