



Rare Iron-bearing Rocks, Potential Precursors as Raw Materials for Pigments in Archaeology

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ABSTRACT

From a geochemical and mineralogical point of view, iron-rich materials do not constitute real deposits but are found as rare inclusions in the carbonate, in the marl of clay formations or pebbles in marine terraces. These minerals have different origins and compositions; they are ankerite, ferroan dolomite and goethite, and substances produced by iron bacteria. The thing they have in common is that they all contain iron in modest to high quantities. These rare minerals and the fact that they are often not present in geological maps and literature often lead to them being overlooked in the search for the raw materials that led to the production of ochre pigments used in prehistoric contexts. The aim of this work is the search for potential raw materials used as a pigment for a red band painted pebble, found when a surface survey in Contrada Mandrascava (Agrigento, Sicily). Since in the area, there are no deposits of iron minerals, we documented and described rare findings of ferruginous colouring materials found in the area.

Keywords: Painted Pebble, Ochraceous Pigments, Raw Materials, Ferroan Dolomite, Iron Nodules, Ankerite.

INTRODUCTION

Humans have used reddish/yellowish ferruginous pigments sometimes called ochres since the Middle Pleistocene (Wadley, Williamson, & Lombard, 2004; Watts, Chazan, & Wilkins, 2016; Hodgskiss, 2020). Many authors describe ochre as a ferruginous rock or as a natural mixture of clay minerals and iron oxy (hydroxy) minerals, possibly containing quartz (Hovers, Ilani, BarYosef, & Vandermeersch, 2003; Iriarte, Foyo, Sánchez, Tomillo, & Setién, 2009; Dayet, Texier, Daniel, & Porraz, 2013; Cavallo et al., 2018; Velliky, Porr, & Conard, 2018; Hodgskiss, 2020). These ochre/ferruginous materials were used as a pigment for cave paintings (Zilhão et al., 2010; Bu, Cizdziel, & Russ, 2013; Velliky et al., 2018; Wolf et al., 2018) and in burial ceremonies (Wreschner et al., 1980; Hovers et al., 2003). As regards the raw material, various iron minerals and lateritic soil were used: goethite, hematite, siderite, lepidocrocite, Terra Rossa, jarosite, ankerite and ochre (Weinstein-Evron & Ilani, 1994; Pomiès, Menu, & Vignaud, 1999; Montalto, 2010; Roebroeks et al., 2012; Dayet et al., 2013; Trajska, 2014; Cavallo et al., 2018) and substances derived from iron bacteria (MacDonald et al., 2019; Garilli et al., 2020). The geochemical characterization of ferruginous pigment is very important to reconstruct its origin (Erlandson, Robertson, & Descantes, 1999; Gil et al., 2007; Popelka-Filcoff, Robertson, Glascock, & Descantes, 2007; Iriarte et al., 2009; Gialanella et al., 2011; Beck et al., 2012; Siddal, 2018; Román et al., 2019; Velliky, Barbieri, Porr, Conard, & MacDonald, 2019; Garilli et al., 2020; Salomon et al., 2021). Consequently, it is essential to recognize whether it was taken from the areas where the people who used it lived or whether it came from other, more or less adjacent areas (Zarzycka et al., 2019). In the archaeological field, especially in prehistory, the search for raw materials is important not only to find the material of origin but also to understand if the materials come from areas very far from the collection site and therefore hypothesize migrations or exchange with other populations. The search for

raw materials to produce ochraceous yellow/red pigments leads to a search for the geological deposits that surround the area and to identify the most suitable materials. It is not always possible to find them and therefore one begins to hypothesize distant origins, but sometimes materials are not considered which are often not indicated in the geological maps, since they are found in very modest quantities in various deposits. Further, these materials are often not uniformly distributed within the strata but localized only in some sporadic parts. This work aims to demonstrate that materials that have often not been investigated in the geological literature can be found basically around the area under consideration. The idea for this work was born, looking for prehistoric material on never-ploughed soils such as clayey gullies in Contrada Mandrascava near Agrigento, (a Sicilian prehistory site, even if the finds are often found on the surface and not in a datable layer) where Gerlando Bianchini has collected, in a marine terrace, a fragment of a fossilised *Quercus* sp. trunk, an elephant molar (*Palaeoloxodon mnaidriensis*) and two lithic artefacts (Bianchini & Mascle 1971; Bianchini, 1972). During the surface survey, several archaeological materials including flints, and a painted pebble were found. It is a yellowish carbonate pebble painted on one side only with fairly regular red stripes (Figure 1). Having found the pebble and the lithic artefacts on the surface, we have no elements to date.

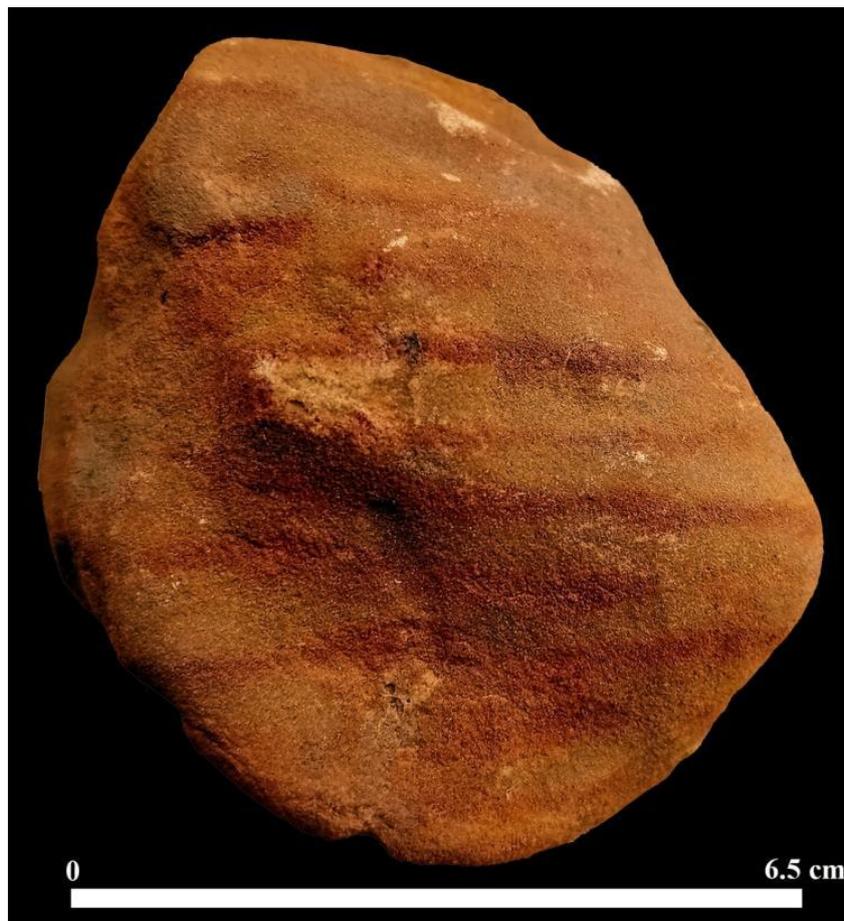


Figure 1. Painted Pebble with Red Stripes PRS; Colour Munsell of Red Pigment 5YR 3/4

Researching what pigment colouring material, they may have used available in the area, the Terra Rossa, which is the most abundant ferrous sediment in Sicily is located many kilometres away where the Mesozoic carbonate formations are present. But in the same area (Figure 2), can be found pebbles that could potentially be used as pigments, in the native form or after being manipulated by grinding and cooking. These materials are rare inclusions, pebbles, or nodules within formations such as marl, clays, or marine terraces.

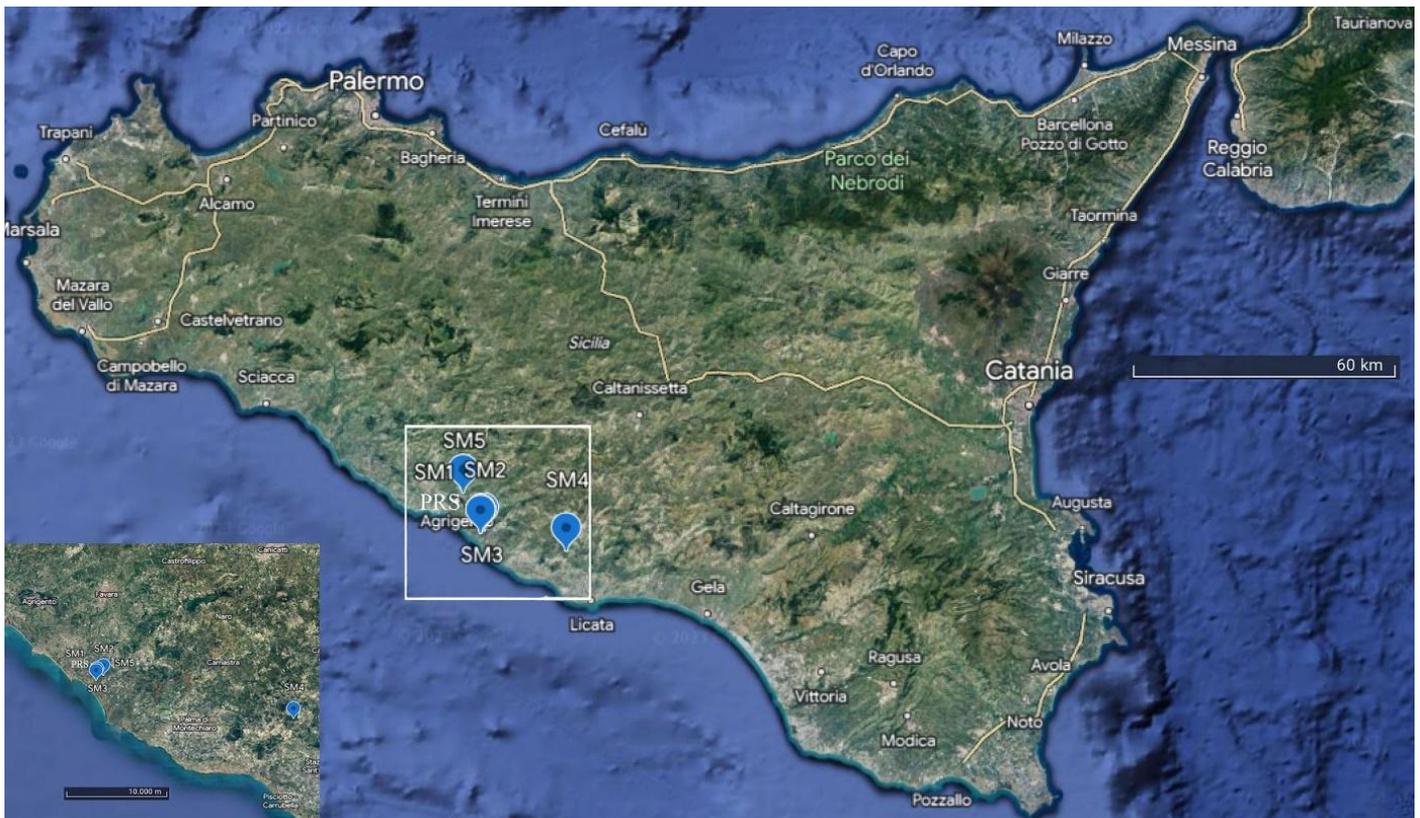


Figure 2. Satellite image of Sicily, the square delimits the area where the samples were collected. In the lower left square, a detail of the area under examination (from Google Earth, modified).

GEOLOGICAL SETTING

The area of the survey is characterised by a series of Geological formations:

Terravecchia Formation (Upper Tortonian): clays, clayey sands, and sands (Decima, Bommarito, La Rosa, & Aiello, 1972).

Gessoso-solfifera Formation (Messinian): at the base is the *Tripoli* consisting of white leafy siliceous marls rich in diatoms, on this is the *Calcarea di base* limestone which consists of compact vacuolar limestones passes heteropically to the *Gessi di Pasquasia*. This latter consists of selenitic gypsum. The succession ends with gypsarenites (Decima et al., 1972).

Trubi (Early Pliocene): marls and globigerine calcareous marls, overlaid and interspersed with clayey breccias incorporating "exotic" pebbles of various origins and ages (Decima et al., 1972). May contain iron sulphates (Dinarès-Turell & Dekkers, 1999).

Monte Narbone Formation (middle-upper Pliocene): grey-blue clayey and sometimes silty clays and marls (Decima et al., 1972).

Agrigento Formation (Early Pleistocene): cross-stratified, yellowish fossiliferous calcarenites (Decima et al., 1972).

Marine Terraces (Upper Pleistocene): consist of sandy, compact silts, with mainly calcareous or quartz arenitic pebbles and to a lesser extent elements of various nature (Decima et al., 1972).

MATERIALS AND METHODS

The samples analysed were collected by us except for the RM4 sample kindly provided by Calogero Verde. The data about locations, colours and dimensions are summarised in Table 1, while the samples are represented in Figures 1 and 3.

Table 1. Macroscopic Characteristics of the Examined Samples and their Respective Dimensions

Sample	Discovery location	Macroscopic description	Size
PRS	Contrada Mandrascava, Agrigento, Italy. In the soil on a clayey gully	Painted pebble with red stripes	6.5-7.5 cm, thickness 3 cm
RM1	Contrada Mandrascava, Agrigento, Italy. In the soil on a clayey gully	Rounded hard pebble of dark red colour with a few black spots.	6.4.5 cm, thickness 2.8 cm
RM2	Contrada Mandrascava, Agrigento, Italy. In the soil on a clayey gully	Sub-rounded porous, soft pebble of pale yellowish colour.	6.4 cm, thickness 2.2 cm
RM3	Contrada Mandrascava, Agrigento, Italy. In the soil on a clayey gully	Rounded compact pebble of yellowish colour, slightly soft on the surface.	4.2.5 cm, thickness 2.5 cm
RM4	Contrada Durrà, Licata, Italy. In the soil in a hilly area	Rounded nodule of reddish colour. In the section, it presents concentric layers.	7.5.5 cm, thickness 5 cm
RM5	Contrada Mandrascava, Agrigento, Italy. On the bank of a river	Dried red coloured mud	200 g

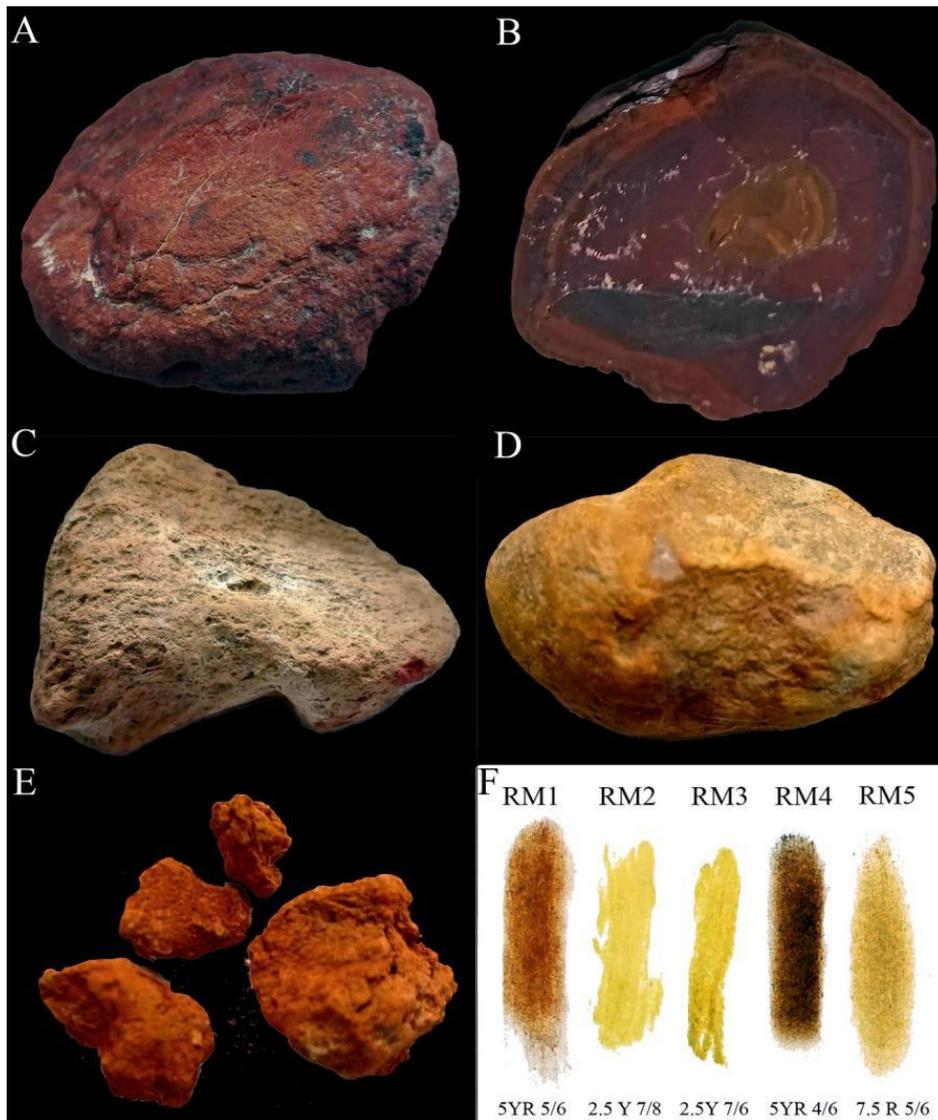


Figure 3. General view and details of the examined samples. (A) RM1 sample. (B) RM4 sample. (C) RM2 sample. (D) RM3 sample. (E) RM5 sample. (F) Colour differences of the tested samples on a sheet of paper. Below are the respective Munsell colours.

To test their potentiality as pigments, tests were carried out on a sheet of paper. Samples RM1, RM4 and RM5 were ground and the powder we used to finger paint over the sheet without adding fixatives. Samples RM2 and RM3 were smeared over the sheet without the need for grinding, they left a line very similar to a coloured pencil (Figure 3F). The colours range from yellow to red-brown, but shades of yellow can be transformed into orange or red after firing at different temperatures. The iron hydroxides tend to transform into hematite at temperatures

above 250-300° (Pomiès et al., 1999; Rzepa, Bajda, Gawel, Debiec, & Drewniak, 2016; Cavallo et al., 2018). The corresponding Munsell stains were researched on these coloured strips.

A non-invasive investigation on PRS painted pebble by portable X-ray fluorescence (p-XRF) was performed with an AMETEK spectrometer consisting of a Mini-X2 X-ray tube equipped with an Au anode and a SDD solid-state silicon drift detector with a Be window and a typical resolution of 125 eV. Analytical measurements were performed with a voltage of 40 kV and current of 15 μ A, a working distance of about 90 mm from the sample, and acquisition times of 150 s (GEOLAB laboratory). EDS analyses were performed to characterise the chemical composition by Quanta 200 SEM coupled with energy-dispersive X-ray spectroscopy (SEM/EDXS). This instrument was used both in backscattered electron (BSE) and secondary electron (SE) mode to investigate the microstructure and to measure the relevant elemental composition. Selected representative samples were analysed using a series field emission gun (FE-) SEM, equipped with an EDAX microanalytical system using the standardless ZAF quantification method, A procedure in which corrections for atomic number effects (Z), absorption (A) and fluorescence (F) are calculated separately from suitable physical models. The operating conditions were as follows: accelerating voltage 20 kV, beam current 40 mA and working distance 15.8 mm. A Phenom proX SEM was used for EDS analyses aimed to investigate the chemical composition of the bacterial structures found in the studied springs and the Palaeolithic ochre. The same instrument was used for SEM imagery. X-ray diffractometry (XRD) analyses have been performed on all samples by PANalytical X'pert Pro at the Geolab (Carini, Palermo). Analyses were conducted by PANalytical X'pert Pro (voltage 40 kV, anode Cu, filter Ni, current 30 mA, scan 8-60° 2 θ , Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) with a scan speed of 2 $\theta = 5 \text{ min}^{-1}$) at the Geolab (Carini, Palermo) to evaluate the mineralogical composition.

Colours have been determined at natural lighting conditions by spreading powdered pigments or applying the colour directly with the pebbles on a sheet. The Munsell Soil Colour Charts (Munsell Color Company, 1988) were used to standardize the colours of all the studied samples.

RESULTS

The XRF analysis of the painted pebble revealed the predominance of calcium in the part not covered by pigment and iron in much smaller quantities. In the red stripes, iron is predominant and calcium from the substrate appears secondary (Figure 4). No other elements were detected probably due to the modest quantities. Therefore, we can deduce that the pigment of the stripes is an iron oxide or iron hydroxide, probably hematite or goethite. The calcium detected comes from the carbonate composition of the pebble.

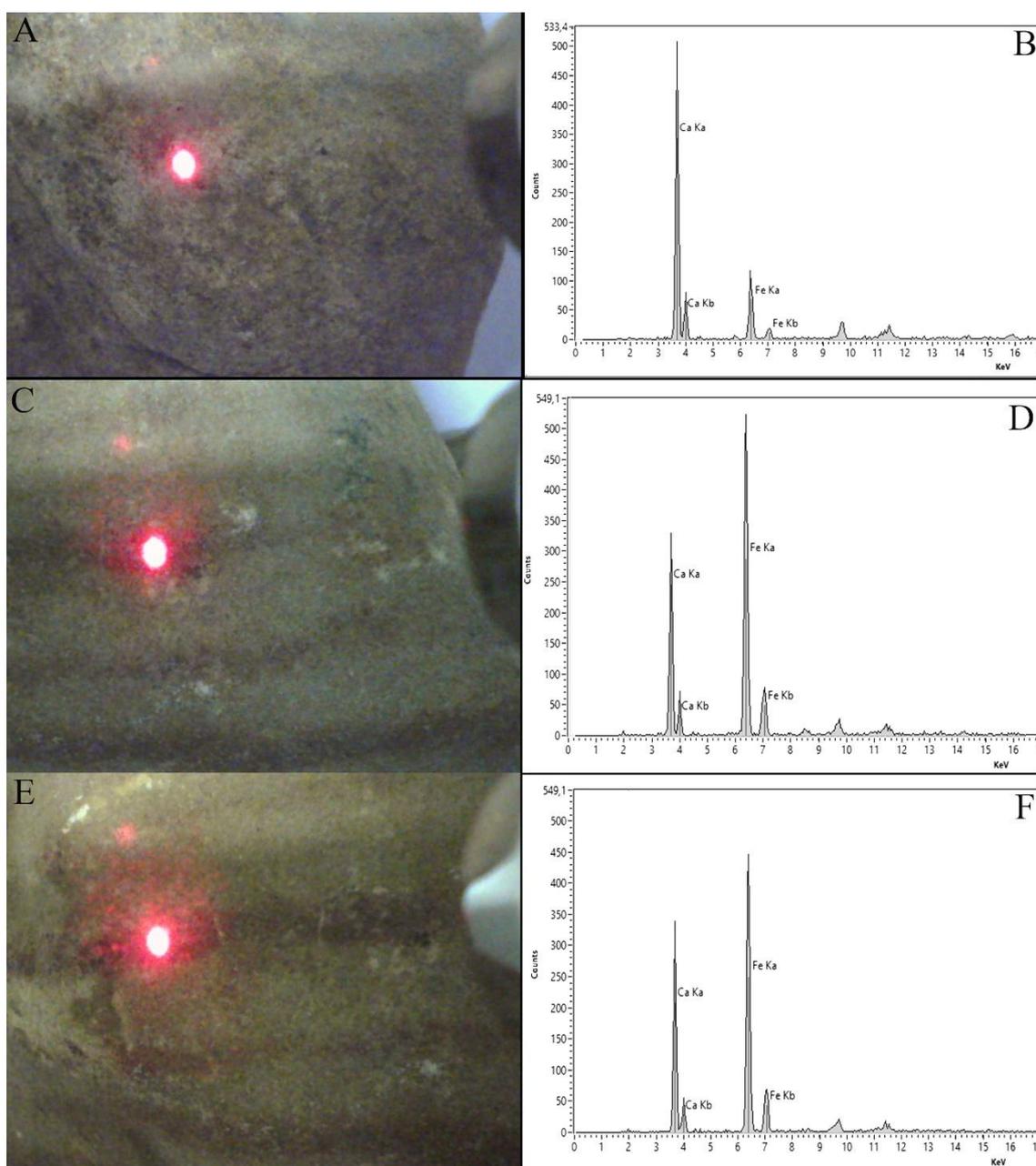


Figure 4. XRF analysis point-and-shoot and related spectrum of PRS. (A) pebble without pigment point-and-shoot; (B) pebble without pigment spectra; (C) point-and-shoot 1 on the red stripe; (D) point 1 spectrum; (E) point-and-shoot 2 on the red stripe; (F) point 2 spectra.

XRD analyses of the samples are represented in Figure 5 and the results of XRD and chemical analyses EDS are summarised respectively in Table 2 and Table 3. The SEM images are represented in Figure 6.

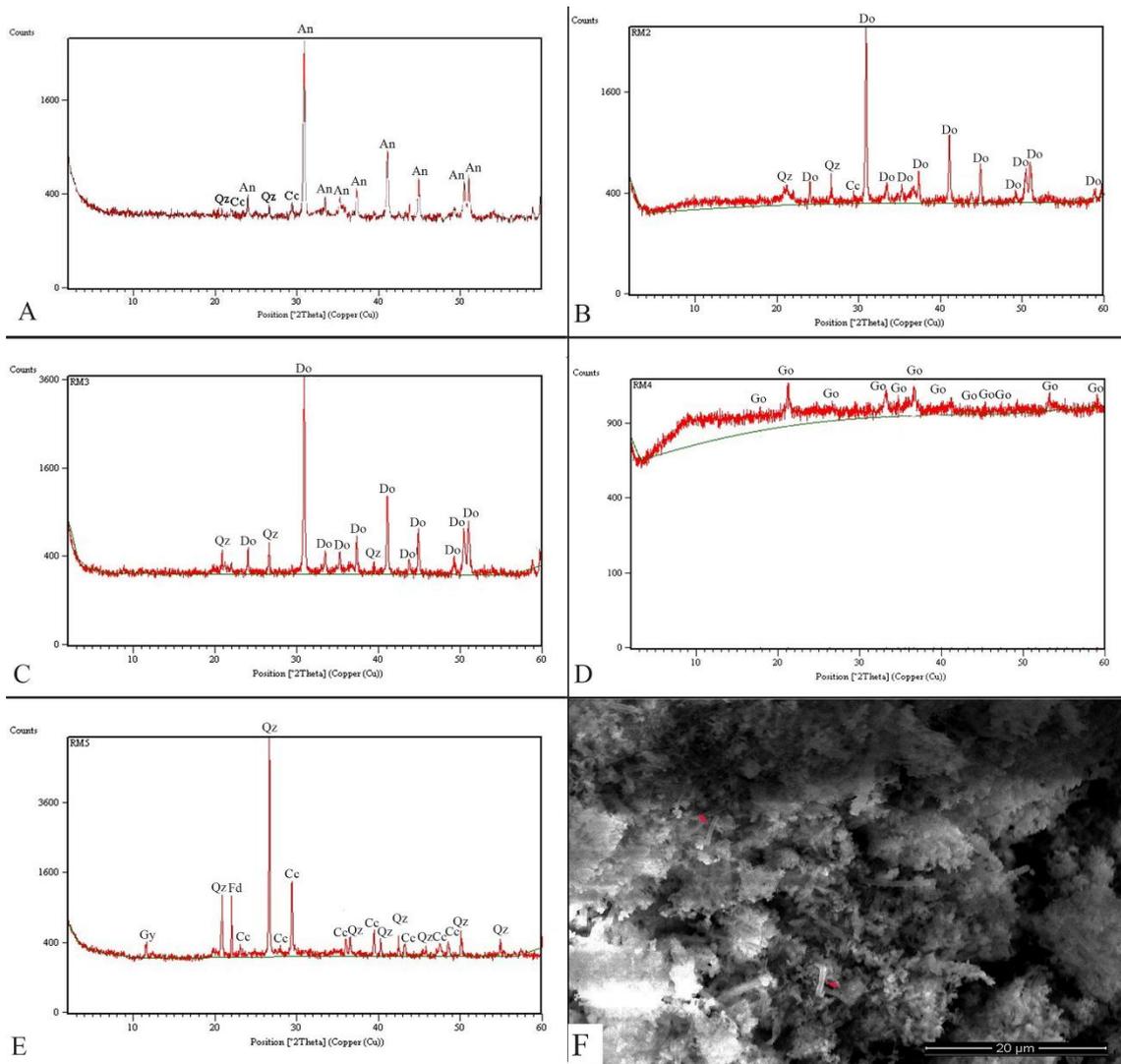


Figure 5. Diffractograms of the examined samples (A) RM1; (B) RM2; (C) RM3; (D) RM4; (E) RM5; (F) SEM image showing iron bacteria (indicated with red arrows).

Table 2. Quantity of the Various Crystalline Minerals that Constitute the Rocks Examined

Sample	Qz	Cc	An	He	Go	CM	Fd	Dol	Gy
RM1	+	+	+++	nd	nd	nd	nd	nd	nd
RM2	+	+	nd	nd	nd	nd	nd	+++	nd
RM3	++	nd	nd	nd	nd	nd	nd	+++	nd
RM4	nd	nd	nd	nd	+++	nd	nd	nd	nd
RM5	+++	+	nd	nd	nd	+	++	nd	+

Note: Legend - He: hematite; An: ankerite; Dol: dolomite; Go: goethite; Qz: quartz; Und. CM: undetermined clay mineral (mixed-layer); Fd: feldspar; Cc: calcite; Gy: gypsum. +++: Main phase; ++: secondary major phases (>10%); +: minor phases (<10%); nd: not detected.

Table 3. Percentage of Atoms of Major Elements, Identified by EDS

Sample	C (%)	O (%)	Na (%)	Mg (%)	Al (%)	Si (%)	Cl (%)	K (%)	Ca (%)	Fe (%)	Mn (%)	Mg/Fe
RM1	8.64	60.64	bdl	7.33	0.37	0.98	0.7	bdl	13.03	8.3	bdl	0.61
RM2	8.13	58.85	0.87	8.24	0.3	0.88	0.99	bdl	15.23	6.51	bdl	1.26
RM3	9.43	61.05	0.1	8.47	1.09	3.27	bdl	0.24	11.12	5.24	bdl	1.62
RM4	5.47	56.84	bdl	1.27	1.83	2.98	bdl	0.31	0.99	24.49	5.82	-
RM5	7.57	57.67	2.01	1.47	2.83	9.33	1.96	bdl	2.94	14.51	bdl	-

Note: bdl = below the detection limit.

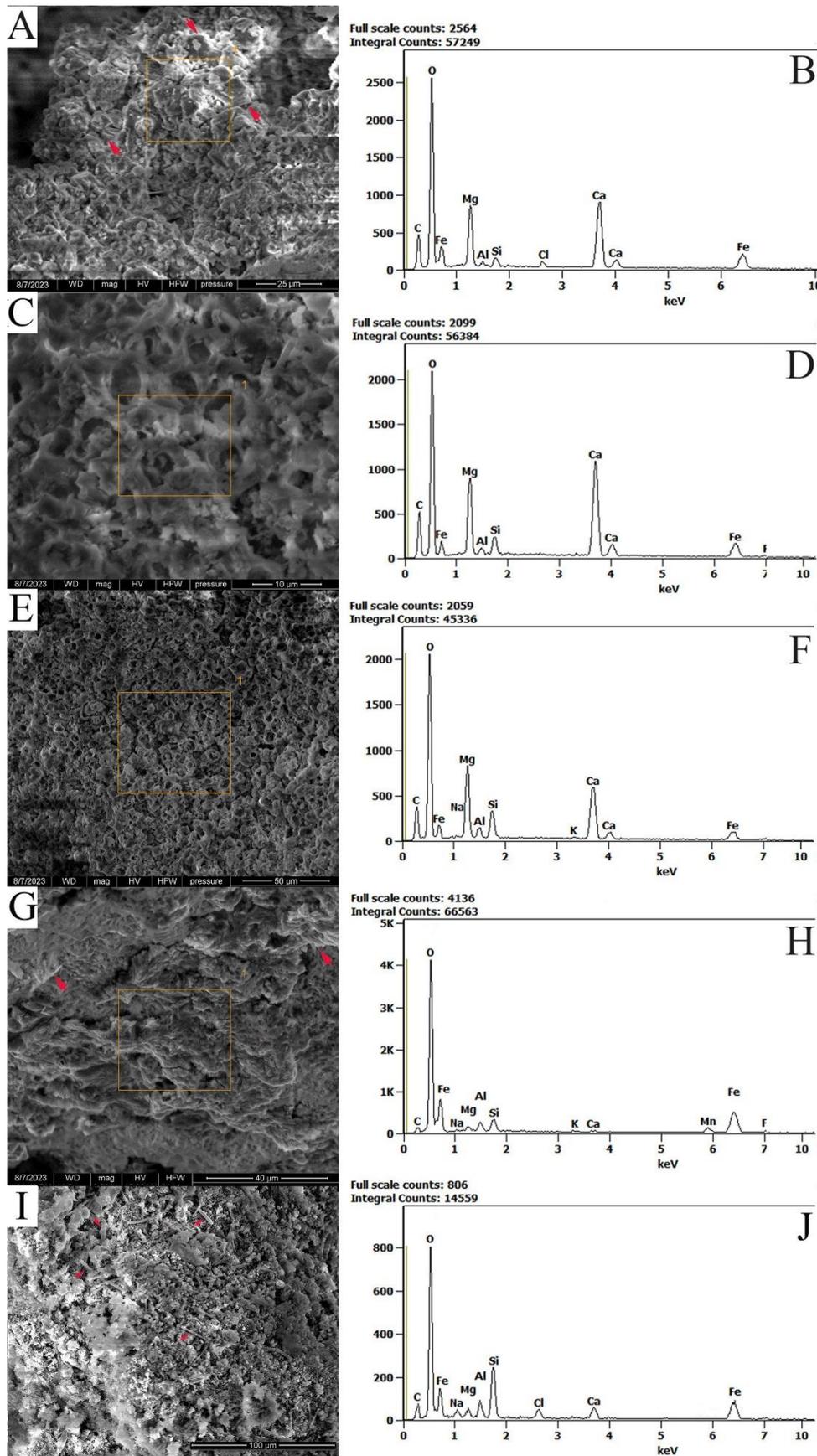


Figure 6. (A) The SEM image of sample RM1 shows a compact structure in which euohedral-subohedral rhombic microcrystals can be seen (red arrows). The square indicates the area in which the atom count was made. (B) RM1 EDS. (C) SEM image shows a vacuolar structure of the RM2 sample. (D) RM2 EDS. (E) Vacuolar structure of RM3 sample. (F) RM3 EDS. (G) RM4 sample shows a compact structure composed of pseudo-acicular microcrystals. (H) RM2 EDS. (I) SEM image showing filaments of iron bacteria (red arrows). (J) RM5 EDS.

The chemical composition for the first three samples is quite similar, there are high percentages of Ca, Mg and Fe while Al and Si have low percentages. In RM4 we have a high percentage of Fe and the other elements except Mn (Table 2), have percentages below 3%. A different case is RM5 since it is impossible to isolate the bacterial deposit from the underlying river sand; silica and iron predominate. The iron content has a range that goes from a minimum of 5.4% for RM3 to a maximum of 24.49% for RM4. In the XRD analysis of sample RM1 (Figure 5A), the predominant mineral is ankerite, while in RM2 and RM3 (Figure 5B-C) it is dolomite. Deer, Howie, and Zussman (1962), distinguish the ferroan dolomites, for which the Mg: Fe ratio is higher than 4, from the ankerites for which this ratio is less than 4. So, according to Deer et al. (1962), since the Mg/Fe ratio is less than 4, all three should be ankerites, even if in the first sample iron is more abundant than magnesium, and vice versa in the other two (Table 3). Ferroan dolomite $\text{Ca}(\text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ is a relatively common Fe-bearing variety of dolomite in which the content of $\text{Mg} > \text{Fe}^{2+}$ (Ptáček, Šoukal, & Opravil, 2021). So RM2 and RM3 will probably be ferroan dolomites. This means that it is very difficult to distinguish these minerals on XRD. As regards the SEM images, RM1 (Figure 6A) present a compact structure in which microcrystals aggregate in a cumulative texture with rhombus euhedral-subhedral (Figure 6A, red arrows) shapes can be glimpsed. RM2 and RM3 instead have a vacuolar structure (Figure 6C-E), which probably denotes a biological origin. RM4 also has a compact structure, the pseudo-acicular microcrystals (Figure 6G, red arrows) have a very fine size. In the RM5 sample, we note the presence of bacterial filaments (Figure 5F and 6I, red arrows), quartz granules and clay minerals.

DISCUSSION

The characterization of ferruginous geomaterials is complex and difficult. Considering that these rocks can also form within sedimentary rocks, under hydrothermal alteration, in igneous rocks, and can also be found in metamorphic rocks, they potentially present heterogeneous petrological characteristics (Dayet, 2021; Salomon et al., 2021). In our study, we characterized the red pigment with which the PRS pebble was painted and we tried to trace the raw material. A pebble is very similar in colour, parallel lines and use of a single face was found in Epigravettian levels in a cave in central Italy (Astuti, 2012). As regards the pigment used to paint the PRS pebble, we have excluded Terra Rossa, both due to the distance of the deposits and mainly for the chemical composition. Sicilian Terra Rossa contains aluminium, potassium, and silicon (Vita, Schimmenti, & Sineo, 2022). When searching for raw materials, it is essential to consult the geological map, but a collection of materials along watersheds, along rivers, and in areas where rainwater concentrates pebbles must not be neglected. In these accumulations of pebbles, minerals are often found that are uncommon in many areas. So prehistoric populations could encounter these raw materials for pigment while searching for flints or quartzites without the need to transport or exchange them with other populations. Our research focused on the materials found in the area even if not present in large quantities. We are dealing with nodules or pebbles that are found as rarely included in geological formations such as limestone, clay, or marl. The characteristic that unites these materials is the presence of iron minerals, it is precisely this element that gives the rocks or minerals shades ranging from yellow to orange and red. Among the materials studied, we have three similar pebbles from a compositional point of view, the first RM1 in XRD is ankerite, while RM2 and RM3 are composed of ferroan dolomite. Ferroan dolomite can be found within carbonate formations (H. Xu et al., 2018) and recent studies have shown that it may have a bacterial origin (F. Xu, You, Li, & Liu 2019). Authigenic nodules of dolomite and ferroan dolomite are found in Spain within marls, methane would have contributed to their formation (Pierre, Rouchy, Blanc-Valleron, Etoubleau, & Fouquet, 2015). The structure of the RM2 sample which is very porous, could lead to the formation of a bacterial process. Dolomite cylinders with internal vacuolar patterns formed by discontinuous concentric rims have been found in lacustrine evaporitic deposits in Spain. These cylinders are interpreted as the dolomitized cells of a widespread microbial community (Bustillo, Armenteros, & Huerta, 2017). In anoxic muds, micrite is rich in microbial organic matter and these conditions would lead to an organo-dolomite process (Slaughter & Hill, 1991; Mazzullo, 2000). So RM1, RM2 and RM3 could come either from the clays of Monte Narbone, with water erosion they can be found along streams or in the soil. Ankerite and ferroan dolomite have been found mixed with goethite and hematite in Palaeolithic ochres of northern Italy (Cavallo et al., 2017), since they have a limited diffusion, they did not have a great use in prehistory and later periods. Iron-manganese nodules or iron minerals are present in Sicily in the limestone and more rarely in the marls, therefore the RM4 nodule will be derived from the erosion of carbonate (Jenkyns, 1970) or marly rocks such as Trubi (Dinarès-Turell & Dekkers, 1999). This nodule in its crystalline phases is almost exclusively composed of goethite, a mineral widely used in prehistory. It usually has a yellow colour, but it is sometimes heated to become red (Pomiès et al., 1999; Rzepa et al., 2016; Cavallo et al., 2018), in our case, it already naturally has a red colour. Several studies have been interested in iron nodules as pigment precursors. In Germany, various potential raw materials of prehistoric ochres were sampled,

among which the iron nodules were identified (Velliky et al., 2019). Also in Spain, the analysis of pigments in cave paintings has led to the assumption that the materials of origin were iron nodules (Martín-Ramos, Cuchí-Oterino, & Bea-Martínez, 2023). The latter were also examined in Calabria to evaluate whether they were used as pigments during Magna Graecia (Miriello et al., 2010). Both goethite and ankerite have been used as yellow pigments in wall paintings at Zeugma in Turkey (Akyol, Kadioğlu, & Demirci, 2011). The RM5 sample has a clear bacterial origin, deduced from the SEM images where filamentous bacteria are seen (Figure 5F, 6I). The presence of iron bacteria can be found in streams, rivers or springs, the waters must be oxygenated and iron must be present in the water. The occurrence of Fe in RM5 is due to the activity of chemoautotrophic iron-oxidising bacteria FeOB (Cullimor & McCann, 1978; Garilli et al., 2020) as this chemical element be found in the bacterial sheaths (Emerson & Ghiorse, 1993; Suzuki et al., 2012). The reason we do not see iron minerals in XRD is that these organic iron compounds are often amorphous (Garilli et al., 2020). The use of organic compounds of iron as a pigment produced by iron bacteria is documented both in the Palaeolithic and in the Holocene (MacDonald et al., 2019; Garilli et al., 2020).

CONCLUSION

From the results of the potential raw materials, it was found that all the analysed samples can be used as pigments, with shades ranging from yellow to reddish. Some samples require grinding and powders can be used as is. From the chemical comparison of the pigment on the pebble and the materials we studied, the potential raw material could be an RM4 nodule as iron is abundant while the other scarce elements could not be detected by XRF. We believe that this study is important because often when documented deposits are not found on geological maps, we begin to search in distant areas, neglecting any resources that, although modest, are found in the vicinity of the area in which the archaeological material was found.

AUTHOR CONTRIBUTIONS

All the authors contributed to this paper. G. V. did the sampling. G. V. with A. M. and L. S. prepared and edited the manuscript. G. V. drew pictures. G. V. and M. A. V. performed the laboratory analyses. All the authors discussed and revised the manuscript.

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DATA AVAILABILITY STATEMENT

Data is available on request from the authors.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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