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Conservation of Paleontological Finds: the Restoration Materials of the "Problematica Verrucana"

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Abstract. The materials used in the historical restoration of a fossil collection named "Problematica Verrucana", have been studied in order to contribute to the creation of a catalogue of restoration materials used in the past. Due to the complexity of the mixtures used with different purposes to restore fossil finds, an extractive technique has been employed in order to separate the compounds soluble in solvents with different polarities. Using this procedure several components, even when found in small amounts, have been identified. The chemical composition of the organic and inorganic compounds used in the restoration material has been determined using extractive procedure, FT-IR and ^{1}H-NMR spectroscopies. A preliminary macroscopic characterisation and mineralogical and petrographical analyses have also been performed on the inorganic filling materials found in several samples. The different compositions of various materials used in the restoration of this fossil collection might be related to the particular conservative and esthetic functions of the product applied on the find.

Keywords. Fossil collection, restoration materials, petrographical analyses, spectroscopic analyses, paleontological museum.

1. INTRODUCTION

Paleontological museums usually preserve recently acquired finds beside ancient and historical collections, where some fossils could have suffered from serious alteration processes due to prolonged storage in depositories and warehouses, while other fossils could have been "restored" during the centuries.[1,7] Furthermore, in order to be conserved into a museum, natu-

ralistic finds need to undergo a specific process, called *preparation*. In the past, the *preparation* and restoration of damaged pieces were generally made by the paleontologists themselves, often in an empirical and artisanal way[3,8] with materials and procedures which have rarely been documented.

The *Natural History Museum* of Florence hosts a fossil collection named *Fucini Collection* or "Problematica Verrucana". This collection is composed of fossil tracks and fossil seaweeds found by Alberto Fucini, geologist and paleontologist of the University of Florence, on the Monti Pisani during the first decades of '900[9]. The peculiar feature of this collection consists in the fact that the majority of finds show signs of historical restoration, probably performed by Fucini himself, perhaps with the aim of facilitating the study of the finds. Unfortunately, no documentation about the products applied during these interventions is conserved at the *Natural History Museum*.

The aim of this research was to identify the materials used for the historical restoration of this collection. With this purpose, several samples recovered from restoration materials were studied by means of chemical and mineralogical analyses.

2. MATERIALS

2.1 The Finds

The *Fucini Collection*, or "Problematica Verrucana", is made up of more than one thousand pieces; the samples for this study were taken from 17 finds, as described in Table 1, with the aim of identifying different kinds of materials.

This collection is composed for the most part of fossil imprints or marks that animals have left in their habitat in the past. The comparison between the *Problematica Verrucana* tracks and those of several tetrapods has not been completed yet[10-13]. Actually the majority of finds have been identified as either impress or reverse marks (the relief of the impress in the specular portion of the sediment) of small dinosaurs. Besides, marks of vegetal rests are also conserved in the Fucini Collection, principally seaweeds like *Sewardiella* e *Gothaniella* (Figure 1).

The term "*Problematica*" refers to the difficult interpretation of the type of traces left behind, while the adjective "*Verrucana*" derives from the term *Monte Verruca* (in the *Monti Pisani* between *Pisa* and *Lucca* - Italy), as does the term *Verrucano*, a geologic period con-

Table 1. Finds and samples.

Find name	IGF[a]	Type of find	Sampling zone	Sample
Gothaniella sphenophylloides Fucinii, forma piumosa	10351	fossil seaweed	junction	Sample 1
Chondrites Fucillatus	10368	print of a prehistoric reptile	junction and back	Sample 2
Thecodontiehnus verrucae	5152	hand-print of a small carnivorous reptile	lateral part	Sample 3
Sewardiella Verrucana	10323	fossil seaweed	lateral, right, part	Sample 4
Sewardiella Verrucana Fucinii, forma multiradiata	10298	fossil seaweed	superior part	Sample 5
Sewardiella Verrucana Fucinii	10301	fossil seaweed	front and lower part	Sample 7
Undefined find	516T	undefined track	back	Sample 8
Undefined find	748T	undefined track	back	Sample 9
Sewardiella Verrucana Fucinii	10302	mold of fossil seaweed	back	Sample 10
Sewardiella Verrucana Fucinii, forma fasciculosa	10315	mold of fossil seaweed	lateral, left, part	Sample 11
Undefined find	692T	undefined track	back	Sample 12
Sewardiella Verrucana Fucinii, forma rotata	10299	mold of fossil seaweed	lateral, left, part	Sample 13
Thecodontiehnus Fucinii v. Huene	5149	hand-print and foot-print of a reptile similar to varan	back, lower part	Sample 17
Undefined find	not catalogued	-	back	Sample 18
Rhinocecephalichnus	5195	hand-print and foot-print of a reptile	lower part	Sample19
Sewardiella Verrucana Fucinii, forma lateradiata	10292	fossil seaweed	lower part	Sample 20
Undefined find	348T	undefined track	back	Sample 21

[a]IGF Catalog number of Natural History Museum

Figure 1. Examples of animal and vegetal finds of Fucini Collection: find IGF 5152, a) hand-print of a small carnivorous reptile: The codontiehnus verrucae; b) IGF 1036, a fossil seaweed: Gothaniella sphenophylloides Fucini.

sidered as a synonym of *Permiano*, which characterises the relevant area.

2.2 Description and Function of Restoration Products

According to their macroscopic aspect and main functionality, the restoration materials used in the Fucini Collection can be divided in four classes, each one containing different kinds of products. Products belonging to the same class may vary in colour or aspect of the aggregate. Sometimes several pieces of the same materials were sampled, for example when a product was apparently used for different functions (Table 2) (Figure 2).

Class A: light-yellow substances with or without aggregate used as adhesive to reconnect separated parts of finds. Materials belonging to this class can be divided in three different categories, all containing an adhesive material, either used alone (Product A), mixed with aggregates having smaller grains (Product B) or larger grains (Product C). Product A is a yellow-orange amber, transparent and hard material. Products B and C are similar to Product A. Product B is used to attach broken parts of medium-dimension finds; it is applied alone or with paper or fabric. Product C is used for pieces of medium and big dimensions. It is rarely used with paper or fabric.

Class B: hard materials used for junctions and for moulds, which appear of two colours (green or gray). The difference between these two products, classified as Product H and Product G, is macroscopically limited to the colour. The two products appear like hard and porous mixtures, of light green or gray colour, and of crumbly aspect. The presence of some drops suggests that the product has been applied in a liquid state. The same product has been sampled in finds in which it worked as adhesive, and in moulds. The gray material has been defined "sulphor" by Fucini [9]. These materials have been used to lend adhesion to broken pieces and to make moulds.

Class C: gummy pastes used for support purposes. These materials appear as rubbery adhesive pastes probably used for integrations (especially Product E) or to create a layer in the back of the finds. Product E appears as a partially hardened rubber. The colour is brown. It was probably used for integrations. Product F appears like a completely hardened rubber. It appears in the form of small, quite flat, cushions. The shape suggests that the product was applied with the pressure of the fingers. It is found only in the back of the finds: it looks as if it was used to create a support base for photographic sessions.

Class D: filling materials of various colours. They are five materials which appear as inorganic products used to assemble broken pieces or to reconstruct lacking parts. Product K is of dark grey colour and it is hard to the touch. Product L and Product M have similar aspects, they are hard and compact, but they have different pigmentations (the first one has a grey colour, the second is brownish-red). Product N is dusty and friable and of brownish-orange colour; it seems hard, but it is not compact, it appears fragile and dusty. Product O

Table 2. Description of the samples: class, product and number of finds.

Sample	Class	Product	Description
Sample 1	Class A	Product A	Light-yellow, hard and poorly compact product, present in 76 finds
Sample 2			
Sample 3		Product B	Light-yellow, hard and quite compact product, present in 169 finds
Sample 4			
Sample 5		Product C	Light-yellow, hard and very compact product, used only for big pieces, present in 8 finds
Sample 9	Class B	Product G	Hard and glassy mixture of grey color, present in 11 finds
Sample 10			
Sample 11			
Sample 12		Product H	Hard and glassy mixture of green color, present in 20 finds
Sample 13			
Sample 7	Class C	Product E	Gummy product of brown color, present in 7 finds
Sample 8		Product F	Gummy product of black color, present in 10 finds
Sample 17	Class D	Product K	Dark-grey filling, present in 2 finds
Sample 18		Product L	Grey filling, present in 22 finds
Sample 19		Product M	Brownish-red filling, present in 23 finds
Sample 20		Product N	Brownish-orange filling, present in 3 finds
Sample 21		Product O	Whitish-grey filling, present in 1 finds

Figure 2. a) Example of Class A materials (Product C); b) Class B (Product H); c) Class C (Product F); d) Class D (Product M).

appears, also at a macroscopic level, considerably different than the others: the binder appears of grey-whitish coloration, the aggregate is poorly sorted (dimensions from the micron to the centimetre).

3. EXPERIMENTAL SECTION

CDCl$_3$ (Aldrich, purity 99,9% in D), D$_2$O (Aldrich, purity 99.9% in D) and DMSO-d$_6$ (Aldrich, purity 99.8% in D) were reagent grade and were used without further purification.

^{1}H NMR spectra of solutions were recorded at 399.92 MHz on a Varian Mercury 400 or at 199.985 MHz on a Varian VXR 200. All spectra were reported in ppm using solvent residual peak as reference.

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum BX model, using the Spectrum v. 3.02.02 program. The FT-IR spectra of all solid materials were recorded using a mixture of sample (3 mg) and KBr (100

mg). The solutions were analysed using KBr or CaF$_2$ plates after deposition and solvent evaporation. In the extraction tests, 12 mg of each sample were introduced into a round bottom flask, equipped with a magnetic stirrer, with 0.7 ml of deuterated solvent (CDCl$_3$ or D$_2$O) and maintained at room temperature under magnetic stirring for 24 hours; then the solid and the solution were separated by filtration. At the end, an extraction with D$_2$O was also performed at 85°C for 6 hours. The solutions were analysed by ^{1}H-NMR spectroscopy and then by FT-IR spectroscopy as reported above. The solid residues were washed with the corresponding non deuterated solvent used in the extractive procedure, dried under vacuum and analysed with FT-IR spectroscopy as reported above.

The macroscopic analyses were carried out with a stereomicroscope (Zeiss KL 1500 Electronic). The mineralogical compositions were determined through powder X-ray Diffraction (XRD) using a Philips PW 1050/37 diffractometer, with a Philips X'Pert data acquiring system, operat-

ing at 40 kV-20 mA, with a Cu anode, a graphite mono-chromator and with 2°/min goniometry speed, in interval 2θ between 2°-62°. The petrographic description was performed using a polarised light Microscope ZEISS D7082 OBERKOCHEN (OM) on thin section (30 μm thickness); the microscope photos were taken with a Nikon Coolpix 4500 with a magnification of 10× and 2,5×.

4. RESULTS AND DISCUSSION

The chemical composition of the products used in the historical restoration of the *Problematica Verruca-na* was studied by means of FT-IR and ^{1}H-NMR spectroscopies. In order to identify all products, also when found in small amounts, some extractions with solvents of various polarity were carried out on the fragments of samples, as reported in the experimental. A preliminary macroscopic characterisation and mineralogical and petrographical analyses were also performed on the inorganic filling materials found in the products of Class D.

4.1 Characterisation of Class A Products

The chemical composition of the different samples identified as Class A (**Products A**, **B** or **C**) was analysed by FT-IR spectroscopy on the KBr mixture.

The same organic compound, probably used as adhesive, was present in all products of class A as main component (Product A, samples 1 and 2) or as ligand for inorganic fillers (Product B, samples 3 and 4; Product C, sample 5). The FT-IR data [3428 (broad, vs), 2924 (m), 1631 (m), 1423 (m), 1030 (vs) cm^{-1}] suggested the presence of a polysaccharide compound and in particular

the fingerprint region of the FT-IR spectrum was similar to the Arabic gum spectrum (Figure 3).

Bands attributable to inorganic fillers could not be found in the spectra of Product A (samples 1 and 2), whereas different inorganic fillers were detected in the FT-IR spectra of the other Class A products. In fact, bands attributable to calcium carbonate [2512 (w), 1799 (m), 1423 (vs), 874 (m), 712 (w) cm^{-1}] and silica [1083 (vs), 794 (m), 778 (m), 694 (w), 517 (w), 467 (s) cm^{-1}] were present in the Product B spectrum (samples 3).

Finally, the presence of some bands of silica [794 (m), 778 (m)] and mica [3628 (m), 1028 (vs), 755 (sp) cm^{-1}] was observed in the Product C spectrum (sample 5), while other bands were not detectable due to their overlap with those of low amounts of polysaccharide.

4.2 Characterisation of Class B Products

A complete absorption of infrared radiations, in the 4000-1000 cm^{-1} range, was observed for **Product G** (samples 9, 10 and 11) and for **Product H** (samples 12 and 13), also with a lower concentration of this sample in the KBr mixture. The presence of specific functional groups could not be detected and only a single band at 464 cm^{-1} was noticed.

After extraction with CDCl$_3$, no organic compounds soluble in this solvent were found. In fact, no signals were present in the ^{1}H-NMR and FT-IR spectra recorded on this fraction. Nevertheless, a yellow solid was recovered in the NMR tube, which suggested the probable presence of sulphur. No changes were observed in the FT-IR spectrum of the solid insoluble in CDCl$_3$.

The behaviour of these samples suggested the presence, as main component, of a grey product, not trans-
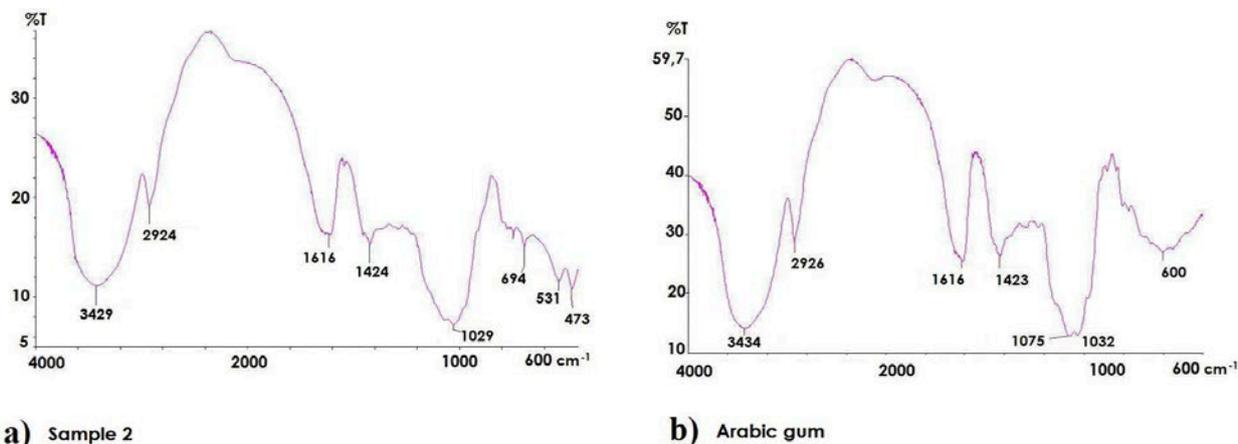
Figura 3. Product A, sample 2. – a) FT-IR spectrum; b) FT-IR spectrum of arabic gum.
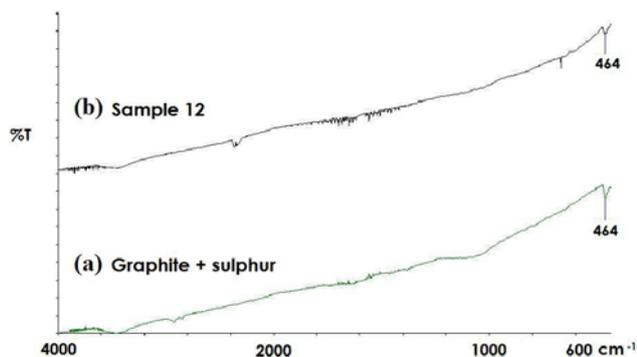
Figure 4. FT-IR spectrum of a graphite/sulphur mixture (a) compared with that of sample12 Product H (b).

parent to the infrared radiation as graphite. Because of the presence of this compound, it was not possible to observe other characteristic absorption bands. In order to confirm the hypothesis identifying graphite as the grey part of the solid and sulphur as the yellow part, a mixture containing graphite and sulphur was prepared and analysed by FT-IR spectroscopy. The FT-IR spectrum recorded on this mixture was identical to that recorded on sample 12 (Figure 4). Moreover, the colour appeared analogous with the sample material one.

4.3 Characterisation of Class C Products

The FT-IR spectrum of **Product E** (Sample 7) showed several bands attributable to the presence of a mixture of different organic products [2919 (vs), 2849 (s), 1734 (vw), 1710 (w), 1538 (vs), 1458 (m), 1398 (m), 1032 (w) cm^{-1}], probably waxes (1734 cm^{-1}), terpenoids (1734, 1710 and 1398 cm^{-1}) and salts of saturated and monoun-

saturated fatty acids (1538 cm^{-1}). Furthermore, gypsum (CaSO$_4 \cdot$2H$_2$O) [3529 (w), 3404 (w), 1116 (w) cm^{-1}] was identified in lower amounts as inorganic material. The ^{1}H-NMR and FT-IR spectra of the CDCl$_3$ solution (Figure 5), obtained by extraction from the solid material at room temperature, suggested the presence as main components of salts of saturated and monounsaturated fatty acids [band at 1538 (vs) cm^{-1} in the FT-IR and signals at 0.89 (m, CH$_3$), 1.27 (m, CH$_3$-C̲H̲$_2$), 1.65 (m, CH$_2$-C̲H̲$_2$- CH$_2$-COO), 2.00 (m, C̲H̲$_2$- CH=CH -), 2.38 (m, C̲H̲$_2$-COO), 5.41 (m, -C̲H̲=C̲H̲-) in the ^{1}H-NMR]. Low amounts of free fatty acids or terpenoid acids and esters can also be found (band at 1731 (w), 1710 (m) cm^{-1}), whilst glycerol, linoleic and linolenic acids, free or esterified in triglycerides, were not detected in the ^{1}H-NMR spectrum. The solid residue contains gypsum [3535 (m), 3405 (m), 1623 (w), 1116 (vs) e 670 (w), cm^{-1}] together with mica [3613 (w), 1030 (vs), 750 (w) cm^{-1}], while the contemporary presence of silica can be identified for the weak bands at 797 (w), 777 (w), 531 e 472 cm^{-1}. The bands at 2925 (w) and 2851 (w) cm^{-1} were attributable to the presence of an organic compound insoluble in CDCl$_3$.

Several bands were found in the FT-IR spectrum of **Product F** (sample 8), attributable to a mixture of several organic and inorganic compounds [3445 (m), 2917 (vs), 2849 (vs), 1736 (s), 1709 (m), 1496 (m), 1465 (s), 1244 (w), 1173 (w), 873 (w), 854 (w), 718 (w), cm^{-1}]. The presence of waxes [1736 cm^{-1} in the FT-IR and signals at 0.89 (m, CH$_3$), 1.27 (m, CH$_3$-C̲H̲$_2$), 1.65 (m, CH$_2$- C̲H̲$_2$- CH$_2$-COO), 2.38 (m, C̲H̲$_2$-COO), 4.06 (m, O-C̲H̲$_2$-) in the ^{1}H-NMR] as main component, probably along with terpenoids (1736 and 1706 cm^{-1}), was identified in the fraction soluble in CDCl$_3$. In the spectrum of the solid resi-

a)

b)
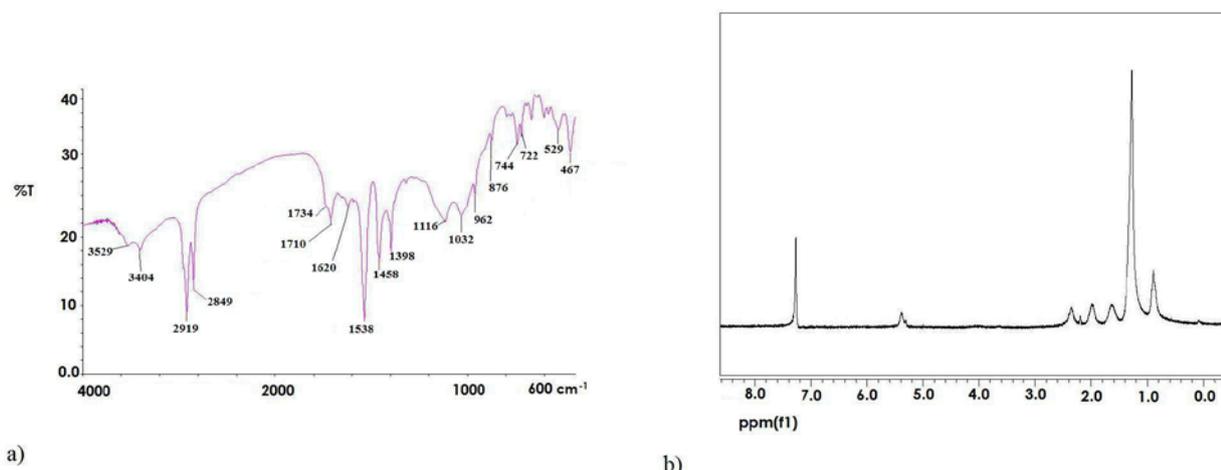
Figure 5. Product E, sample 7 - a) FT-IR spectrum; b) Soluble fraction in CDCl$_3$, ^{1}H-NMR (CDCl$_3$) spectrum.

due, insoluble in chloroform, bands [3434 (m), 2918 (s), 2849 (m) cm^{-1}, 1496 (vs), 873 (w), 712 (w) cm^{-1}] attributable to a mixture of an organic compound and calcium carbonate were found. In particular, the organic compounds could be diterpenes (sandarac, rosin) polymerised due to ageing, according to their low solubility in chlorinated solvents.

4.4 Characterisation of Class D Products

The inorganic filling present in the products of class D was characterised using mineralogical and petrographical analyses.

Under stereomicroscope observation, **Product K** (sample 17) appears shiny on the surface. It is possible to observe that it is constituted by a binder and the aggregate. The binder is of grey colour and compact. In the aggregate three different typologies of grains are distinguished: the first one presents crystals of fine dimension, white colour, scaly fracture, and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Finally, it is possible to observe traces of red particles of fine dimensions. The presence of hemihydrate gypsum as main component with low amounts of bi-hydrate gypsum was detected by FT-IR spectrum [3608 (m), 3564 (m), 3400 (m), 1623 (m), 1152 (vs), 659 (s), 601 (s) cm^{-1}]. Low amounts of a protein (1650 and 1549 cm^{-1}) used as binding material were also identified. No compounds soluble in $CDCl_3$ or D_2O at room temperature were detected. It is possible to hypothesise that Product K has a binder which is probably constituted by gypsum and protein, while the aggregate might be constituted by dolomite. In fact, the mineralogical analy-

ses (XRD) of sample 17 reveal the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$) and dolomite ($CaMg(CO_3)_2$). However, petrographical analyses were not carried out due to the small dimension of the sample and it was not possible to carry out a complete characterisation.

Product L (sample 18) was sampled from a piece of large dimensions (not catalogued). It was removed from the back of the find. Under stereomicroscope observation, it is possible to distinguish a binder and the aggregate. The binder is of white-yellowish colour and it appears compact. The aggregate is constituted by two different typologies of grains: crystals of white colour with a scaly fracture and greasy surface and a fine particulate of black colour and rounded shape. Hemihydrate gypsum as main component and lower amounts of gypsum were identified in the FT-IR spectrum [3611 (s), 3549 (s), 3404 (m), 1622 (m), 1150 (vs), 659 (s), 601 (s) cm^{-1}], together with a protein in small amounts (1650 and 1549 cm^{-1}). The mineralogical analysis (XRD) of sample 18 reveals the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and traces of quartz (SiO_2). The observation under the polarised light microscope in thin section shows a binder of grey colour, which is mainly composed of gypsum. The porosity is medium and of irregular shape. The aggregate shows crystals of sub-euhedral shape and fine dimensions (prevalence of 50 μm and rare of 100 μm); the composition is mainly constituted by little needles of gypsum and traces of quartz and calcite. Iron oxides with opaque and globular appearance, probably Magnetite (Fe_3O_4), are present. The binder/aggregate ratio is 1/2 (Figure 6). Therefore, Product L is constituted by gypsum and protein substances as binder, along with an aggregate main-
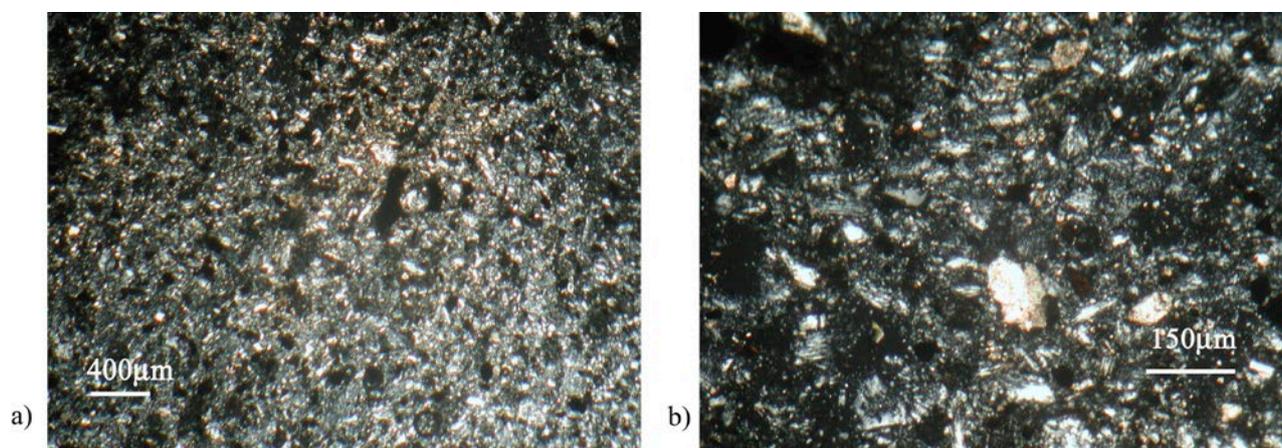
Figura 6. Product L, sample 18 – a) Cross nicols image: general view of the plaster with gypsum in the binder and in the aggregate; b) Cross nicols image: particular of the binder of dark colour, constituted by gypsum; it is visible aggregate, with prevalence of gypsum and trace of quartz and calcite (in colour brown in the top of image).

ly composed of gypsum, iron oxides (probably responsible for the darker pigmentation) and subordinate quartz and calcite.

Under stereomicroscope observation, **Product M** (sample 19) appears shiny on the surface. It is possible to recognise a binder and the aggregate. The binder is of brick-red colour and compact. The aggregate is constituted by three different typologies of grains: the first one presents crystals of fine dimensions, white colour, scaly fracture and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Furthermore, it is possible to observe traces of particles of fine dimensions and of red colour. Bands attributable to the presence of hemihydrate gypsum as main component with lower amounts of gypsum were present in the FT-IR spectrum [3610 (m), 3546 (m), 3404 (w), 1622 (m), 658 (s), 601 (s) cm^{-1}]. A protein as organic binder was present in small amounts (1546 cm^{-1}) and the presence of an iron oxide (hematite, 537 cm^{-1}) was also observed. The mineralogical analysis (XRD) reveals the presence of bassanite (CaSO$_4$·1/2H$_2$O), gypsum (CaSO$_4$·2H$_2$O), and traces of quartz (SiO$_2$). The observation under polarised light microscope in thin section, shows a binder of brownish-red colour, with anisotropic appearance and mainly constituted by gypsum. The porosity is medium, with irregular shape. The aggregate presents dimensions between 50-100 μm in prevalence and rarely 200 μm, of sub-angular shape. It is constituted by gypsum, quartz and traces of calcite and mica. Iron oxides are present. The binder/aggregate ratio is 1/3 (Figure 7). Therefore, Product M is constituted by gypsum and protein substances as binder, along with an aggregate composed mainly of gypsum, iron oxides (probably responsible for
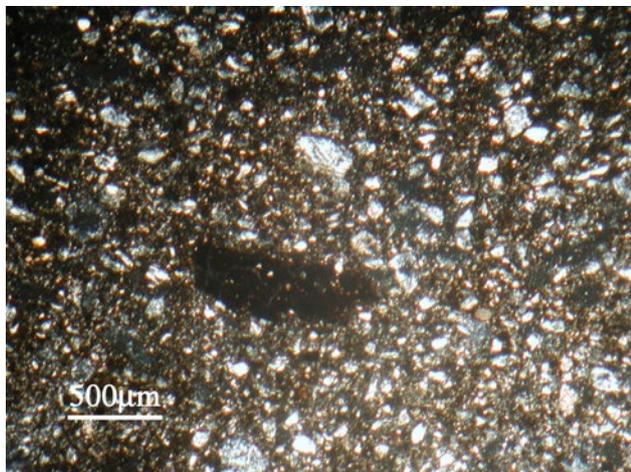
the brownish-red pigmentation) and subordinate quartz, calcite and mica.

The stereomicroscope observation of **Product N** (sample 20) shows a binder and the aggregate. The binder is of yellow colour and compact. The aggregate is constituted by three different typologies of grains: the first one shows crystals of fine dimensions, white colour, scaly fracture and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Moreover, it is possible to observe traces of particles of fine dimensions and of red colour. Gypsum hemihydrate as main component and lower amounts of gypsum were identified in the FT-IR spectrum [3610 (m), 3549 (m), 3400 (w), 1622 (m), 1151 (vs), 659 (s), 601 (s) cm^{-1}]. The presence of calcium carbonate and traces of a protein were also observed. The mineralogical analysis (XRD) of sample 20 reveals the presence of bassanite (CaSO$_4$·1/2H$_2$O), gypsum (CaSO$_4$·2H$_2$O) and calcite (CaCO$_3$). The presence of quartz (SiO$_2$) is also probable. The observation under polarised light microscope in thin section shows a binder of brownish-orange colour, with anisotropic appearance and constituted mainly by calcite and minor amounts of gypsum. The porosity is low and of irregular shape. The aggregate, of variable grain size from 50-300 μm, is constituted by gypsum, calcite and iron oxides. The binder/aggregate ratio is 1/3 (Figure 8). Therefore, Product N is constituted predominantly by calcite, low amounts of gypsum and protein substances as binder, with an aggregate composed mainly of gypsum, iron oxides (responsible for the brownish-orange pigmentation) and subordinate calcite.

Figura 7. Product M, sample 19 - Cross Nicols image: particular of the gypsum binder with brownish red colour for the presence of iron oxides. Gypsum and quartz, constituting the aggregate, are visible.
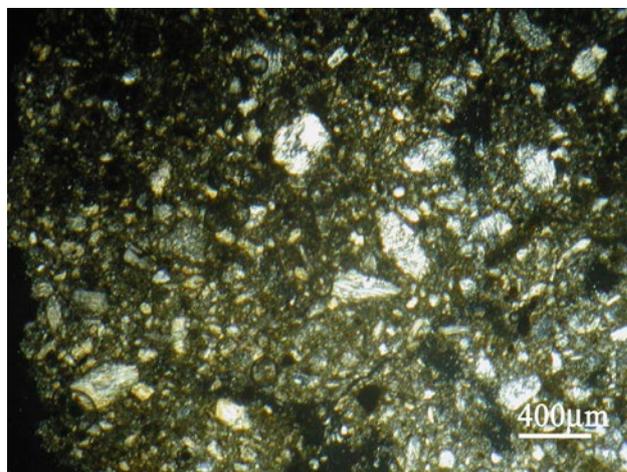
Figura 8. Product N, sample 20 - Cross Nicols image: particular of the binder of brown colour constituted by lime and gypsum; gypsum, calcite and iron oxides are visible in the aggregate of bigger dimensions.

Product O is only applied on the catalogued piece IGF 348T (indefinite trace). It was removed (sample 21) from the back of the find. Under stereomicroscope observation sample 21 shows a binder and the aggregate. The binder is of whitish-grey colour and compact. The aggregate is composed by grains of extremely variegated shape, typology and dimension. The FT-IR spectrum suggested the presence of calcium carbonate [2514 (w), 1432 (vs), 875 (s) and 712 (m) cm^{-1}] and of polysaccharide [3441 (m), 1028 (m), 469 (w) cm^{-1}] as binder. No organic products soluble in CDCl$_3$ were detected. The mineralogical analysis (XRD) of sample 21 shows the presence of calcite (CaCO$_3$), quartz (SiO$_2$), plagioclase-albite (NaSi$_3$AlO$_8$) and traces of fillosilicates. The presence of larnite (Ca$_2$SiO$_4$) is probable. The petrographical analyses were not carried out due to the small dimension of the sample. Therefore, one can hypothesise that Product O has a binder which is probably constituted by a hydraulic lime (for the presence of larnite) and polysaccharide; the aggregate might be constituted by quartz, plagioclase and fillosilicates, but it is not possible to carry out a correct characterisation without a petrographical analysis.

4.5 Conservation Properties of Products

Class A products are composed of a polysaccharide either used alone as adhesive (Product A) or thickened with different inorganic materials as aggregate (calcium carbonate and silica for Product B and silica and mica for Product C). Each different composition of the three products of Class A corresponds to a different use of the materials. In fact, rubber is used alone when it is applied as an adhesive, whereas it is mixed with an inorganic aggregate when the product is used to fill internal or external gaps and to reconnect big and irregular pieces (plaster).

The presence of calcium carbonate in Product B may also be attributable to carbonation of lime; in fact, lime could have been added to polysaccharides to improve mechanical properties. This formulation was probably chosen with the purpose of giving a mimetic effect and finishing touch in spite of a mechanical support and was used for finds of small and medium dimensions. On the contrary, Product C which contains an aggregate with larger grains and has a composition with quartz and without calcium carbonate, is preferred to Product B, as the dimensions of the find increase.

Class B materials (Products G and H) are compounds used for the fabrication of moulds and junctions. As confirmed by the analysis of a standard mixture, their composition reveals the presence of sulphur and an

amorphous carbon product as graphite. These products are also used as plasters; in this case the adhesive properties are conferred to the composite by the presence of graphite.

Class C materials (Product E and F) are mixtures of organic and inorganic compounds. Product E is composed of terpenes, waxes, salts of fatty acids, and gypsum. Product F is composed of terpenes, waxes, and calcium carbonate. Gypsum and calcium carbonate could have also been used as aggregate, especially in Product F, where no further aggregate is present to fulfill this function. In Product F the presence of carbonate could also be ascribable to lime carbonation. Lime could have been added to the mixture to enforce the grip or the hardness of the product [14, 15].

From the comparison of chemical, mineralogical and petrographical results for **Class D** materials, one can infer that Product K, Product L and Product M have gypsum and protein substances as binding materials with gypsum, iron oxides (Product L and Product M) and quartz, calcite and mica (mica only for Product M) as aggregates. For Product K, a correct identification of the aggregate cannot be performed due to the absence of petrographical analyses; it is only possible to hypothesise (by XRD analyses) a dolomitic composition. The composition of Products K, L and M is in agreement with a standard glue-gypsum plaster. In particular, in Product K the presence of protein is more copious than expected and it is in agreement with a major hardness of the material.

Product N differs from the former products of Class D; in fact, it can be defined as a plaster with a binder constituted by lime and gypsum; the aggregate (gypsum, calcite and iron oxides) has higher granulometry. Probably the presence of lime along with gypsum, the abundance of aggregate and the higher granulometry allowed the development of a tougher structure (in fact the plaster has been used to repair a long fracture in the find) [16-21]. Product O is probably an hydraulic mortar (for the presence of larnite), perhaps cementitious[22] and with a polysaccharide as additional binder. Furthermore its function is different: Product O was applied to create a firm base to maintain the finds in vertical position during the photographic sessions of Fucini, therefore the use of a mortar with higher resistance is to be deemed correct for this purpose.

Therefore, the products of Class D (except for Product O with only a particular function of support) were realised by Fucini as plasters with a prevalent presence of aggregates with a variable granulometry and the addition of glue to improve the hardness of the material. Furthermore, Fucini took into account other factors than

the compositional characteristics, mainly the colour of the filling, giving importance to the similarity of the pigmentation between restoration products and the finds.

Products A, K, L, M, N can be compared with similar ancient recipes mentioned in literature. Product A is mainly a polysaccharide material, according to the recipe of Cecchini[23], which contains Acacia gum (the Cecchini recipe specifies "Acacia gum, sugar and honey"). Product K is a standard glue and gypsum plaster as, for example, the recipe mentioned in Arcolao[14]. Products L and M are glue and gypsum plasters with iron oxide for the pigmentation and sand for the aggregate, in agreement with the traditional recipe of Cecchini [23]. Product N is a plaster realised with lime, gypsum and glue, sand for the aggregate and iron oxides for the pigmentation, and similar products are described in the literature ("lime, glue, gypsum, sand, pigments, alum") [25].

5. CONCLUSIONS

Important pieces of information were obtained analysing the products used for the fossil restoration of the *Fucini Collection*. The results show an example of application of traditional recipes in a yet unexplored field. Moreover, even among the wide variety of organic and inorganic materials, this study adds new information regarding some combinations of products; for example in the case of plaster of polysaccharide rubber with inorganic aggregate[24,25].

The possibility to identify materials used in old restorations represents a starting point for the study of conservation of paleontological finds of ancient collections. Further insights on these products and especially the extension of this research towards other classes of compounds will allow to obtain a more complete picture on the restoration techniques used on fossils in the past.

Moreover, some products (especially Class D materials and Product A) seem to fulfill exceptionally well, even one hundred years later, their conservative and esthetic functions. A dedicated study would also permit to evaluate their applicability to current restorations of paleontological finds. Knowing products and techniques, evaluated according to the present status of conservation, will allow to develop operative protocols for the conservation of paleontological material.

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REFERENCES

1. F. Howie, *Museum climatology and the conservation of paleontological material*, The Paleontological Association, London, **1979**.
2. B. Kummel, D.M. Raup, *Handbook of Paleontological Techniques,* W.H. Freeman and Company, San Francisco and London, **1978**.
3. P. Leiggi, P. May, *Vertebrate paleontological techniques, Volume 1,* Cambridge University Press, Cambridge, **1994**.
4. L. Azzaroli, A. Berzi, P. Brandinelli, S. Ciruzzi, *I musei scientifici a Firenze. Problemi di restauro e ricomposizione museale. Parte prima.* UNIEDIT, Biblioteca di Architettura, **1984**.
5. G. Merla, *Il Giornale dell'Università,* **1951**, *anno I, n. 12*, 345.
6. U. Schiff, *Archeion,* **1928**, *Vol.IX,* 1.
7. H. Howard, *Handbook of Paleo-Preparation Techniques (revised by Russell McCarty),* Florida Paleontological Society, Gainesville Florida, **1994**.
8. C. Cipriani, *Appunti di Museologia Naturalistica,* Firenze University Press, Firenze, **2006**.
9. A. Fucini, *Problematica verrucana. Tavole Iconografiche delle vestigia vegetali, animali, fisiche e meccaniche del Wealdiano dei Monti Pisani, Vol. I, II, III,* Industrie Grafiche V. Lischi & figli, Pisa, **1936**.
10. F. von Huene, *Eglogae Geol. Helv,* **1940**, *32 (2)*, 184.
11. F. von Huene, *Zentralblatt f. Min. Geol. u. Pal.*, **1940,** *Abt. B., 11,* 3492.
12. F. von Huene, *N. Jahrb. f. Min. Geol. u. Pal.*, **1941**, *Abt. B.,* 86.
13. M. Mazzini, *Guida del museo di Geologia e Paleontologia - Università di Firenze,* Landi, S. Giovanni Valdarno, **1982**.
14. C. Arcolao, *Le ricette del restauro,* Marsilio, Venezia, **1998**.
15. E. Schiele, Berens, L. W. *La calce.* Ed. Tecniche ET, **1976**.
16. A. Cagnana, in *A. d. costruzione.*(Edizioni S.A.P. srl), **2000**.
17. DOC.UNI-NORMAL11176. *Beni Culturali. Descrizione petrografica di una malta,* **2006**.
18. DOC.UNI-NORMAL10924. *Beni Culturali. Malte più elementi costruttivi e decorativi. Classificazione e terminologia,* **2001**.
19. DOC.UNI-NORMAL11189. *Malte storiche da restauro. Metodi di prova per la caratterizzazione chimica di una malta,* **2006**.
20. L. Fieni in *Le ricette del restauro,* (Edizioni all'Insegna del Giglio), **2002**.
21. T. Turco, *Il gesso. lavorazione, trasformaione, impieghi,* Hoepli, Milano, **1985**.

22. E. Pecchioni, F. Fratini, E. Cantisani *Le malte antiche e moderne: tra tradizione ed innovazione*. Pàtron Ed. Bologna, **2008**.

23. G. Cecchini, G. Giordano, Milani, *Materiali tradizionali per il restauro dei dipinti. Preparazione e applicazione secondo il manuale di Giovanni Secco Suardo*, Associazione Giovanni Secco Suardo, Lurano (Bg), **1995**.

24. M. Matteini, A. Moles, *La chimica nel restauro: i materiali dell'arte pittorica*, Nardini, Firenze, **1989**.

25. A. Bralia, F. Cancelli, C. Manganelli Del Fa, E. Pecchioni, *Museologia Scientifica*, **1990**, 175.