

NON-DESTRUCTIVE IDENTIFICATION OF PREHISTORIC ADHESIVES BY HS-SPME-GCXGC-TOFMS: PRELIMINARY STUDY

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Introduction

The earliest evidence of the use of glue in hafting appears during the Middle Palaeolithic (MP) (ca. 300,000 to 40,000 years ago) in particular from about 80,000 years onwards. The chemical identification of glue is important as it reveals essential aspects of prehistoric technology and sheds light on past human behaviour. Traditionally, gas chromatography (GC) is used to identify glues, however, it has major drawbacks because of its destructiveness and the difficulty to analyse small samples such as those typically found on MP stone tools¹. In this study, we try to develop a new identification method of prehistoric glues by using headspace solid phase micro extraction combined with comprehensive GC – time-of-flight mass spectrometer (HS-SPME-GCXGC-TOFMS), which is in essence non-destructive to the glues. Furthermore, we tested if the stone raw material influences the chromatography pattern of the glue mixture consisting of Pinus resin and Beeswax.

Materials & Methods

- Samples:
 - Adhesives: Birch tar, Pinus *pin*ea resin, Beeswax, Hide glue (dried chips), Arabic gum (powder) -> in 20 mL vial
 - Mixture: Pinus *pin*ea resin:Beeswax (70:30) -> droplet on stone piece (raw material: obsidian (O), dolerite (D), quartz (QZ), quartzite (QE))
- GC: Pegasus GC-4D (LECO corporation) GCxGC-TOFMS equipped with a secondary oven and a quad-jet, dual stage thermal modulator and an Agilent 7890 GC.
 - Rxi-624sil MS (30 m x 0.25 mm i.d. 1.4 µm d_f) x Stabilwax (2 m x 0.25 mm i.d. 0.5 µm d_f), 40 °C-240 °C, 5 °C/min, P_m 4s, ²D oven offset +15 °C, modulator offset +10 °C.
- Sample prep: Multipurpose sampler (Gerstel) with a HS-SPME option. A 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (Supelco) SPME fibre was used².
 - Incubation at 50 °C for 10 min, absorption for 25 min, desorption at 270 °C for 3 min.
- MS parameters: transfer line: 230°C, ion source: 230°C, 70 eV, 30-550 m/z.

Results & Discussion

- The HS profile of the different adhesives shows a distinct elution pattern with the same elution program (Fig. 1)
 - Possible to differentiate between glues based on HS measurements in combination with GCxGC-MS
 - Hide glue and Arabic gum needed more sample preparation by dissolving in MilliQ water.
- Resin mixture on stone
 - Each stone raw material is measured in triplicate
 - The Principal Component Analysis (PCA) shows a difference for each raw material (Fig. 2)
 - Indicating that the raw material influences the chromatography results.
 - Further investigation is needed regarding the influence of raw material when trying to detect glues
 - The Hierarchical Clustering Analysis (HCA) dendrogram shows the grouping of the samples, quartzite seems to be separate from the other samples.

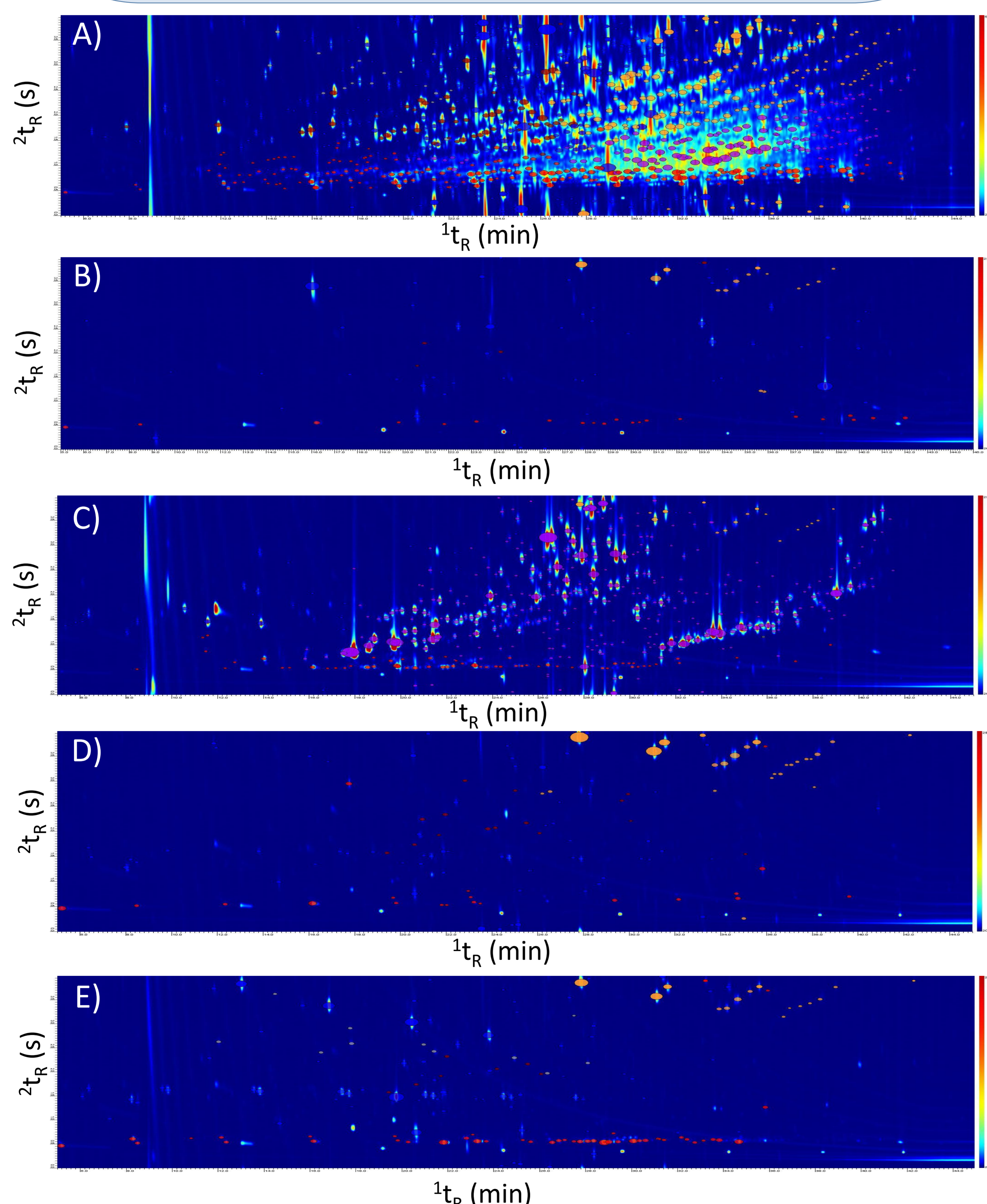


Fig 1. A) Birch tar, B) Arabic gum, C) Pinus *pin*ea resin, D) Beeswax, E) Hide glue
○ – oxygenates, ○ – terpenes, ○ – aromatics, ○ – naphthalenes, ○ – hydrocarbons, ○ – nitriles

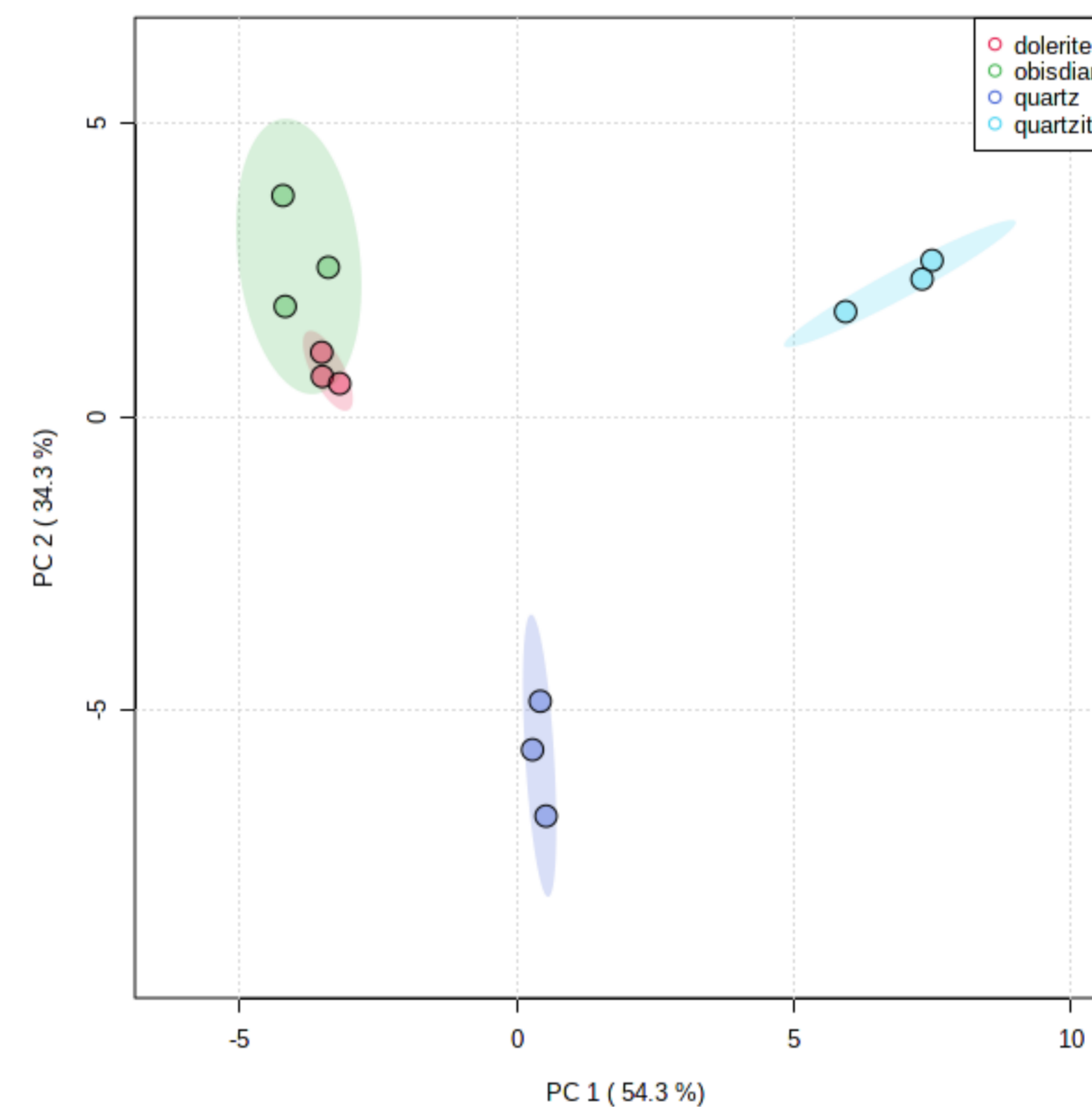


Fig 2. PCA result of the different stone types, only the most important (F-values > 20) features were selected.

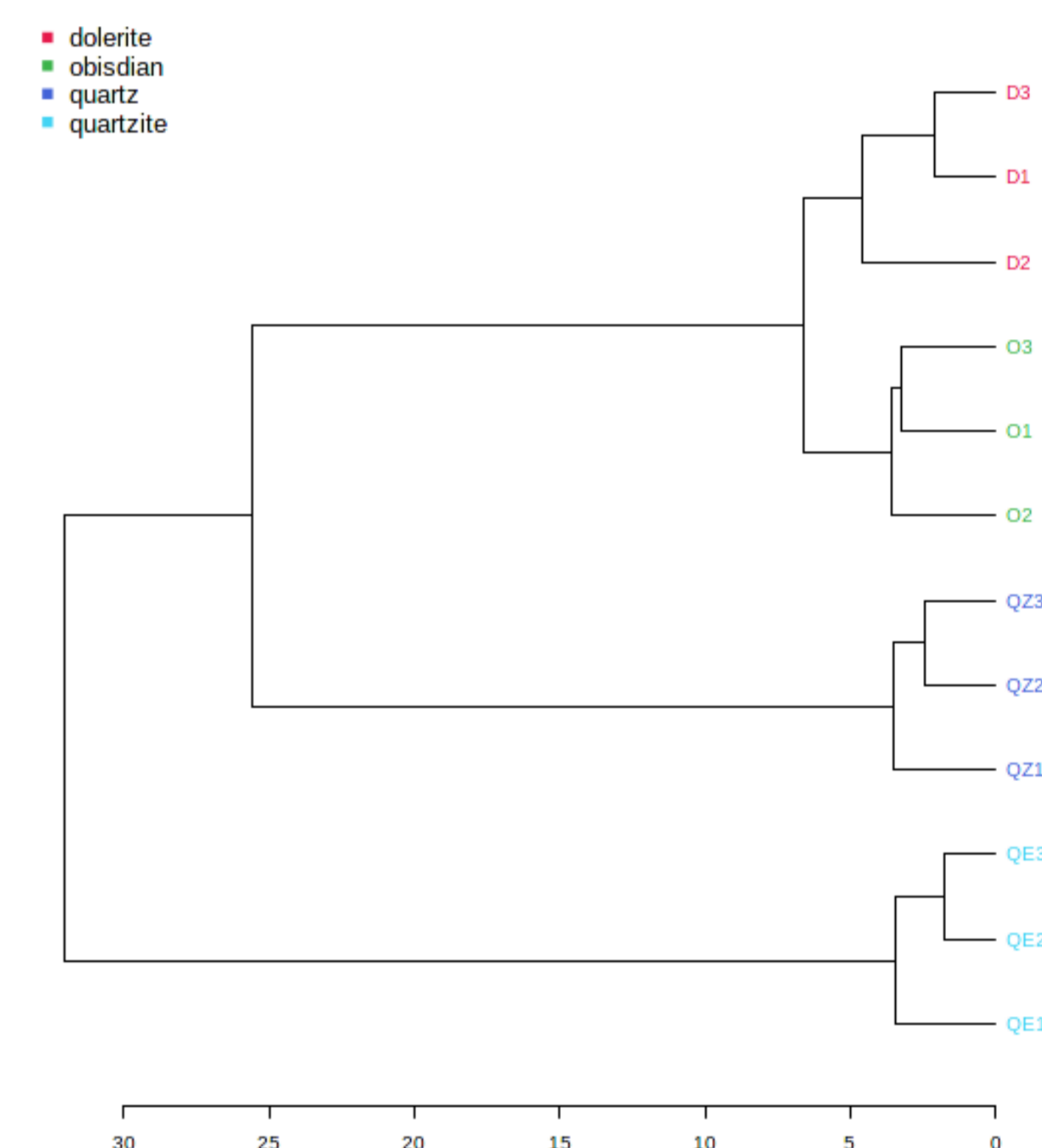


Fig 3. HCA dendrogram of the features using the Euclidean distance calculated based on the intensities of the highest features (F-values > 20).

Conclusion & Perspectives

The first results of HS-SPME-GCXGC-MS show that SPME is a good technique for discriminating between glues that are possibly used in prehistory. However, there are concerns that HS-SPME might not be sensitive enough when studying archaeological stone tools dating to the Palaeolithic period. Therefore, we currently investigate the usage of dynamic headspace for these glues.

Surprisingly, the PCA results show that the stone raw material influences the chromatographs. This is also supported by the HCA dendrogram. Currently, the reason for this is still unknown and more research is planned.

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