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First evidence of vivianite in human bones from a third millennium BC *Domus de Janas*: Filigosa tomb 1, Macomer (NU), Sardinia

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ABSTRACT

Sardinia is an island located in the middle of the Mediterranean Sea. Due to its position geologically acquired in the Middle Miocene (around 16 Ma ago), this island had a very strategic position in antiquity, as it was involved into all the trade routes that crossed the Mediterranean Sea; however, it developed original archaeological features up to the Iron Age. During the Final Neolithic, the Ozieri's Culture developed throughout the Sardinian territory, with diffusion of typically hypogea graves named Domus de Janas. The study was conducted inside the *Domus de Janas* at Filigosa necropolis, located on a tuffaceous hillside near the village of Macomer in the area of Marghine, Central-Western Sardinia. Tomb 1 dating back to the beginning of the third millennium BC had been excavated by Professor E. Contu in 1965 At the time of first excavation, this tomb showed very particular conditions that had enabled an excellent conservation of several osteological and wooden samples.

This paper focuses on the presence of vivianite deposits on human bones and its origin. For such a mineral to be formed an interaction between phosphate, iron and water has to occur. These findings can be considered the first evidence of such mineral in a Sardinian archaeological site, and one of the most ancient findings of this mineral in Italy, as well as the first evidence observed in prehistoric sites related to a period before the introduction of iron use.

1. Introduction.

Vivianite is a hydrated iron phosphate mineral (chemically, $Fe(PO_4)_2{\cdot}8H_2O$) which crystallizes in a monoclinic system. Colourless when unaltered, vivianite ranges from grey to indigo, green or dark blue when subjected to oxidation whereas, depending on its oxidation state, it ranges from a vitreous to a pearly lustre.

This mineral was first described in 1817 by Abraham Gottlob Werner, who named it 'Vivianite' after John Henry Vivian, the first mineralogist to discover such specimen in Cornwall (UK) (Werner, 1817).

Vivianite findings in archaeological contexts have been reported since 1800, although only in 2006 McGowan and Prangnell reported on its relevance in archaeology (McGowan and Prangnell, 2006).

The oldest known evidence of vivianite in archaeology is associated with the iceman mummy Oetzi (Pabst and Hofer, 1998), who presented small amounts of this mineral into his lungs and on his skin.

In Italy, other archaeological evidence about this mineral relates to Bronze Age, Iron Age and Roman contexts; in two of these sites, the *Terramare* Bronze Age site of Fondo Paviani, Verona, (Nicosia et al., 2011) and the Roman harbor of Como (Ferrario et al., 2015), vivianite was found in sedimentary stratigraphic soils, whereas in three Iron Age sites in Campania, Longola-Poggiomarino, Sarno river valley and Castel Vetrano necropolis, (Balassone et al., 2009), it was detected in metal artefacts.

The ideal conditions for this mineral's formation in archaeological contexts require aqueous environment and the presence of phosphates and iron ores. Therefore, archaeological sites usually presenting vivianite pertain to Ancient or Modern History, where human and/or faunal remains in swampy environments are associated to iron goods:

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formation of vivianite could not be formed unless such conditions are met.

This research represents the first archaeological evidence of vivianite in Sardinia found in a prehistoric grave cut (usually called *Domus de Janas*) dating from the Chalcolithic period, around the early third millennium BC, located in the archaeological site of Filigosa. The relevance of this research is the absence of ferrous objects among goods retrieved from Tomb 1: thus it might be considered the first evidence in prehistoric archaeological context. Therefore, as in the case of Oetzi, the iron ore should rather be identified with the bedrock composition of the tomb.

Domus de Janas are prehistoric rock-cut graves found specifically in Sardinia, dating from the Recent Neolithic (also locally known as the San Ciriaco culture), namely around the fourth millennium BC (Tanda, 2009). The subsequent Ozieri culture, which developed during the Final Neolithic, represents the first Sardinian culture with a regional diffusion, which sees homogeneous rituals and ceramic traditions from the north to the south of the Island (Melis, 2009).

The most recent surveys reported about 3,500 *Domus de Janas* (Tanda, 2009), including both single tombs and necropolis, carved out of different bedrocks and provided with either a single or multiple cell, thus presenting different sizes. In addition, these tombs might or may not present sculptures and mural decorations, which often imitated the structure of ordinary houses.

The *Domus de Janas* necropolis of Filigosa, located over a hillside near the village of Macomer, Central-Western Sardinia, in the sub-region called Marghine (Fig. 1) consists of 4 rock-cut graves. It represents the first necropolis where a specific Eneolithic culture from 3264 to 2915 cal BC[1], later indicated as Filigosa culture, was first acknowledged (See Figs. 2 and 3).

The site was discovered in 1960 following some illegal excavations that affected a small portion of the *dromos* in Tomb 1 and it was excavated again by Contu in 1965 (Contu, 1965; Foschi, 1986).

At the moment of its discovery, the tomb presented with some water and a thin layer of mud, that had likely seeped through the tuffaceous rock of the necropolis; these conditions, noted in the relevant excavation log and confirmed by its associated pictures (Fig. 4), allowed the ideal conditions for the conservation of any organic materials, including the renowned miniature wooden vase currently exhibited at the National Archaeological Museum “G. A. Sanna” in Sassari.

The specificity of the materials found in this tomb lies in the ideal conditions that allowed the conservation of different materials, such as human remains as well as biological material from plants and of entomological and mineral origin, which represent unique finding from Sardinian prehistory to date.

The focus of this paper is the analysis of skeletal remains found in Filigosa Tomb 1 presenting crystal-shaped encrustations, grey/black/bluish in colour.

2. A geological perspective

2.1. *Sardinian geology*

2.1.1. *The Palaeozoic Era*

The geological history of Sardinia (Carmignani et al., 1992) started at the beginning of the Palaeozoic Era (541–251 Ma ago), more specifically in the Cambrian series 2: the large majority of the rocks which sedimented when Sardinia was still submerged crops out in the Southern part of the island called Sulcis-Iglesiente and can be accurately dated to that era. The dating was possible due to the presence of relevant fossils such as Trilobites and Archaeocyatha in those predominantly arenaceous and carbonate rocks.

Since that period, the marine sedimentation had consistently settled until the Middle Ordovician, when the sea levels dropped; upon the pre-Variscan tectonic processes, which can be included in the so-called ‘Sardinian Phase’, those sediments that had previously settled were deformed and uplifted resulting into the first ancient group of emerged continental layers heavily eroded by exogenous agents during the Cambrian-Ordovician series.

In the Early Ordovician, the sea spilling again over into the whole island resulted in the recovery of the sedimentation activity, predominantly involving carbonate and clay-rich rocks that can be clearly identified in the Silurian and Devonian rocky outcrops. By the end of the Lower Carboniferous, a new phase of tectonic processes occurred in Sardinia, which grew in power and intensity in the Mid-Carboniferous: the thousands-metres thick successions from the Palaeozoic that had previously sedimented, underwent pressure and temperature increase, bending and overturning movements, taking on a schistose structure and a Barrovian metamorphism. By the last phases of the orogenesis (320–315 Ma), massive magma bodies climbed up through the fractures and faults of the deformed rocks and crystallized as granite at middle crustal levels, locally leading to the deformation of Variscan rocks and triggering thermic metamorphism phenomena.

At the end of the Mid-Carboniferous Sardinia’s emerged areas were mountains, part of that Variscan chain extending across Central Europe and the Western Mediterranean, to which the island was firmly connected. Finally, the severe Permian erosion activity, at the end of the Palaeozoic Era, completely levelled the Sardinian area.

2.1.2. *The mesozoic era*

The end of the Variscan orogeny marked the beginning of a long volcanic and tectonic stagnation in the Mesozoic Era (251–66 Ma ago). During this Era, the sea levels raised again, although submerging Sardinia only for short periods during the Jurassic Era. The rocks formed during this age, predominantly limestones, can be identified in large outcrops located in the sub-region called Nurra, in the Supramonte, in Monte Albo, in the small island of Tavolara, and in the sub-regions called Ogliastra and Sarcidano.

2.1.3. *The cenozoic era*

In the Cenozoic Era (66 Ma ago to present day), Sardinia started to get its own characteristic appearance, differentiating itself from the rest of Europe. Constant dislocations due to fractures and orogenic uplifts related to the third of the major orogeny phases, called the Alpine orogeny, split the Sardinian crust into different blocks.

In the Early Miocene, the block formed by modern Sardinia and Corsica broke away from Continental Europe and moved toward the Western Mediterranean until it reached its current position (Middle Miocene), finally becoming an island.

Sardinia’s drifting is marked by various volcanic activities, predominantly including andesitic lava which became increasingly massive while amassing together with other marly and arenaceous sediments into the ‘Sardinian Rift’, namely a large depression which goes through the island, from the Gulf of Asinara to the Gulf of Cagliari.

Following a relative calm during the Mid-Upper Pliocene, in Sardinia the Rift Campidano Valley started to lower and to take its current shape, while the volcanic activity was resumed especially on Monte Arci and Monte Ferru, followed by the abundant basaltic emissions from which originated the large plateaus in the Central and Northern part of the island (i.e. Gesturi and Campeda).

During the Quaternary (1,8 Ma ago to present day) the erosion accumulation activity operated by the sea, rivers and brooks, the wind and other exogenous agents have shaped the current conformation of the island, which had already been broadly set up during the Pliocene.

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[1] Data obtained as a part of the project "Nutrition and society at the origins of nuragic civilization" (CRP_661), funded by a Grant to Young Researchers, Autonomous Region of Sardinia, awarded to Dr. Luca Lai, presented during the following study: Sample UniCa 143, individual 5, Oxford laboratory code Radiocarbon Accelerator Unit, Oxford University OxA-25337, ™^{13}C‰ $= -19.51$; conventional years BP = 4401 ± 32.

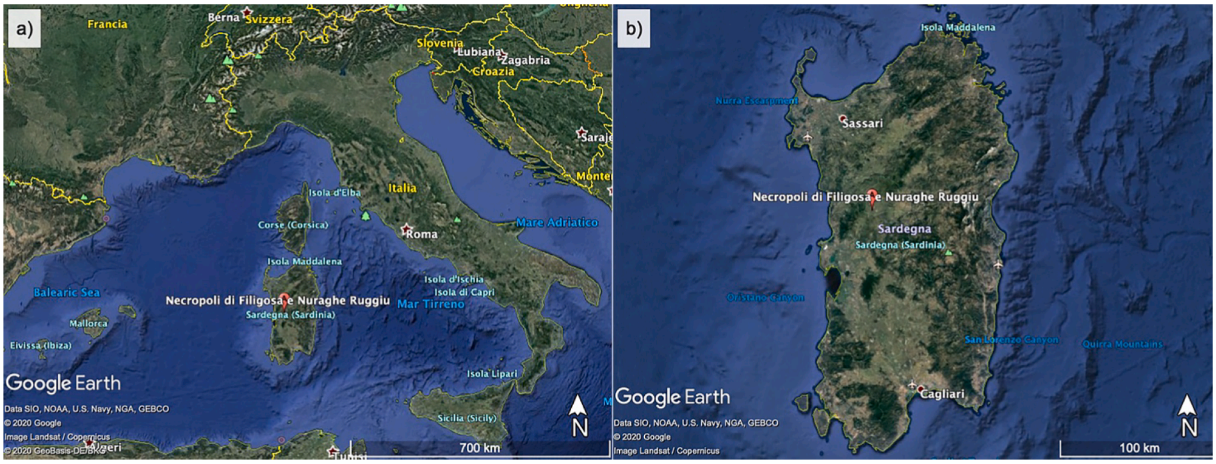

Fig. 1. a) The position of Sardinia in the Mediterranean; b) the position of the Filigosa necropolis on the Island map.

Fig. 2. Tomb 1, Filigosa (ph. Donna Nuragica).

2.2. *Geology of Filigosa's territory*

The geology of the area can be distinguished in two fundamental elements of the landscape: the Abbasanta plateau and the Marghine chain. The first is an important basaltic plateau of Quaternary age, constituted through mainly linear emission centers. The second is a mountain range due to an important OSO - ENE tectonic dislocation that determined the tilting towards the NW of the ignimbritic coulters of the Oligo-Miocene. From a geological and morphological point of view, the region has a limited variability; the substrate includes exclusively volcanic lithologies, covered by sedimentary deposits due to the modelling of the slopes occurred in the Quaternary. In its reciprocal movement, the fault distinguished a lowered part, subsequently covered by continental and volcanic deposits, and a raised part, which now forms the chain. The raised part was further tilted towards NO. In fact, the main peaks of the Marghine are facing SE, or in the diametrically opposite direction where more steep slopes are found, while on the other side the chain slopes more gently. The oldest part of the chain, not included in the municipal area, consists of a crystalline basement of intrusive and metamorphic rocks dating back to the Paleozoic era. In particular, granodiorites whose placement is to be traced back to the Variscan orogeny are found, encased in a metamorphic complex consisting of schists, phyllites and marbles. Tertiary volcanics, due to highly explosive volcanic phenomena are found above the Paleozoic rocks. Fiery clouds are made up of an emulsion of gas, lava and solid parts that emerge from linear fractures at temperatures around 900 °C with speeds of several tens of kilometers per hour, these paroxysmal activities are capable of destroying any life form making every trace of it disappear by sublimation. The lithic product that is generated by cooling is ignimbrite characterized by a typical bank geometry and recognizable in the countryside by the characteristic "flames" of light color generated by hot collapse of the pumice. Alternating with these paroxysmal phenomena there were other more "peaceful" ones characterized by the ejection activity of ashes and pumice. The final result is an alternation of reddish hard rocks, the ignimbrites, and softer rocks, the tuffs, gray, gray greenish and pinkish. The tertiary volcanites, inclined towards the NW as already mentioned, occupy the whole top part of the chain and characterize the profile of the mountain with broken slopes due to the heads of the ignimbritic banks, alternating with gentler slopes due to the softer rocks. During the tectonic movement, substantial flows of basaltic chemistry flowed from the primary and secondary faults. Some emission centers are present in the studied area and have been mapped, the outcrops of these old volcanoes are characterized by the presence of considerable quantities of boiling and very light slag.

As already mentioned, the part lowered by the fault was subsequently filled with continental deposits. First of all, sediments of alluvial and fluvio-lacustrine origin were deposited, generated by the dismantling of the important chain just raised. Above these sediments, during the Plio - Quaternary, basaltic lavas were placed in expansions that gave rise to the Abbasanta plateau. The basaltic lavas have the characteristic of being, at the time of placement, very fluid therefore they often filled paleo depressions leaving a tabular morphology at the top. Erosion then affects the edges of the expansion selectively, especially if the substrate is soft or even loose as in this case, thus implementing the inversion of the relief: what was previously at the bottom of the valley becomes a summit area and vice versa. In the recent quaternary, the modelling phenomena of the slopes were completed, with the accumulation of detrital deposits. The erosion, transport and sedimentation phenomena were triggered by the newly raised volcano-tectonic reliefs. The so formed debris accumulated at the foot of the slopes, filled the concavity of the ground or accumulated in the valley bottoms. In general, these sediments are classified in relation to the morphogenetic action that determined them, the extent and type of transport.

Into the detail of our study area, the lithologies observed are part of the Volcanic District of Bonorva - Macomer Unit (OER). In the outcrop, pyroclastic flow deposits can be distinguished in ignimbritic facies, welded, with structures from vitroclastic to eutaxitic; in banks alternating with pyroclastic flow, fall and basal wave deposits. (K / Ar 21.6 ± 1.1 Ma (Aquitanian): Lecca et al., 1997). Pyroclastic flow, fall and surge levels (OERb).

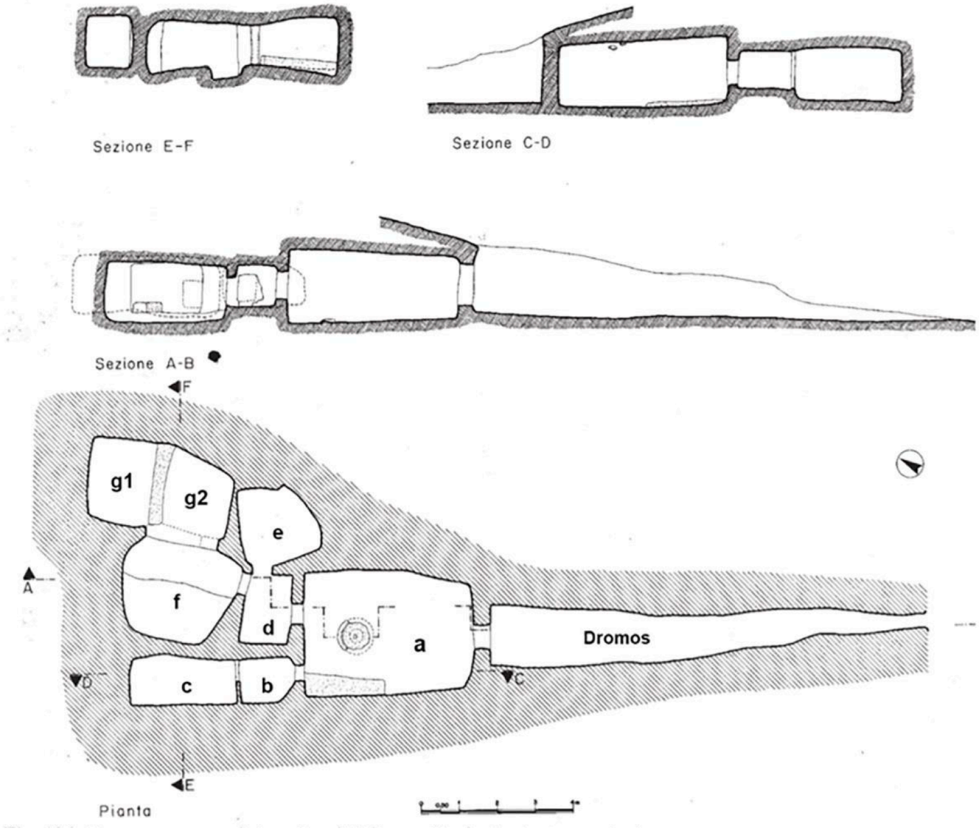

Fig. 3. Tomb 1 plan and section (Moravetti, 1998).

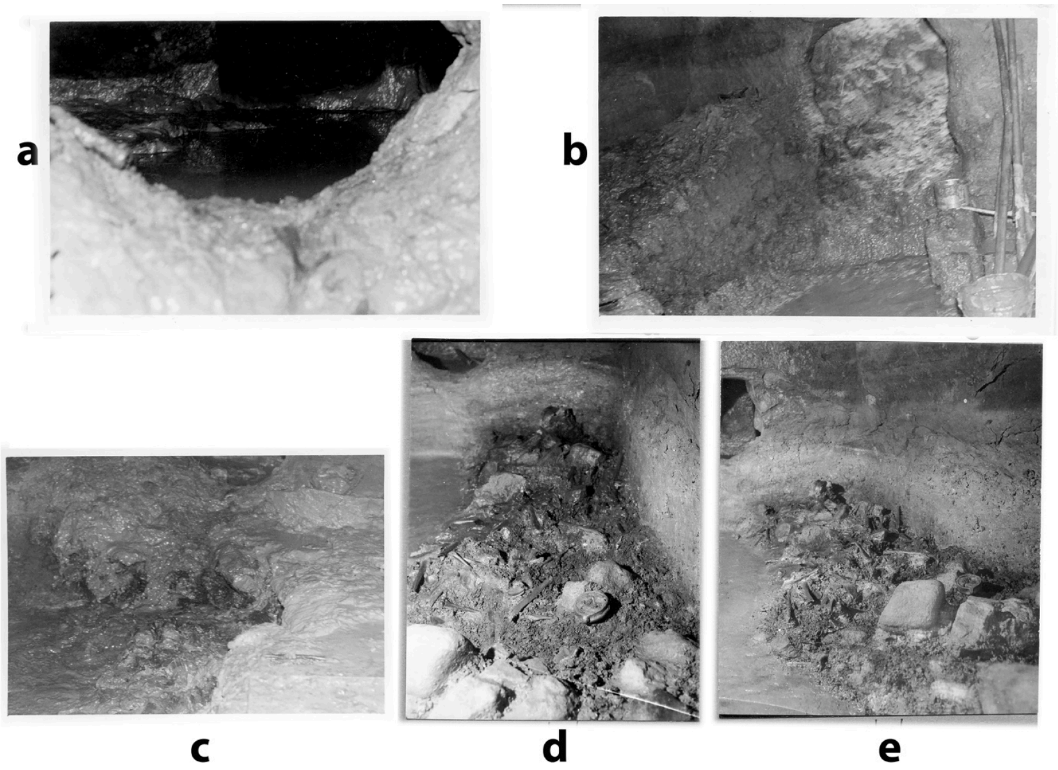

Fig. 4. Tomb 1 - first excavation in progress: a) flooding of internal burial rooms, view from cell A; b) deposits in the tomb's dromos, view from cell A; c) cell A Eastern wall's deposits; d-e) cell A Eastern wall's excavation in progress: water and mud; bones and vases still in situ. (note: On the concession of the Ministero per i beni e le attività culturali – Soprintendenza archeologia, belle arti e paesaggio per le provincie di Sassari e Nuoro. Any further reproduction or duplication is forbidden).

3. Materials and methods

3.1. Material

The human remains recovered from the tomb consist on 1700 fragments of human bones, 103 of which were covered by a mineral encrustation (Fig. 5); seven of them were subject to further in-depth analysis (XRD, petrographic thin sections and SEM analysis).

Samples were prepared through conventional laboratory procedures, including dry cleaning or with cold water without direct immersion, with soft bristle brushes and wood utensils, drying at air without heat source (to avoid deformation of the sample). Reconstitution of the fragmented parts when possible using the tape “Scotch 3 M”, reversible with alcohol, or Paraloid B72 in 20% solution for the consolidation of fragile pieces.

Once clean, bones were catalogued and inventoried by a permanent marker on enamel base an acronym identifying each piece with the code of the reservoir (e.g. FIL by Filigosa), the number of the tomb, the number of the box or the number or letter of identification of the cell (if and when we have it indicated) and they are entered in a register to facilitate subsequent reviews or studies.

Since the graves corresponded to multiple burials, first a calculation of the minimum number of individuals (NMI) was performed (Duday, 2000, 2005). The first step to calculate the NMI is to group the bones by typology, distinguish them by laterality, define their sex (Acsádi and Nemeskéri, 1970; Borrini, 2007; Buikstra and Ubelaker, 1994; Ferembach et al., 1977–79; Rodríguez Cuenca, 1994; Walker, 2008) and age range (Black and Scheuer, 1996; Brooks and Suchey, 1990; Brothwell, 1981; Campillo and Subirà, 2004; Gindhart, 1973; Langley-Shirley and Jantz, 2010; Lovejoy et al., 1985; Maresh, 1970; Scheuer and Black, 2000; Stloukal and Hanáková, 1978; Ubelaker, 1989). Then we proceeded following a criterion of “maximum parsimony” attempting to eliminate any possibility of double counting of the same individual. The taphonomic characteristics have been highlighted, useful for interpreting the post-depositional events of the bone remains (Borrini et al. 2011).

Vivianite encrustations were also observed over a wooden fragment recovered in the same site (Fig. 6).

3.2. Mineralogical and petrographic methods

To perform the petrographic observation, some bones fragments hosting submillimeter- to millimeter-sized dark green/blue crystals were cut in thin slices, incorporated in epoxy resins and bound on a petrographic glass slide. Bone slices were then reduced up to 30 μm in thickness and polished with 1 μm alumina powder and the optical analyses were performed through polarizing microscope.

Moreover, some bone fragments have been analysed in low vacuum with Fei Quanta 200 Scanning electron microscope (SEM) operating at 20 kV.

Mineralogical characterization was made through XRD powder diffraction analyses, after pulverizing small portion of the dark green/blue mineralization collected in contact on the bones. Experimental setting of the diffractometer PANalytical X’Pert Pro was 40 kV and 40 mA, theta-theta geometry, radiation Cu-Kα_1 (1.540598 Å), scan range 3.484–70.998, step-size 0.167113, and 0.19 s per step. The software used for mineralogical identification and analysis was X’Pert HighScore Plus version 2.1b (Degen et al. 2014).

4. Results

The anthropological study (Rodriguez doctoral dissertation in process) showed an NMI (White and Folkens, 1991) of 49 adults in Tomb I, calculated based on their most significant bones (complete preserved right tibia, or at least complete for 2/3 proximal and distal extensions); and 33 for non-adults, as follows:

- foetal: probably 1 individual to whom a scapular fragment may belong.
- Infant I (0–6 years old): 11;
- infant II (7–12 years old): 10;
- 13–16 years old: 11 individuals.

A post-depositional taphonomic study was carried out on all individuals (Rodriguez doctoral dissertation in process). The analysis showed that the taphonomic syndromes mainly observed on the examined skeletal material include a dark colour of the samples, both biotic (of biological, plant and entomological origin) and abiotic encrustations (e.g. minerals, carbonated deposits) such as post-mortem fractures, erosion and exfoliation. In addition, it should be noted that the weight of each specimen is above average, in accordance with their long underwater permanence. As previously remarked, water was constantly present in Tomb 1: the examined samples were found covered in mud, and regardless the fact that the tomb is currently opened and empty, seepage still occurs and humidity exudes from the rocks, as evidenced by musk on the walls and on the floors in different burial rooms.

Out of the 1,700 bone fragments of various sizes found on-site, about 6% (1 0 3) showed evidence of crystal presence. The excavation log hand-written by the archaeologist during his inspection did not mention such crystals probably because of the vivianite’s lack of visibility until its oxidation, or likely due to the presence of mud over the bone samples; unfortunately, it did not describe where the bones’ surface appeared, as

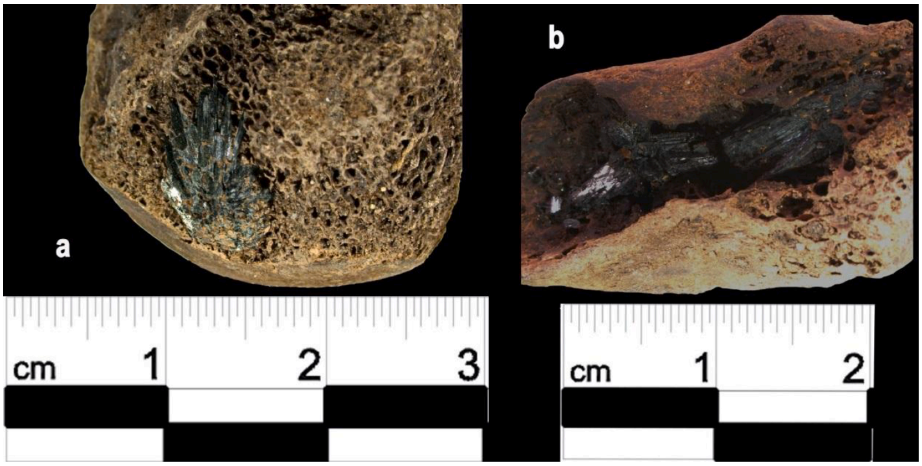

Fig. 5. a) Calcaneus vivianite encrustation; b) Vivianite encrustation on humeral shaft.

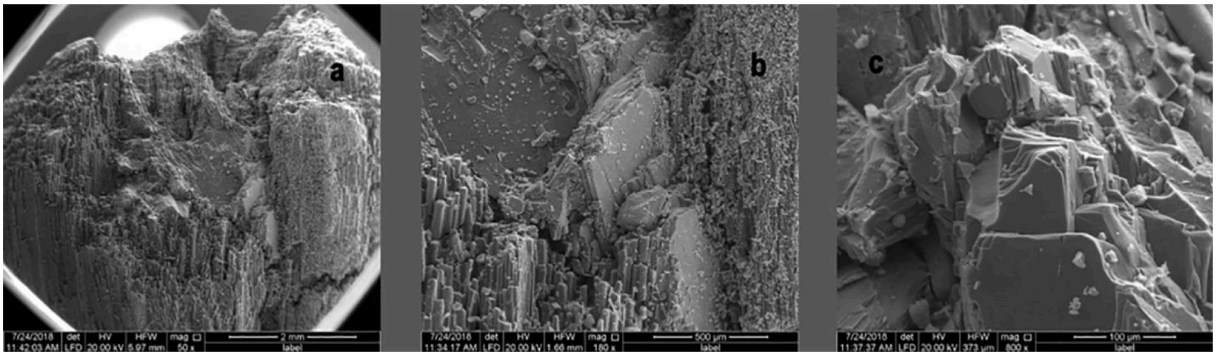

Fig. 6. Various magnifications of SEM images showing a wooden fragment presenting vivianite encrustations.

well as it did not specifically mention the place where the samples were collected or the different conditions presented by the whole archaeological context. The bones examined showed some crystals only over a portion of their surface, sometimes closely connected to the inner trabeculated bone tissue: this might suggest that on such portion of the bone surface where the encrustations appeared might have occurred the ideal conditions for a greater water saturation and the best anaerobic conditions for the formation of vivianite crystals. Furthermore, the presence of vivianite on these samples might also help in the taphonomic interpretation of human remains since it can provide relevant information about the methods used for deceased individuals deposition.

4.1. Mineralogical characterization

Thin section observation shows the high porosity of the bones due to the decay of soft tissues. The pores are separated by osseous septa, yellowish to brownish, with irregular shapes and a structure characterized by concentric lamellae around the pores.

Dark green/blue crystals develop within the pores commonly filling them and assuming their shapes (Fig. 7a, b) or more rarely preserving a euhedral shape (Fig. 7c). In the sections perpendicular to the rhombic prism (00 l) a perfect cleavage oriented parallel to the major diagonal is observed. The same cleavage system can be observed parallel to the faces of the prism (hk0). A fracture system, perpendicular to the c-axis, is rarely found. The most striking feature of these crystals is the strong pleochroism that changes from pale yellow to green/brownish to cobalt blue (Fig. 7a, b). Some crystals are patchy-colored from brown to blue. At crossed polar interference colors are masked by the absorption of the mineral and extinction angle ranges between first and third. The patchy-colored zones observed at single polar can be detected also in crossed polars, manifested by faint bluish to pinkish third order colors (Fig. 7d). The above described features are compatible with vivianite (General Formula: $Fe^{2+}_3 (PO_4)_2 8{\cdot}H_2O$) and/or metavivianite (General Formula: $Fe^{2+} Fe^{3+}_2 (PO_4)_2 (OH)_2 6{\cdot}H_2O$), two iron phosphates sometimes found

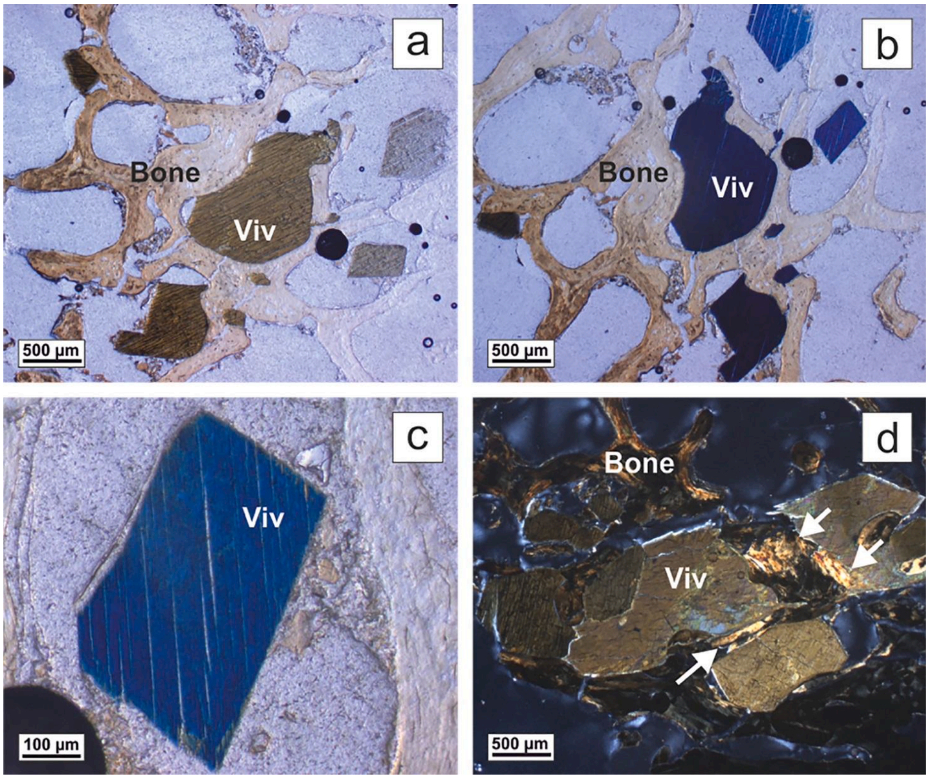

Fig. 7. Photomicrograph of bones with vivianite/metavivianite crystals: a) panoramic image showing crystals that fill the pores in sharp contact with osseous trabeculae (single polar); b) the same portion of bone shown in a but rotated of about 45°, note the strong pleochroism (single polar); c) detail of euhedral crystal with perfect cleavage traces (single polar); d) complex interaction between vivianite and bone with some reaction border highlighted by with arrows (crossed polars).

in human and animal bones.

Diffractometric analyses showed a pattern that is compatible to the two above mentioned species, vivianite (ref. code ICSD 00–030-0662) and metavivianite (ref. code ICSD 00–026-1137). Both phases share the higher intensity peaks located at 13.0750° 2θ (rel. int. 100%), at 13.2160° 2θ (rel. int. 27.68%) and at 18.1546° 2θ (rel. int. 5.02%). However, the presence of both phases can be inferred by the position of minor peaks that can be attributed exclusively to one or to the other phase (Fig. 8).

5. Discussion

During the anthropological study (Rodriguez doctoral dissertation in progress) evidence emerged that

they demonstrate a collective burial, as claimed by the NMI, while there is no trace of scarification rituals, in fact the remains of skin adhering to the bones indicate a primary type burial.

So, the vivianite’s concretions might help in the interpretation of this archaeological context. The identified mineral has a colour ranging from white to blue, turning into ‘blue-green’ when exposed to air. It can be formed in archaeological contexts rich in iron, phosphate and water, but poor in sulphides and oxygen, with a stable pH range between 5.5 and 8.5 (McGowan and Prangnell, 2006); it can also be “vivianite formed after bone hydroxylapatite in a relatively acidic and reduced environment, controlled by complex relations among organic matter distribution and degradation, water supply and circulation rate. Slag and iron flakes provided abundant Fe^2, which was mobilized in acidic conditions” (Maritan and Mazzoli, 2004).

In the case of the samples collected from the Filigosa necropolis, the contact between the vivianite/metavivianite and the bones is commonly sharp and in some cases there is a border of reaction (Fig. 7d, Fig. 9), suggesting that vivianite forms at the expense of the bones (McGowan and Prangnell, 2006). The red circle in Fig. 9 highlights the mineralogical neo-formation of vivianite/metavivianite (general formula Fe^{2+} Fe$^{3+}_2$ (PO$_4$)$_2$ (OH)$_2$ 6·H$_2$O), the reaction could be triggered due to the phosphate (PO$_4$)$^{3-}$ release from the hydroxylapatite (general formula Ca5(PO4)$_3$OH), that is the main inorganic constituent of the bones.

The mineralogical characterization clearly indicates the presence of iron phosphate phases like vivianite and metavivianite. The presence of both phases, detected by XRD analyses, is further supported by optical observation; indeed, the patchy change of color is likely due to the different oxidation state of iron.

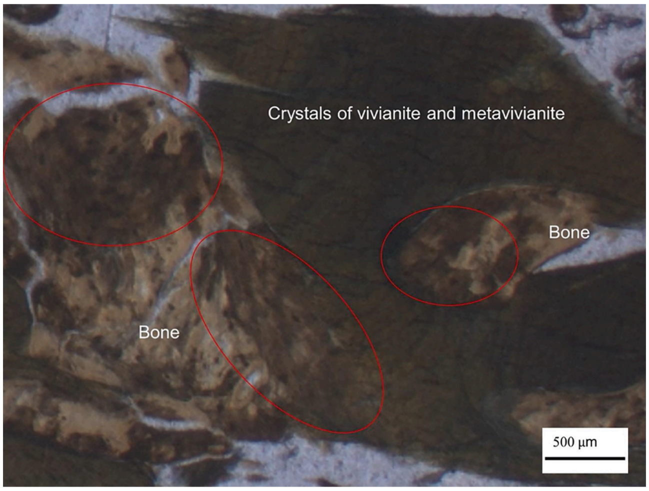

Fig. 9. Photomicrograph showing the relation between bones and vivianite/metavivianite crystals: in the area dotted by red circles the reactions of bones composed by hydroxylapatite and neo-formation of vivianite/metavivianite can be recognized.

The finding of vivianite or metavivianite in the archaeological context of Filigosa Tomb 1 confirms that all the necessary requirements for formation of this mineral were met: presence of water: namely a swamp or submerged ambience, either intermittently or continuously. In fact, at the time of its first excavation, the tomb contained a large amount of water and mud (Fig. 4); an environment with reduced oxygen concentrations, preserving artefacts and/or human remains that would otherwise have decomposed in case of higher concentrations. The finding of the miniature wooden vase currently displayed at the National Archaeological Museum “G. A. Sanna” in Sassari, as well as of other materials of plant origin that are currently subjected to further studies,

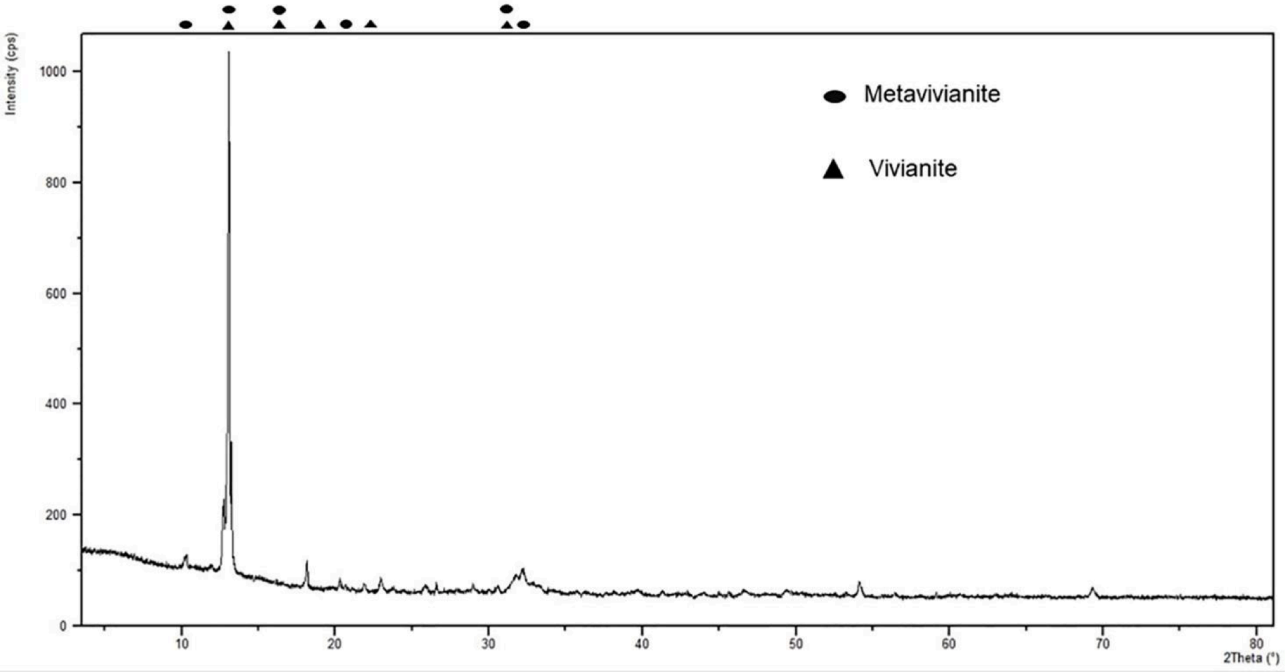

Fig. 8. XRD pattern of vivianite/metavivianite crystals. Note that the minor peaks can be assigned to one or to the other phase exclusively.

are a clear evidence of the reduced oxygen concentration in this archaeological context;

close proximity with phosphates: this includes human and/or faunal remains, and leather. In the archaeological context examined herein, human remains were the largest finding (outnumbered only by ceramic remains which, however, are not included in this study), whereas the tomb also presented a small number of animal remains (sheeps, goats and lagomorphs), as well as biological materials of human origin which will be subjected to further studies; close proximity with iron ores: namely, iron artefacts or materials directly originating from the enclosing rocks. In this case, the examined tomb pertains to the Filigosa culture, dating back to Copper Age, when iron was still an unknown material, thus suggesting the iron enrichment occurred in accordance with the latter hypothesis (originating from the surrounding rocks); Vivianite formation pattern is crucial; this is a in situ formation occurred in close proximity with phosphates and iron ores or at the edge of excavated facilities from which it might have been transferred as a solution containing phosphates and iron. In this case, the conversion of hydroxyapatite contained in the bones -major source of phosphate-reacting with water inside the tomb and with the iron contained by the surrounding rocks enabled vivianite crystal formation. This might also provide further information for the interpretation of depositional rituals, hopefully confirming also the anatomical connection of the available skeletal remains. Unfortunately, at the time of writing, this corroboration is not possible for Tomb 1 since this tomb was used by two different cultures in chronological succession (the Filigosa culture and the following Abealzu culture), condition which may have partially altered the previously existing burials either because of the post-depositional movements caused by the mud penetrating the grave cuts; another limitation in confirming such hypothesis is caused by the lack of appropriate documentation pertaining the tomb's excavation (e.g.: plants, georeferenced pictures), which might have allowed a later interpretation of this archaeological context. However, there is no evidence of the presence of iron elements from Abealzu culture.

6. Conclusions

For the vivianite formation interaction between phosphate, iron and water is needed. An interaction clearly exists between phosphate contained in bones and water, but explaining the interaction with iron it is more difficult at archaeological level. In any cases exist iron elements as a goods. This aspect differentiated vivianite formation in this setting compared to other archaeological settings.

For vivianite to be stable there should be low sulphide rates; this would allow the conservation of metallic objects, which could have been corroded by the sulphuric acid produced by sulphate-reducing bacteria. Specifically, this archaeological site did not include any metallic artefacts; however, the presence of specimens of plant origin, as the abovementioned wooden miniature vase and the other specimens currently subjected to further studies, in case of higher tannate levels might have contributed to the sulphide reduction, thus enabling vivianite formation.

Although the source of the phosphate seems to be clear from the petrographic evidences, the source of iron remains unclear and more analysis and field observation are warranted to find, for instance, a lithogenic source.

CRediT authorship contribution statement

Consuelo Rodriguez: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing - original draft. **Luigi Sanciu:** Writing - original draft, Validation, Investigation, Visualization. **Alfredo Idini:** Writing - original draft, Investigation, Formal analysis, Writing - review & editing. **Dario Fancello:** Writing - original draft, Investigation, Formal analysis, Writing - review & editing. **Clizia Murgia:** Methodology, Validation. **Ilenia Atzori:** Writing - original draft. **Vittorio Mazzarello:** Writing - review & editing, Resources, Supervision. **M. Eulalia Subirà:** Methodology, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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