A geological collection and methodology for tracing the provenance of Palaeolithic colouring materials

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Abstract:

Although prehistoric sites frequently contain numerous fragments and traces of many different kinds of colouring matter, intensive study of this type of archaeological remains began only recently. Such studies, aimed at determining how raw materials formed and changed over time, and how they were transported by the groups of humans who used them, are extremely valuable as they reveal shared strategies, that is, cultural traditions and the spaces in which they developed. The scope of this paper focusses on the description of the main geological contexts in which ferruginous colouring materials form and are found. In the framework of a collective research program called Pigmentothèque (iron- and manganese-rich rocks and minerals library), geological surveys are conducted taking into consideration the geological settings in which colouring materials are present and using a common record and sampling methodology which is followed by petrophysical, mineralogical and chemical analyses based on a shared procedure and vocabulary. In order to go beyond descriptions based solely on colour and chemical composition, we describe the great variety of iron-rich materials that can be used to obtain colouring matter. This diversity in the formation and evolution of iron-rich materials must be taken into account when trying to understand past humans’ choices of raw materials, their provenance and the anthropogenic and natural modifications they have undergone. We also describe criteria for recognising cohesive remains of colouring matter during archaeological excavations, so these artefacts can take their place alongside other mineral resources in helping improve our understanding of past societies.

Keywords: iron-rich materials; provenance; sourcing; ochre; pigment; Palaeolithic; reference samples; petroarchaeology


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1. Introduction

Scholars have been interested in the utilisation of colouring matter since the earliest days of research into prehistoric cultures (e.g., Lartet & Christy 1875: 60-61, 94, 109, 297; Moissan 1902; 1903; de Mortillet & de Mortillet 1900: 555; Rivière 1887: 196), but studies of this category of archaeological remains from the perspective of chaînes opératoires began only about a decade ago. Colouring matter is often referred to as “ochre”, a term with a multitude of sometimes contrasting meanings that has been applied to everything from black pigments derived from manganese-rich materials to the reds, oranges and yellows obtained from iron-rich substances. This lack of precision can be attributed partly to the word’s roots in the Greek ῥκρα, from ῥκρα, which simply means pale, haggard or wan. Another, perhaps more important, explanation for ochre’s widely divergent, almost antithetical meanings, is the fact that it has long been used interchangeably to refer to colour, colouring matter and raw material (Salomon 2009: 46, 51-52; Triat 2010: 16-17; Tromeur 1998: 5-9). This lexical vacillation is omnipresent, but it means the term ochre (ocher in US English) provides little information about either the colour or hue (yellow, orange, red, brown, light, dark, etc.) or the material (in its natural state or transformed by humans, pigmentaceous minerals, rocks rich in pigmentaceous minerals).

In addition, colouring matter occurs in numerous forms, ranging from blocks and fragments, either in their natural state or modified by human actions, to its most common form: small flakes or powders, in varying states of preservation. Powders are found mixed into sediment, daubed on rock walls and applied to the surfaces of all types of artefacts, including knapped and unknapped stone tools, tools made from hard animal tissue, body ornaments, portable art pieces, and, in some funerary contexts, on skeletons. Nevertheless, despite the wide occurrence of colouring matter, scholars have only recently begun investigating its provenance and production. As for siliceous matter and shells, studies of archaeological colouring matter can provide insights into the journeys undertaken by past humans and thereby throw light onto patterns of movement of human groups within a geographical area, and even patterns of land use.

The first step in understanding Palaeolithic supply strategies, the exploitation of colouring matter, where it was used, and the individual and collaborative effort invested in the technological and value systems involved is to identify the different raw materials available in the environment and the characteristics they acquired as they evolved. By analysing raw material exploitation methods, technological possibilities and constraints, and individual and collective skills, it is possible to determine shared strategies and knowledge, and technical practices and cultural values. Identifying the sources and characteristics of the resources used is fundamental to understanding chaînes opératoires. It also provides insights into the choices the resources’ users made and the links between sequences (procurement, technical transformation, utilisation).

A Collaborative Research Project (PCR) called Pigmentothèque (a colouring matter library), led by Emilie Chalmin and Hélène Salomon (financed by the Auvergne-Rhône-Alpes Regional Council Department of Cultural Affairs), was set up to address these issues. This paper presents an overview of the wide diversity of the geological contexts in which iron-containing materials may be found. It describes the methodological framework drawn up for the Pigmentothèque’s research and presents the project’s collection of iron-rich rocks in order to show how this approach can be used to investigate ferruginous-matter procurement strategies (Chassin de Kergommeaux et al. 2021). Although the examples presented in the following are mainly French, they can be applied to a wider geographical and geological area (for instance, Dayet et al. 2017; MacDonald et al. 2018; Mauran et al. 2021; Velliky et al. 2019).
2. The issue of provenance: of territories and materials

2.1. Colouring raw materials, circulation networks and territory

Prehistoric territories are defined by identifying cultural groups with codes and norms founded on shared knowledge (Aubry 2005; Bon 2009: 250). Although the notion of territory differs from one discipline to another, prehistoric archaeologists consider a territory to be a culturally occupied space (recognized by groups that live within the space) that is exploited economically and where culture, rituals and socially-constructed and material resources are handed down from generation to generation (Binford 1979: 259; Godelier 1984: 101-115; 1986: 90-102; 2009: 97). By ensuring access to mineral and living resources, groups of humans staked out territories that were constructed and deconstructed over time and which can be seen as networks of places made of relationships between materials, humans, settlements and movements (Binford 1980; Bon 2009: 254; Delvigne et al. in press; Gould & Saggers 1985). Although this is a major issue in prehistoric archaeology, identifying the area of prehistoric territories on the basis of linear links between supply location and settlements where materials were left comes up against major pitfalls. Indeed, the transport of resources between one point and another can be handled by: (i) several different groups not recognising a common identity, but exchanging raw materials from one group to another, or (ii) one group crossing the territories of other groups in order to obtain resources. Therefore, the movement of raw materials cannot be seen as a direct reflection of the territorial hold of a given group. For these reasons, we are not able to distinguish direct acquisitions and exchange, and thus to establish the limits of territories through the acquisition of raw materials. On the other hand, the approach allows us to reconstruct networks of resources’ circulation and, by extension, networks of human circulation at a given period. Hence, studies of prehistoric societies are based on recognising systems for exploiting resources within networks of places e.g., between several human settlements, mineral deposits, rock art sites (Bourdier 2013; Monney 2012).

The few ethno-historical and ethnographic documents that mention the procurement of colouring materials (mostly red) tell of how costly such expeditions were for human groups, whether because of the difficulty of the journeys (long, dangerous), the exchanges of goods that took place during them, or the sometimes violent contacts with other groups that held sovereignty over the resources being sought. Jones (1984) recounts the quest of “ochre seekers” in Australia, small groups separated from their tribe that travelled up to 1,000 km across adversaries’ territories, paying rights of way and obeying the access rules and codes needed to obtain a red material (called “ochre”) that was considered sacred and known for its quality. Other scholars have described similar expeditions by the OvaHimba in Namibia (Rifkin 2012a) and by various hunter-gatherers in North America (Kenyon 1980: 151). But these epic journeys are unlikely to be the rule. Because the subject of how nomads obtained the colouring raw materials they needed has rarely been addressed, it is the most surprising practices that have grabbed the attention of observers, who have described these practices without specifically considering the material being sought. Thus, cases of collecting materials close to dwellings may not have been described. Moreover, it is control over socially constructed and material resources, not the distances travelled, that define living spaces and frequented places (Godelier 1984: 105-106; 1986: 93-94).

2.2. History of research on the provenance of colouring matter used during the Palaeolithic

Unlike the provenance of the siliceous raw materials used to make tools, which has been studied since the earliest days of prehistoric research (Damour 1865), the geological and
geographical origins of the raw colouring matter found in prehistoric settlements and rock art sites has only recently attracted the interest of researchers. Because prehistorians’ interest in colouring matter initially focused on authenticating, conserving and producing replicas of decorated caves (Moissan (1902; 1903); Courty (1902); then Couraud & Laming-Emperaire (1979) at Lascaux; Cabrera-Garrido (1978) at Altamira), it was not until the 1980s and 1990s that scholars began paying attention to colouring matter and coloured materials in contexts without proven rock art (Lower and Middle Palaeolithic, settlements; see Audouin & Plisson 1982; Beyries & Inizan 1982; Beyries & Walter 1996; Couraud 1983, 1991; Demars 1992; Onoratini 1985; San Juan 1990). The scientific value of these remains has now been generally accepted, following a multitude of studies aimed at analysing and characterising the vast corpus of cohesive colouring matter that has retained its petrographic structure, whether it is raw or mechanically processed, rather than colouring matter applied to tools, portable art objects or rock walls (Beck et al. 2012; Billard et al. 2016: 17-20, 221-226; Dayet 2012; Pradeau 2015; Pradeau et al. 2014; Regert 1995; Salomon 2003; 2004; 2009). To date, these studies have tended to adopt a site-centred approach, focusing on an area around a specific archaeological site. Pradeau’s (2015): 166-170 systematic study of certain types of ferruginous rocks is a notable exception to this rule.

In addition, most studies have focused on chemical and mineralogical analyses of colouring materials, especially elemental analyses (see Salomon et al. 2016, for a summary), and neglected the rocks’ petrographic characteristics. However, elemental analyses alone rarely provide sufficient information to confidently attribute an archaeological object to a geological formation or a source (Beck et al. 2012; Dayet et al. 2015; Eiselt et al. 2011; Goemaere et al. 2016b; 2016c; MacDonald et al. 2018; Pradeau 2015: 248-254; Pradeau et al. 2016; Salomon et al. 2014; 2016). Hence, geochemical and mineralogical analyses must be combined with petrographic analyses, which can throw light onto how materials have evolved, both chemically and physically, between their formation and their discovery at an archaeological site. Comprehending the multiplicity of these rocks and minerals, taking into account both the great diversity of modes by which they formed and evolved and the variability that occurs within deposits, is a prerequisite for determining the source of a sample of colouring matter. The present paper helps meet this need by providing brief descriptions of the materials used as colouring matter and the main settings in which they formed.

3. Rocks and minerals used as colouring matter during the Palaeolithic

Materials used as colouring matter contain a mineral pigment that, when reduced to a powder, can give its colour to other materials, either by masking the initial colour or by blending with the substrate (Pradeau 2015: 35-36). The colouring materials used during the Palaeolithic were derived from a wide variety of rocks (Onoratini 1985), most of which were composed of or coloured by iron ox(hydrox)ides (reds, yellows, browns, oranges, purples, blacks) or manganese ox(hydrox)ides (browns and blacks). Such rocks form in many different settings. Hematite (α-Fe₂O₃, red to violet) often occurs in association with goethite (α-FeO(OH), yellow to brown) and with mixtures of other iron ox(hydrox)ides showing greater-or-lesser degrees of hydration and crystallisation (formerly called limonite) (Cornell & Schwertmann 2003: 9-19). Manganese oxides and hydroxides (blacks), either pure or containing barium and other cations, are components of many minerals (Chalmin 2003: 41-76).

Although Palaeolithic humans used only a small number of colours, they occur in a wide range of shades due to differences in the crystallinity, granulometry and relative proportions of each mineral, mixing with different mineral phases within a rock, and the rock’s porosity (Cornell & Schwertmann 2003: 409-468; Routhier 1963: 700-788; Salomon et al. 2019; Triat
As mentioned earlier, ochre is often used to designate all colouring materials that are rich in iron (or manganese) ox(hydrox)ides (or kaolin in some cases), whatever their colour (Brooks et al. 2018; David et al. 2019; Mackay & Welz 2008; Rifkin 2012b: 149; Watts 2002; Wreschner 1980). Nonetheless, other authors describe these materials more precisely as natural mixes of clay minerals and iron ox(hydrox)ides, possibly containing quartz (Bar-Yosef-Mayer et al. 2009; Cavallo et al. 2017; Cuenca-Solana et al. 2016; Dayet et al. 2017; Eisel et al. 2011; d’Errico et al. 2010; 2012; Glavenchuk 2012; Henshilwood et al. 2009; 2011; Hodgskiss & Wadley 2017; Hovers et al. 2003; Iriarte et al. 2009; MacDonald et al. 2018; Popelka-Filcoff & Charrison 2012; Rifkin 2012a; Rosso et al. 2014; Sañó et al. 2015; Velliky et al. 2018; Wadley 2013; Zipkin et al. 2017). However, the settings in which pigmentaceous materials formed, whether sedimentary (marine, continental, regolithic) or associated with magmatic, metamorphic or hydrothermal activity, vary greatly and thereby produce different mineral suites (Blot 2002; 2004; Denayer 2016; Jébrak & Marcoux 2008: 42-45; Rossi & Gasquet 2014). This is why the term ochre is no more suitable as a general term for all iron-rich pigmentaceous materials than as a description of their colour. Hence, ochre should not be used in place of more precise terms, especially because the great genetic and evolutionary variety of pigmentaceous materials makes them excellent geomarkers (Blot 2004; Dayet et al. 2017; Denayer 2016; Goemaere et al. 2016a; Jébrak & Marcoux 2008: 42; Pradeau et al. 2016; Rossi & Gasquet 2014; Thiry et al. 2006), as this paper aims to show in the case of ferruginous materials.

Iron-rich formations can be classified into three main types according to the source of the iron and the segregation mechanisms to which it has been subjected. In most of these formation types, bacteria may have contributed to (or even are responsible of) the concentration or oxidation of iron (Audra et al. 2011; Cavallo et al. 2018; Dubinina et al. 2012; Lenehan et al. 2017; Levett et al. 2020; MacDonald et al. 2019; Mamet & Boulvain 1990; Mamet & Préat 2003; Préat et al. 1999; 2000).

3.1. Type I: Sedimentary iron formations

Type I: Sedimentary iron formations (Figure 1: 1) contain iron that was deposited at the same time as the sediment or that was mobilised during diagenesis (Denayer 2016; Jébrak & Marcoux 2008: 344-352; Rossi & Gasquet 2014).

Banded-iron formations (BIFs) are Precambrian rocks formed by the chemical precipitation of iron and silica. They consist of alternating layers of iron oxides (hematite or magnetite, often black or silver) and red cherts, sometimes interbedded with calcareous shales (Figure 2: a-b), although they may also contain iron carbonates (siderite), silicates (garnetite or minnesotaite) or sulphides (pyrite). BIFs are the source of most of the world’s commercially exploited iron ore, with particularly large deposits in Australia, Canada and Africa (Cornell & Schwertmann 2003: 409 & 416; Jébrak & Marcoux 2008: 346; Robb 2005: 302-309).
Figure 1. Diversity of iron formations and evolution of deposits. Without attempting to be comprehensive, this diagram shows the main types of formation and most important weathering situations, in order to illustrate the idea of an evolutionary chain (Fernandes & Raynal 2006). Diagram: C. Chanteraud and A. Chassin de Kergommeaux, modified after Chanteraud (2020: 46).
Figure 2. a-b) Banded Iron Formation, Rio Tinto’s Marandoo mine, Western Australia, c-d) Oolitic ironstone (Clinton type) interbedded between Frasnian and Lower Famennian shales, Huy, Wallonia, Belgium, c) about 6 m high, d) scale bar: 2 mm e-f) Lias ferruginous marl interbedded with limestone, Molière, Gard, France, scale bar: 20 cm. Photos: a & b: A. Chassin de Kergommeaux, c: E. Goemaere, d to f: H. Salomon.

Oolitic ironstones (Figure 2: c-d) are sedimentary rocks containing iron derived from continental weathering. Most oolitic ironstones formed during the Phanerozoic. They frequently occur as red-to-brown, oolite-rich lenticular bodies interbedded with calcareous, clayey or sandy rocks that were deposited in shallow marine environments or, very rarely, lakes (Cornell & Schwertmann 2003: 416-420; Denayer 2016; Dreesen et al. 2016; Robb 2005: 300-301). Oolitic ironstones are composed of iron-rich ooids, which are small (less than 2 mm in diameter), concentrically layered spheroidal grains that form around a nucleus,
which may be a mineral grain, bioclast or lithoclast. The layers or the nuclei (or both) are made of iron ox(hydrox)ide (goethite, hematite), iron carbonate (siderite), iron silicate (berthierine) or iron chlorite (chamosite). Oolitic ironstones are divided into two types - called Clinton and Minette - on the basis of their composition and how they formed (Dreesen et al. 2016; Evans 1993: 257). For example, in Europe, Clinton-type oolitic ironstones formed during the Ordovician, e.g., in Normandy, France, (Dreesen et al. 2016; Goemaere et al. 2016a), during the Devonian, e.g., in southern Belgium and in the Eifel Mountains of Germany (Dreesen et al. 2016; Denayer 2016; Goemaere et al. 2016a) (Figure 2: c-d), during the Hettangian, e.g., in the Ardèche, France (Cayeux 1909: 720-726, 767-786), and during the Toarcian, e.g., in the Aveyron and Deux-Sèvres, France; deposits include ferruginous oolites with ferruginised ammonites, often called Ammonitico Rosso (Galbrun et al. 1994). Minette-type deposits formed during the Upper Bajocian, e.g., in Normandy (Pavia et al. 2015) and during the Aalenian and Bajocian, e.g., in Lorraine, France, and in Luxembourg (Dreesen et al. 2016; Waterlot et al. 1973: 186).

Ferruginous marls, mudstones, siltstones and sandstones (Figure: 2 e-f) are red or yellow, continental or marine sedimentary formations, most of which formed during the Upper Palaeozoic, Lower Mesozoic or Upper Cenozoic. These formations stand out clearly in the landscape. The iron, which may be of detrital or diagenetic origin, permeates the sediment and cements the grains. Diagenetic, authigenic and automorphic iron ox(hydrox)ides form by the oxidation of pre-existing minerals such as glauconite, magnetite, biotite and ferromagnesian minerals, or by the pseudomorphosis of goethite, biotite or pyrite (Cornell & Schwertmann 2003: 413-416; Vinchon 1984: 268-274).

Iron ox(hydrox)ide-rich matter also forms in other, more localised, mostly continental sedimentary formations. Bog iron stones (Denayer et al. 2011; Thelemann et al. 2017) are recent or sub-recent deposits that form in northern-hemisphere lakes and marshes when oxidation-reduction reactions result in iron precipitating out of iron-rich waters (Stanton 1972: 398-399).

3.2. Type II: Formations associated with mineralisations

Type II: Formations associated with mineralisations are mostly of hydrothermal origin. They are most frequently deposited as veins when minerals precipitate from hot aqueous fluids as they percolate through discontinuities in the rock (joints, faults, see Figure 1: 2 and Figure 3: a-d). Some syndiagenetic deposits are stratified. Iron in these mineralisation deposits is often associated with lead, zinc, silver, antinomy, barium, gold, copper, etc. (Blot 2002; Jébrak & Marcoux 2008: 57-63, 198-203, 333-342; Kholodov et al. 2012; Rossi & Gasquet 2014). Deposits are of limited geographical extent, measured in hundreds of metres, and geological maps do not always show their presence unless they are known to have been mined. In which case, maps tend to show the material extracted, rather than mineral composition of the ore body.

Mineralisations can form many different types of metallic body (shape and composition), including iron-lead-zinc deposits and iron oxide-copper-gold (IOCG) deposits, which are composed mostly of iron oxides and sulphides (Rossi & Gasquet 2014). Contact metamorphism allows mineralising fluids to penetrate the surrounding wall rock to a depth of a few centimetres (Figure 1: 2).
In addition, metasomatism, either by percolating fluids or by solid-state diffusion, can result in rocks being permeated, to a greater or lesser extent, by iron oxides, e.g., the ferruginous limestones at Pierremorte, Gard, France (Figure 1: 3 and Figure 3: e-f). Iron may be derived either from outside sources or from minerals within the surrounding rock (Jébrak & Marcoux 2008: 46-47).

Ferruginous springs (Denayer 2011) bring to the surface mobile iron, which then oxidises and precipitates to form crusts. Bacteria contribute to the oxidation and mineralisation of iron present in high concentrations in the water (Garilli et al. 2020; Handley et al. 2010; James & Ferris 2004; Mustoe 1981).
3.3. Type III: Formations containing concentrations of iron liberated by the continental weathering of pre-existing rocks

Type III iron oxide-rich rocks are common. This transformation, outlined below, is particularly favoured by warm, humid climates (Beauvais & Colin 1993; Kholodov et al. 2012; Triat 2010: 116-143; Widdowson 2007):

1. Leaching of soils and rocks by percolating rainwater, biological activity and hydrolysis;
2. Dissolution of iron-rich minerals (glauconite, pyrite, chlorite, phyllosilicates, etc.) and transport of the liberated iron ions;
3. Deposition, concentration and trapping of iron when Eh and pH conditions change due to contact with either carbonate rocks (limestone, dolomite) or different lithologies, and precipitation of iron in the form of sulphides and carbonates, which then oxidise (goethite, hematite).

These modifications give rise to formations composed of successive leached and iron-enriched horizons, with iron-rich hardpans, ferricretes, duricrusts or ferricrusts, layers of iron ox(hydrox)ide-rich pisoliths and lithoclasts, ferruginous-clay horizons and horizons containing fragments of weathered parent rock (Figure 4).

3.3.1. Type III A: Weathering profiles

Type III A: weathering profiles (Triat 2010: fig. 10; 123) are often referred to generically as laterites, alterites or ferrallitic soils (Figure 5: a-b).

- In-situ weathered horizons (alterite) (Beauvais & Colin 1993; Gourdon-Platel et al. 2000) occur when the weathered material conserves the architecture of the parent rock. These horizons generally contain fragments of the parent rock mixed with inherited minerals, newly formed minerals, including iron ox(hydrox)ides, and various types of concretions (Lozet & Mathieu 2002: 20).
Figure 5. Iron oxide formation in weathering profiles: a-b) Palaeosol formed on basalt, Mirabel, Ardèche, France, c-d) Iron crust formed in a Middle Cenomanian sand containing kaolinite and ferruginous sandstone horizons, La Capelle-et-Masmolène, Gard, France, e-f) Ochre profile, weathered Albian-Cenomanian glauconitic sand, Roussillon, Vaucluse, France, e) top: ferricrust with underlying hematite-rich clayey sand; bottom: leached kaolinite-rich horizon, f) yellow goethite-rich and red hematite-rich horizons, g-h) Terra Rossa on Upper Gargasian-Clansayesian calcareous-marl, Maury, Pyrénées-orientales, France. Photos: H. Salomon.
- Ferricrete, also known as iron duricrust, ferricrust or hardpan, occurs within well-developed weathering profiles (Figure 1: 4, Figure 4 and Figure 5: c-d) (Widdowson 2007).

- Laterite (Figure 4: a) is formed by the surface weathering of iron- and manganese-rich igneous rocks under wet tropical or equatorial conditions, which are conducive to intense chemical weathering. Lateritic soil profiles are characterised by alternating aluminium-rich (in the form of gibbsite and kaolinite) and iron-rich (in the form of iron oxides and iron hydroxides) horizons, with basal horizons containing numerous fragments of the parent rock (saprolite). Laterites subject to alternating wet and dry conditions are capped by an iron duricrust (Beauvais 1999; Beauvais & Colin 1993; Lozet & Mathieu 2002: 264-265; Petersen 1971; Triat 2010: 117).

- Ochres (Figure 4: b and Figure 5: e-f) are glauconitic sands or sandstones (hence of marine origin) that have been subject to continental weathering in warm, humid climates during laterization. The iron is derived mostly from the hydrolysis of glauconite into kaolinite. This weathering substantially alters the mineralogy and composition of the original rock, which becomes enriched in kaolinite (and other aluminium-rich minerals) and in iron oxides and hydroxides (Guendon & Parron 1985; Onoratini,1985; Triat 2010: 134).

- Terra Rossa (Figure 1: 5 and Figure 5: g-h) is a rarely used term describing the red clay residues left by the dissolution of limestones and dolomites (decarbonatation), with SiO₂ depletion and Fe₂O₃ enrichment. Terra Rossa forms on top of carbonate beds. This type of weathering (fersiallitisation) typically occurs in warm, sub-tropical or Mediterranean climates with variation between seasons (Lozet & Mathieu 2002: 457).

- Iron weathering deposits in limestone (Figure 6: a) form by the direct weathering of limestone into iron-rich clay and iron crusts. They occur on the surface of the limestone or as coatings in depressions and karst cavities (Salomon & Pomel 2005). The breccia structure is produced by weathering breaking up iron deposits that accumulated in the karst (Figure 6: a-4).

- Bauxite (Figure 4: c and Figure 7: a-b) is a sedimentary or residual rock composed of ox(hydrox)ides of aluminium accompanied by iron ox(hydrox)ides, clay minerals (kaolinite) and titanium dioxide minerals. It varies in structure but is often pisolithic. Bauxite may be either autochthonous (primary), produced by in-situ lateritic weathering of the parent rock (marl, calcareous mudstone, argillaceous limestone, schist), or allochthonous (redeposited), formed by materials from ferrallitic weathering deposits that are transported downstream, redeposited, often in karsts, and subject to further weathering (Guendon & Parron 1985; de Lapparent 1930: 176-191; Nicolas 1968; Valeton 1996: 55-182).

- Siderolithic iron or Bohnerz: the term “siderolithic” describes both a stratigraphic period (i) and a formation mode (ii): (i) a long-abandoned stratigraphic division corresponding to a period marked by strong continental weathering that was long believed to take place during the Eocene-Oligocene but, according to latest studies, can also be linked to the great late Jurassic-early Cretaceous regression (Théveniaut et al. 2007; Thiry 2011: 19-33; Thiry et al. 2005; Yans 2003), and (ii) to products of this type of weathering (lateritic duricrusts) that have been reworked to varying degrees and possibly stored in karst cavities and other sedimentary traps. They are often composed of goethite and hematite pisolithes, wrapped in ferruginous clays (Gourdon-Platel & Lambert 1986; Gourdon-Platel et al. 2000; Nicod 1996; Rosenthal 1991; Simon-Coinçon et al. 2000; Thiry et al. 2006).
Figure 6. Formation of a) Iron weathering deposits in karst: 1-2) Direct weathering of limestone to iron-rich clay minerals, 3) Leaching and precipitation of iron at strata surfaces or in karsts, 4) Erosion of upper strata and iron precipitation and accumulation in karst depressions; b) Cryptokarstic iron deposits: 1) Glauconite-rich sand deposit over older limestone strata, 2) Growth of tropical vegetation - leaching of iron by percolating acidic waters, limestone weathering and cryptokarst formation, 3) Humid, tropical climates accelerate karstification and iron precipitation at the contact between sandstone and limestone, 4) Quaternary erosion and weathering of iron formations. Diagram: A. Chassin de Kergommeaux (after Quinif 1993).
Figure 7. a-b) Allochthonous bauxite trapped in a Middle Jurassic karst, Cazouls-lès-Béziers, Hérault, France, c-d) Ferruginised limestone, Aalenian, La Rousse, Ardèche, France, e-f) Alluvial iron-oxide-rich pebbles in recent and Cretaceous alluviums, Vagnas, Ardèche, France, g-h) Colluvium with fragments of Eocene lateritic crust, Cussac, Périgord, France, g) white scale bar: 20 cm, h) pebbles measures around 5 cm. Photos: H. Salomon.
3.3.2. Type III B: Weathered mineralisation deposits

Gossan, also called iron cap (Figure 1: 6), is the oxidized cap of a mineral vein or ore deposit with Fe, Pb, Zn, Cu sulphides. Weathering of a sulphide body produces iron ox(hydrox)ides and segregation of leached elements, creating a characteristic cementation zone. Remarkable textures of sulphides replacement are often seen in the form of boxworks: honeycomb patterns of a mixture of hydrous iron and manganese oxide minerals that remains in the cavity after a sulphide mineral has dissolved. Their colour varies according to their mineral composition: Fe-ox(hydrox)ides (brown to red), Mn-ox(hydrox)ides (black), Cu-carbonates and sulphates (blue-green)(Blot 2004; Haldar 2018; Jébrak & Marcoux 2008: 475-484; Kholodov et al. 2012; Rossi & Gasquet 2014).

3.3.3. Type III C: Iron deposits formed by trapping

- Cryptokarstic deposits form when materials weathered in wet tropical climates (mostly weathered glauconite sands) accumulate in karst cavities (Figure 6: b). Percolating waters not only attack the limestone, accelerating karstification under vegetal cover, they also leach iron from glauconite in overlying sediments, which is then redeposited as a coating or crust at the limestone-sand contact (Quinif 1993; Salomon & Pomel 2005).
- Strata-bound replacement iron mineralisation (after Routhier 1963: 700-704) is an old expression. It occurs when goethite and iron hydroxide minerals showing various degrees of hydration and released by the weathering of overlying sediments precipitate at the contact between strata of different lithologies (e.g., limestone and shale), following a bedding plane (Figure 1: 8).

3.4. Other deposits formed by a combination of diagenesis, alteration and weathering

- Lahn Dill is a type of iron ore consisting mostly of hematite and quartz that was first described in the Dill and Lahn Valleys in Germany (several occurrences are also present in Central Europe as in the Renan massif, Harz, Eastern Thuringia and in the Eastern Sudets). It is produced by a combination of volcano-sedimentary deposition, diagenesis, and late hydrothermalism (Flick & Nesbor 1988; Flick et al. 1990; Nesbor 2007).
- Ferruginous and ferruginised limestones are limestones (Figure 7: c-d) in which the original calcite was partly or entirely replaced by iron ox(hydrox)ides during sedimentation or diagenesis, or as a result of hydrothermal injection, e.g., the Hettangian crinoidal limestones of Thoste (Boirat et al. 1980; Cayeux 1909: 7-33; Salomon 2019).
- Ferruginous hardgrounds (Figure 1: 9) are iron and manganese-rich crusts that form on top of, and cover all or part of, a carbonate layer when sedimentation slows greatly or stops, thereby allowing the sediment to lithify before subsequent beds are deposited. Intense chemical and biogenic weathering leads to the precipitation of iron and manganese ox(hydrox)ide. Hardgrounds may also contain traces of biological activity (Préat et al. 1999).
- Alluvial (Figure 1: 10 and Figure 7: e-f) and colluvial (Figure 1: 11 and Figure 7: g-h) deposits are large accumulations of allochthonous material, with grains up to the size of pebbles and cobbles, transported by flowing water (alluvium) or gravity (colluvium). Alluvial deposits contain rounded concretions, pebbles and cobbles which may be cemented into puddingstone (Figure 8: a). Colluvial deposits consist of angular to sub-rounded fragments and concretions (Figure 8: b) that accumulate at the foot of slopes or on gently sloping hillsides to form layers of intermittent extent and variable thickness (Denayer 2011: 37).

The rocks and minerals formed in the settings described above may then be highly modified by further weathering (Figures 1 and 8: c-d).
3.5. Deposits rich in non-oxidised iron and magnetite

Deposits in which iron-rich minerals occur mostly in the form of iron sulphides (pyrite, marcasite, mispickel, see Figure 8: e-f), sulphates (jarosite), carbonates (siderite), phosphates (vivianite) or silicates (chlorites, glauconite) are more or less (glaucnite, jarosite), even non-pigmentaceous. However, they may contain some pigmentaceous matter due to weathering and heating partially oxidising these minerals into hematite and goethite. Black magnetite may also oxidise into hematite.
4. The Pigmentothèque

In order to catalogue both this genetic diversity and the vertical and horizontal variability within deposits and geological formations, it is necessary to put in place a sampling strategy suited to each situation. Analyses of the samples collected, including their physical and chemical properties, and assessments of their accessibility, reveal the myriad types of potential resources and provide data that can be used to decipher the criteria that guided prehistoric humans’ choices of raw materials, which were governed by the availability of different resources and their intended use (Pradeau et al. 2016; Salomon 2019).

With this in mind, at the beginning of the 2000s several researchers began cataloguing deposits capable of supplying the types of colouring matter used at Palaeolithic rock art sites near the Ardèche River (N. Aujoulat, J. Monney). The Pigmentothèque was set up in 2016 to extend the area covered by this work and to further systematize the collection and analysis of samples. This Collective Research Project combines a research programme to develop and apply investigative methods and apps with a resource centre that houses data (photographs, measurements, quantifications, standardised descriptions), identification keys and collections of samples (both unprocessed and prepared) that can be used to answer questions about the colouring matter used in the past. The Pigmentothèque has also built up a database of the physical characteristics of rocks (including criteria that make a material exploitable, such as its mechanical properties, appearance, texture, etc.) for use in experimental and functional studies. The methodology developed by the Pigmentothèque is based on experience gained by the “Réseau de Lithothèques” interdisciplinary Collective Research Project (Delvigne et al. 2020; Fernandes 2015; Fernandes et al. 2019; Tuffery et al. 2019) and existing methodologies for studying archaeological colouring matter (see Chalmin & Salomon 2019; Chalmin et al. 2021a; Salomon et al. 2019, for detailed methodology and vocabulary).

4.1. Prospection: collecting information in the field

Possible sampling sites are identified by combining information contained in the French Bureau of Geological and Mineralogical Research’s (BGRM) archives with other sources of information, such as place names and satellite and aerial photographs taken at different periods (infoterre.brgm.fr, remonterletemps.ign.fr).

An app and field datasheets originally created for silicites (Chalmin et al. 2021a; Delvigne et al. 2020; Salomon et al. 2019; Tuffery et al. 2018; 2019) have been adapted to the needs of research on iron- and manganese-rich materials, which occur in a wide range of geological settings and lithologies. (The step-by-step documentation of the sampling spots are detailed in Salomon et al. (2019) and Chalmin et al. (2021a), were the attributes used with the app in the field and the definitions for each attribute are presented). Initial studies of the sources of raw materials used as colouring matter involved inspecting and describing fresh and weathered samples collected in the field, while checking parameters relating to each resource’s origin and stratigraphic position (stratigraphy, site effects, patina, geomorphology, geological and mining documents) (Delvigne et al. 2020).

4.2. Methods for characterizing colouring materials

The Pigmentothèque houses samples in the form of unmodified cohesive blocks, prepared blocks (polished sections and thin sections) and powders that can be subjected to petrographic, mineralogical, chemical and geochemical analyses (see available list and descriptions in Chalmin et al. 2021a; b; Chassin de Kergommeaux et al. 2021; Salomon et al. 2019).
4.2.1. Visual examinations on different scales

Following an iterative description at different scales from surface to volume enables to replace in a chronology the different characteristics (stigmata and compositions) inherited and acquired by the colouring matter during specific events of its “evolutive chain” (as proposed by Fernandes (2012: 172) and Delvigne et al. (2020)) (Figure 9):

- genesis: Intrinsic characteristics of the materials reveal their formation context: grains and other clasts, binding phases (cement and matrix), primary mineral assemblage, texture, etc.

- gitology: examination of the stigmata due to weathering and transport of the raw material prior to its collection give clues on the geomorphological location of the procurement.

- human modifications (techniques): techniques implemented in the past to transform the raw material such as separation, heating, powder production, mixing with other substances leave recognisable stigmata on and within the colouring matter (Figure 10).

- taphonomy: post-depositional modification of the colouring matter is marked by addition and loss of compounds and matter (Figure 10).
Lithological, petrographic, mineralogical (nature and association of minerals within the rock, degree of crystallinity) and geochemical (proportions of major, minor and trace elements) analyses are used to determine a signature for each formation, bed, horizon, or outcrop rich in iron or manganese ox(hydrox)ides and recorded in standardised description sheets (Chalmin et al. 2021a; Salomon et al. 2019). In addition, experience has shown the importance of first describing each sample’s mesoscopic characteristics (x10 to x150). Indeed, the first things prehistoric humans would have noticed about a rock, mineral, soil or weathering profile would have been its visual and tactile properties (colour(s), hardness, compactness, homogeneity/heterogeneity, colouring power). Preparing these descriptions is a simple procedure that can be used to document and analyse large archaeological collections in their entirety (Billard et al. 2016: 17-20, 221-226; Chalmin et al. 2021a; Dreesen et al. 2016; Pradeau 2015; Pradeau et al. 2016; Salomon 2009, 2019; Salomon et al. 2014, 2019).
All types of rock and colouring and coloured archaeological remains should be inspected visually - naked eye, stereomicroscope, polarising (transmitted and reflected) microscope, scanning electron microscope - as these analyses provide information on weathering of rocks and minerals both before, they were collected and after they were used. They also guide subsequent chemical and geochemical analyses, whether conducted on the object as a whole or on selected parts. Geological samples are categorised according to criteria set out in classification tables (e.g., Choquette & Pray 1970; Cojan & Renard 1999: 192-197, 402; Dott 1964; Dunham 1962; Folk 1959; Lundegard & Samuels 1980; Mount 1985; Pettijohn 1975: 543; Pettijohn et al. 1987; Prothero & Schwab 2014 :498; Udden 1914; Wentworth 1922), which enable most of the intrinsic quantitative and qualitative characteristics of colouring matter to be described (Chassin de Kergommeaux et al. 2021): the detail routine of macro- to microscopic description accompanied by the common vocabulary (in English and French), definitions (only in French for the moment), as well as qualitative and quantitative charts may be found in Salomon et al. (2019) and Chalmin et al. (2021a).

4.2.2. Chemical analyses

Complementary to petrographical determinations, elemental and structural analyses may give additional clues for cohesive colouring matter provenance (Beck et al. 2012; Chalmin et al. 2021b; Dayet 2021; Dayet et al. 2015; 2017; Goemaere et al. 2016b; c; MacDonald et al. 2018; Mathis et al. 2014; Mauran et al. 2021; Popelka-Filcoff et al. 2008; Salomon et al. 2016). X-ray diffraction provides semi-quantitative analyses that indicate the presence or absence of certain crystalline phases and their approximate relative abundance. Most elemental analyses of Pigmentothèque samples are carried out by proton induced X-ray emission (µPIXE) spectrometry and inductively coupled plasma (ICP) spectrometry, as these two methods have satisfactory detection limits (unlike portable X-ray fluorescence, which is commonly used in archaeometry) (Chanteraud et al. 2021). We systematically use the six geological internal “standards” presented in PCR Pigmentothèque’s reports. They were selected for their singular petrophysical and geochemical characteristics in order to compare analytical settings and campaigns, as well as measures obtained on diver sample types: cohesive non prepared blocks and fragments, patinated surfaces and fresh breaks, sections, homogenised powder, applied powder and micro-samples (Chalmin et al. 2021a; Chanteraud 2020: 96-106; Chanteraud et al. 2021; Chassin de Kergommeaux et al. 2021; Salomon et al. 2019).

These analysis methods are suitable for any specimen of geological colouring matter and a selection of archaeological objects, but non-invasive investigations are privileged for these latest. The set of analyses can be used to determine a geochemical signature that is linked to how the raw material formed and how it has transformed over time (Ambrosi & Nahon 1986; Beauvais 1999; Byrne & Kim 1990; Dill 1985; Dupuis & Beaudouin 2011; Green & Watling 2007; McQueen 2005; Monteiro et al. 2018; Zipkin et al. 2017). Therefore, it seems crucial to implement analytical methods that are sufficiently relevant, sensitive and precise to identify significant chemical signatures in relation to resources that may have been sought and exploited (Beck et al. 2012; Dayet 2021; Dayet et al. 2015; MacDonald et al. 2018; Mathis et al. 2014; Popelka-Filcoff et al. 2007; Salomon et al. 2016). In addition, we argue that these analyses make sense through an iterative approach (Figure 9). Nonetheless, colouring matter applied to an object is most frequently in powdered form, so it cannot be subject to petrographic analysis. In such cases, the chemical composition of colouring matter samples has to be compared with that of reference samples taking into consideration the very small quantities of colouring matter in residues and paintings and the environmental input (rock, sediments, post-depositional concretions and coatings, leaching and erosion) (Chanteraud et
al. 2021). With these numerous anthropogenic and post-depositional modifications, being able to systematically identify the type of geological formation from which a sample of powdered colouring matter was obtained is an obstacle that has rarely been overcome (Eiselt et al. 2011; Lebon et al. 2014). This is why we currently combine detailed, standardised descriptions of archaeological raw materials with chemical analyses conducted using standardised protocols, which we compare with appropriate reference samples (see for instance geochemical analysis presented in Chalmin et al. 2021a; Chanteraud 2020: 146-189; Salomon et al. 2019).

5. Conclusion

The general analytical methodology developed by the Pigmentothèque for studying archaeological collections is based on the need to determine the transformations a material has undergone, whether before collection by its prehistoric user, during its use or after it was discarded. Because these modifications destroy many of the raw material’s original properties, it is essential to identify them in order to determine the material’s fundamental signature and thereby ascertain its geological and geomorphological origin. As Figures 1 and 10 show, pigmentaceous rocks and minerals may be primary deposits, which are subject to transformations by circulating fluids and leaching. Erosion may also result in primary deposits being transported (by gravity, by runoff, etc.) and deposited in a new environment to form secondary deposits, where they are again weathered. After being collected by prehistoric humans, they may have been heated, ground into powders, separated, mixed with other substances and applied to different substrates. Leaching, erosion, capping and encrustation continue to modify these materials on rock walls and in sediments. Hence, the first step in retracing circulation networks and prehistoric supply strategies is to identify the different characteristics materials acquired as they evolved (Delvigne et al. 2020; Fernandes 2012: 22, 122-124). The fundamentals presented in this paper should be followed by other papers reporting examples illustrated at different scales, from the outcrop to the microscopic scale. Comparisons of chemical compositions can thus be based on the reality of these materials, taking into account the variability of the lithologies present within an outcrop or a formation and individualising the petrographic, mineralogical and geochemical signatures most likely to allow comparisons with archaeological remains (Chalmin et al. 2021a; b; Chanteraud 2020: 146-189).

Although ascertaining the geological and geographical provenance of colouring matter can throw light on geological knowledge and technological skills that are now lost, the processing of colouring matter to enable its use and the small quantities preserved make this endeavour extremely complex. Nevertheless, the wide diversity of lithologies from which these materials were obtained (formation and facies), each with its distinct petrographic, chemical and mechanical properties, makes it possible to recognise the criteria governing past choices and to relate these choices to cultural and economic factors, which were themselves conditioned by a combination of the material’s intended use and technological possibilities. These past knowledge and preferences may then be replaced in a chronological framework and spatial envelope.

Moreover, recourse to iron-rich pigmentaceous materials was not restricted to the Palaeolithic; their use has continued throughout history. Hence, the Pigmentothèque is also a valuable resource for scholars investigations focusing on more recent periods (Mesolithic, Neolithic, Bronze and Iron Ages, Antiquity, Middle Age, etc.), or on different geographical areas, studies of mural and easel paintings, and work to restore and create replicas of heritage objects and sites.
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Data accessibility statement

The data used here are from the ownership of the authors, and the others are cited. Reviewed annual reports of the Pigmentothèque project are available online in open access at the open archive HAL (repository of scholarly documents from all academic fields): https://hal.archives-ouvertes.fr/.

Access to the geological references for purposes of research must be arranged with E. Chalmin and H. Salomon.

Spectroscopic references are available in open access on SSHADE (OSUG Data Center). https://www.sshade.eu/db/pig. doi:https://doi.org/10.26302/SSHADE/PIG

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