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NO BONES ABOUT IT

Fossilized bones help scientists not only identify the age of rocks, but also to determine the ancient environment and climate in which ancient humans and animals once lived. One just needs to know the right methods to use.

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Animal bones are a common find. During excavations, especially in caves, but also in former hunting camps, settlements, medieval towns and dump sites. Human bones are rarer, found only at certain archaeological sites, mainly cemeteries. They are crucial in research in archeology, anthropology, paleontology and geology, as they contain important information about the Quaternary (the most recent geological period) and earlier periods.

Bones are used in biostratigraphy to determine the age of rocks, through the identification of fossil markers (species characteristic for specific geological periods). There are limitations to using this method for the Quaternary period, due to its relatively short duration, in which not many important evolutionary changes have occurred. Fossil bones are much more

useful in the chronostratigraphy of this period, determining the absolute age of layers in years (more often in thousands, tens of thousands, or hundreds of thousands of years). They offer a good research tool, especially for radiocarbon and uranium-thorium dating, as they accumulate radioactive carbon throughout the organism's lifetime and uranium isotopes during burial time. Lastly, bone-based studies are useful for analyzing environmental changes (climate, landscapes, and ecosystems), as they help to determine the composition of ancient biocenoses and ancient environments based on the species composition of the fossils. Also, biogeochemical analysis of bones can provide information on the paleoecology and climate, gleaned by analyzing the stable isotope ratios of carbon, oxygen, hydrogen, sulfur and nitrogen, which in turn reflect the diet and the environment of the animals or humans.

Wandering bones

For such comparative research of fossil bones to make sense, we need to be certain of their homogeneity. Regardless of the purpose and type of research, the bones



The mandible of a cave hyena found in the Perspektywiczna Cave in the Częstochowa Upland. Although hyenas are associated with Africa, they once lived in Central Europe and became extinct in this area about 40,000 years ago. However, this bone was found in a layer that was deposited only a thousand years ago. This is a telling example of re-deposition, involving the secondary displacement of objects between geological layers.

must be of the same age and from the same period of sediment accumulation. Otherwise, we would not be analyzing a set of bones from a given period, but a random collection of bones from various environments and ecosystems.

Polish scientists have long treated fossil bones in Quaternary sediments as relatively homogeneous, assuming that they were originally deposited in the same layers in which they were found during excavation. Meanwhile, numerous studies conducted abroad, as well as research begun in Poland by the present author and observations made by other researchers, have demonstrated that certain sets of bones found in late Quaternary sediments in Poland were not actually found *in situ*, in other words in the location of their original deposition.

Bones can be transferred between layers for various reasons, mainly by animals who mix up the sediment when building burrows, digging up or burying bones in the process. The freezing process can also have a great impact, as bones and other objects can slip into the crevices formed in a deeply frozen settlement, or they can be “frozen out,” slowly pushed up to the surface out of the ground by ice lenses form-

ing every winter. Their location may also be affected by geological transport: erosion, especially by rivers, and slope denudation can damage layers of various age and transport them, finally depositing bones from different layers together in a new location. Certain geological environments are particularly susceptible to the mixing of bones from different periods, especially riverbeds and the bases of slopes. But even in places

What is diagenesis?

Bone is one of the few vertebrate tissues that can survive degradation and be preserved in a fossil state. The total transformation that the bone undergoes from the time it is first buried is called fossilization or diagenesis. It begins immediately after the death of the individual organism and can last for millions of years, transforming the bones into fossils. In general, the process can be divided into early and late diagenesis. The boundary between these two stages is fluid, but this division is useful in taphonomic research. Early diagenesis occurs when the bone still retains its original structure and vital components. Late diagenesis occurs in fossils, in other words in already heavily altered remains.

where sediment accumulation proceeds calmly, for example in caves or where deposits are blown in by the wind, mixing can occur as a result of secondary post-sedimentation processes.

Test limitations

There are several ways to determine if bones from a given assemblage are actually of the same age. The simplest way is to analyze their general macroscopic properties, including color, brittleness, degree of cracking and the existence of mineral precipitations. However, this method is so subjective that it can only be used for preliminary analysis.

Another way to study a set of bones is through paleoecological analysis, which is based on the obvious assumption that the bones of individuals who lived together must have belonged to the same ecosystem. Thus, the bones of animals from very different environments, such as tundra animals (e.g. the muskox or lemming) and typical forest dwellers (the lynx or squirrel), must come from different geological periods. If the remains of animals from different ecological environments are found together, it clearly shows that the deposits have been mixed. However, this method fails if the mixed bones come from similar environments, as well as in the case of extinct species (of which we have little ecological knowledge).

The best method is physicochemical dating, because it allows us to determine the period in which each bone was deposited. Radiocarbon dating is the most accurate technique. It allows us to identify not only the degree of homogeneity, but also the time when the deposition took place. However, this method has significant limitations. Firstly, it is expensive. Secondly, the protein component of the bone, which contains the organic carbon that is the basis for the dating, must be well preserved, and it is this compo-

nent that is most easily decomposed. Thirdly, after about 50,000 years, the number of still decaying C-14 radioactive carbon atoms is so low that it is impossible to measure.

There is one more method of determining the homogeneity of fossil bones: studying the geochemical changes caused by diagenesis (the process by which the sediments are turned into sedimentary rocks, and the remains of organisms into fossils).

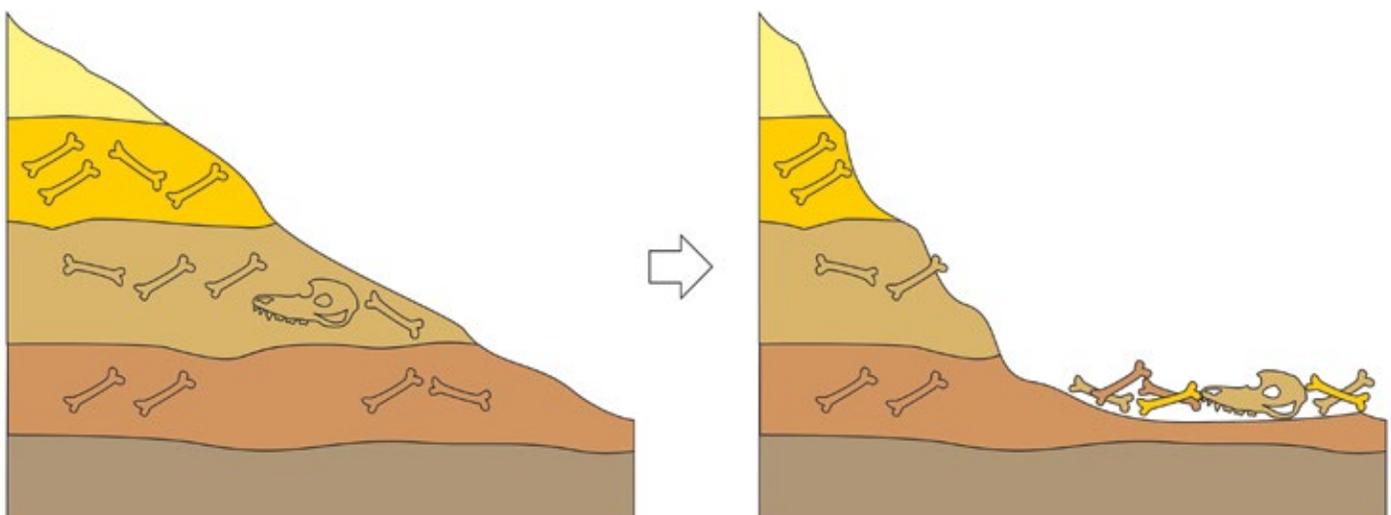
Chemical differences

When studying Quaternary bones, which are relatively young on the geological time scale, the processes of early diagenesis are important. These consist in:

- dissolution or hydrolysis, leading to the removal of organic or mineral bone components, depending on the moisture content of the sediment and the pH of the water filtering through the bone;
- recrystallization, or the dissolution and renewed crystallization of apatite (phosphate mineral, a bone component), leading to the reduction of porosity and changes in the chemical composition of crystals due to introducing ions from the environment;
- the absorption and adsorption of ions from groundwater, altering the chemical composition of the apatite;
- permineralization, or the precipitation of new minerals, most often calcite, pyrite, gypsum and others;
- fragmentation and compaction, or bone distortion due to the mechanical pressure exerted by the surrounding sediment.

Diagenesis alters various bone parameters, such as its chemical and mineral composition, degree of crystallinity, porosity, tissue structure, fragmentation and size. Each of these can be used in analyzing homogeneity.

The concept of "geochemical fingerprint": bones deposited in different geological layers exhibit differing chemical compositions. After erosion and re-deposition in a new location, bones from different layers can be mixed together, but the original chemical features acquired during early diagenesis remain and allow the researcher to determine the specimen's origins.



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Studies to date have shown that bones from different layers have a different chemical composition of apatite. This is due to exposure to external conditions, such as humidity, porosity, pH and redox potential of the sediment, as well as the varied availability of ions in the environment. This phenomenon, known as the “geochemical fingerprint,” can be used to determine which layer a bone comes from and, consequently, to evaluate the homogeneity of a given assemblage of bones.

Tracing traces

Bone apatite, also known as bioapatite, exhibits the textbook formula for the mineral hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. However, this formula shows only a simplified chemical composition, because it does not include trace elements that are always present in bioapatite in small amounts. Metals such as Na, K, Mg, Sr, Ba and lanthanides occur as substitutes for calcium, phosphate is partially replaced by carbonate, sulfate and hydrogen phosphate, while F^- , Cl^- and O^{2-} ions occur as substitutes for the OH^- group. The content of the main elements in apatite, including calcium, phosphorus and oxygen, does not change significantly during diagenesis, but the trace elements do exhibit significant variations.

An important question that arises when talking about using such chemical changes in homogeneity tests is how fast and where they occur depending on the sediment. I conducted an experiment to study this problem: fresh animal bones were buried in containers with various types of sediments, such as sand, loess, clay, peat and silt. They were then kept in a laboratory under controlled temperature and humidity conditions for 2.5 years, after which they were dug out and the changes to the chemical composition of the bones were studied. It turned out that even over such a short time, in comparison with the hundreds and thousands of years we use to measure time in geology and archaeology, the bones underwent significant changes, which varied depending on the type of sediment and humidity. This allowed to determine the types of diagenetic changes the bones undergo depending on the ambient conditions. The experiment also proved

that the chemical composition mainly develops in the first years the bones are in the earth. This means that if the bones are mixed between the various layers later on, they will already bear a characteristic chemical composition that will allow their original location to be identified.

Laying doubts to rest

Homogeneity studies are currently being carried out at several Polish archaeological and paleontological sites, including in the Biśnik, Nietoperzowa and Perspektywiczna caves, in which there are several layers containing fossil bones. They are also being carried out on the medieval strata in Kraków’s market square and at the site of mammoth and reindeer hunters in Jaksice.

The method used in the project allows us to analyze bones regardless of the degree of collagen loss, and there are no age limits, as there are in radiocarbon dating. It is also a much cheaper method, which is significant when studying numerous sets of bones. It does not allow us to determine the absolute age (in years), but does allow us to determine the relationships between relative ages, such as whether the bones are of the same age or not.

A crucial area in which this method can be used is the selection of bones for further radiocarbon dating or other research, such as U/Th dating, measuring stable isotope ratios or the genetic analysis of ancient animals and humans. It can help to eliminate any uncertainties about the origins of bones, which are always present in this type of research. It will also help determine which layer a given specimen belongs to, which is important when it comes to such human bones from the Paleolithic era, the bones of rare or index species, those with traces of anthropogenic processing, as well as those of unknown or uncertain affiliation (with lost or damaged records, coming from previous old-fashioned research), recovered from theft, etc. Indirectly, conclusions derived from analyzing bone remains can point to the possible mixing of other archaeological artifacts, such as flint products.

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Experimental research on chemical changes in bones. On the left, containers with various sediments and fragments of fresh bones being prepared for burial. On the right, example bones dug up after two and a half years. The first specimen is a comparison bone, not buried. The most-modified specimen, with reddish hue, was buried in peat.

Further reading:

- Krajcarz M.T. (2013). Geochemical evidence for postsedimentary re-deposition of animal bones at multilayered sites. The case of Biśnik Cave, southern Poland. *Archaeologia Polona* 49 (2011): 153–162.
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