

Enigmatic, biogenically induced structures in Pleistocene marine deposits: A first record of fossil ambergris

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ABSTRACT

Probable fossil ambergris occurs within early Pleistocene shallow-marine clay deposits in western Umbria (central Italy). More than 25 large, permineralized structures are scattered over an area of ~1200 m². These are commonly convex to elongated, helicoidal to concentric, calcium carbonate-rich structures, 30–60 cm high and 60–120 cm wide. Permineralized squid beaks and altered organic matter occur inside these structures. Preliminary chemical data reveal the presence of organic molecules compatible with the degradation of cellular lipids, whose cholic acids indicate the presence of mammalian gastric or intestinal activity; eight free amino acids were also found. The results allow the identification of these structures as intestinal products of sperm whales living ~1.75 m.y. ago. The described fossil structures represent the only known example of Pleistocene sperm whale coprolites.

INTRODUCTION

The early Pleistocene marine clay of southwestern Umbria (Allerona, northern Apennines, central Italy) was deposited within a broader shallow-marine context, no deeper than 150 m, from late Pliocene to early Pleistocene time (Baldanza et al., 2011). The beds consist of gray to blue, massive to thinly laminated clay and contain more than 25 large, permineralized structures, which are the subject of this study (see Fig. DR1 and the Appendix in the GSA Data Repository¹). A very rich fossil assemblage includes invertebrates (mainly molluscs, echinoderms, serpulids, and corals; Brocchi, 1814; Malatesta, 1974) and fragments of vertebrates (mainly fish teeth, ray fragments, and cetacean bones). Both odontocetes and mysticetes, as skeletal fragments, and scattered whole ribs have been documented in the study area from the 19th century onward (Capellini, 1883; Soprintendenza per i Beni Archeologici dell'Umbria, 2010) but have received little attention until now. Following the recent discovery of whale bones very close to the permineralized structures described here (Fig. 1A), a preliminary investigation has revealed the consistent presence of a mollusc assemblage typical of whale-fall communities, comparable to those reported in Tuscany by Danise et al. (2010) and Dominici et al. (2009) (Table DR1 in the Data Repository).

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¹GSA Data Repository item 2013298, Figures DR1–DR4, Tables DR1 and DR2, and an Appendix, is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

DESCRIPTION OF THE STRUCTURES

We discovered 25 structures spread out over ~1200 m² at 355 m above sea level on Pleistocene clay badlands of Allerona (42°50'13"N, 11°58'22"E). These deposits are calcium carbonate-rich, equant to elongate structures of different types and shapes emerging as cones from the clayey sediment. The dominant type (60% of the total) consists of large hummocks with concave, irregular centers, 30–60 cm high

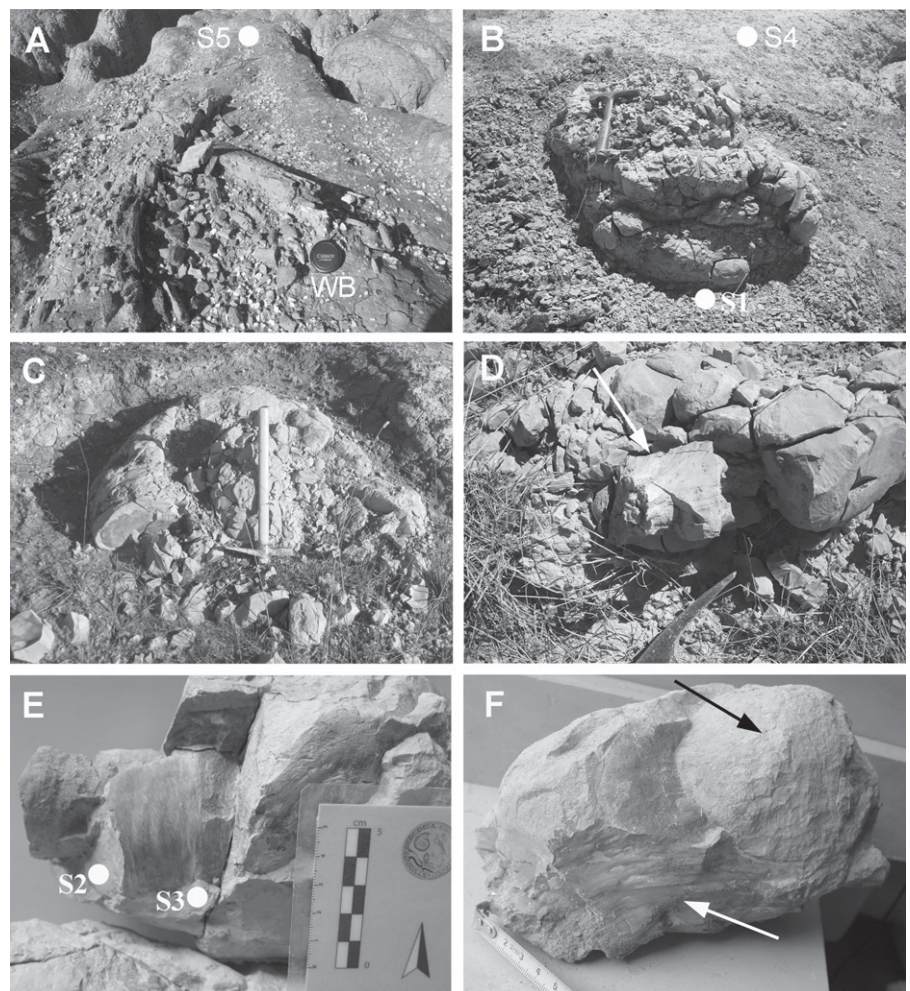


Figure 1. Enigmatic structures in Pleistocene sediments of Allerona (western Umbria, Italy). **A:** Close-up view of whale bones (WB). **B,C:** Hummocky-shaped structures consisting of tangle of irregular tunnels or mud slabs. **D:** Detail showing tapering and converging striae (arrow) of large structure. **E:** Side view of structure showing helicoidal arrangement and striae similar to those of modern ambergris. **F:** Subcircular lumps (black arrow) similar to rognons described by Clarke (2006) in modern ambergris, with striae (white arrow) and tapered end, similar to structures occurring in ambergris as it is remodeled in a whale's rectum (scale bar = 5 cm). S1 to S5 indicate chemical samples.

and 60–120 cm wide, with subcircular to elliptical outlines, each consisting of a tangle of rough tunnels or mud slabs, commonly rotated, with disparate organization (Figs. 1B–1F). Color varies from yellowish to red or whitish to light gray, commonly with different gradations in the same structure. Simpler structures (~40% of total) are isolated in clay, 30–50 cm wide, and up to 100 cm long (with a few up to 130 cm), each exhibiting an outer subcircular shape and commonly obliquely oriented (20°–30° on bedding plane). Although externally they resemble vertebrate and invertebrate burrows, such as the Eocene–Oligocene aestivation burrows of lungfish described in France by Gaillard et al. (2013, their figures 6 and 8) or the Early Jurassic (Pliensbachian) shafts of *Tisosa siphonalis*, also of France (van de Schootbrugge et al., 2010), the Allerona specimens are distinguished from burrows by important differences. For example, the internal arrangement of the Allerona structures is helicoidal to concentric around a central nucleus (usually a dark gray clay core), a feature lacking in most burrows (e.g., simple or columnar carbonate concretion in *Tisosa siphonalis*; van de Schootbrugge et al., 2010). Moreover, a well-cemented series of concentric rings, commonly with oxidized reddish or yellowish crusts and very similar to those present in modern ambergris specimens, are common in the Allerona specimens (Figs. 2A and 2B). Very frequently, longitudinal sets of striae 3–5 cm wide and up to 12 cm long, commonly converging toward an apex, have been observed in our specimens (Figs. 1F and 2D). These striae differ from those of burrows (e.g., those illustrated by Gaillard et al. [2013]) because those of the latter are parallel and regularly spaced, while striae in the Allerona structures are convergent toward the apex (Fig. 2D). These features are, however, well known in modern ambergris. Clarke (2006) observed that the thinner end of each mass of ambergris may be tapered, or shaped like a thick bobbin protruding from the main mass, with a somewhat rounded terminus. Notably, the orientation of ambergris specimens, which is known only from two finds from the *Southern Harvester* floating factory during the Antarctic whaling season of December 1953 (155 kg and 421 kg specimens), is with the smaller end pointing toward the anus and the larger end pointing toward the stomach of the whale. Similarly, the end of each Allerona structure is tapered and exhibits wide and deep convergent striae (Fig. 2D), as in ambergris described by Clarke (2006) (Fig. 2C). Subcircular lumps and protruding structures are common in the outer part of the Allerona structures (Fig. 1F), just as in the “rognons” found in present-day ambergris (Clarke, 1954; Clarke, 2006, his figure 4; Johnson, 2001; Perrin, 2005; Vogt, 2011). Rare cases of rudimentary branching have been found at Allerona. Branches display an asymmetric Y-shaped form, showing

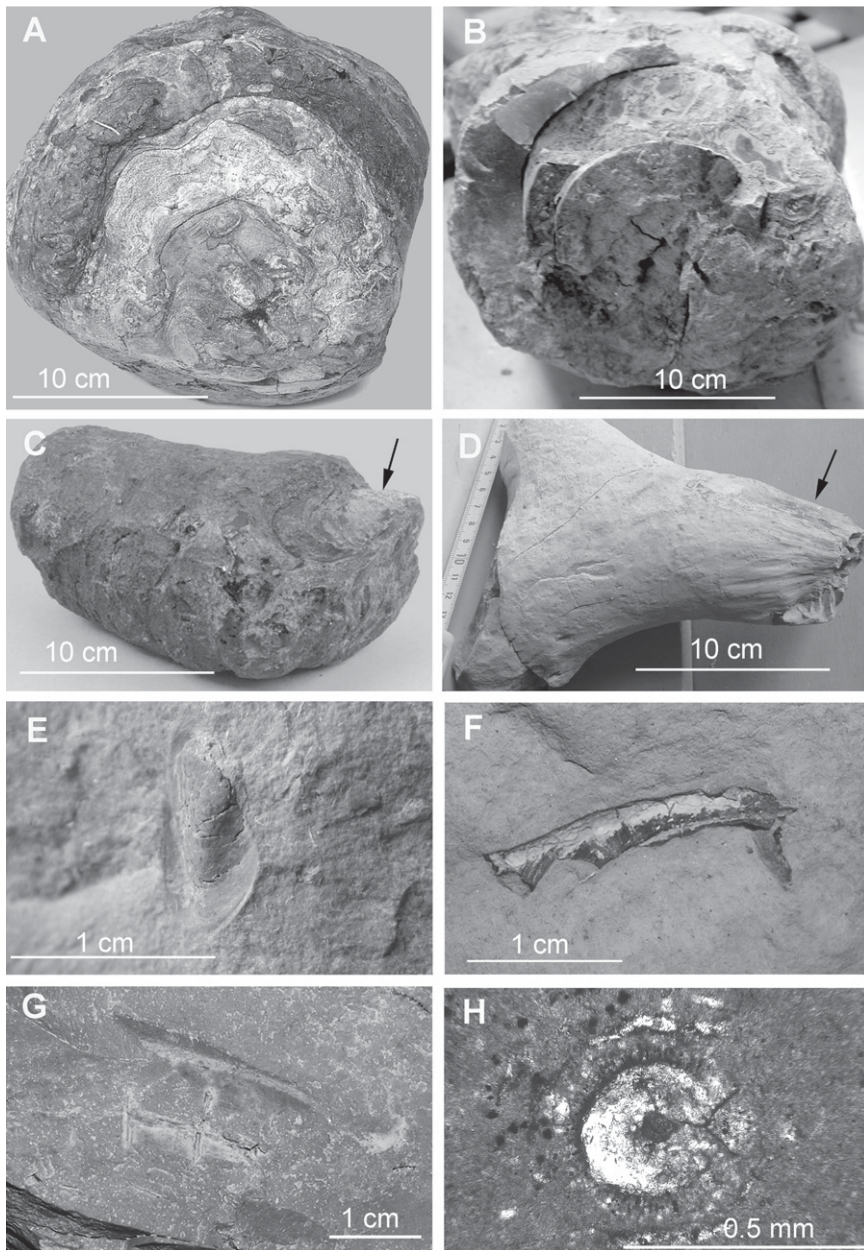


Figure 2. A–D: Comparison between modern ambergris and permineralized structures of Allerona (western Umbria, Italy), showing transverse view of modern (A) and fossil (B) ambergris with concentric rings, and side view of modern (C) and fossil (D) ambergris with tapering end and converging striae (see arrows). E–G: Fossil remains of permineralized squid beaks from Allerona. H: Cross section of squid beak rostrum from fossil ambergris, thin section.

a dark clay nucleus within; a typical narrowing and a slight tapering are both only near the apex, where deep, converging longitudinal striae are common. Comparable features have not been previously reported in the paleontological and ichnological literature. Dimensions and morphological features (Figs. 2A–2D) link our enigmatic structures to ambergris as well (Clarke, 1954, 2006; Baynes-Cope, 1962). The presence of squid beaks, permineralized with pyrite or calcite in the interior of several lumps, underscores this link (Figs. 2E–2H). The lower beaks are better preserved than the upper ones

(Xavier and Cherel, 2009); lower squid beaks, ranging from few millimeters to 2–3 cm in size, represent 80% of all squid beak remains, while upper beaks represent only ~20%. The presence of fossil squid beaks inside almost all of these enigmatic structures suggests the association with modern sperm whale ambergris masses. A closer comparison with modern ambergris is thus worthwhile.

PRESENT-DAY AMBERGRIS

Ambergris, known as *ambra grigia*, *ambregris*, *ambergrease*, or *gray amber*, is a solid,

waxy, dull gray or blackish flammable substance usually associated with sperm whales (*Physeter macrocephalus* Linnaeus, 1758; syn. *P. catodon* Linnaeus, 1758) and more rarely with pygmy sperm whales. Several theories of its origin have been proposed; nevertheless, because of the presence in the whales' gut of beaks and pens of squid (Fig. DR3), the whales' principal food, the metabolically induced origin of ambergris is widely accepted. The well-known, eagerly hunted and precious ambergris (Murphy, 1933; Clarke, 2006; Kemp, 2012) is usually collected from coastal sand or found floating at sea, occurring in lumps of various shapes (Figs. 2A and 2C) and sizes weighing from 10 g to 50 kg or more (Clarke, 1954, 2006). It is occasionally found within the abdomens of dead whales (Clarke, 2006). Because cephalopod beaks commonly occur within ambergris (Clarke, 2006), it has been hypothesized that the whales produce the substance within the gut to protect it from indigestible sharp objects (Santos et al., 1999, 2001; Clarke, 2006; Fernandez et al., 2009; Spitz et al., 2011). Despite this consensus, the origin of ambergris is still debated, although the theory that it forms as a pathological "concretion" (*sensu* Clarke, 2006) of fecal material is now generally accepted (Lambertsen and Kohn, 1987; Clarke, 2006). Present-day ambergris is reported worldwide; e.g., on the Atlantic coasts of the Bahamas, Belize, Brazil, and Argentina as well as in the Indo-Pacific region (Clarke, 2006). The soft, fatty precursor of ambergris is pale white, commonly streaked with black, and with a strong fecal smell. After months to years of floating in the pelagic environment, photo-degradation and oxidation gradually harden the ambergris, which turns dark gray, yellowish, or black, with a crusty and waxy consistency. Concentric, irregularly enveloped, protruding structures (rogons) are also common (Baynes-Cope, 1962; Clarke, 2006). Ambergris as old as 3–4 k.y. is known, mostly from Egypt, Arabia, and China, and has been used in perfume making and as a drug (Murphy, 1933; Clarke, 2006; Kemp, 2012). Like other coprolithic structures (Seilacher, 1964; Frey and Pemberton, 1985), ambergris is expected to be preservable in the fossil record; however, fossil ambergris has never previously been documented.

PRELIMINARY CHEMICAL ANALYSES

With the aim to find organic traces from the original substances (ambrein) and to support the hypothesis that our structures are fossil ambergris masses, five selected samples (S1–S5) were subjected to preliminary chemical examination (details of which are reported in the Appendix). Transmission infrared fluorescence spectroscopy (FTIR) and liquid chromatography analyses were carried out on mineralized fossil structures and neighboring clay sediment. Samples of both the inner gray (S2) and the outer red or yellow

(S3) parts of the structures were analyzed by FTIR. Two definite spectral patterns were recognized in both types of samples, evidencing different percentages of CaCO₃ and aluminum silicates. The FTIR analysis showed a relatively low amount of aluminum silicates within the fossil structures (Fig. DR2). In contrast, the enclosing clay sediments showed a low content of CaCO₃ (<15%); CaCO₃ in the enigmatic structures is interpreted as biogenically precipitated due to local enrichment in organic matter (Castanier et al., 1999; Douglas, 2005). Liquid chromatography analysis (see the Appendix) was carried out on a methanolic extract of samples S1–S5 (Figs. 1A, 1B, and 1E): clay sediments sampled under fossil structures (S1), two samples of permineralized fossil structures (S2, S3), and neighboring clay sediments (S4, S5). Several organic compounds of lipid derivation were found, with a variable distribution in each sample. Several cholic acid species that might be indicative of mammalian gastric activity, and are compatible with cellular lipid degradation, were discovered in samples S1, S2, and S3.

Traces of eight free amino acids attributable to squid beak composition were found, with values in micrograms per gram (Table DR2), specifically comparable with analyses of jumbo squid (*Dosidicus gigas*) beaks (Miserez et al., 2007). The unexpected finding of free amino acids demonstrates the ability of sediments to preserve organic substances 1.75 m.y. old that originally were present in biogenic structures.

INTERPRETATION

The enigmatic structures presented here show several important similarities with contemporary ambergris masses: (1) the overall forms and striation of the structures, (2) the presence of fossil squid beaks, and (3) the presence of organic molecules derived from mammalian gastric activity and from the alteration of squid beaks. The fossil organic compounds, many referable to squid beak composition and the presence of anandamide, an endogenous substance produced only by mammals, support an odontocete origin and affinity with present-day ambergris, though the role of diagenesis must be considered.

Unfortunately the chemical analyses are not conclusive, as they did not reveal substances directly correlated to ambrein, the diagnostic precursor to compounds used in perfumery (Governato et al., 1977). But the diagenetic processes that induced the precipitation of CaCO₃ could have obliterated ambrein-derived molecules. As reported by Clarke (2006), the distribution of ambrein is very different from outer to inner layers of ambergris; the black ambergris of the outer layers, of poor quality for perfumery, is low in ambrein and other ether-soluble constituents, but has the highest mineral content (phosphorus, magnesium, and calcium oxides),

while magnesium ammonium phosphate crystals (such as struvite) occur in fresh samples.

Although more detailed analyses are required, the affinity with modern ambergris seems convincing. We suggest that the enigmatic structures of Alleronia are fossils analogous to the large ambergris masses found within the abdomens of dead sperm whales.

Still, it is difficult to justify such a concentrated accumulation of ambergris masses in a surface of only ~1200 m². Several hypotheses can be proposed, from pandemics to environmental stress, and further analysis is needed to identify the causes of death and of concentration. In reconstructing a possible scenario, significant evidence is provided by molluscs characteristic of whale-fall communities close to the whale bones and around all the ambergris masses. The presence of whale-fall mollusc assemblages in this context is suggestive of a distinct mass mortality of sperm whales. The carcasses that originally accumulated on the seafloor are not preserved. The presence of more than 25 coproliths of variable size and shape may be the only record of this mass mortality, the causes of which have still not been identified. The lack of cetacean remains around the structures can probably be ascribed to several processes that have contributed to destruction of whale carcasses in modern whale falls in the Pacific and Atlantic Oceans (Smith and Baco, 2003). According to Smith et al. (2002), the ecological succession of scavengers and other opportunistic taxa proceeds more quickly at shallower depths than in deep-sea whale falls. At shallow depths, the higher water temperature enhances bacterial activity, shortening the duration of the sulphophilic stage (Fujiwara et al., 2007). Shallow depth and higher water temperature, both identified in the Alleronia site, seem to be important factors that accelerate carcass degradation (Smith et al. 2002; Fujiwara et al., 2007).

As ambergris accumulates in the intestine of a sperm whale, it generates a progressive obstruction that may cause the rupture of the rectum wall, inducing the whale's death and the release of ambergris into the sea (Clarke, 2006). However, this can only be considered a contributory cause, and it is not sufficient to explain a mass die-off of sperm whales. According to Gannier et al. (2002), living sperm whale populations in the Mediterranean Sea largely prefer the water overlying the continental slopes, with sightings occurring less than 10 km from the –200 m isobath. Even so, they do chase squid into shallower depths along the coast. The paleogeographic configuration of the Alleronia area, a narrowly elongated northwest-southeast bay (a "cul-de-sac") with a maximum depth of 150 m and subject to river influx (Bizzarri, 2006; Bizzarri and Baldanza, 2009; Baldanza et al., 2011), may have been a natural trap for pods of sperm whales chasing schools of squid (Fig. DR4).

Thus, any of several combined factors, whether paleoenvironmental or related to the biology of sperm whales, could have contributed to this mass mortality event. Although research is still in progress and more systematic analyses will be carried out on mammal coproliths, the Alleron site uniquely suggests the abundance and sudden death of sperm whales in this area during the early Pleistocene. The discovery of these masses of ambergris increases our knowledge of the distribution and activity of sperm whales in the ancient Tyrrhenian Sea 1.75 m.y. ago. As a result, the Alleron site, exhibiting a very high concentration of sperm whale coproliths, is the first fossil documentation of sperm whale ambergris anywhere in the world.

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