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Flint Patina as an Aspect of "Flaked Stone Taphonomy": A Case Study from the Loess Terrain of the Netherlands and Belgium

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This paper describes recent research into variable patinas observed on lithic artifacts from the loess-mantled region of Southern Limburg, The Netherlands and Belgian Limburg. There, patina intensity and artifact typology and technology have long been used as indicators of the relative age of surface finds. Though it is true that Neolithic and later flint surface finds never possess the intensity of patina observed on Paleolithic artifacts, this study indicates that sub-aerial exposure likely plays a marginal role in flint patination. Rather, type and degree of patina development appear more closely related to depositional context. We consider data from local surface sites, inferences about the geochemical influence of plant roots, humic acids, soil pH, temperature, and site aspect; and microscopic analysis of thin sections produced from a small sample of artifacts. Finally, we propose a simple model of the flint patination process based on empirical and experimental research on glass hydration. This is a preliminary, conceptual study aimed at developing a working protocol for more extensive flaked stone taphonomy research. Excavations, lithic artifact assemblage analyses, and geochemical studies are currently ongoing, and continue to build on the results of this preliminary research.

Keywords: STONE TOOLS, ARTIFACT TAPHONOMY, FLAKED STONE TAPHONOMY, CHERT, FLINT, PATINA, PALEOLITHIC, THIN SECTIONS.

Introduction

The term "patina" originated to describe the greenish film that spontaneously forms on copper or bronze objects resulting from exposure to humid atmospheric conditions, technically a veneer of "malachite," a hydrated copper carbonate mineral. Within Stone Age archaeology, however, the term is used in a far more general sense, referring to any film, rind, encrustation, or layer produced on the surface of flint due to chemical weathering. Using the term in this general

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sense is helpful, provided that its user understands that patina refers to any process of alteration of any type of flint taking place anywhere at any time. Unfortunately, there is still a tendency within archaeology to view patination as a progressive weathering process taking place at the ground surface and creating a rind, the thickness of which can be used as a surrogate for the passage of time. This narrow use of a broad term has led to a proliferation of misunderstandings. Furthermore, stone artifact taphonomy typically focuses on post-depositional processes at the physical level, including use wear, edge damage, artifact breakage, and displacement patterns (e.g. Villa & Courtin, 1983; McBrearty *et al*., 1998; Bordes, 2003; Borrazzo, 2011; Eren *et al*., 2010, 2011; Jennings, 2011; Parteger, 2011; Parteger & Bradfield, 2012). Much remains to be learned at the petro-chemical level (e.g. Fernandes *et al*., 2008).

In this paper, we specifically address two components of a recently proposed definition of "flake stone taphonomy": "…as the subfield identifying and analyzing the processes affecting the appearance and context of lithic artifacts subsequent to their cultural use lives." (Eren *et al*. 2011:202). We focus on the aspects of "appearance" and "context" of lithic artifacts due to post-depositional processes, and argue that depositional context has profound effects on the appearance of flaked flint artifacts by facilitating the process of patination. It is well acknowledged that the patination of flint artifacts is a result of context-dependent, post-depositional processes of weathering and diagenesis, notably silica and quartz dissolution and re-precipitation. However, the relationship between depositional context and patina formation processes is complex, and many variables have not yet been investigated.

Our main purpose is to call attention to the complexity of patination processes on artifacts from the loess mantled region of South Limburg (NL) and Belgian Limburg (Figure 1). Following a review of the patination processes relevant to our study area, we present two case studies. The first is quantitative, a comparison of two assemblages at the Paleolithic site of Lauw, Belgium. The second is qualitative, a microscopic examination of a small sample of patinated artifacts of different age – set within the context of the regional geology, climatology, and archaeology. Finally, based on a review of empirical and experimental research we propose a revised simple model for the flint patination process in depositional context. We conclude that patination is more related to depositional context than sub-aerial surface exposure, and hypothesize that with further research, variable patina characteristics can eventually serve as proxies for reconstructing depositional context.

Flint patination

Definitions

Flint is a vernacular term for a form of chert, a rock type formed by the aqueous precipitation of micro-crystalline quartz, usually with associated impurities like water, clay minerals, carbonates, iron and manganese oxides, aluminum, and organic compounds (Hurst & Kelly, 1961, references in Sieveking & Hart, 1986; Leudtke, 1992). Though chert (or flint) forms in a variety of depositional contexts ranging from discrete strata in abyssal settings to nodules within host rocks, its formation requires the re-precipitation of silica dissolved in ground and connate water, and obtained from a silica-bearing source. In northern Europe,

Figure 1. Map of Europe showing location of the Netherlands and study area. Detail showing Southern Limburg, the Netherlands and Belgian Limburg, and sites mentioned in the text.

the term flint usually refers to the slightly translucent variety of chert ranging in color from light brown to black, often with a blue tinge. Typically, they originate as secondary replacements in Cretaceous limestone formations (references in Sieveking & Hart, 1986; Zijlstra, 1987; Madsen & Stemmerik, 2010).

True weathering rinds, or 'cortex' on flint nodules from Cretaceous or Tertiary contexts are not considered as a form of patina in this study. We restrict the term to surfaces that have been worked by humans in the past.

A distinctive patina was one of the first observations made at the outset of Paleolithic research, when flint artifacts were found in association with the remains of Pleistocene mammals within primary and reworked loessic contexts in France and England (e.g. Prestwich, 1859, 1892).

In our study area of Dutch and Belgian Limburg, De Puydt (1885), Ubaghs (1887), and Ophoven (1938) were among the first to publish on patina characteristics of flint artifacts. Since their work, many terms have been informally adopted to characterize the range of different types of patina (e.g. Stapert, 1976; Rottländer, 1989). In this paper we utilize the following terms:

- Color patina: orange, dark brown, to black coloration.
- Gloss patina (*glanzpatina*): smooth, shiny reflective surface that may cover all or parts of an artifact.
- White patina: granular, chalky white coating on an artifact's surface.
- Porcelain patina: white, glossy reflective coating that may also present features like pits.
- Dendritic patina (*vermiculé*): curvilinear, asymmetrical pattern of thin white lines on a background of original raw material hue, or other patina types. Rottländer (1975) suggested its likeness to the patterning of plant roots.

Gloss patina is generally thought to be a product of silica dissolution (Rottländer, 1989; Howard 1999, 2002). Unlike 'desert varnish' or 'wind gloss' it is not due to contact with fine to coarse granular particles, where corrasion induces a glossy, sometimes discolored surface, although corrasion and silica dissolution can combine to form gloss patina (Stapert, 1976; Howard, 1999; Howard, 2002). Gloss patina has been observed to inhibit the development of other kinds of patina or weathering rinds (Rottländer, 1975; Stapert 1976; Howard, 1999), yet this hypothesis has not been empirically tested.

While all of the patinated artifacts described here present some degree of gloss, the focus of this paper is on porcelain and *vermiculé* patinas. We do not address locally observed "Neolithic patina" (e.g. Ubaghs, 1887; Ophoven, 1938; Sieveking *et al*., 1972). This is typically a white patina as described above that appears on artifacts dated on typological grounds to the Neolithic time period, and is distinguishable from patinas observed on Paleolithic finds. However, it is important to note that in our research area, the majority of patinated Neolithic finds are frequently encountered in the vicinity of Neolithic flint mines in forested settings, and not commonly in plowed fields. The formation of this patina may therefore be related to both the increased temperature and humidity of the forest floor context. Soils in these settings are likely enriched with carbonates and have elevated pH due to near-surface chalk outcrops, and chalk displaced by Neolithic flint-miners and reworked into soils.

Multiple patina types can occur within discrete artifact collections, or on individual artifacts.

Little attention, however, has been given to this complication.

Physio-chemical factors

Many researchers have studied flint patination in laboratory settings (e.g. Hue, 1929; Bellard, 1930; Curwen, 1940; Kelly & Hurst, 1956; Schmaltz, 1960; Hurst & Kelly, 1961; Rottländer, 1975, 1989). Schmaltz (1960) replicated 'heavy white patina' on English flint in the lab, using concentrated alkaline (sodium hydroxide) solvents at high temperatures (78°C). Rottländer (1975, 1989) differentiated and replicated the conditions of color-patinas and gloss-patinas, replicating the former in a laboratory context simulating that of a peat-bog. These and other studies isolated and investigated the most important geochemical factors associated with flint patination: the pH of rainfall or soil water; the humidity of atmospheric or soil air; the integrated thermal history above, at, or below the ground surface; the duration of exposure to patina-producing factors, including sunlight; the degree to which the aqueous chemical system is open or closed; and the internal structure of the raw material (Hue, 1929; Bellard, 1930; Schmaltz 1960; Honea, 1964; Rottländer, 1975, 1989). Importantly, these laboratory studies concluded that neither the thickness nor variety of patina could be used to date archaeological materials, a conclusion later corroborated by field workers (e.g. Kelly & Hurst, 1956; Goodwin, 1960; Hurst & Kelly, 1961; Stapert, 1976; Van Nest 1985; Rottländer, 1989; Sheppard & Pavlish, 1992; Burroni *et al*., 2002).

The main geochemical processes of flint weathering that produce patina are dissolution, hydration, oxidation, leaching, and chemical and mechanical disaggregation (Schmaltz, 1960). Since the pioneering studies described by Hue (1929), and the seminal works of Schmaltz (1960) and Rottländer (1975, 1989), much has been learned about the chemical details, namely the dissolution kinetics of both quartz and amorphous silica in aqueous solutions at ambient temperatures (c. 0–25°C) (e.g. Bennett *et al*., 1988; Dove, 1994, Dove & Nix, 1997; Dove, 1999; Icenhower & Dove 2000; Dove *et al*., 2008).

Patinated flint artifacts are commonly present within upland limestone terrains because the increases in pH (alkalinity) and temperature raise the rate of quartz dissolution and the concentration of dissolved silica at chemical equilibrium (e.g. Birkeland, 1999; Bennett *et al*., 1988; Dove, 1994, Dove & Nix, 1997; Dove, 1999; Icenhower & Dove, 2000; Dove *et al*., 2008). The steady supply of dilute alkaline groundwater solutions through such terrains enhances the mobility of dissolved silica, which leads to both the formation and transformation of patinas (Curwen, 1940; Schmaltz, 1960; Dove, 1994).

Exposure to UV radiation also increases the dissolution rates of the cryptocrystalline quartz within flint (Rottländer, 1975). This has led many researchers to conclude that sub-aerial exposure is a major factor in patina development (e.g. Burroni *et al*., 2002). Anecdotally, this seemed to be the case at the Early Middle Paleolithic site of Maastricht-Belvédère, (Limburg, Netherlands) where 'fresh' flint artifacts began to patinate within minutes of excavation and exposure to sunlight, enough to obscure use-wear traces under magnification (van Gijn, 1988). In contrast, the relatively minimal patination of flints from exposed Roman walls in the same region suggests that sub-aerial exposure is of limited importance. A more complex scenario is suggested by upland surface, plow soil contexts in which both intensely patinated (i.e. Paleolithic) and un-patinated (i.e. Neolithic) artifacts co-occur. While Rottländer (1975, 1989) noted the effects of acute doses of UV light in producing 'grey-white' patina, the respective roles and relative importance of light and atmospheric humidity in patina development have yet to be rigorously tested.

Pedologic settings

The aspect, angle, and topographic position (summit, shoulder, back, or toe) of a slope play a critical role in its thermal exposure, moisture regime, and chemistry (e.g. Birkeland, 1999, especially Figures 9.4 and 9.26). Owing to their higher temperatures, south and southwest-facing slopes and summit, shoulder, and backslope positions all promote elevated clay and $CaCO_3$ content at higher relative depths in soil catenas than at north-facing or foot slope positions. Mineral salt and carbonate content are generally higher at foot slope positions compared to the summit, shoulder, or backslope. All things considered, increased clay content, alkalinity, and temperature enhance the rate of patination and its style in upland settings.

Chemical and mechanical weathering of flint is enhanced within the 'rhizosphere,' the zone of plant root growth and die-back. The bulk organic chemistry of this zone influences the rate of patination, largely through the effect of alkalinity. Organic and amino acids associated with plant roots influence silica dissolution rates, an effect that has been measured quantitatively for basalt (Hinsinger *et al*., 2001). More specifically, Rottländer (1975) speculated that the so-called 'basic' amino acids histidine, arginine, and lysine – frequently present in humic soil contexts (Schreiner & Shorey, 1910) – could be responsible for the development of both an enhanced rate of patination, and a dendritic pattern. Kowano & Obokata (2007) showed that these amino acids are concentrated at the time of root degeneration. Chemically, such 'basic' amino acids have the ability to interact electrostatically with the negatively charged surfaces of amorphous silica, and this interaction weakens the Si-O-Si bonds of the structural framework, increasing the dissolution rates in a manner similar to that of alkali and alkaline earth cations. At the millimeter scale, the die-back of roots creates voids, which can fill in with carbonates and salts, thereby contributing to strong micro-gradients. The pH of the soil is also influenced directly by organic acids. Citrate, oxalate, and acetate – the exudates of plant roots (Jones, 1998; Jones & Darrah, 1994) all increased quartz dissolution rates in solutions of dilute organic acids at 25°C, generally similar to soil temperature and organic acid contents (Bennett *et al*., 1988). This increase in the micro-local pH in the rhizosphere increases quartz dissolution and general mineral weathering rates at the root-zone scale (Drever & Stillings, 1997).

We hypothesize that the combined processes of amino acid and organic acid interaction, and carbonate influx at plant root sites, are likely responsible for producing the typically dendritic, *vermiculé* patina. Within our study region, this patina type is unique to Paleolithic artifacts, and is a patina variety that is missing from most discussions in the published literature on flint weathering. The frequent observation of one surface of an artifact displaying a dendritic patina pattern while another surface presents porcelain patina may be the consequence of asymmetry within the soil environment, with roots restricted to one side only. More specifically, horizontally oriented artifacts near the surface of a soil may have roots attached to the uppermost surface, promoting dendritic patina; whereas their bottom surfaces may collect carbonates and moisture, promoting a porcelain patina (see Figure 8). Given the many mechanisms involved, patina processes should vary with the controlling attributes of slope, depth, and soil type.

Patina need not form at the ground surface. In fact, heavily patinated artifacts are often associated with buried unconformities, usually represented by stone lines or gravel lenses. In Dutch and Belgian Limburg, many Paleolithic artifacts have been found in association with a conspicuous gravel deeply buried beneath loessic silt loams that contains high frequencies of patinated flint clasts (the so-called 'patina layer'; A.J. Groenendijk, J.P. De Warrimont, pers comm.; Meijs, 2011). Regardless of its geomorphic interpretation, being a zone of enhanced permeability and storativity, this buried gravel lens holds and transmits translocated water, carbonates, and salts, thereby increasing the micro-local pH, and invigorating bulk patination processes. The same would be true for any zone of elevated groundwater mobility. The majority of upland Palaeolithic sites that have been excavated in our research area are likely associated with buried gravelly contexts, or other unconformities. Surface and excavated assemblages also present patina type frequencies that are not statistically different.

Case Study: Comparing Artifact Assemblages at the Paleolithic Site of Lauw, Belgium

At the site of Lauw, a large and relatively dense surface scatter of flint artifacts considered to be of Paleolithic age is located on an eroding loess-covered plateau overlooking the Jeker River, a tributary of the Maas River (Figure 1). In 1981, the Katholieke Universiteit Leuven conducted test excavations at the site, and four trenches were excavated up-slope of the surface accumulation (Gijselings & Dopere, 1983). Paleolithic artifacts were concentrated well beneath the plow zone at slightly more than one meter below the modern surface, and were associated with a gravelly layer (see Figure 2; Gijselings & Dopere, 1983). A sample of artifacts from the surface assemblage (n=317) and the excavated assemblage, with associated three-dimensional data (n=101) were recently re-analyzed by the first author.

Lacking chronometric dates, the surface and excavated artifact assemblages were assigned to the Paleolithic based on artifact analysis. Middle Paleolithic tool forms are numerous in both surface and excavated assemblages and include one biface considered a *Keilmesser*, diagnostic Mousterian scraper forms, as well as retouched flakes classified as notches, denticulates, and bifacially worked pieces (cf. Bordes, 1961; Bosinski, 1967; Debénath & Dibble, 1994). The most numerous artifact classes in both surface and excavated assemblages are complete and broken flakes. Flake scar pattern analysis suggests that the most common methods of reduction were the discoidal and Levallois techniques, and a chi square test comparing the flaking technology between the surface and excavated assemblages indicates that the assemblages are not statistically different (χ^2=3.467, df=8, P < .05; Table 1).

The most frequently represented patina types in both the surface and excavated assemblages are a combination of color, *vermiculé,* and gloss patina, and a combination of porcelain and gloss (Figure 3). A chi square test comparing patina type data from the surface and excavated assemblages indicates that there is no significant difference between the assemblages (χ^2=5.37, df=4, P < .05; Table 2).

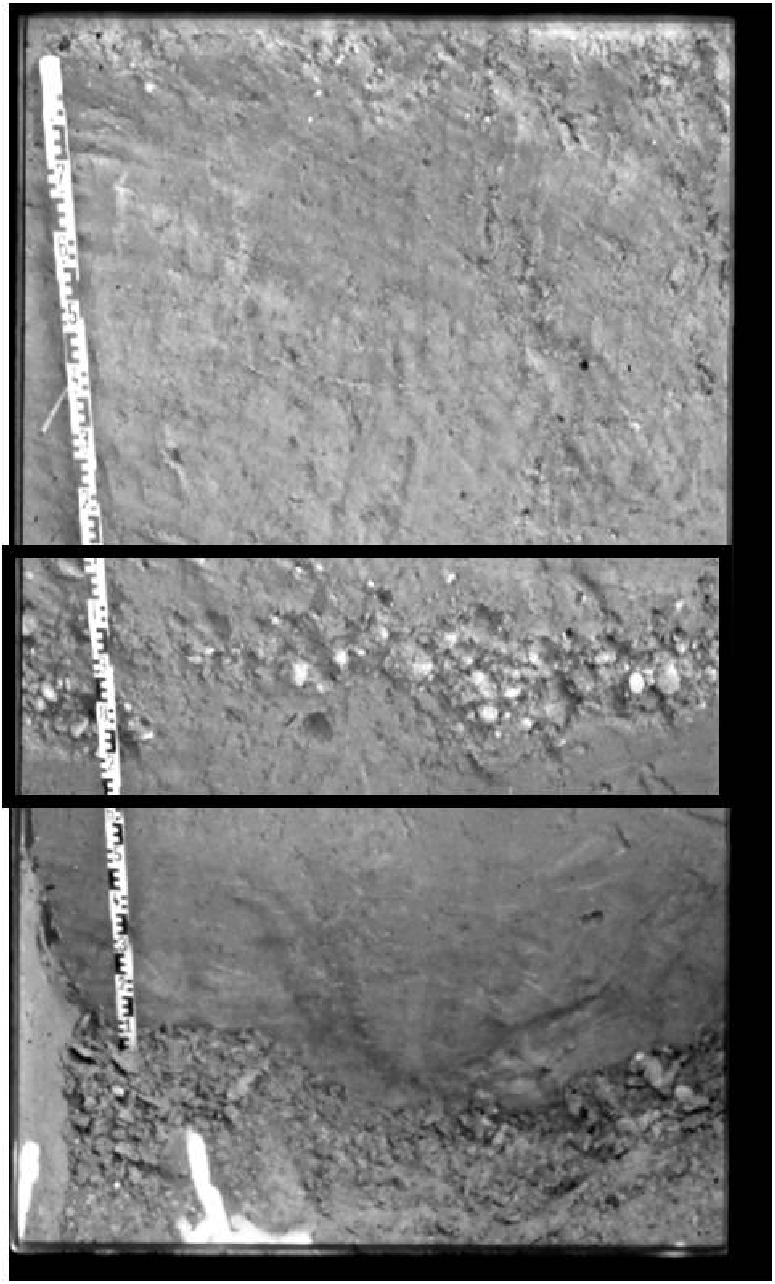
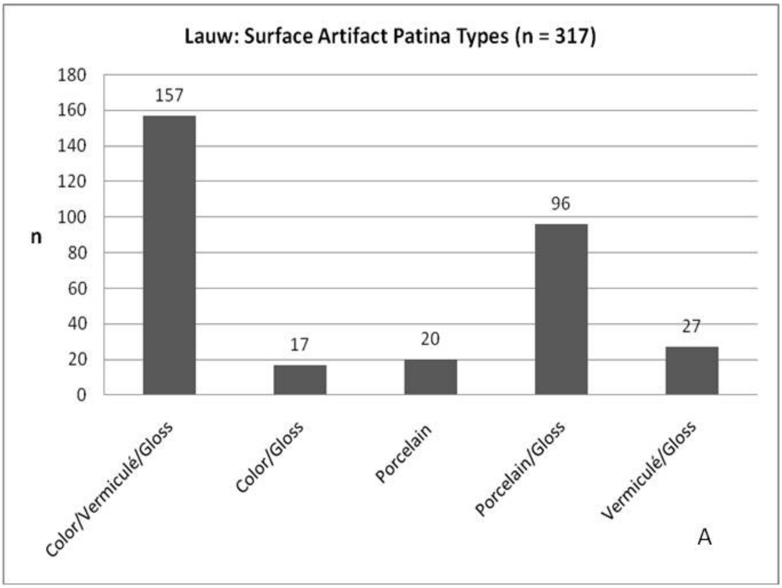


Figure 2. Lauw: archaeological profile. Find horizon indicated by black box. (Photo courtesy of P.M. Vermeersch, KU Leuven).



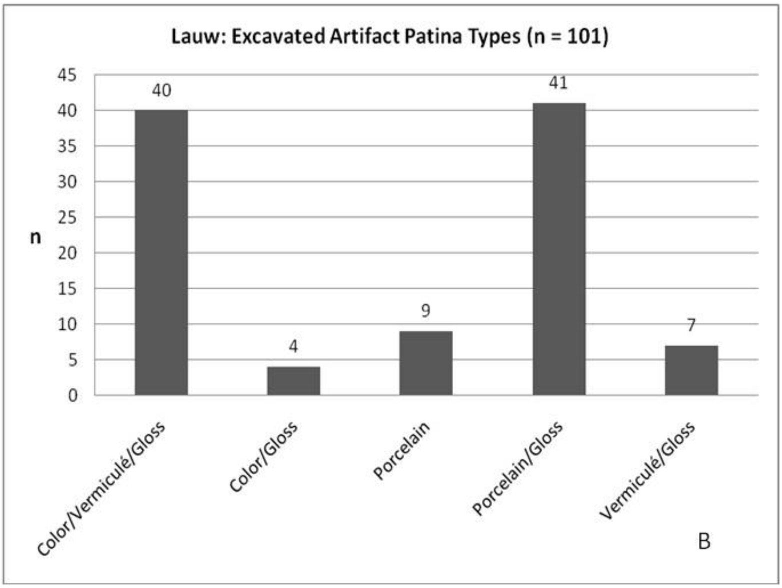


Figure 3. A. Lauw surface assemblage patina types. B. Lauw excavated assemblage patina types.

In this example, the similarity in patina characteristics between the surface and buried assemblages of similar Paleolithic artifacts refutes the notion that patination was due to sub-aerial exposure in connection with recent erosion processes on the modern surface. It also raises the question of depositional context. In this case, the buried, gravelly depositional context of the excavated artifacts may have influenced the translocation of salts and minerals, promoting subsurface patination. Alternatively, given the high frequencies of *vermiculé* and color patinas on the Lauw artifacts, some artifacts now present in the buried palimpsest at the gravel layer could have patinated in their primary soil contexts, and were then displaced to their current context.

Case Study: Patina Formation in Dutch South Limburg and Belgian Limburg Regional Considerations

Paleolithic, Neolithic, and more recent artifacts are widespread in the provinces of South Limburg, The Netherlands, and Belgian Limburg (Figure 1). This area lies in northwest Europe, at around 50° 52 N latitude, within a northwestern extremity of the Eurasian loess belt. There, three main patina types are frequently observed on technologically or typologically Paleolithic surface finds. A 'porcelain' or white, shiny patina; a '*vermicul*é' or 'spaghetti'-like patina with a dendritic pattern of white patination superimposed on the darker background of the original raw material color; '*glanzpatina*', or gloss patina, a shiny film on the surface of artifacts that may cover other patina types, or un-patinated surfaces (Stapert, 1976; Roebroeks, 1980). Color patina is also observed, but is less frequent in the research area than in regions to the north (Stapert, 1976), and will therefore not be treated specifically in this paper.

Table 1. Lauw surface assemblage flake reduction technology.

Lauw Surface Flakes		
	n	**%**
Discoid	43	21.5
Retouched Discoid	1	0.5
Levallois	74	37
Retouched Levallois	3	1.5
Retouched Flake	12	6.0
Core Trimming Element	4	2.0
Blade	2	1.0
Normal	5	2.5
N/A	56	28.0
Total	200	100

The three main patina types can appear concurrently on any given artifact. It is notable that many artifacts can present one side with a porcelain patina, while the other surface displays *vermicul*é patina. This likely indicates an original horizontal orientation of the artifact that underwent differential patination.

Geologically, the study area sits on a tectonic unit called the 'South Limburg Block'. It is situated in the fault block area between the Dutch *Central Graben* (which continues into Germany as the *Ruhrtal Graben*), and the Ardennes Massif (Kuyl, 1980). Beginning in the Early Pleistocene, uplift in the southeast caused the Maas River to shift course from its original northeasterly direction to its present orientation. The Maas achieved its current south-north orientation by the Middle Pleistocene. Uplift and lateral migration of the Maas promoted the down-cutting of the Cretaceous and Tertiary

Table 2. Lauw excavated assemblage flake reduction technology.

Lauw Excavated Flakes		
	n	**%**
Discoid	19	20.2
Retouched Discoid	1	1.1
Levallois	30	31.9
Retouched Levallois	1	1.1
Retouched Flake	7	7.4
Core Trimming Element	1	1.1
Blade	2	2.1
Normal	1	1.1
N/A	32	34.0
Total	94	100

limestone bedrock and formation of terraces and plateaus.

There are two main flint-bearing limestone formations in the region: the Maastricht and Gulpen Formations (Kuyl, 1980). The Gulpen Formation is present in the southwest of Southern Limburg, while the Maastricht Formation is present to the north (Buurman & van der Plas, 1971; Kuyl, 1980). For the purposes of this case study, the Gulpen Formation is considered the general source for all of the flint studied here. This is because the locations of the finds are associated with the geographical distribution of this formation, and it is generally richer in high quality flint than the Maastricht Formation (Kuyl, 1980).

During glacial periods of the Pleistocene, loess blanketed the region with thicknesses up to twenty meters on the tops of plateaus and terraces. The stratigraphy of the loess sequence for the last 300,000 years has been revealed by its quarrying (for brick making) and other digging activities (e.g. at Maastricht-Belvédère (Roebroeks, 1988), Veldwezelt-Hezerwater (e.g. Bringmans, 2006), and Kesselt-Op de Schans (van Baelen *et al.*, 2007), Haesaerts, 1985; Meijs, 2002). Hypothesized sequences correlate the loess stratigraphy with Oxygen Isotope Stages (OIS) documented in marine and glacial ice cores, based on regionally correlated litho- (pedo-) stratigraphy, biostratigraphy, and micromorphology (e.g. Haesaerts, 1985; van Kolfschoten & Roebroeks, 1985; Huizer, 1993; Haesaerts, & Mestdagh, 2000; Meijs, 2002).

Subsequent alluvial and colluvial erosion, especially associated with agricultural tillage has created a denuded landscape consisting of low, rolling hills, with the loess being thin or non-existent at plateau edges (Bolt *et al.*, 1980). Modern construction of roads and escarpments also affects the erosion regime in the region (de Roo, 1993). Where the loess cover is thin or missing, weathered chalk deposits and terrace gravels are commonly exposed along with Paleolithic and Neolithic surface finds, which are especially common on south or southwest facing slopes (Groenendijk & De Warrimont, 1995; Kolen *et al.*, 1999).

The present northwest European climate ranges from cool to cold winters with high precipitation to relatively warm summers with moderate precipitation. During the Pleistocene, the regional climate fluctuated between glacial and interglacial conditions. Cold and dry climate with steppic vegetation and small, clumped populations of arboreal species typified glacial periods. Interstadial conditions promoted the moderate return and expansion of coniferous tree species populations, but were relatively short lived. Interglacials saw warm to temperate climatic conditions with the re-establishment of dense mixed deciduous forests (van Andel & Tzedakis, 1996; Caspers & Freund, 2001). Ecological and climatic stability during interglacials is represented in low elevation loess sequences in the form of palaeosols, while thick, massive loess deposits and cryogenic features indicate paraglacial conditions. Erosion occurred during both climatic regimes, but is thought to have been most severe during the onset and decline of interglacial stages.

The earliest documented occupation of the region comes from the sites of Kesselt-Op de Schans in Belgian Limburg and Maastricht-Belvédère in Dutch Limburg (Roebroeks, 1988; van Baelen *et al*., 2007). These sites have revealed hominin presence, in the form of flint knapping debris, between 300–250,000 years ago, and possibly earlier. Paleolithic hunter-gatherers are commonly thought to have preferred lower elevation fluvial contexts for habitation (e.g. Gamble 1999), but the abundance of Paleolithic surface sites found in the uplands of most northwest European river catchments indicates a varied use of the entire landscape (e.g. Roebroeks & Tuffreau, 1999; Kolen *et al*., 1999; Glauberman, 2006). Around 8,000–6,000 years ago, the first Neolithic farmers to inhabit the region built settlements on the tops of plateaus and terraces, deforesting these areas (e.g. de Grooth, 2005; Schreurs, 2005). Two more waves of deforestation occurred during the Roman and Medieval occupations due to implementation of intensive cultivation of most areas of the landscape with low slope angles (Renes, 1988). Deforestation of the uplands led to erosion and subsequent deposition of loess (silt loam) in the low elevation parts of the landscape.

Within the region of Dutch and Belgian Limburg, there are a few identifiable flint varieties based on macroscopic characteristics of color and texture (Buurman & van der Plas, 1971). The varieties are usually named after locations of Neolithic or recent flint and limestone quarry sites. The most common flint type in the region is known as Rijckholt flint, named after the extensive Neolithic flint mine complex located near Sint Geertruid, The Netherlands. This black, grey, or bluish flint originates predominantly in the upper beds of the Gulpen limestone Formation. The context of prehistoric procurement for this flint type ranged from chalk outcrops, to river gravel contexts, to *eluvial* or weathered chalk deposits. Based on cortex characteristics within Paleolithic artifact assemblages, it is common to encounter flint that originates in eroded weathered chalk deposits, fluvial flint nodules with a smooth rolled outer surface, and low frequencies of fresh chalk flint. However, flint mining during the Neolithic produced vast amounts of fresh chalk flint. During Roman times, flint was also mined in large quantities for use as building material, and presents a typical chalky-white, fresh outer surface. Thus at different times, people accessed different flint beds within the local limestone stratigraphy.

Microscopic Analysis

To characterize the variability of flint patinas in the Limburg region, we collected and analyzed a small sample of five artifacts (Table 3). With respect to chronological age, we assign them to the Paleolithic, Neolithic, and the Roman periods, based on occurrence and typology. With respect to raw materials, we consider them all to be Rijckholt flint, a dark grey to blue flint, with fine, light colored inclusions. All of our sample locations were near the Neolithic Rijckholt flint mines, and local natural exposures exhibit a similar lithology. With respect to site setting, with one exception the artifacts were collected from plowed surfaces in either south-

Table 3. Sample artifacts studied for this research.

Artifact	Patina Description
Roman Wall Flint	Extremely light to No Patina
Neolithic End Scraper	No Patina
Paleolithic Flake	Ventral = Porcelain Dorsal = *Vermiculé*
Paleolithic Biface Fragment	All Surfaces Porcelain
Paleolithic Flake Fragment	All Surfaces *Vermiculé*

southwest facing, summit, shoulder, or backslope positions. The Roman wall flint was collected from a grassy surface, and had fallen out of a wall that faces southwest.

Thin sections (thickness=30 µm) were cut from all artifacts in the sample, with the cuts designed to capture patina exposures at right angles. The sections were studied using a petrographic microscope under normal and cross-polarized light, at magnifications ranging from 4–40X. Descriptions of the artifacts consist of general overviews of technological and typological features, followed by descriptions of the thin sections. Figures 4–13 contain artifact and thin section descriptions, and results are summarized below.

1. A variety of patina types were present.
2. Paleolithic artifacts are characterized by a stronger patina, but not necessarily because they are older. Rather, they were formerly in a moist buried setting.
3. A porcelain patina, typified by smooth and dense bands of lighter-leached and darker-dispersed materials, is related to an intense and regular pattern of surface weathering. The depth of weathering indicated by the lowest dark band of dispersed ferruginous material is usually deeper than that observed for other patina types.
4. *Vermiculé* patina is strikingly different from porcelain patina. Viewed in thin section, the white dendritic pattern reflects localized whitenings surrounded by the matrix of dispersed dark material.

Discussion

The variability in patina types observed at Lauw, and within our sample of artifacts of different ages corroborates the previous interpretation that neither the type nor the degree of patination can be used to date artifacts, unless all other variables are controlled for. This is demonstrated quantitatively for the Lauw site, where we found no significant difference in patination between surface and buried artifact assemblages.

Paleolithic and Neolithic surface finds are estimated to have been exposed on the surface since at the earliest Neolithic times, but more likely since medieval times when deforestation and agriculture began in earnest. Paleolithic surface finds most likely originate in layers beneath meters of loess deposited during the last glacial maximum of the Weichselian, upon which the Holocene soil has formed. It logically follows that Paleolithic finds in this scheme would have spent much more time in a buried matrix setting than the more recent artifacts.

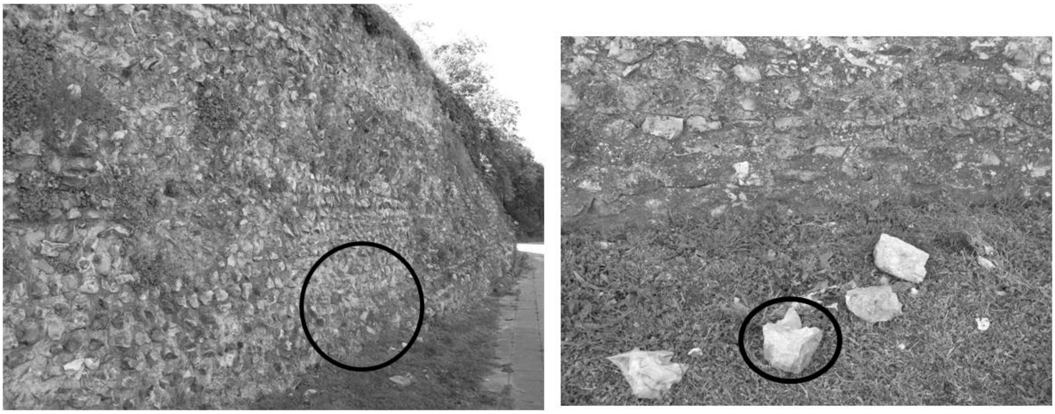


Figure 4. Roman Wall Flint: Nodule of Rijckholt flint found in a Roman wall in Tongeren, Belgium (Maximum Dimension=111.6 mm, Maximum Thickness=61 mm). Black circles indicate location of nodule. Cortex is present on two surfaces of nodule. Exposed surface was fractured during manufacture of wall. Thin section was cut to capture this exposed surface.

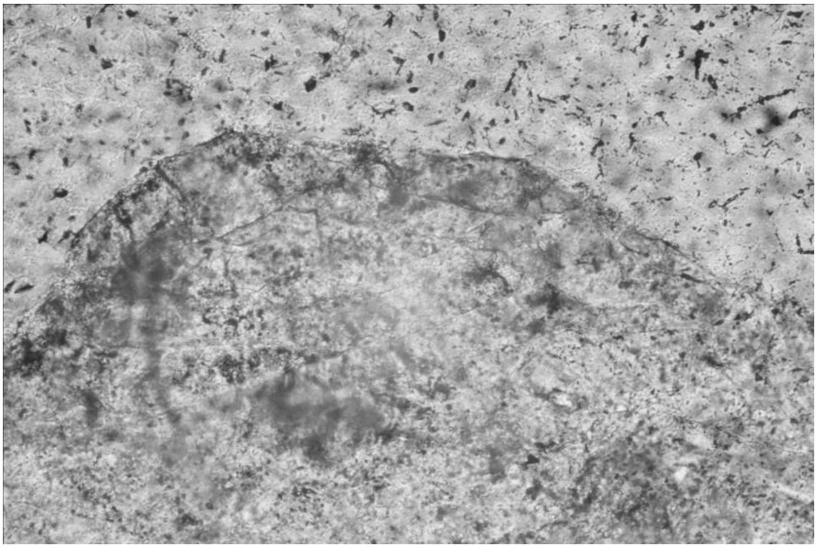


Figure 5. Thin Section 40 X, Plain Polarized Light (PPL); Field of View: 350 µm. This sample does not present any form of patination discernable with the naked eye. In thin section, the edge of the sample does not indicate any dispersal of ferruginous materials, and no zones of leaching can be observed. The flint is homogenous throughout, and no indications of the development of a weathering rind can be observed.

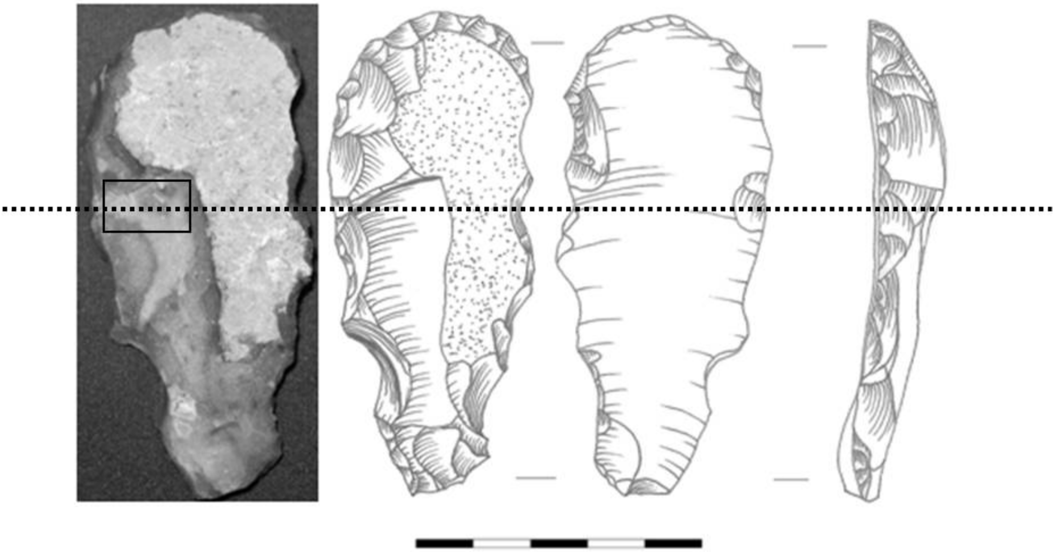


Figure 6. Neolithic End Scraper: The retouched end scraper, typical of the Michelsberg culture (E. Rensink pers. comm., 2004), was manufactured on dark grey-black Rijckholt flint (Length=90.3mm, Width=37.2 mm, Thickness=10.4mm). This artifact does not present any patina to the naked eye. Location of thin section indicated by dashed line. Scale bar=5cm.

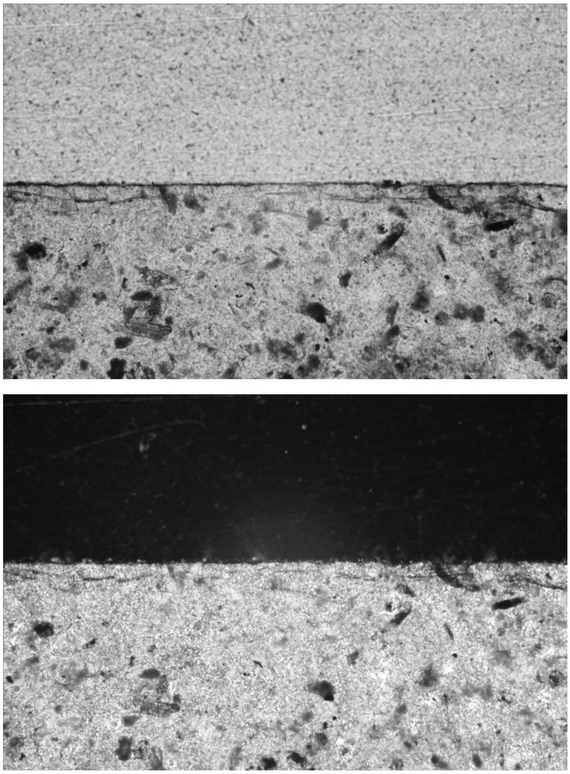


Figure 7. Thin Section: Top: 40X, Plain Polarized Light (PPL); Field of View: 350 µm. Bottom: 40X Cross Polarized Light (XPL); Field of View 350 µm. In thin section, the structure of the flint is homogenous. The worked edges do not present any evidence of dispersal of ferruginous materials, or leaching, nor the development of patina.

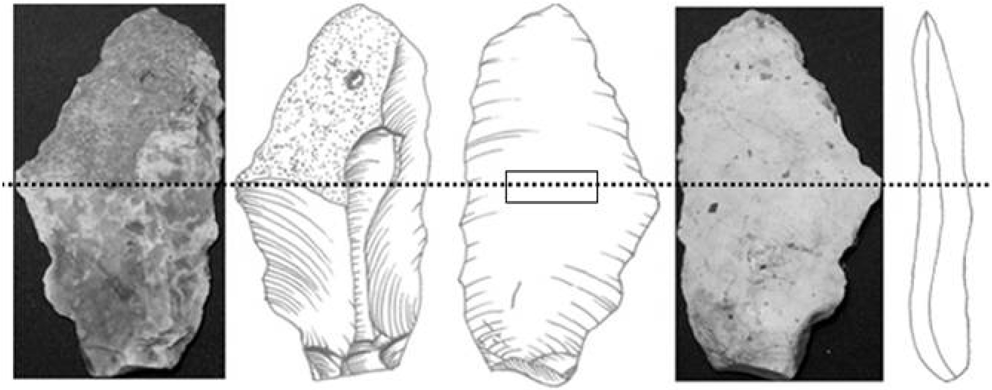


Figure 8. Paleolithic Flake: This artifact is determined to be of Paleolithic age based on technological characteristics. The flake is long and thin (Length= 87.5 mm, Width=44.6mm, Thickness= 10.7 mm), and was struck at an earlier stage of core reduction, as cortex makes up about 25% of the dorsal surface. The three flake scars on the dorsal surface present a convergent scar pattern suggests an early stage within a Levallois reduction sequence. The flake's ventral surface fits the typical porcelain description. The dorsal surface presents a *vermiculé* patina. Location of thin section indicated by dashed line. Scale bar=5cm.

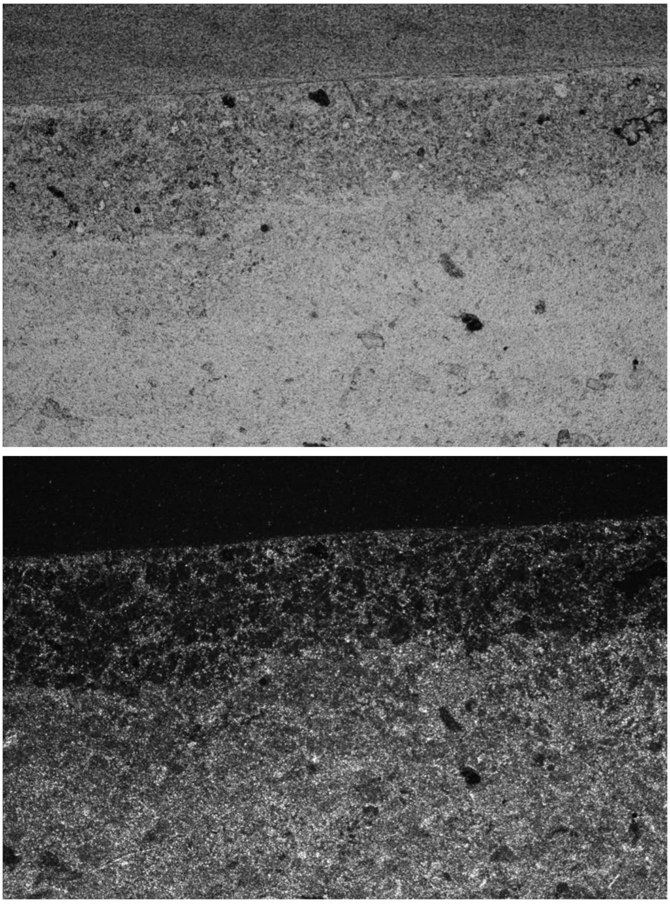


Figure 9. Thin Section: Top: 10X, PPL; Field of View: 1620 µm. Bottom: 10X, XPL; Field of View: 1620 µm. n thin section, the porcelain patinated ventral surface edge shows a distinct solid grouping of dispersed ferruginous material beneath and along the edge. Iron oxides are present within this layer. This indicates a relatively deep depth of weathering, and the morphology of the banding is relatively regular and well developed. Exterior to this is a lightly developed band of leached material indicated by the lighter color.

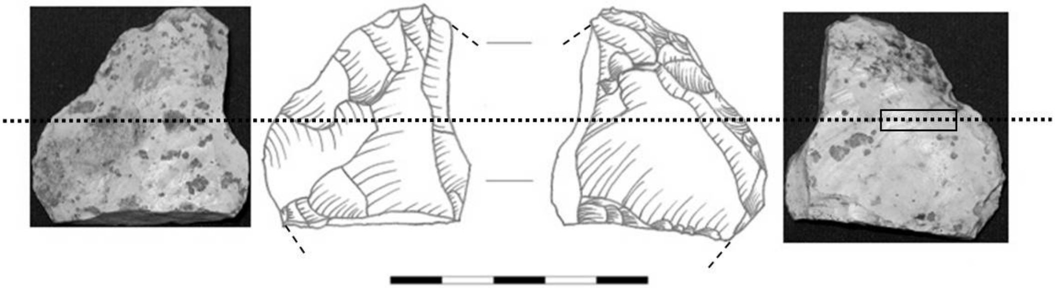


Figure 10. Paleolithic Biface Fragment: This artifact is determined to be of Paleolithic age based on technological and typological features. It is worked on both surfaces, and is quite thin (Length=45.1 mm, Width=42.2 mm, Thickness=13.5 mm). A convex, slightly retouched or shaped edge is still remaining on the piece. It is broken on two of three edges, all of which are patinated. Its patina is of the porcelain type on all faces. Location of thin section indicated by dashed line. Scale bar=5cm.

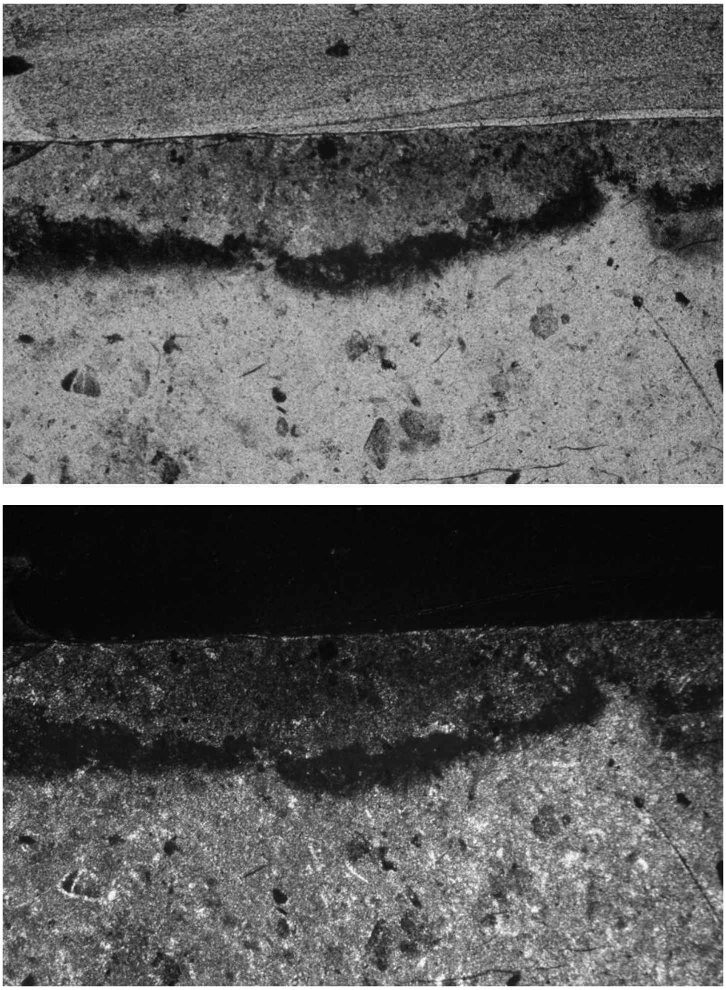


Figure 11. Thin Section: Top; 10 X, PPL; Field of View: 1620 µm. Bottom: 10X, XPL; Field of View: 1620 µm. The edge shown here presents a deep depth of weathering indicated by a relatively solid and continuous band of dark dispersed ferruginous material. The absolute edge of the artifact displays a darkened cloudy appearance, sometimes with a thin band of light material along the edge. The deep location of the dark band of dispersed ferruginous material indicates intense patination of this artifact that is relatively homogenous on all major surfaces.

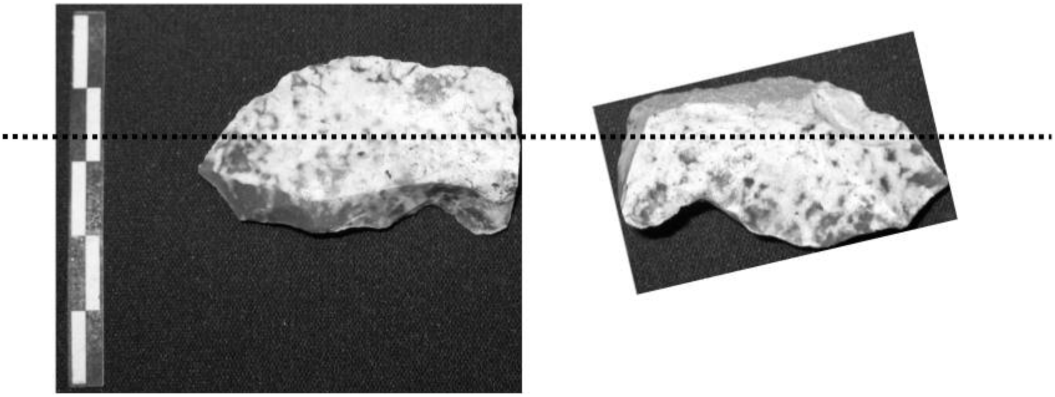


Figure 12. Paleolithic Flake Fragment: This artifact is a broken flake with a *vermiculé* patina on all surfaces (Length=37.8 mm, Width=42.7 mm, Thickness=10.4 mm). Location of thin section indicated by dashed line. Scale bar=5cm.

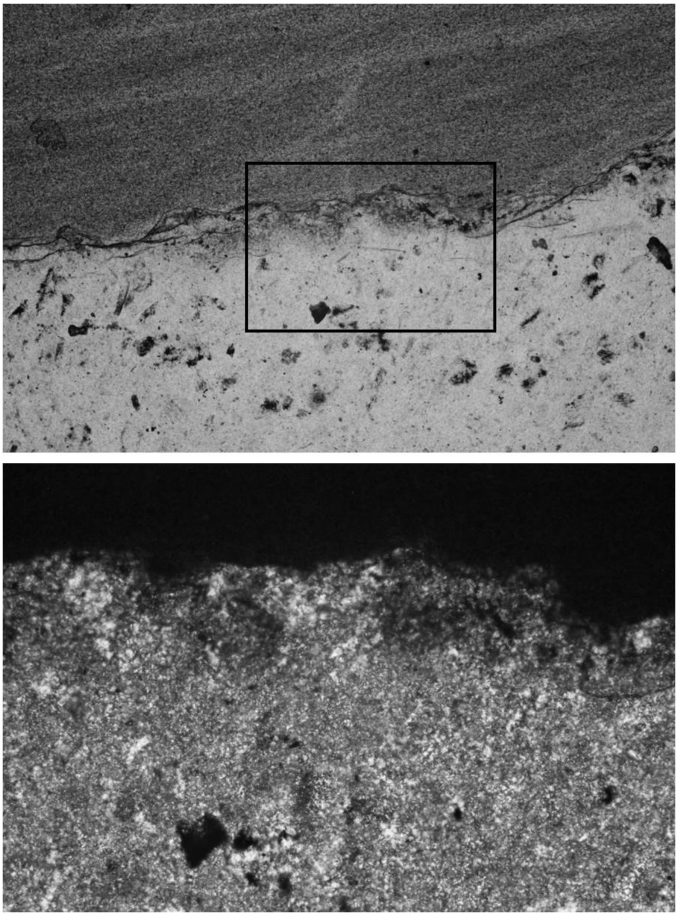


Figure 13. Thin Section: Top: 10X, PPL; Field of View: 1620 µm. This specimen allows for the examination of typical *vermiculé* patina on all major surfaces. Viewed in thin section, there exists a light colored band at the edge of the piece that is disconnected and interrupted with darker material. A darker cloudy layer lies beneath this followed by a lighter layer of leaching. The leached horizon is then followed by a darkened, diffuse and cloudy band of dispersed ferruginous material. Box indicates area under higher magnification in bottom figure.

Bottom: At higher magnification, (40X; XPL; Field of View; 350 µm) it is clear that the exterior dark band interrupts the lighter material at the edge. These interruptions are the locations where the section intersected the white dendritic pattern typical of *vermiculé* patina. Blown up area indicated by box in top figure.

The sample of Roman wall flint analyzed in this study acts as a 'natural experiment' in patina formation under sub-aerial conditions. According to Vanvinckenroye (1985), the Roman wall surrounding the town of Tongeren (Belgian Limburg) was built around 200 AD. In c. 500 AD the Romans used the town as a quarry, and removed all of the limestone blocks from the exterior of the walls. Since flint nodules set in a limestone based mortar were used to compose the inner structure of the wall, from 500 AD until the present the flint was exposed to the elements, and provides a historically documented time range of sub-aerial exposure of flint, outside of a soil context, of roughly 1500 years. The limestone quantity and geo-chemical make-up of the mortar is unknown. However, if the limestone in the mortar was a factor concerning patination, then the flints should be intensely patinated due to increased alkalinity. Since this is not the case, it is suggested that the mortar is not creating an especially favorable micro-environment for flint patination.

The review and case studies presented here indicate that depositional context is a far more important control on the type and degree of patination than is the duration of sub-aerial exposure. The clearest examples come from the Paleolithic artifacts originating in buried gravelly layers, as at the site of Lauw. They are intensely patinated, despite being buried for much of their taphonomic history. Artifacts with a porcelain patina on all surfaces may indicate more intense, regular patination, likely within a buried setting where the ambient groundwater is pervasive and alkaline. In contrast to speculation that patina *formation* is associated with erosional processes, we find it a more parsimonious explanation that the weathering of artifacts discovered in unconformable contexts occurred in their relict depositional settings and not as a direct result of the erosional activity responsible for unconformities.

Specimens within our sample exhibiting a *vermiculé* patina are also diagnostic of formative environment, in this case the root zone, especially for those artifacts with asymmetric patterns. Finally, that variables other than sub-aerial exposure must account for differences in patina is illustrated by the great variety of patina types, degree of development, and asymmetries, all for collections of comparable age.

In Figure 14, we provide simple visual model for the flint patination processes of silica/quartz hydration, dissolution, and re-precipitation in diverse depositional settings. This model is based on synthesis of results of experimental studies on silica/quartz dissolution and diagenesis as discussed above, and the formation of hydration layers on pure silica glass (Yanagisawa *et al.*, 1997: Figure 7: 1168). We cite the processes of biogenic silica diagenesis and precipitation of quartz that originally form flint nodules in carbonate sediments (e.g. Zijlstra, 1987) as similar to those that contribute to patina formation. We envisage patinas as developing through dissolution and re-precipitation of silica in the form of a thin film or weathering rind, in reaction to unique depositional micro-environments. This model is in line with seminal research on flint patination and gloss development (e.g. Hue, 1929; Bellard, 1930; Curwen, 1940; Kelly & Hurst, 1956; Goodwin, 1960; Schmaltz, 1960; Hurst & Kelly, 1961; Rottländer, 1975, 1989; Howard, 1999, 2002). In contrast to pure silica glass however, as silica/quartz dissolution proceeds in flint, impurities such as carbonates, clay minerals, iron and iron sulfide, and manganese oxides are dispersed and collect at variable depth and density beneath the weathering edges of

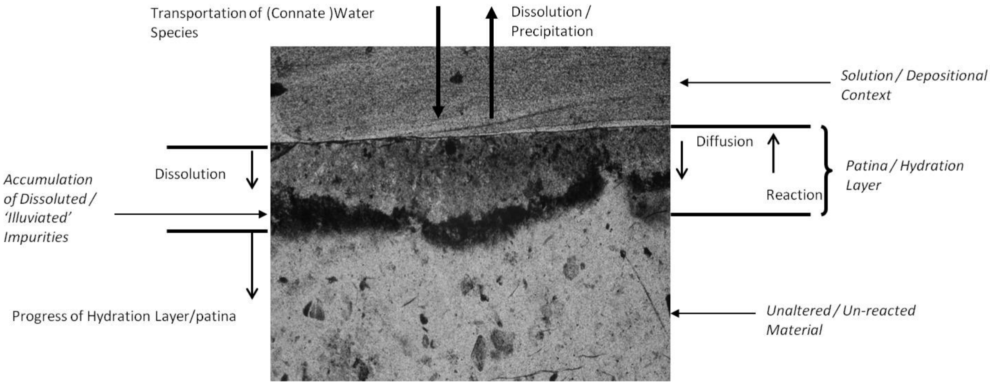


Figure 14. Simple dissolution model for patina formation process. Based on model of hydration layer formation during dissolution of silica glass (Yanagisawa *et al*., 1997, Figure 7: 1168), and using Figure 11 as an example.

artifact surfaces (see Figure 14). In taphonomic terms, once a flint nodule is removed by humans from its context of procurement, fractured in the act of knapping, and after artifacts are discarded and enter a depositional context, 'fresh' surfaces are subject to dynamic physiochemical micro-environments. If micro-environmental conditions are conducive, surfaces in contact with depositional matrix begin to undergo renewed silica/quartz dissolution, hydration, and re-precipitation. The intensity, localization, and duration of these processes are related to the internal structure of the raw material, its interaction with the geochemically dynamic surrounding matrix, and archaeological site setting and formation processes.

Conclusion

We hope that these preliminary quantitative and qualitative case studies inspire future bio-geochemical research on the patination of flint artifacts and depositional contexts, in order to tease apart the many variables involved. Continuing this line of research, regional artifact assemblage analyses, excavation sampling, and geochemical studies are ongoing, including enlarging the sample of thin sectioned artifacts. Research already underway by colleagues is focused on building a large sample set of variable patinas described in thin section. Further laboratory and fieldwork using a variety of analytical methods to better define correlations among patina types and depositional contexts are ongoing. We hypothesize that continuing these lines of inquiry into patinas within the framework of "flaked stone taphonomy" will aid in reconstructing relict depositional contexts from patina features on artifacts in secondary or surface contexts. After considering preliminary observations from a small sample of thin sections, data from local surface sites, and inferences about the geochemical influence of temperature, site aspect, plant roots, humic acids, and soil pH, we were unable to falsify this hypothesis.

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