ΕΓΕ 2019
15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. **7** Ext. Abs. GSG2019-387

Mineral Staining In Excavated Bone: The Case of Dispilio, Greece

E. Stathopoulou[1,2], M. Mallouchou1, E. Margariti[1]

(1) Department of Historical Geology & Palaeontology, Faculty of Geology & Geoenvironment, University of Athens, Panepistimiopolis, 15784 Zographou, Greece, estathop@geol.uoa.gr
(2)Wiener Laboratory, American School of Classical Studies at Athens ASCSA, 54, Souidias str., 106 76 Athens, Greece.

Background

Mineral staining of buried bone is a diagenetic procedure, which involves mainly Fe and Mn oxides (Stermer et al., 1995; Stathopoulou et al., 2013; Bradfield, 2018). Manganese is usually the most present in soil and can occur in several oxidation states, each resulting in different colouration of the bone surface with which it has come into close proximity. Specifically, reduced manganese will tend to produce darker brown to black stains (Dupras and Schultz, 2014). Iron oxides in the sediment typically result in bone turning a deep chocolate brown colour, while well-drained soils conducive to oxidizing conditions can result in bright red to brown discolourations. The mineral composition of soils, soil solution, unique chemistry and pH play an important role on bone staining (Shahack-Gross et al., 1997). Moist, acidic conditions are conducive to corrosion (Janaway, 2008) and it is in these environments that a variety of bone discolourations are expected.

Possible causes of oxide staining may include: 1) microbial activity and more specifically activity of Mn, Fe-oxiding bacteria. The optimal conditions preferred by these bacteria are moist environments that are aerobic with near neutral pH. Manganese origin is often associated with soil humification following a human occupation. The presence of clay minerals is also important, since the bacteria can adsorb on them and use nutrients that also absorb on clay. The bacteria concentrate metals from their environment, most probably from water. The bones themselves may serve as a source of nutrients for the Mn- oxidizing bacteria (Marin Arroyo et al., 2008; Shahack-Gross et al., 1997), and 2) alterations of pH and Eh that may cause precipitation of Fe –Mn oxides. For instance, iron oxides can be produced due to the oxidation of pyrite. Bacterial solubilization and oxidation of iron from pyrite has also been determined. An increase in pH and intensification of oxidizing conditions (associated with dry, well-aerated soils) may favour a change in manganese towards insoluble forms. On the contrary, with a decrease in pH, the manganese may be reduced, increasing its solubility. An increase in the pH can, in turn, be due to burial causes, lack of humidity, the evolution of the soil itself, or other types of causes that may have an anthropogenic origin, such as combustion produced in hearths (Caldeira et al., 2010; Marin Arroyo et al., 2008).

The identification of mineral staining at a site is important, as bone discolouration may also be connected to burning. The use of fire within a prehistoric settlement or site is one of the major issues of geoarchaeological research (Asmussen, 2009), as it proves the presence of man. The identification of archaeological burnt bones has commonly been based on changes such as their colour, crystallinity, shape, histology, as well as the presence of cracks and a black char with characteristic chemical properties. The most easily identified colour, indicative of burning, is also black (Shipman et al., 1984).

Objectives

This paper presents the interdisciplinary study on the origin of “black bones” at the Neolithic lakeside settlement of Dispilio, Greece (5500–3500 BC), where discoloured animal bones have been recovered from a waterlogged and organic soil-matrix containing charcoal, ash and burnt cultural remains. In the past, this has been interpreted as the result of the destruction of the village by fire and abandonment. This study aims to examine whether the colouration of the material at the site can be explained by this theory, through the distinction of burnt vs. oxide stained bones.

Material-Methods

Forty four (44) groups of fish bones and nineteen (19) mammal bone samples were selected for this study. The fish bones included fragments from the neurocranium, the branchiocranium and the spine (vertebrae, costae, etc) as well as bone parts from the pectoral, pelvic and fin skeleton. The species most represented were Cyprinus carpio and Silurus glanis. The mammal bone samples were shafts of long bones (tibia, humerus, etc), and of metapodials, as well as fragments of short bones. They were pieces not identified to species, and pertained predominantly to smaller animals. Material was mainly chosen based on colour, in an attempt to cover all types of bone discolouration present at Dispilio (light-coloured/yellow to dark-coloured/black), but also the different cultural contexts found at the site (lacustrine phase C, early-pre-destruction and late-destruction) and amphibian phase B (post-destruction layer; terrestrial phase). By means of comparison, two modern bone reference samples were used (NIST bone meal sample Reference material 1486 and an exhumed relatively fresh bovine bone).

All bone samples were examined through Optical Microscopy, Scanning Electron Microscopy (SEM), X-ray Microanalysis (EDS), X-ray Diffraction (XRD) - Rietveld Analysis, Infrared Spectroscopy (ATR, NIR) and chemical analyses (ICP-MS). Alterations of histology, mineralogy, chemistry, crystallinity and structural parameters due to diagenesis and/or possible burning are presented and correlated to the intriguing regional geochemical context.

Results-Conclusions

The various analytical techniques employed on mammal and fish bones did not offer any proof that any of the chosen material is burnt, based on specific features described in relevant bibliography. Rather, all the observed alterations concerning cracking, histology, colour, crystallinity etc. in the samples, could be attributed to diagenesis.

Our study showed that bones have certainly been affected by Mn and Fe oxide staining and owe their colour to this procedure. The soil-matrix at the site, which is very rich in charcoal and ash but at the same time waterlogged and organic, may have played a role in bone colouration, in combination with the aforementioned phenomena. Oxide staining is a very common phenomenon in sites that appear rich in organic matter abandoned as a result of consumption activities. With respect to the origin of Mn and Fe in the area and based on the mineral phases traced within the surrounding sediment in the polished sections, it can be suggested that these elements come from the rocks and sediments of the surrounding area. It is also possible that part of the Mn does not have a geological origin, and an anthropogenic source should be considered, namely the accumulation of vegetable and animal organic matter. Ions of the metal could be released during decomposition of the organic matter, and then enter the sediments in which the bones are buried (Marin-Arroyo et al., 2008; Shahack-Gross et al., 1997).

Regarding the colour based grouping (dark vs. light-coloured bones), it also corresponded to a number of different diagenetic features. In general, light-coloured bones seem to be less affected by diagenesis and exhibit features concerning chemistry, crystallinity etc, that resemble those of fresh bone, which proves that these bones were buried in a totally different geochemical environment to the dark-coloured ones.

On the other hand, fish samples exhibited some different characteristics to those of mammal bones. This can be explained by the different histological structure of fish bones, in terms of increased porosity and thus higher susceptibility to dissolution, degradation and interaction with the surrounding sediment.

Concerning the stratigraphy of the studied samples, there does not seem to be a specific diagenetic trend, other than those described based on the colour of the bones. Light-coloured bones, come mainly from phase B which represent the terrestrial part of the site, while dark-coloured material derived from all phases, but mostly C early and C late which represent the waterlogged part.

Acknowledgements

The authors are indebted to late Prof. G. H. Hourmouziadis for providing access to the material, to Panayiotis Karkanas for geting the project off the ground. Funding was provided by the Wiener Laboratory (American School of Classical Studies at Athens). Thanks are owed to Dr. G. D. Chryssikos and Dr. V. Gionis from the Applied Spectroscopy Laboratory, of the Theoretical and Physical Chemistry Institute at the National Hellenic Research Foundation, for their ideas and specialized knowledge, as well as for the application of vibrational techniques on our material.

References

Asmussen, B., 2009. Intentional or incidental thermal modification? Analysing site occupation via burned bone. Journal of Archaeological Science 36, 528–536.

Bradfield, J., 2018. Some thoughts on bone artefact discolouration at archaeological sites. Journal of Archaeological Science: Reports 17, 500–509.

Caldeira, C.L., Ciminelli, V.S.T., Osseo-Asare, K., 2010. The role of carbonate ions in pyrite oxidation in aqueous systems. Geochimica et Cosmochimica Acta 74, 1777–1789.

Dupras, T., Schultz, J., 2014. Taphonomic bone staining and color changes in forensic contexts. In: Pokines, J., Symes, S. (Eds.), Manual of Forensic Taphonomy. CRC Press, Florida, 315–340.

Janaway, J., 2008. The Decomposition of Materials Associated with Buried Cadavers. In: Tibbett, M., Carter, D. (Eds.), Soil Analysis in Forensic Taphonomy: Chemical and Biological Effects of Buried Human Remains. CRC Press, Florida, 153–201.

Marin Arroyo, A.B., Landete Ruiz, M.D., Vidal Bernabeu, G., Seva Román, R., González Morales, M. R., Straus, L.G., 2008. Archaeological implications of human-derived manganese coatings: a study of blackened bones in El Mirón cave, Cantabrian Spain. Journal of Archaeological Science 35, 801–813.

Shahack-Gross, R., Bar-Yosef, O., Weiner, S., 1997. Black-coloured bones in Hayonim Cave, Israel: differentiating between burning and oxide staining. Journal of Archaeological Science 24, 439–446.

Shipman, P., Foster, G., Schoeninger, M., 1984. Burned bones and teeth: An experimental study of color, morphology, crystal structure and shrinkage. Journal of Archaeological Science 11, 307–325.

Stathopoulou, E. T., Theodoropoulou, T. and Phoca-Cosmetatou, N., 2013. Black fish bones in waterlogged deposits: the case of the Neolithic lake settlement of Dispilio, Greece. Archaeofauna 22, 51-74.

Stermer, E., Risnes, S., Fischer, P., 1995. Trace element analysis of blackish staining on the crowns of human archaeological teeth. Eur. J. Oral Sci. 104, 253–261.