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Decorated Prehistoric Pottery from Castello di Annone (Piedmont, Italy): Archaeometric Study and Pilot Comparison with Coeval Analogous Finds

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Abstract

Prehistoric pottery decorated with incisions or impressions filled with white and seldom coloured inlays is well documented in the archaeological literature, but the related in-depth archaeometric studies are sporadic. 43 decorated ceramic shards, dating from the Neolithic to the Bronze Age, and an Iron Age fibula from the archaeological site of Castello di Annone (Piedmont, North-Western Italy) were analyzed with FTIR, Raman and XRPD for characterization of the ornamental pigments forming these inlays. Few white components were used as fillers, namely talc and bone ash (hydroxyapatite – Bone White), often as a mixture and seldom accompanied by other pigments (i.e. kaolinite and calcite). Comparison with freshly-heated biogenic hydroxyapatite proved that ancient Bone White pigment was calcined at about 900°C. Such a process was kept separate from pottery firing as these white mixtures show absence of talc degradation by-products and sporadic presence of kaolinite, implying these ceramics were decorated only after firing in furnace. Actual presence of fluorapatite in bone ash could allow dating with the Fluorine Method, but lack of fluorine detection with SEM-EDS causes such an attempt to be impracticable so far. A pilot comparative study with a restricted but representative group (11) of coeval finds from other sites of Piedmont suggests that while recurrence of talc prevails in Castello di Annone from the Neolithic throughout the Bronze age, massive use of bone ash (Bone White) becomes widespread in the close Iron Age settlements, possibly consequent to a more efficient handling of its production technology.

Keywords: Ceramics; Inlay-filled incision; Talc; Hydroxyapatite; IR-spectroscopy; X-Ray powder diffraction.

1. **Introduction**

The practice and tradition in prehistory to painstakingly fill incisions and/or impressions on pottery with inlays (more frequently white, seldom coloured) is well documented in the archaeological literature. A huge number of related finds, covering all the chronological intervals from the Neolithic to the Iron Age, were described from locations dispersed all over the world. The recurring motif adorning such artefacts is characteristic of specific historical periods and often helps the archaeologists in accurately dating these ceramics. Besides, it is commonly reputed that the choice of the materials, colours and techniques used to manufacture such decorations and inlays can be related to both aesthetical and technological reasons (Campbell, 1989), being eventually inspired to specific forms of symbolism (De Hostos, 1919; Plog, 1980; Topping, 1987; Tiné, 1988; Baird, 1991; Blasco, 1994; Martìn and Delibes, 1989; Gibson and Woods, 1997; Gibson, 2002, 2006; Laing, 2003; Prieto-Martìnez et al., 2003). In spite of such a widespread diffusion, few papers have been focused so far on the archaeometric characterization of the materials used by our ancestors to realize such ornamental motifs. As far as Italian finds are concerned, samples of white inlays from the Piedmont site of Casalnoceto (AL) were previously analyzed with XRPD techniques, which revealed the presence of talc (Venturino Gambari 1998; Venturino Gambari 2004). A more recent work (Giustetto, 2008) evidenced possible use of kaolinite in white inlays applied on incised ceramic shards coming from Pecetto (TO). Use of bone ash (Bone White) was detected on ceramic shards from Switzerland (Rychner-Faraggi & Wolf, 2001; Giustetto, pers. comm.) and Spain (Odriozola and Hurtado-Pérez, 2007). Analogous scientific studies on artefacts coming from different countries are similarly rather scarce (Noll et al., 1975; Hagstrum, 1985;

Jernigan, 1986; Swann et al., 2000; Mohammed-Ali and Khabir, 2003; Striova *et al*., 2006; Bugoi et al., 2008; Katsaros et al., 2009; Curtis et al., 2010).

This paper is focused on the in-depth archaeometric characterization of decorated fragmental pottery from the prehistoric site of Castello di Annone (Piedmont, Italy; Fig. 1) and includes a detailed archaeological description of the stylistic shapes and decorating motifs recurring in all investigated periods. The exhaustive characterization of the materials used to realize these ornaments, which cover a chronological period from the Neolithic to the Iron Age, brought to significant extrapolations concerning the manufacturing process and the techniques adopted to produce such artefacts.

To achieve such a goal a multi-disciplinary, micro-destructive analytical approach was adopted in order to preserve, as much as possible, the integrity of the pottery remnants. In addition to identification purposes, efforts were dedicated towards the possible detection of binding agents or other vehicles used to fix these inlays on the underlying ceramic body.

The outcomes obtained from the Castello di Annone pottery were further compared with analogous data collected on a restricted but representative group of ceramic implements from other almost coeval archaeological sites (Chiomonte, Fossano and Castelletto sopra Ticino; Fig. 1), all located in Piedmont but differentiated from the cultural, technical and aesthetic points of view. Such a pilot study, although preliminary, allowed the individuation of specific chronological periods or geographic areas in which some pigments were preferentially used.

(INSERT FIGURE 1)

2. **Materials and methods**

2.1 *Materials and Archaeological Case Study*

A significant number of decorated ceramic shards and/or implements (55) were extracted from the remnants of each archaeological site and selected for analysis. The material forming these white inlays appears non-homogeneously distributed but evident in those areas where it still abounds. For analytical purposes, two specimens were collected from each shard by scraping the surface with a fine scalpel, labelled by a prefix attesting the provenance (CdA: Castello di Annone; Ch: Chiomonte; F: Fossano; CT: Castelletto Ticino) and accompanied by an odd (inlay) or even number (underlying ceramic body).

(INSERT FIGURE 2)

2.1.1 Decorated pottery from Castello di Annone

43 ceramic shards and a bronze fibula bearing decorative incisions or impressions filled with white inlays were selected among the thousands of fragmental pottery from the site of Castello di Annone. Attribution to a specific chronological period was based on the peculiar shapes and decorating motifs and brought to the following partition: Neolithic (29), Copper Age (10), Bronze Age (4), Iron Age (1 fibula).

Located on a hill district alongside the Tanaro river, this site saw several occupational phases dating from the middle Neolithic (4500 BC) to the middle Iron Age (VI - V century BC) until the post-medieval epoch. Continuity for the anthropic settlement was favoured by propitious environmental conditions, fit for human activities. The village position over the surrounding areas allowed control of the whole Tanaro Valley, favouring agriculture development in alluvial soils suitable for cereal growing even with the raw ancient techniques. The archaeological features of the analyzed ceramic shards are detailed hereafter for each of the investigated periods, together with the description of a bronze fibula dating to the Iron Age.

Middle to Late Neolithic (ca. 4600 - 4200 BC): a sprawling and enduring anthropic settlement gave rise to flourishing lithic and pottery industries. The former saw presence of flint, quartz and obsidian splintered stone implements, sandstone or gabbro grindstones and eclogite or Na-pyroxenite polished greenstone implements (mainly axes or chisels) (Giustetto et al., 2008), in the form of finished or semi-finished handmade articles (Venturino Gambari and Zamagni, 1996; Salzani, 2005).

Among the thousands of fragmental pottery dating back to the Neolithic village, 29 shards bearing incisions or impressions filled with white inlays were selected (Fig. 2.a). 88% of these ceramics belongs to the so-called phase II (meander-spiralic style) of the 'Vasi a Bocca Quadrata' ('Square Mouth Vase': VBQ hereafter) culture (27 specimens; see Supplementary Material, Table S1), which can be divided in two fractions: i) a finer one, with predominant square or round mouth bowls decorated with motifs showing homogeneous syntaxes (i.e. excised triangles); ii) an accompanying fraction, where round mouth shapes (bowls, vases, cinerary urns) bear notched rims and/or wall-dragging decorations. No VBQ culture – phase I remnant was found, although some fragments differ from the others due to adoption of peculiar manufacturing techniques and decorative motifs, sometimes accompanied by different impastos. This atypical material can be further divided in two groups (termed 2 and 3): i) group 2 ceramics show decorations which outline banded or stripped motifs, realized with the incision technique and showing traits leading back to the Varese Isolino VBQ facies; ii) group 3 ceramics can be referred to intervened contacts with the phase III of VBQ culture, occupying quite a restricted geographic area (eastern Lombardia, Veneto and Trentino). Finally, some ceramics shards are consistent with the plastic elements style due to presence of ashlars and elongated grips applied on sumptuously decorated VBQ shapes, apparently contradicting those features typical of other sites belonging to phase III (Salzani, 2005).

Arrival of people from the low and medium Rodano valley between 4400 and 4200 BC caused the VBQ traits to be contaminated by Western features. These materials form the residual 12% of the Castello di Annone ceramics (2 specimens: CdA33 and CdA81; see Supplementary Material, Table S1) divided in two groups: i) with traits leading back to the St. Uze style (deep shapes decorated with plastic elements); ii) with motifs typical of the ancient Chassey Culture (painted lattice-disposed triangles, bands filled by vertical lines, seldom with irregular geometric motifs). These implements show fine to medium-grained impastos and polished surfaces, with distinctive shapes (decorated rectilinear, convex-profile or brim-bordered bowls prevailing on globular or egg-shaped jars, neck-shaped vases or cups). Graffito decorations are characterized by canaliculated handles and single or multiple pierced grips, together with persistence of ribbon-shaped handles (Padovan, 2005).

Copper Age (ca. end of 3000-2000 BC): in the Eneolithic period a reduced human presence is apparently observed in the whole Piedmont region, probably because of a more enhanced mobility of the human groups. In Castello di Annone evidences about the knowledge of copper metallurgy were found, accompanied by new decorative typologies for ceramics, characterized by irregular and rough surfaces and by a composite syntax of ornaments in the form of plastic cordons. Influences from the Varese Isolino and from the French Culture of Chassey can be noticed throughout the whole III millennium BC, while decorative features typical of the bell-jar Culture appear only in the 2^{nd} half.

Ten Eneolithic ceramic shards (bowl side fragments) were analyzed (Fig. 2.b; see Supplementary Material, Table S1), mainly characterized by metopal incised decorations filled with white to yellowish inlays.

Bronze Age (ca. end of 2000-1000 BC): a vast number of ceramic shards referred to all four chronological periods (Ancient, Medium, Late and Final) of such an Age (2^{nd}

millennium BC) were found, consistently with an existing pile-dwelling and ‘terramaricole’ civilization. Between the end of the XVIII and the XVII Century, passing from the Ancient to the Medium Bronze Age, the more evident characteristic about the ceramics manufacture is the wide diffusion in the whole Italian peninsula of the axe-shaped handle superelevation which occurs in bowls. Such a feature (which appears in the Castello di Annone ceramics as well as in those coming from Mercurago and Chiomonte), though not directly related to any specific Culture, must be considered as an influence exerted by the Italian style also in the Cisalpine area. During the Late Bronze Age, fibulae in bronze and other metallic alloys begin to appear. Four ceramic shards (bowl sides), bearing parallel or zigzagged incised decorations filled with a white to yellowish inlay, were analyzed (Fig. 2.c; see Supplementary Material, Table S1).

Iron Age (ca. 1st Millennium BC): in addition to ceramic implements, several fusions in bronze can be found during the following Iron Age, such as fibulae, buckles, pendants and arrow tips. Some fibulae show different and peculiar features (i.e., snaked or Celtic bark wire) possibly used to relate these implements to specific cultures (i.e. the ‘Ligures’ people, for those fibulae found in the protostoric burial ground near Chiavari). As representative of this period, a bronze fibula (CdA67) bearing round-shaped incised decorations filled with a whitish inlay was analyzed (Fig. 2.d; see Supplementary Material, Table S1).

2.1.2 Decorated pottery from other coeval archaeological sites

A representative group of analogously decorated pottery implements from other archaeological sites of Piedmont [Chiomonte (Ch): one shard; Fossano (F): 4 implements; Castelletto sopra Ticino (CT): 6 implements] was also sampled and labeled accordingly, in order to be analyzed for comparative purposes. Ceramics from Chiomonte date back to the Neolithic age (between 6.000 and 3.500 BC), whereas implements related to the other two sites date back to the Early to Middle Iron age (VIII-VI century BC and 825-675 BC for Fossano and Castelletto sopra Ticino respectively). A brief archaeological description of these ceramics is reported hereafter. (INSERT FIGURE 3)

2.1.2.1 *Chiomonte/La Maddalena*

Located in the higher part of Susa Valley, this site lies at the base of a slope facing South, disposing of water and soils suitable for cereals and legumes cultivation (Padovan and Thirault, 2007). An archaeological excavation, hurriedly performed during a motorway construction, brought to light different occupational phases running from the Neolithic to the Middle Age.

An important enduring settlement attributed to a transalpine group of Chassey Culture (Bertone et al., 1986) that dates back to the late Neolithic, has been related to commercial exchanges of both flintstone and greenstone implements, together with the development of high-altitude itinerant stock-rising. Ceramics from this period show convex bottom vases, bearing single, double or multiple grips, pierced and located close to the border and along the body, with fine to medium-grained impasto. Recurrent shapes are frustum of cone bowls and ovoid or globular vases with short, cylindrical neck and brimmed dishes, incised by graffito or impressed decorations with white or coloured inlays (red, brown or black; Padovan and Thirault, 2007; Bertone and Fozzati, 2002). A single ceramic shard from Chiomonte (Ch1) was investigated, dating back to the Late Neolithic (ca. 3700 BC) and bringing a scratch decoration filled with a red inlay (Fig. 3.a, see Supplementary Material, Table S2).

2.1.2.2 *Fossano*

This site is located on a plateau near the Stura di Demonte river, in a position suitable for anthropic settlement thanks to the presence of water resources, soils for cultivation/breeding and visual control on the surrounding landscape. Recent archaeological surveys discovered traces of a continuous occupation from the Neolithic to the Iron Age. In the Bronze Age, a cultural and economical development favoured the rise of commercial relationships with other transalpine areas and Golasecca, causing social differentiation evidenced by appearance of typical Ligurian crematory rites (Gambari, 2004). Use of river navigation as commercial paths allowed these Ligurian groups to control the access to the coast and alpine passes. The influence exerted by Etruscan groups is testified by prestige objects found in Ligurian territories from VII century BC, when Fossano became a startling example of demographical crowding.

The related ceramic shapes (VIII-VI century BC) show short-rimmed cups, deep-tanked bowls, big frustum of cone-necked vases decorated by banded incisions, ovoid vases with protruded rim and digitally impressed cord between rim and shoulder. Decorations are infrequent and consist of incised bunches of short lines/grooves and zigzagged motifs, sometimes filled with a white inlay (Venturino Gambari et al., 1996). Both of these motifs can be found on the four white-decorated analyzed finds (F1, F3, F5, F7; Fig. 3.b, see Supplementary Material, Table S2),

2.1.2.3 *Castelletto sopra Ticino*

This site, together with Varallo Pombia, saw the development in the IX century BC of the so-called Golasecca Culture in an area covering the actual borderlines of Piedmont, Lombardy and Canton Ticino, where also previous cultures had arose (i.e. the Canegrate Culture in the XIII century BC, equivalent of transalpine cultures, and the Cisalpine Culture, defined as Protogolasecca, in the final Bronze Age - XII-X century BC). The Golasecca Culture developed during the Iron Age in an area surrounding the commercial lines directed North-South (Ticino-Verbano e Agogna-Cusio-Toce systems; Gambari, 1988) and gradually became the *trait d'union* between the Mediterranean Sea and Continental Europe. In the VII-VI century BC the richness of these communities favoured the demographical growth of Castelletto Ticino, Sesto Calende, Golasecca and Como (Gambari and Cerri, 2009), which acquired proto-urbane dimension hosting most pre-roman necropolis of the North-West of Italy. Prestigious objects were found both in Golasecca and in Celtic transalpine areas, testifying the well developed commercial system existing among Etruscans, Celts and Greeks (De Marinis, 1991; Kruta, 2003, 2004).
The Golasecca culture covers three chronological periods (I, II and III), each characterized by peculiar ceramic decorations. All six analyzed implements (handmade ovoid or spheroid bi-conic cinerary urns with scarcely depurated impastos and incised decorating motifs filled by white inlays; Fig. 3.c) belong to the first, more ancient period, which can be further articulated in Golasecca I A (between IX and VIII century BC), I B (end of VIII and beginning of VII century BC) and I C (half of VII to beginning of VI century BC). A sharper attribution can

be made by keeping into account the evolution of the decorative motifs. Three cinerary urns (CT7, CT9 and CT11; Fig. 3.c, see Supplementary Material, Table S2) belong to the I A sub-period and bear in the upper half a repetitive ‘thin rope’ decorating motif, showing two stripes of reversed triangles incised by oblique parallel impressions (‘wolf-tooth’ decoration). These decorations are filled by a white inlay and divided by two or more gridded or zigzagged thin stripes (De Marinis, 1982). In the Golasecca I B sub-period, the ‘thin rope’ decorated bi-conic urns have been substituted by incisions showing ‘wolf-tooth’ decorations divided by a single stripe with network motifs (CT1, CT3 and CT5; Fig. 3.c, see Supplementary Material, Table S2). The following Golasecca I C and II periods bring to predominance of typical globular or ovoid urns bearing ‘*stralucido*’ decorations, characterized by larger and more complicated ‘wolf tooth’ motifs which tend to disappear in the III period.

2.1.3 Synthetic talc/hydroxyapatite mixtures

Freshly synthesized white mixtures of known wt% composition were prepared by grinding talc and hydroxyapatite. Talc powders were obtained by crushing of a natural specimen coming from the ‘Nuova Fontane’ mining concession, near Perrero, Prali and Salza di Pinerolo (Piedmont, Italy). Biogenic hydroxyapatite was obtained by thigh bovine bones according to the method proposed by Herliansyah et al. (2009). After cleaning and boiling three times (30 min, each time changing water), the bones were sun-dried for three days, cut with a hacksaw and calcined in a box furnace at 900° for 2 hours (5°C/min heating ramp) to remove organic matrix and avoid soot formation. The calcined bone fragments were cooled at room temperature and ground in an agate mortar. The degree of purity for both talc and hydroxyapatite was checked by XRPD, which showed absence of accessory mineral phases.

2.2 Analytical methods

A multi-disciplinary, micro-destructive analytical approach – comprehending FT-IR, Raman, X-ray diffraction and SEM-EDS – was adopted to achieve an exhaustive archaeometric characterization of all colorizing agents forming these inlays. Such an evidence is often hardly reached by using a single technique, due to the intrinsic limits which inevitably affect each method. X-ray diffraction allows a sharp mineralogical analysis of the studied specimen, but is strongly biased by the high intensity of those reflections related to heavy-scattering materials (such as quartz, feldspars and micas, quite abundant in the ceramic body) which may cover signals related to the white pigments. Though less affected by such an inconvenient, an exclusive characterization by means of vibrational spectroscopies (FTIR and Raman) may be troublesome, due to dubious attribution of the related absorption bands and consequent sharp phase identification. An undisputable identification needs therefore to be supported by a cross-checked convergence of data collected with different methods. In addition to pigment identification, vibrational spectroscopies were also used to possibly identify those binding agents (presumably organic) used to fix the colouring agents on the underlying ceramic body.
IR absorption spectra were collected on a FT-IR Bruker Vertex 70, equipped with an ATR attachment with a resolution of 2 cm^{-1}, collecting 32 scans for each spectrum.
FT-Raman spectra were collected on a Renishaw in Via Raman Microscope with a laser emitting at 785 nm. Photons scattered by the sample were dispersed by a 1200 lines/mm grating monochromator and simultaneously collected on a CCD camera; the collection

optic was set at 50X objective. The spectra collection setup of 75 acquisitions, each taking 50 s, was adopted.

X-ray powder diffraction (XRPD) data were collected on hand-ground specimens in an agate mortar using an automated PW3050/60 PANalytical X'Pert-PRO diffractometer, with θ-θ setup and an RTMS (real Time Multiple Strip) detector using monochromatized Cu-Kα radiation. The use of capillary has been prevented from the scarcity of the samples; for this reason diffraction data were collected on a zero-background, Si-monocrystal flat sample holder. Preferred orientation effects were attenuated by suspending the crushed powders in a non-volatile inert solution (amyl acetate + 5% collodion), thus maximizing the statistic disposition of the crystallites.

Quantitative analyses, restricted to the mutual talc and hydroxyapatite weight% amounts forming the ancient white pigment mixtures, were extrapolated by comparing the intensities of the experimental diffraction data with those collected under the same conditions (powders dispersed in amyl acetate + 5% collodion on a zero-background sample holder) on purposely prepared mixtures of known wt% composition (see Supplementary Material, Fig. S1). Multiple calibration curves were independently computed by calculating the ratio between the integrated intensities of several couples of non-overlapping talc and hydroxyapatite reflections [i.e. between the (002), (004), (006) and (0010) peaks of talc and the more intense (211) peak of hydroxyapatite] in each of the synthesized control mixtures (see Supplementary Material, Fig. S2). These curves were applied in reverse on the experimental data collected on the ancient specimens, thus obtaining an estimate of the mutual wt% talc-hydroxyapatite amounts for each couple of reflections (generalized Reference Intensity Ratio – RIR method). All computed estimates were further averaged so to possibly smooth the residual preferred orientation biasing the (00*l*) peaks of talc (only ones visible in the experimental data). The Diffrac Plus (2005) evaluation package was used for both qualitative and quantitative mineralogical analyses.

Scanning Electron Microscopy was performed using a SEM Stereoscan 360, Cambridge Instrument, coupled with an EDS Link Pentafet Oxford instrument equipped with a 'thin window' detector, that allows qualitative/quantitative chemical analyses of light elements (down to Boron). Working parameters were: acceleration voltage 15 kV, working distance 25 mm, probe current 1 nA and spectra acquisition time varying from 60 to 300 s. Standardization was performed using a pure Co specimen. Chemical data collected on unpolished and carbon coated fragments of the white inlays scraped from the ancient ceramics were processed with the Inca 200 Microanalysis Suite Software, version 4.08.

3. **Results**

Despite the scant mass of each scraped specimen (few mg), the adopted analytical approach allowed in most cases an exhaustive characterization of all white pigments used for the manufacture of these inlays, together with other polluting phases possibly related to the underlying ceramic body (whose presence is justified by the objective difficulty in sampling the scarce and extremely thin superficial white layer). Presence of contaminating materials can also be related, in specific cases, to impurities of the pigment mixture. A complete list of all materials detected in the analyzed Castello di Annone inlays, together with a concise archaeological description of each ceramic shard, is given in Table S1 (see Supplementary Material).

The pilot comparative study conducted by matching the Castello di Annone outcomes with those of analogous pottery from other anthropic settlements in Piedmont, although suffering from a restricted statistic, sketched an extremely appealing picture about the possible recurrence-predominance of specific materials in particular areas or periods. The complete list of ceramic implements coming from other sites of Piedmont (Chiomonte, Fossano and

Castelletto sopra Ticino) and analyzed for comparative purposes, comprehensive of all above mentioned data, is listed in Table S2 (see Supplementary Material).

3.1 Castello di Annone

Analytical data collected on 43 ceramic shards and one bronze fibula from Castello di Annone are commented hereafter for each of the adopted techniques.

3.1.1 Vibrational spectroscopies

FTIR evidences suggest that at least two different materials were mainly used as white fillers to produce these inlays. The recurring presence, in several spectra, of the δ(OH) absorption band at 669 cm^{-1} leads to possible presence of talc ($Mg_3Si_4O_{10}(OH)_2$) (Farmer 1974, Wilkins 1967). Traces of the talc signature were unequivocally detected in 17 out of the 44 analyzed archaeological finds (for example CdA1, CdA7, CdA11, CdA23, CdA37, CdA39, CdA41 and CdA49 – see Supplementary Material, Table S1; Fig. 4). Other samples show presence of a different kind of hydroxyls [bands at 3572 - ν(OH) and 630 cm^{-1} - δ(OH)], coupled with bands related to presence of CO_3^{2-} (signals at 1460, 1419 and 873 cm^{-1}; Fowler, 1974) and PO_4^{3-} groups (1040, 1093 and 962 cm^{-1}; Babot and Apella, 2003). A broad band at 1640 cm^{-1} is related to δ(H_2O), whose stretching counterpart forms a broad feature between 3250 cm^{-1} and 3500 cm^{-1}. All these evidences point to possible presence of a phosphate/carbonate phase such as hydroxyapatite [$Ca_5(PO_4)_3(OH)$] and carbonate-hydroxyapatite [$Ca_{10}(PO_4)_5CO_3(OH)$], mineral components of bone. This suggests possible use of Bone White, an ancient synthetic pigment obtained by calcination of animal bones, teeth and antlers. Unequivocal detection of hydroxyapatite spectral signature was detected in 5 out of the 44 analyzed specimens (i.e CdA3, CdA5, CdA17, CdA25, CdA53; see Supplementary Material, Table S1; Fig. 4).

Raman spectra unfortunately evidenced strong fluorescence in all analyzed specimens, which basically prevented an easy interpretation of the collected data. Presence of Bone White is however further supported by the typical phosphate band, systematically emerging from the convolute background at about 961 cm^{-1} (not shown; Silva and Sombra, 2004) in those specimens marked by recurrence of the typical hydroxyapatite IR absorption bands.

In some specimens FTIR absorption bands related to both talc and hydroxyapatite were observed (i.e. CdA51, CdA65; see Supplementary Material, Table S1), implying that a mixture of these two materials was possibly used to realize these white inlays. An unambiguous attribution of each signal to a specific colouring agent, however, is not easy because bands related to the main component tend to mask those of the subordinate material, which appear only as weak shoulders (i.e. CdA9; CdA23; CdA85; see Supplementary Material, Table S1).

Sporadic IR evidences (bands at 1436, 1088 and 874 cm^{-1}) about presence of calcite, possibly as the result of secondary, post-burial deposition processes (rather than an additional white agent) were also recorded twice (i.e. CdA27, CdA51; see Supplementary Material, Table S1).

In some cases (i.e. CdA13, CdA19 and CdA31) spectroscopic data collected on the white fillers specimen strongly resemble those of the corresponding ceramic body (CdA14, CdA20 and CdA32 respectively), suggesting a contamination during sampling. Such a limitation, dictated by the scarcity of the residual layer of inlay, generally did not prevent an accurate characterization of the white components (with some due exceptions, i.e. CdA19, CdA75, CdA87; see Supplementary Material, Table S1).

In addition to white pigments and ceramic components, other weak bands were often observed probably related to presence of proteins (i.e CdA7, CdA11 and CdA21). Though unequivocal identification could not be achieved, presence of these signals could possibly be related to residual traces of binding agents apt to favour adhesion of the inlay to the substrate. In some cases traces of a consolidant resin (paraloid) were also detected, consequence of an intervened restoration (i.e. CdA19).

FTIR data collected on the decorated bronze fibula (CdA67) evidenced presence of a multi-component white mixture, including bone ash (hydroxyapatite) and calcite.

(INSERT FIGURE 4)

3.1.2 X-Ray Powder Diffraction

The enhanced sensibility granted by XRPD towards detection of the bulk composition allowed a more exhaustive characterization of all mineral phases forming the studied decorating motifs, together with the description of all contaminating phases related to the underlying ceramic body and/or pigment impurities.

Adoption of essentially two different white components for the manufacture of these ornaments is basically confirmed by XRPD. On the basis of their mineralogical composition, all investigated specimens can be approximately divided in three main groups: i) exclusively talc-constituted inlays (15 out of the 44 total samples: for example CdA1, CdA7, CdA23 and CdA37 – Fig. 5.a); ii) presence of talc and hydroxy–/carbonate-hydroxyapatite (bone ash) mixtures (18 specimens), which can be the sole components (14 samples, such as CdA9, CdA11, CdA29 and CdA85 – Fig. 5.b) or combined to additional white agents (4 cases, such as CdA13 with kaolinite or CdA51 with calcite), with variable quantities in different specimens; iii) exclusive presence of pristine Bone White (3 specimens, i.e. CdA3, CdA5 and CdA17 – Fig. 5.c). An exception to such a rule is offered by CdA27, which showed an atypical calcite + kaolinite composition. For 7 specimens an unequivocal characterization could not be achieved, due to insufficient sampling or heavy contaminations from the ceramic body.

A mixture of two white components, namely talc and bone ash (calcined hydroxyapatite), is therefore likely to have been used in most cases. The mutual amounts of talc and hydroxyapatite in such mixtures were extrapolated, whenever possible, by comparing the intensities of the related diffraction peaks with those of control mixtures of known composition. The related results, expressed as absolute talc and hydroxyapatite wt%, are reported in Table 1. Despite the relatively high standard deviations [computed by averaging the compositional estimates obtained on different couples of reflections, in an attempt to smooth the residual preferred orientation inevitably affecting the (00*l*) talc reflections], it is worth noting that throughout all the investigated chronological periods (from the Neolithic to the Bronze Age) the amount of talc usually exceeds or approximately equals that of hydroxyapatite (bone ash), with few exceptions (i.e. CdA13, CdA15 and CdA25).

(INSERT TABLE 1)

Among those inlays containing only pristine talc, it has to be pointed out that although this composition is unequivocal in unpolluted samples (such as CdA1, CdA23 and CdA39), it is objectively difficult to assess whether small amounts of bone ashes are present when strong contamination occurs. The diffraction signatures of high scattering materials from the ceramic body, in fact, tend to mask those signals related to low scattering hydroxyapatite, possibly thwarting its accurate characterization (i.e. CdA43 and CdA69).

Subordinate amounts of contaminating components were observed, in addition to the white pigments, in almost all investigated specimens. Presence of chlorite $[(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8]$, often coupled to talc in natural outcrops, was sporadically recorded (i.e. CdA7) and related to an impurity of the pigment itself. Peaks related to quartz, micas (biotite and muscovite) and feldspars (orthoclase and plagioclase), detected in most specimens, can conversely be justified by intervened contaminations from the ceramic body during sampling, an hypothesis confirmed by the diffraction data collected on the bulk of the ceramic shards (specimens labelled ‘CdA’ and followed by an even number). As mentioned above, strong contaminations could occasionally prevent an exhaustive characterization of all decorating agents (for example in CdA19, CdA55 and CdA75).

Diffraction data collected on the white inlay scraped from the Iron Age bronze fibula (CdA67) evidenced contextual presence of predominant talc, abundant calcite ($CaCO_3$) and subordinate hydroxyapatite, together with the detection of hydrocerussite [$(PbCO_3)_2Pb(OH)_2$] and negligible quantities of contaminant phases (such as quartz and feldspars). Possible traces of hydrocerussite were also observed in the CdA83 specimen (see Supplementary Material, Table S1).

(INSERT FIGURE 5)

3.2 Comparison with decorated pottery from other archaeological sites

A brief but exhaustive analytical report concerning the restricted group of prehistoric decorated ceramic shards and implements coming from the three additional sites of Chiomonte, Fossano and Castelletto sopra Ticino, studied for comparative purposes, is exposed hereafter.

3.2.1 *Chiomonte/La Maddalena*

The FTIR pattern of the unique Late Neolithic (ca. 3700 BC) ceramic shard from Chiomonte (Ch1), decorated by incisions filled with a reddish inlay (Fig. 3.a), shows a strong absorption band at 1082 cm^{-1} together with minor features appearing at 1166, 798, 778 e 694 cm^{-1}, possibly related to quartz. The broad band peaking at 3400 cm^{-1} can be related to ν(OH), suggesting possible presence of a hydroxylated mineral such as hydroxyapatite or kaolinite. Minor features appear at 1032 (Si-O-Si), 1009 (Si-O-Al), 938 and 914 (Al-O-H) cm^{-1} (Fig. 6). Though no direct IR evidence was found, detection of quartz and other minerals may suggest presence of red ochre (hematite, Fe_2O_3) as the possible colouring agent (Bikiaris *et al.* 1999). Such a hint is confirmed by the appearance of weak reflections related to hematite in the XRPD pattern (not shown). Traces of hydroxyapatite and subordinate talc were also detected, but no kaolinite was found. As suggested by FTIR, massive presence of quartz together with feasible traces of a spinel-like phase [$Mg(Al,Fe)O_4$: d = 2.031 Å] were observed.

(INSERT FIGURE 6)

3.2.2 *Fossano*

The four white-decorated finds (F1, F3, F5, F7; Fig. 3.b) show FTIR and Raman patterns quite similar. In all cases, vibrational modes related to hydroxyls (3572 and 630 cm^{-1}), phosphate (1093, 1040 and 962 cm^{-1}) and carbonate groups (1460 and 875 cm^{-1}) lead to presence of hydroxy–/carbonate-hydroxyapatite phases, suggesting pristine Bone White as the sole pigment forming these inlays (Fig. 7.a). This assumption is basically confirmed by XRPD, which however shows that variable amounts of talc are also present in all specimens in addition to bone ash (hydroxyapatite; Fig. 7.b). The mutual talc-bone ash amounts, inferred from XRPD data, show that the talc quantities are sensibly lower than those observed for Castello di Annone, only occasionally reaching worth mentioning values (i.e. F7: ≅ 20%; Table 2). The observed compositional monotony is consistent with the excellent purity of the samples; minor traces of quartz and orthoclase, residues of the ceramic body, can only be observed in addition to white pigments.

(INSERT TABLE 2)

(INSERT FIGURE 7)

3.2.3 *Castelletto sopra Ticino*

The FT-IR and Raman spectral features of all six analyzed decorated pottery implements show absorption maxima related to hydroxyls (3572 and 630 cm^{-1}), phosphate (1093, 1040 and 962 cm^{-1}) and carbonate groups (1460 and 875 cm^{-1}), leading to presence of hydroxy–/carbonate-hydroxyapatite phases (Bone White pigment). Some specimens show traces of a Paraloid contamination, possibly applied during the conservation work, as certified by a weak feature at 1732 cm^{-1} (Fig. 8.a). Massive presence of both hydroxy–/carbonate-hydroxyapatite is unequivocally confirmed by XRPD, though in all samples subordinated amounts of talc are also detected. The mutual talc/hydroxyapatite amounts in these mixtures, inferred by XRPD (Table 2), show that bone ash is always predominant; talc is very scarce, only occasionally reaching 15 wt% (i.e. CT1 and CT7; Fig. 8.b). The essential purity of the analyzed specimens is corroborated by the scarce presence of contaminant phases (quartz, feldspars and micas) from the ceramic body.

(INSERT FIGURE 8)

4. **Discussion**

The analytical survey performed on the Castello di Annone fragmental pottery shows that the white fillers used to manufacture these inlays can be essentially traced to a restricted variety of natural and/or synthetic pigments, mainly represented by talc and bone ash (Bone White). The former, in particular, is the most frequently used, appearing as the exclusive colouring agent in 34% of the investigated specimens. An even more relevant fraction (41%), however, shows presence of talc and hydroxyapatite mixtures, mostly with no further addition (32%) and seldom with the sporadic contribution of other colouring agents (9%) such as kaolinite, calcite (presumably of secondary origin) and/or hydrocerussite. Generally these mixtures are formed by approximately equal weighed quantities of talc and bone ash (50% of the investigated specimens), but frequently (33%) talc is more abundant (Table 1). Pristine Bone White inlays (7%) are also observed (Figure 9.a and 9.b).

(INSERT FIGURE 9)

The recurrent use of talc/bone ash mixtures is basically confirmed by data collected on decorated ceramics from other archaeological sites of Piedmont (namely Fossano and Castelletto Ticino; Table 2), although in this case sheer predominance of hydroxyapatite on talc is observed (Figure 9.b).

Talc is a frail phyllosilicate mineral formed by alteration of Mg-bearing silicate rocks in low-degree metamorphic conditions, whose crushing gives a white powder often used as a pigment or extender in prehistory (Swann et al., 2000; Hradil et al., 2003; Chairkina and Kosinskaia, 2009; Pesonen and Leskinen, 2009). Talc outcrops are quite common in Piedmont and surrounding areas located near the actual towns of Ala (TO), Bibiana (TO), Borzoli (GE), Castel Delfino (CN), Chamonix (France), Col de Tende (France), Lanzo (TO), Masone (GE), Monte Rosa (VB), Montjovet (AO), Prali (TO), Traversella (TO), Viù (TO) and Voltaggio (AL) (Barelli, 1835). Another even more suitable source for talc, however, is represented by steatite (or soapstone), a talc-schist metamorphic rock often associated with the ophiolitic rocks typical of the low Piedmont region. Steatite is quite common in the neighbourhoods of the investigated Castello di Annone site and its direct crushing produces a fine, fairly whitish powder (depending on the wt% of talc) directly useable as a pigment.

Bone White is a chemically inert and heat resistant synthetic pigment obtained by calcination at high temperature of animal bones and/or teeth, whose ashes contain a mixture of two similar phosphates, hydroxyapatite and carbonate-hydroxyapatite. In fresh bone tissue, hydroxyapatite accounts for about 40% of the total weight, the remaining 60% being related to H_2O and organic constituents (mainly collagen). When heated, bone loses around 25% of its mass due to loss of H_2O and organic matter combustion; this process does not affect the Ca/P ratio of biogenic hydroxyapatite, which varies between 1.83 and 2.51. Non-biogenic (mineral) hydroxyapatite, conversely, shows an average Ca/P ratio < 1.8 (Shiegl et al., 2003; Zaichicka and Tzaphlidou, 2002). Use of synthetic Bone White as the main constituent of similar inlays filling incisions on prehistoric pottery is known from literature (Roberts et al., 2007; Odriozola and Martìnez-Blanes, 2007; Odriozola and Hurtado Pérez, 2007; Curtis et al., 2010; Parkinson et al., 2010), even in the Far East (Li et al., 2009). In all analyzed specimens, the biogenic origin of this pigment is experimentally supported by appearance of FTIR absorption maxima at 1460, 1419 (CO_3^{2-} substitution of either the OH^- or -PO_4^{3-} groups: Fowler, 1974; Smith, 1999) and 873 cm^{-1} [$\nu(CO_3)$; Dauphin, 1993; Farmer, 1974] (See Fig. 4; CdA5). These bands, in fact, are typical of fossil bones but absent (or weak) in mineral hydroxyapatite, whose natural sources in Piedmont and surrounding areas are scarce. In addition, detection of the 630 cm^{-1} band (OH librational mode) may suggest that bone calcination occurred at high temperature (Odriozola and Hurtado Perez, 2007). This process is known to cause *T*-dependent transformations in biogenic hydroxyapatite, which significantly vary its crystalline degree. In fresh bone tissue (pattern 1 in Fig. 10.a) broad diffraction peaks are observed for hydroxyapatite, a situation which is not significantly affected by natural ageing (pattern 2 in Fig. 10.a). Severe heating (i.e. calcination; Rogers and Daniels, 2002), on the other hand, causes appearance of progressively narrower reflections (i.e. calcined bovine thigh bone, pattern 3 in Fig. 10.a), symptomatic of an increased crystallization analogous to that observed in the ancient inlays made of pristine Bone White (pattern 4 in Fig. 10.a).

(INSERT FIGURE 10)

While XRPD data show that talc and calcined biogenic hydroxyapatite mixtures were used in most cases, FT-IR/Raman techniques seldom evidence contextual presence of both these components in the analyzed inlays.

The mutual talc/bone ash quantities in these mixtures tend to significantly vary in the different investigated sites, leading to important archaeometric extrapolations. Although more or less significant differences can be observed even within the same context, generally in the more ancient Castello di Annone site use of talc appears to be predominant: such a pigment can be exclusive (34% of the analyzed specimens) or mixed to minor or equal hydroxyapatite amounts (40%) (Figure 9.a). Due exceptions are represented by pure Bone White inlays (i.e. CdA3 and CdA5) or mixtures where bone ashes prevail upon talc (i.e. CdA13 and CdA25; Table 1). In the more recent Iron Age locations (Fossano and Castelletto sopra Ticino; Table 2), conversely, hydroxyapatite becomes significantly more abundant than talc, occasionally pertaining an almost exclusive role (Figure 9.b).

The adopted approach makes it impossible to determine whether bone ash and talc were mixed and applied simultaneously or rather be the result of distinct and sequential applications. If the latter hypothesis is true, multiple coats may have been spread by various hands in different ages, possibly due to colour ‘refreshment’ or ‘vintage’ restoration. A careful, in-depth stratigraphic study of these inlays – involving both optical microscopy and SEM-EDS – could possibly shed light on this aspect, although the macro-destructivity of this approach could severely spoil these precious prehistoric relics. Despite the absence of such information, however, it is unquestionable that in Castello di Annone use of talc – alone or mixed to bone ash – was widely adopted throughout all the investigated periods (Neolithic, Copper and

Bronze Age), whereas in the more recent Iron Age sites (Fossano and Castelletto sopra Ticino) an almost exclusive use of hydroxyapatite prevailed.

Massive use of talc/bone ash mixtures brings to other fundamental extrapolations concerning the technology used to manufacture these white inlays. An analytical method was proposed in literature to infer the burning temperature of bone remains from XRPD and FTIR data (Pleshko et al., 1991; Piga et al., 2008) based on the crystal size increase and structural changes triggered by heating of biogenic hydroxyapatite (Bonucci and Graziani, 1975; Shipman et al., 1984). A correlation exists between the Full Width at Half Maximum (FWHM) of selected diffraction peaks and the temperature reached during calcination (Bartsiokas and Middleton, 1992; Person et al., 1995). In crude bone, the (211) and (112) reflections ($2\theta \cong 31.8°$ and 32.2° using Cukα, respectively) are overlapped and virtually indistinguishable while the (300) peak ($2\theta \cong$ 32.9°) appears as a shoulder (Surovell and Stiner, 2001). By gradually heating, the (211) and (112) peaks start to split (700-750°C) until complete separation (850-900°C) whereas the (300) reflection grows in intensity. This sequence is due to progressive transformation with the temperature rise of hydroxyapatite to β-tricalcium phosphate (Grupe and Hummel, 1991; Nielsen-Marsh, 2000; Roberts et al., 2002). All analyzed specimens containing bone ashes (pristine Bone White or talc/hydroxyapatite mixtures), both from Castello di Annone and the other investigated sites, show sharp and distinct diffraction peaks: the computed FWHM of ancient bone ash (211), (112) and (300) reflections (see, for example, CdA5 and CT1 in Fig. 10.b) corresponds to that of fresh biogenic hydroxyapatite calcined at 900°C (OH-apt in Fig. 10.b). Besides, these data are in excellent agreement with those presented by Odriozola and Martìnez-Blanes (2007; Fig. 10.c), further confirming that calcination for preparation of ancient bone ash indeed occurred at 900°C. These values are consistent with the presumed firing temperatures of these ceramics, qualified as low-fired productions (temperature varying between 750 and 900°C) comparable to coeval French and Swiss findings (Covertini, 1996; Morzadec, 1995; Salanova, 2000). While studying Neolithic ceramics from the Middle

Guadiana river (Badajoz, Spain), Odriozola and Hurtado Pérez (2007) assumed that similar ornaments were applied (with or without a binder) as crude bone powder, made into a paste, directly on the uncooked forged implements before firing in furnace: formation of bone ash would therefore be a byproduct of the ceramics firing. Though similar conclusions could be claimed for the pristine Bone White inlays studied here (i.e. CdA3 and CdA5), the recurrent detection of two-components mixtures (talc + bone ash) in variable ratios leads to an alternative interpretation. The thermal decomposition of talc is known to begin at 800°C (Wesolowski, M., 1984; De Souza Santos & Yada, 1988; Bose & Ganguly, 1994), with consequent formation of byproducts such as enstatite ($Mg_2Si_2O_6$), tridimite (SiO_2) and (if higher temperature is reached) cristobalite (SiO_2). If talc had been applied on the unfired ceramics together with crude bone powder prior to firing, the extent of the temperature (≥ 900°C, as inferred from hydroxyapatite calcination) would also have triggered formation of talc derivatives during sintering in furnace. No trace of enstatite and tridimite, however, was ever detected by XRPD in any of the analyzed specimens, implying that these talc-containing inlays (alone or mixed to bone ash) were applied only after firing. Analogous considerations were recently suggested also by Iordanidis and Garcia-Guinea (2011) studying ancient potsherds (XVI to III century BC) from Northern Greece.

Firing of the ceramic implements (750 < T < 900°C) for the current study must therefore be considered a process distinct from bone calcination (T ≥ 900°C), aimed exclusively to preparation of bone ashes: such a material was applied – possibly together with talc – only on the already fired pottery. This assumption is also empirically supported by the fact that the material grinding of fresh bones to prepare crude bone powder is a very tough task (the Authors personally experienced this while preparing freshly-synthesized Bone White pigment for comparative purposes; see § 2.2), but it becomes considerably easier once the bone is calcined. One can guess it was quite inconvenient for our ancestors to keep on crushing crude bones for the resulting powders (made into a paste) to be burned on the uncooked implements, after realizing that the same results could be obtained with a considerably minor effort just by keeping the two processes (pottery firing and bone calcination) separated and applying bone ashes on the already fired ceramics.

A third natural pigment seldom used to produce these white inlays is kaolinite [$Al_2Si_2O_5(OH)_4$], a soft earthy phyllosicate produced by the chemical weathering of Al-silicates such as feldspars. Possible use of kaolinite as a pigment or extender on prehistoric pottery, though infrequent, is not unknown (Sziki et al., 2003; Hradil et al., 2003; Katsaros et al., 2009). In ceramics from Piedmont, presence of kaolinite can be exclusive (Giustetto, 2008) or more frequently mixed in subordinate quantities together with talc and bone ash (i.e. CdA13) or calcite (CdA27). The role of kaolinite as a basic ingredient of the ceramic *impasto* is unrelated to its use as a white pigment, because this mineral undergoes a complete phase transformation during heating. Therefore sporadic detection of kaolinite further supports the above mentioned assumption according to which such inlays were realized for aesthetic purposes only after ceramics firing: application prior to firing would in fact cause such a phase to disappear.

Presence of calcite was also episodically observed (i.e CdA27 and CdA51). Use of this carbonate phase as a Neolithic pigment, possibly associated to other colorizing agents, was seldom reported (Mioč et al., 2004) and its incidental detection would apparently further support the perspective of these ornaments being applied after ceramics firing (at $T \geq 800$°C de-carbonation would cause disappearance of calcite-based pigments applied prior to firing). Its sporadic recurrence, however, suggests that presence of calcite is probably related to post-burial, secondary depositional processes (Constantinescu et al., 2007; Bugoi et al., 2008) rather than purpose addition by prehistoric artists.

Though a fascinating perspective, infrequent detection of hydrocerussite (in addition to talc, hydroxyapatite and/or calcite; Fig. 9.b) is unlikely to be related to use of Lead White. This pigment, in fact, was first produced in ancient Greece as early as 400 BC or even before (Rossotti, 1983), but its use has never been reported so far in Northern Italy in prehistory.

Detection of hydrocerussite on the Iron Age fibula ornament (CdA67) can be possibly related to corrosion of the bronze surface, due to exposure to degrading/bleaching agents (i.e. rain, groundwaters, soil components, etc.), with consequent formation of Pb corrosion byproducts such as lead carbonates (Selwyn et al., 1996; Balassone et al., 2009). Usually high CO_2 contents favor formation of hydrocerussite (Turgoose, 1985) whereas cerussite forms at low pH (Graedel, 1994). Presence of hydrocerussite in the CdA83 specimen, on the other hand, is dubious.

The unique red inlay found on the ceramic shard from Chiomonte (Ch1) shows presence of red ochre (hematite; Fe_2O_3) together with traces of talc and bone ash. A mixture of several components was therefore used to realize such an ornament, which is consistent with previous studies (Judson, 1959; Mioč et al., 2004; Constantinescu et al., 2007; Bugoi et al., 2008; Iordanidis and Garcia-Guinea, 2011). The scarce purity of the red ochre (contamination from Si, Al and Ca-bearing minerals: Bikiaris *et al.* 1999) is known to prevent sometimes the identification with conventional methods. The detection of a spinel-like mineral, besides, certifies possible Fe^{3+} stabilization due to incorporation in a stable hosting phase (Bondioli et al., 1998; Garcìa et al., 2003), thus explaining the low intensity of hematite XRD reflections.

Possible sources for red ochre in Piedmont and surrounding areas are Almese (TO), Apt Ochre Basin (Provence, France), Baio (TO), Brosso (TO), Carouge (France), Germagnano (TO), La Thuile (AO), Maggiora (NO), Orta (NO) (‘lands of the Vercelli and Novara high plains’), Quart (AO), Schieranco (VB), St. Julien (France), Vico (CN), Villa del Bosco (BI) and Villanova di Mondovì (CN) (‘Monregalese land’) (Barelli 1835; Scarsella and Natale 1989).

An accurate study of the variably coloured ceramic inlays from Chiomonte (red, brown, black: Bertone and Fozzati 2002) could hopefully help to shed light on the relationships which in Neolithic occurred between these inhabitants and those of transalpine and cisalpine areas.

In some white inlays from Castello di Annone weak IR-active vibrational modes related to proteic material were observed, possibly related to the addition of a binder or vehicle apt to ensure pigment adhesion to the ceramic body. No certain attribution (i.e. animal fat, resin or egg, in addition to water; Chalmin et al., 2003; Barnett et al., 2006; Williamson, 2000), however, could be attempted. Traces of Paraloid were also observed on some Castelletto Ticino specimens, diagnostic of a recent consolidation process.

In those ornaments marked by an exclusive/predominant use of bone ashes, a careful analysis of XRPD data suggests possible presence of a further phosphate in addition to hydroxyapatite/carbonate-hydroxyapatite, namely fluorapatite [$Ca_5(PO4)_3F$] or francolite [$(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$], a fluorine rich phosphate or phosphate-carbonate phase respectively (i.e. Castello di Annone and Fossano, Figures 5.c and 7.b respectively, magnifications). It is known from literature that hydroxyapatite can gradually transform into fluorapatite (Hagen, 1973; Wei et al., 2003) due to selective OH^-/F^- vicariance, a process which affects the diagenesis of bone remains submersed in sea waters (Nemliher et al., 2003) or interred in soils permeated by F^--rich aqueous solutions (Wier et al., 1972; Reiche, 2006; Stathopoulou et al., 2008). The OH^-/F^- substitution rate strictly depends from the geo-chemistry of the interring soil and rock substratum and is influenced by F^- concentration on local basis. This substitution plays a fundamental role in the dating of buried bone remains with the so called Fluorine Dating Method (Carnot, 1893; Middleton, 1845; Cook and Ezra-Cohn, 1959; McConnel, 1962; Johnsson, 1997; Goffer, 2007; Gaschen et al., 2008; Goodrum and Olson, 2009).

The observed potential splitting of the hydroxyapatite reflections at high 2θ values in the XRPD patterns, however, is also possibly biased by the non-elimination of the Cu-Kα2 wavelength, thus causing detection/quantification of any F^--substituted phosphate phase to be unreliable. In order to possibly detect actual presence of fluorapatite in these white inlays – and evaluate the feasible setting of an alternative dating method for these implements – pristine bone ash grains were scraped from the CdA3 and CdA5 specimens and analyzed with SEM-EDS, The obtained results, despite their semi-quantitative reliability (being collected on unpolished specimens), show that the averaged chemical composition of these samples (see Supplementary Material, Table S3) is consistent with an almost pure hydroxyapatite; no fluorine was detected. All measured weight% Ca/P ratios (see Supplementary Material, Table S4) fall in the range between 2.12 and 2.31 (average: 2.21), further confirming the biogenic origin of this pigment (Shiegl et al., 2003). These evidences disprove any measurable evidence about actual presence of fluorapatite in bone ashes, unless more sensitive approaches are adopted (i.e. PIGE or PIGME; Quattropani et al., 1999). Moreover, the absence of an appreciable fluorapatite content in these Bone White inlays is consistent with the geochemistry of the fluorine-poor Piedmont subsoil, which does not favour subterranean circulation of F-rich groundwaters.

5. **Conclusions**

A detailed archaeometric study was performed, aimed towards the characterization of white inlays filling incisions and/or impressions on prehistoric pottery coming from the archaeological site of Castello di Annone (Piedmont, Italy), dating from the Neolithic to the Iron age.

The collected evidences show that a restricted number of white pigments was used, namely natural talc and synthetic Bone White, with the sporadic addition of other minor components (i.e. kaolinite). Talc, whose recurrence is predominant in almost all analyzed specimens, could be found as pristine mineral or rather derived from direct crushing of steatite (soapstone rock). As a pigment, it could be used alone or (more frequently) mixed with subordinate or equal amounts of bone ash.

Significant archaeometric considerations can be extrapolated from a pilot study which compares the outcomes from Castello di Annone with those collected on analogously decorated pottery coming from other almost coeval sites of Piedmont (Chiomonte, Fossano and Castelletto sopra Ticino). In spite of its limited statistics, this approach shows that in the more ancient Castello di Annone settlement use of talc (black columns in Fig. 9.b) apparently prevails, though frequently coupled to subordinate or equal quantities of bone ash (which episodically becomes exclusive: Bone White). Use of calcined biogenic hydroxyapatite (white columns in Fig. 9.b), on the other hand, appears to be predominant in the more recent Iron Age sites (Fossano and Castelletto sopra Ticino). It is convenient to suppose that in Castello di Annone the adopted decorating techniques underwent no significant development from the Neolithic to the Bronze Age. The procedure leading to preparation of synthetic Bone White, though already experimented, was probably yet to be adequately mastered. Lack of this technological skill possibly caused diffusion of talc to prevail, for which mere crushing and addition to a binder are required. In the close Fossano and Castelletto sopra Ticino settlements, on the other hand, skilled craftsmen possibly managed, during the Iron Age, to set up a convenient procedure for the production of Bone White, thus realizing the sheer advantages granted by such a pigment in terms of artistic yield and gradually supplanting use of talc.

The performed analyses could not establish whether contextual presence of talc and bone ash in mixture could result from a single application or rather multiple coatings of different pigments in separate moments, aimed to ‘refresh’ or ‘restore’ faded ornaments. The latter hypothesis, if founded, may explain the episodic presence of significant quantities of calcined biogenic hydroxyapatite on the more ancient Neolithic artefacts. Absence of talc degradation by-products, however, suggests that these white inlays were applied only after firing of the ceramics in furnace, a process distinct and independent from calcination aimed to bone ash synthesis ($T \geq 900°C$).

Lack of an appreciable fluorapatite/hydroxyapatite substitution in pure Bone White-manufactured ornaments causes the Fluorine Dating Method to be inapplicable. Analysis of analogous coeval potteries interred in different geographic contexts, with soils permeated by fluorine-rich groundwaters (similar white inlays were recently described in Syria by Fornacelli and Memmi, 2012), might cause such an attempt to be worth trying.

The adopted analytical approach seldom detected traces of a protein binder used to favour adhesion of the pigments to the ceramics, but no sharp attribution could be attempted and an alternative protocol should therefore be pursued. Together with such a goal, future perspectives are directed towards extending the archaeometric survey to other coeval anthropic settlements, in order to enlarge the statistical basis and further support the proposed outcomes.

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Table Captions

Table 1: Quantitative amounts (expressed as wt%) of talc and hydroxyapatite in the decorating white mixtures found on the Castello di Annone specimens, as inferred by XRPD analyses.

Table 2: Quantitative amounts (expressed as wt%) of talc and hydroxyapatite in the decorating white mixtures found on the Fossano and Castelletto sopra Ticino specimens, as inferred by XRPD analyses.

Figure Captions

Figure 1. Schematic map of Northern Italy (upper left corner) and physical map of Piedmont bearing indication of the Castello di Annone (AT) prehistoric settlement and the other coeval archaeological sites investigated for comparative purposes [1: Chiomonte (TO); 2: Fossano (CN); 3: Castelletto sopra Ticino (NO)].

Figure 2. Ceramic shards bearing incisions or impressions filled with white inlays from the archaeological site of Castello di Annone (AT), dating to the Neolithic (a), Copper (b) and Bronze age (c). Fragment of a bronze fibula decorated with a white inlay from the same site, dating to the Iron age (d). (Dimensional scale: cm)

Figure 3. Ceramic shards and implements bearing incisions or impressions filled with white or coloured inlays from the archaeological sites of Chiomonte (red-decorated shard) (a), Fossano (b) and Castelletto sopra Ticino (c). (Dimensional scale: cm)

Figure 4. FT-IR spectra of samples CdA11 (talc) and CdA5 (Bone White).

Figure 5. XRPD patterns of exclusively talc-based (dashed lines: CdA1, CdA7, CdA23, CdA37) (a), both talc and hydroxyapatite-based (dashed and dotted lines respectively: CdA9, CdA11, CdA23, CdA85) (b) and exclusively hydroxyapatite-based (dotted lines: CdA3 and CdA5) (c) white inlay specimens from Castello di Annone. Magnification in the (c) upper right corner shows the possible presence of diffraction peaks related to fluorapatite.

Figure 6. FT-IR spectrum of sample Ch1.

Figure 7 FT-IR spectrum of sample F1 (analogous to F3, F5 and F7) (a); XRPD patterns of hydroxyapatite-based (dotted lines) white inlay specimens (F1, F3, F5 and F7) from Fossano; magnification (upper right corner) shows the possible presence of diffraction peaks related to fluorapatite (b).

Figure 8. FT-IR spectrum of sample CT3 (analogous to CT1, CT5, CT7, CT9 and CT11) (a); XRPD patterns of predominant hydroxyapatite (dotted lines) and subordinate talc-based (dashed lines) samples (CT1 and CT7) (b).

Figure 9. Compositional % distribution of the white inlays applied on the 44 analyzed specimens from Castello di Annone; for each fraction, the number of specimens and related % are reported respectively (a). Summarizing histogram concerning the approximate composition of white pigment mixtures (expressed as talc and hydroxyapatite %) for each specimen in the investigated archaeological sites. Sporadic presence of other white components (i.e. calcite, kaolinite and hydrocerussite) is also indicated. Within the same epoch, specimens were ordered from higher to lower talc content. While in Castello di Annone use of talc prevails in all investigated chronological periods, in the more recent Fossano and Castelletto Ticino settlements such a situation is drastically reversed in favour of bone ash (b).

Figure 10. a) Comparison in the 8-70° 2θ region of XRPD patterns collected on fresh pork rib (1), XVI century human rib (2), biogenic hydroxyapatite calcined at 900°C (3) and Iron Age Bone White pigment (F1) from Fossano (4). Calcination causes the diffraction peaks of hydroxyapatite to dramatically reduce their full width at half maximum (FWHM),

consequent to an increase in the cristallinity degree. b) Comparison in the 30-35° 2θ region of the (211), (112) and (300) diffraction peaks of Bone White-based filler inlays (CdA5 and CT1) with the same reflections related to biogenic hydroxyapatite calcined at 900°C (OH-apt), showing similar FWHM and crystallinity degree. c) Consistency of the experimentally collected data with those presented by Odriozola and Martìnez-Blanes (2007), typical of biogenic hydroxyapatite heated at 900°C.

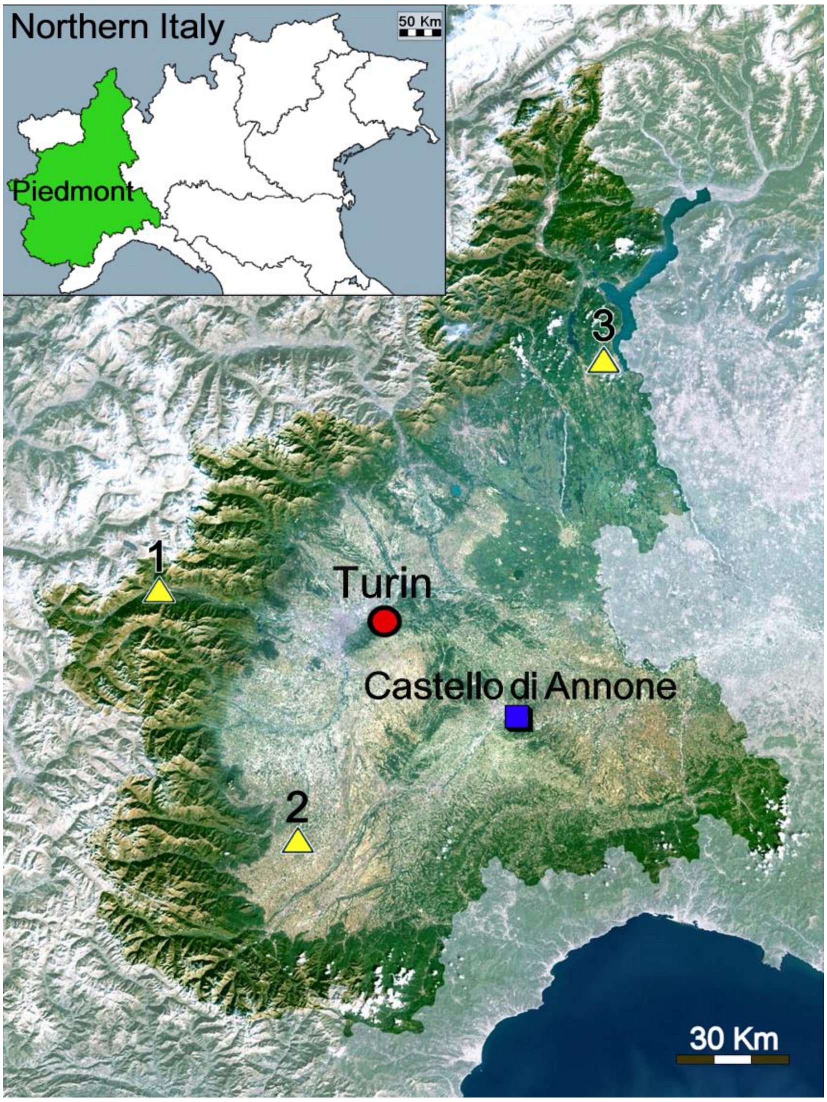


Figure 1

Figure 2

Figure 3

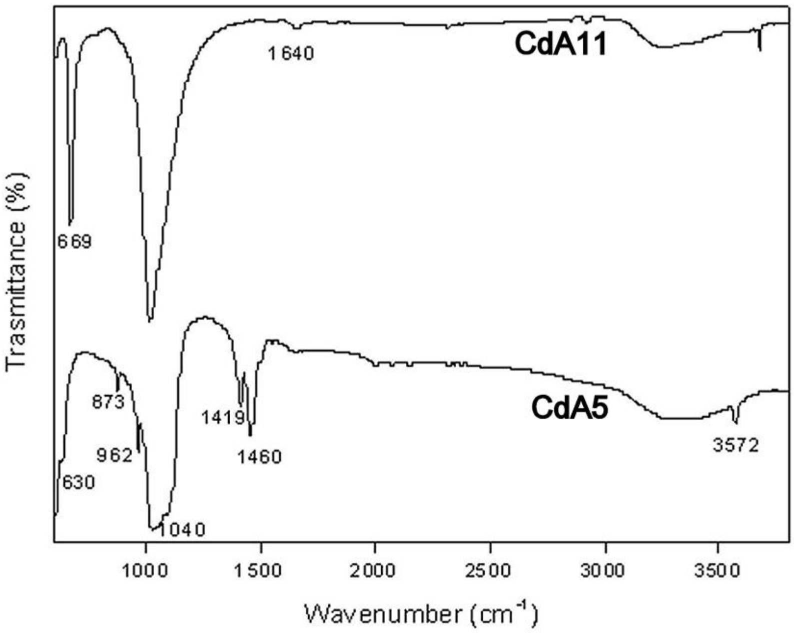


Figure 4

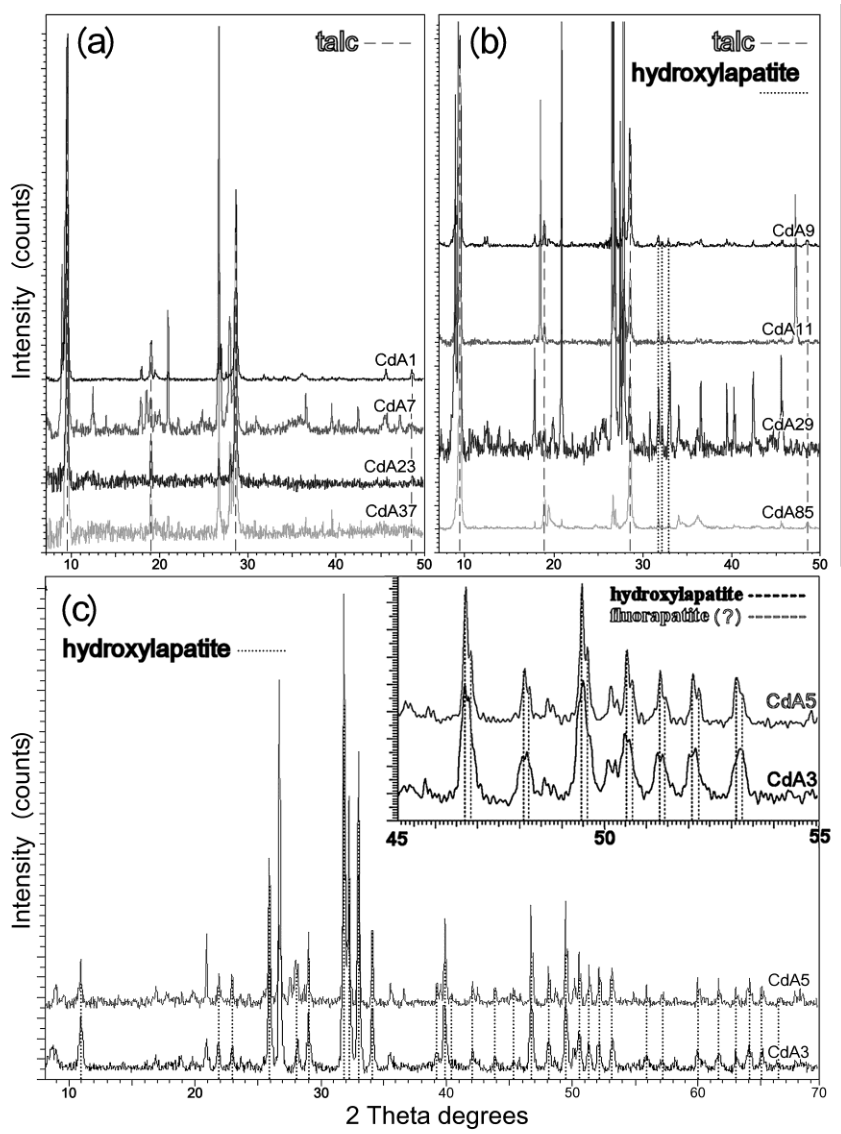


Figure 5

Figure 6

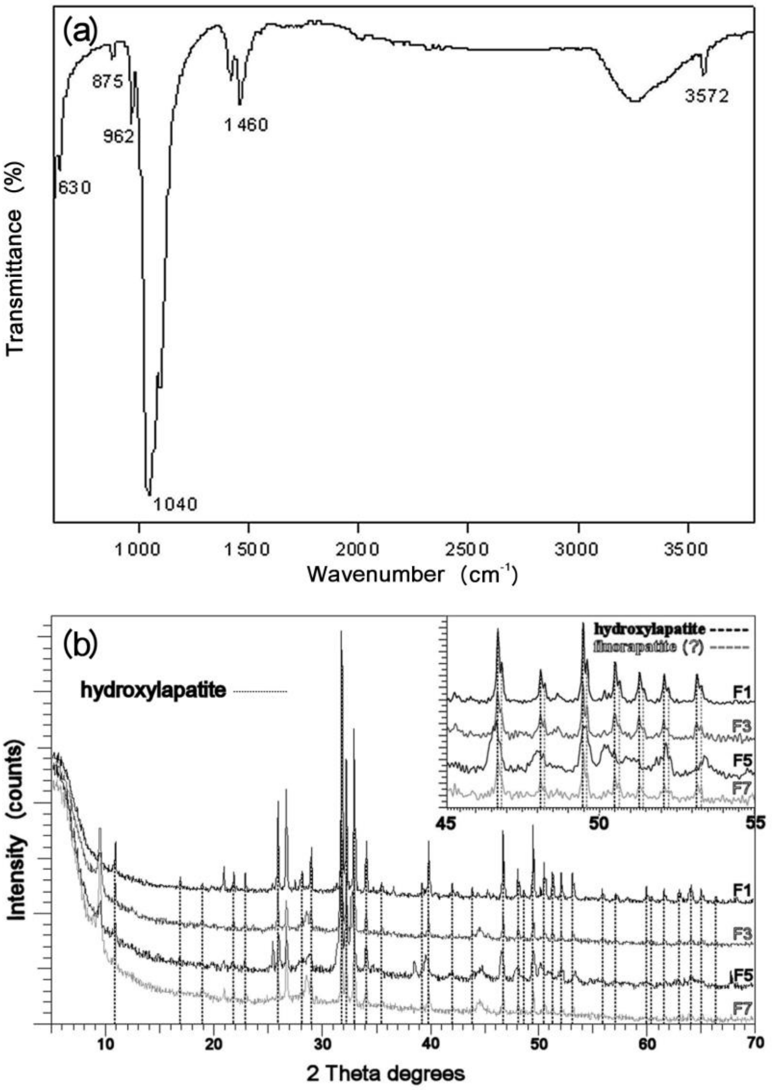

(a)
875
962
630
1460
3572
1040
Transmittance (%)
1000
1500
2000
2500
3000
3500
Wavenumber (cm-1)
(b)
hydroxylapatite
hydroxylapatite
F1
F3
F5
F7
45
50
55
Intensity (counts)
F1
F3
F5
F7
10
20
30
40
50
60
70
2 Theta degrees

Figure 7

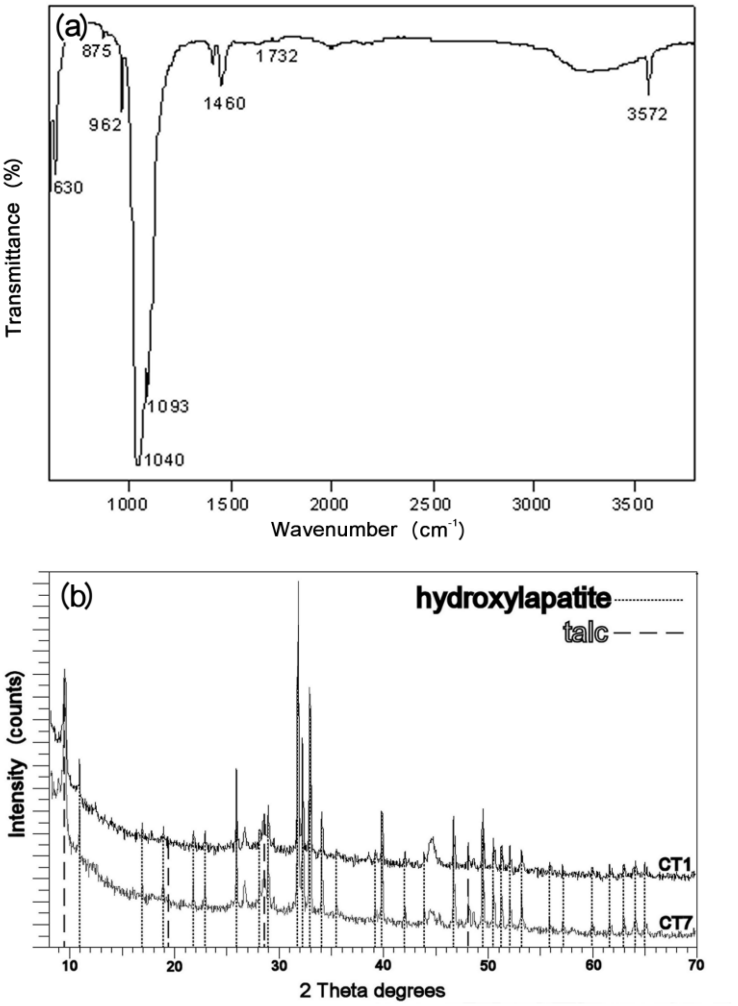


Figure 8

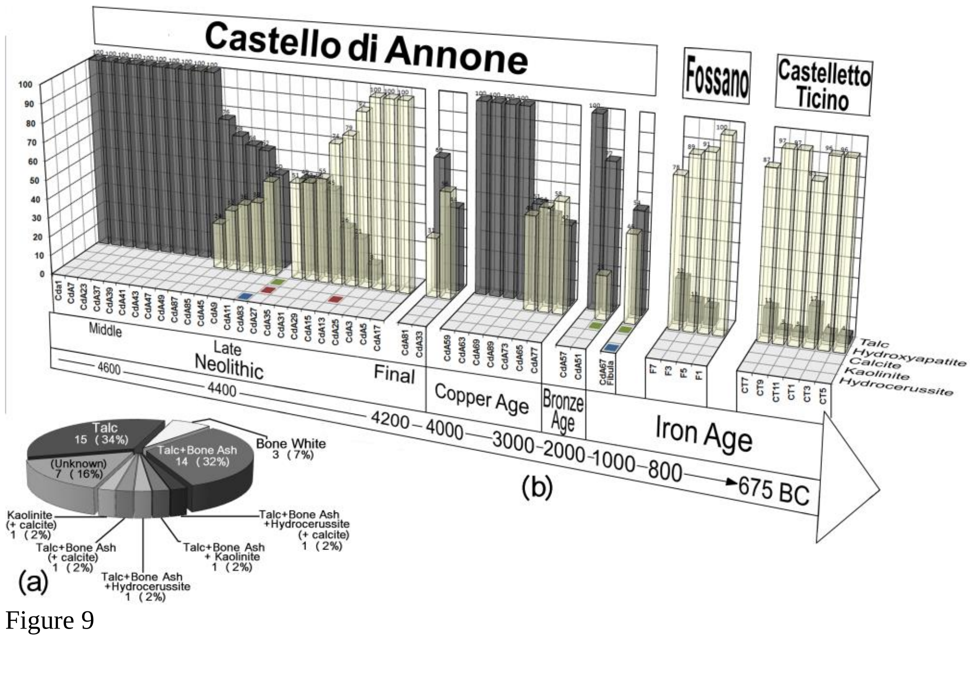
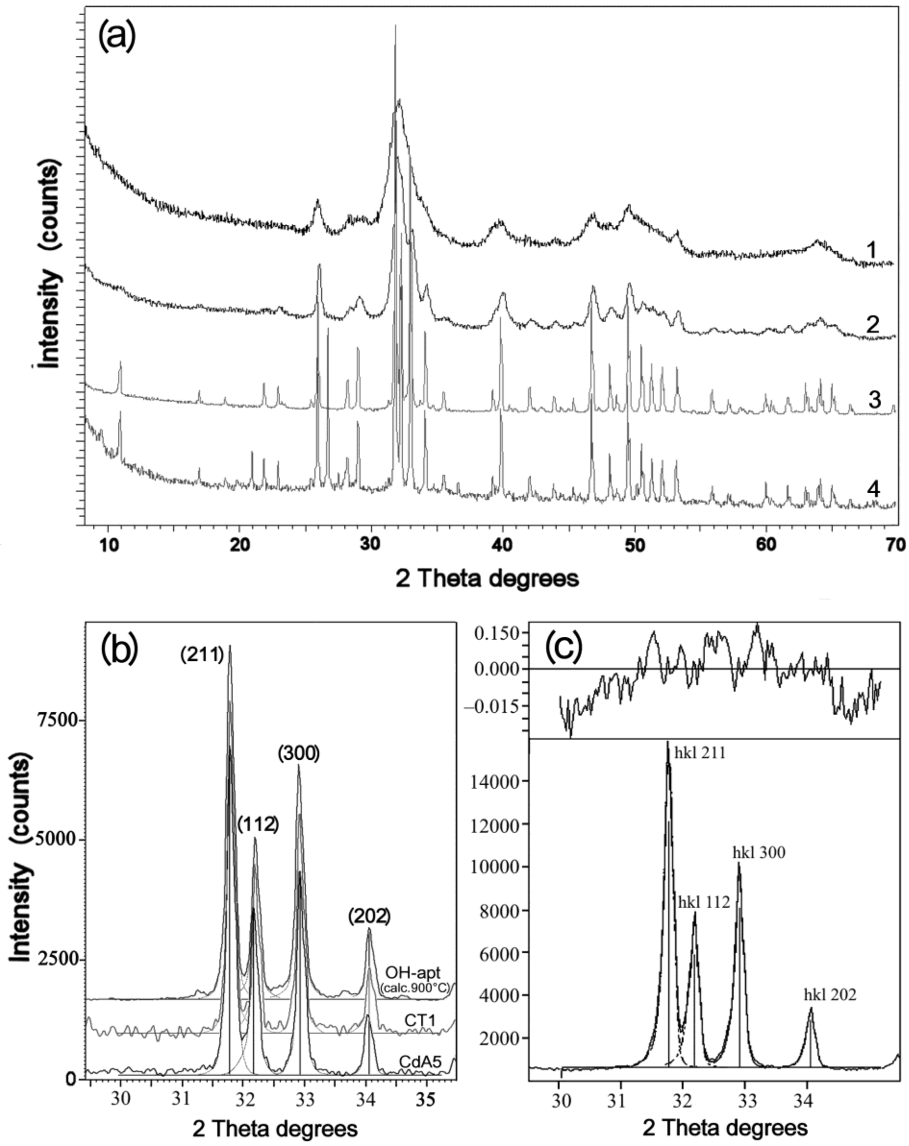


Figure 9



(a)
Intensity (counts)
1
2
3
4
10 20 30 40 50 60 70
2 Theta degrees
(b)
(211)
(112)
(300)
(202)
OH-apt
(calc.900°C)
CT1
CdA5
Intensity (counts)
0 2500 5000 7500
30 31 32 33 34 35
2 Theta degrees
(c)
0.150
0.000
−0.015
hkl 211
hkl 112
hkl 300
hkl 202
2000 4000 6000 8000 10000 12000 14000
30 31 32 33 34
2 Theta degrees

Figure 10

Supplementary Material

Table S1: Chronologic list of all analyzed white inlay specimens from Castello di Annone, complete with both archaeological and archaeometric descriptions (question marks imply uncertain attributions).

Table S2: Chronologic list of all analyzed white inlay specimens from other coeval sites of Piedmont (Chiomonte, Fossano and Castelletto sopra Ticino), complete with both archaeological and archaeometric descriptions (question marks imply uncertain attributions).

Table S3: EDS chemical analyses (expressed as weight% of oxides) on individual analytical spots collected on the CdA3 and CdA 5 Bone White specimens; last column lists the averaged values.

Table S4: Weight% of Ca and P and related ratio resulting from EDS analyses on the CdA3 and CdA5 Bone White specimens.

In order to quantify the mutual talc/hydroxyapatite amounts in the studied white inlays on ancient potteries, control mixtures with measured weight% composition of both phases (from talc 100% – hydroxyapatite 0% to talc 0% – hydroxyapatite 100%, with a 10% sequential step) were prepared and analyzed with an automated PW3050/60 PANalytical X'Pert-PRO diffractometer, with θ-θ setup and an RTMS (real Time Multiple Strip) detector using monochromatized Cu-Kα radiation (Fig. S1). Preferred orientation effects affecting the (00*l*) reflections of talc were possibly smoothed by using a zero-background, Si-monocrystal flat sample holder and suspending the crystallites in a non-volatile inert solution (amyl acetate + 5% collodion), thus maximizing their statistic disposition.

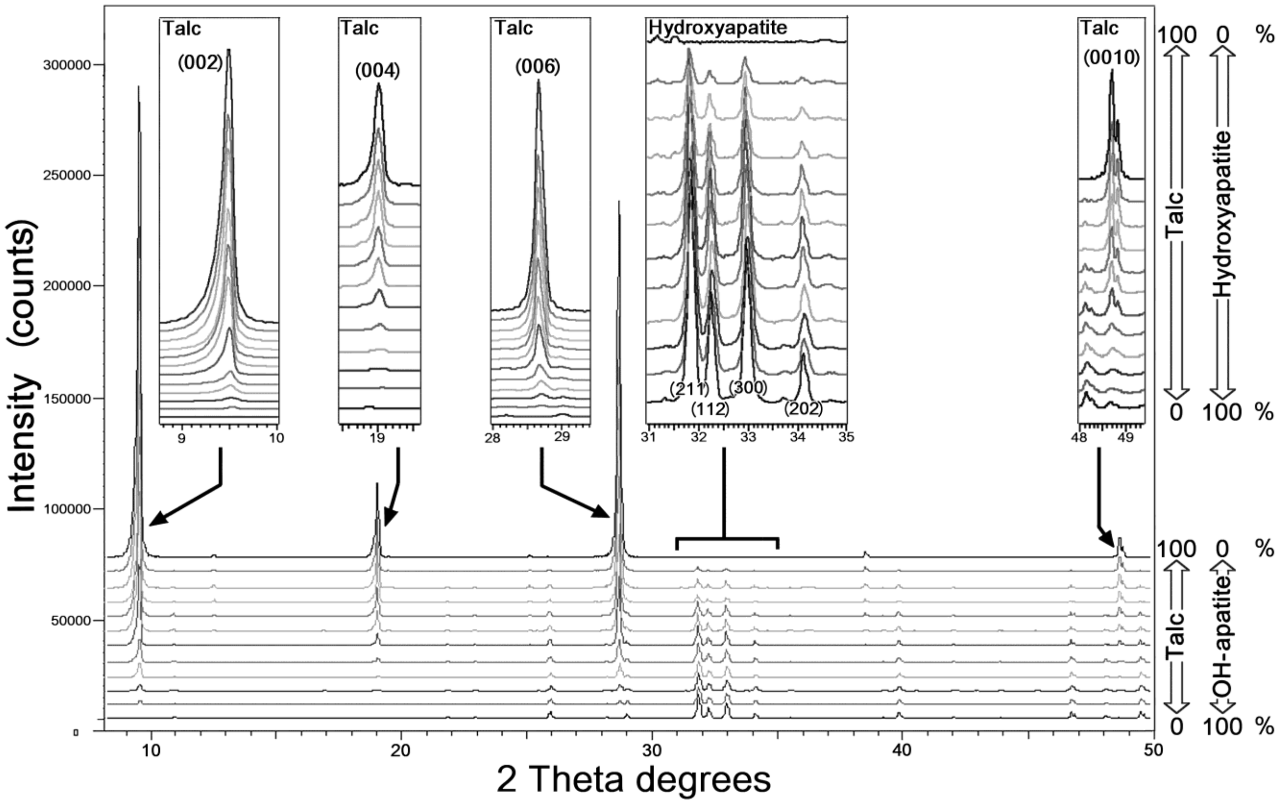


Figure S1. XRPD patterns of synthesized control mixtures with composition ranging from talc 0% - hydroxyapatite 100% (low) to talc 100% - hydroxyapatite 0% (high), each separated by a 10% increase/decrease sequential step. Magnifications indicate the intensity variation trend for all talc [(002); (004); (006); (0010)] and hydroxyapatite (211) reflections considered for the construction of calibration curves.

Feasible calibration curves were obtained by computing, in each of the synthesized control mixtures, the intensity ratios for several couples of independent talc/hydroxyapatite reflections [i.e. between the (002), (004), (006) and (0010) reflections of talc – only ones visible in the ancient white inlays XRD data – and the more intense (211) reflection of hydroxyapatite; Fig. S2). Such curves were then applied in reverse on the ancient inlays XRD data so to obtain reliable quantitative estimates of the mutual talc and hydroxyapatite weight % related to each specimen (generalized Reference Intensity Ratio – RIR method). To further minimize bias related to talc preferred orientation, the compositional values were averaged on all four obtained estimates (related to each couple of talc/hydroxyapatite reflections).

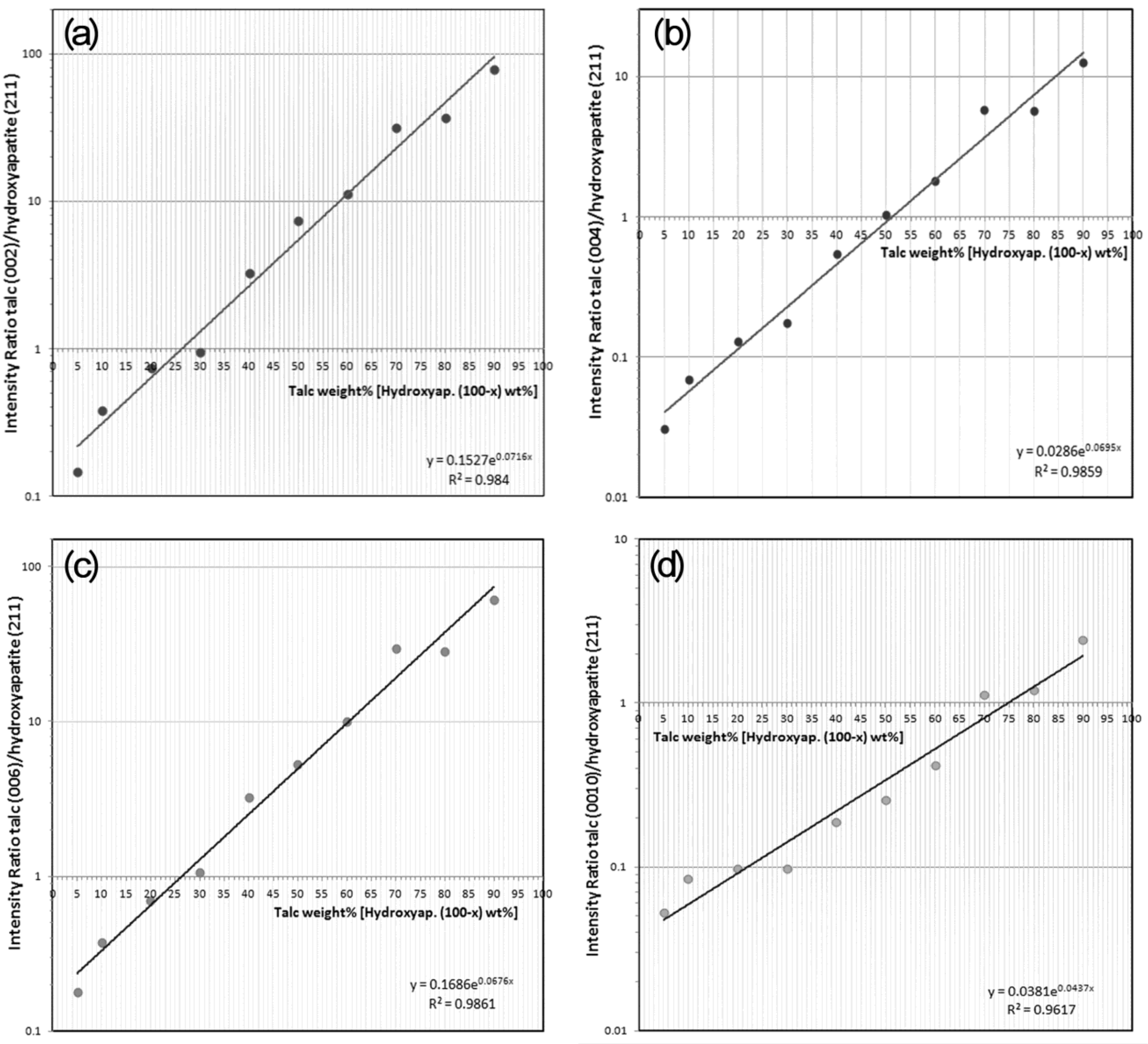


Figure S2. Calibration curves obtained by computing, for each control mixture, the intensity ratios and the related interpolation lines between the (002) reflection of talc and the (211) reflection of hydroxyapatite (a); talc (004) and (211) hydroxyapatite (b); talc (006) and (211) hydroxyapatite (c); talc (0010) and (211) hydroxyapatite (d). (logarithmic scale on Y axis).