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On porosity of archeological bones I — Textural characterization of pathological Spanish medieval human bones

Pedro Bosch [a,*], Carlos Moreno-Castilla [b], Zulamita Zapata-Benabithe [b], Inmaculada Alemán [c], Victor Hugo Lara [d], Josefina Mansilla [e], Carmen Pijoan [e], Miguel Botella [c]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, 0451 México D.F., Mexico
[b] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18002 Granada, Spain
[c] Laboratorio de Antropología, Facultad de Medicina, Universidad de Granada, 18012 Granada, Spain
[d] Universidad Autónoma Metropolitana — Iztapalapa, Avenida San Rafael Atlixco 186, 09340 México D.F., Mexico
[e] Dirección de Antropología Física, Instituto Nacional de Antropología e Historia, Gandhi s/n, Polanco, 11560 México D.F., Mexico

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ABSTRACT

Bone texture may vary as a function of age, pathology as well as on bone treatments; thus absolute values of specific surface area or porosity are not often reported. A review of the anthropological and archeological references reveals that the results obtained with the current methodologies for the textural analysis of bone may be contradictory. Indeed, the characterization of archeological bone is a very difficult task through conventional techniques. Still, it is most relevant as porosity is the symptom of several pathologies, for instance anemia, osteoporosis, hyperostosis or syphilis.

In this work, archeological bone samples – pathological or healthy – were characterized by nitrogen adsorption–desorption isotherms at −196 °C, small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). The studied bones are healthy, osteoporotic, hyperostosic, and syphilitic. Porosity, specific surface area, and morphology as well as non conventional features such as roughness, specific surface or fractal dimension, are correlated with the well known macroscopical reported symptoms. The samples come from Moorish Andalucía (Grenade) and Medieval Catalonia (Poblet Monastery).

1. Introduction

Bone is constituted by connective tissue composed of an organic protein, collagen, and a mineral component, hydroxyapatite (Weiner and Traub, 1992; Labastida Pólito et al., 2006). Collagen appears in bone as beams of white inelastic fibers with an enormous tensile strength. Those fibers include fibrils, which are formed by smaller filaments: the collagen protein that is the most abundant protein in animal tissues. Human collagen protein contains a high percentage (23 to 30%) of proline and hydroxyproline amino acids. The end space of the collagen fibrils is the nucleation center for calcium phosphate, *i.e.*, hydroxyapatite. Depending on collagen fiber orientation, two types of bone are distinguished: cortical which appears in long bones or trabecular that may be found in vertebrae or extremities of long bones. Note that lamellar bone is not restricted to cortical, but refers to the organization of the collagen fibers. Normal adult human trabecular bone is lamellar as well.

Human bones have three main cavities: Harvesian canals (50 μm), osteocytic voids (quasi ellipsoidal and a few μm in size) and canaliculi (found between the lacunae, their diameter is less than one μm). Still, there are other cavities in bone besides these, *e.g.*, the canals of forming osteons, and resorptive bays which are much larger, and vascular canals. The cortical porosity increases from approximately 8% for young individuals up to 24–28% for elderly individuals. Harvesian canals increase significantly with age whereas lacuna porosity decreases slightly (Martin, 1984; Wang and Ni, 2003). There are pathologies such as anemia (Domínguez-Rodrigo et al., 2012), syphilis (Lopes et al., 2010), leprosy (Roffey and Tucker, 2012), or co-deficiency of vitamin C and B_{12} (Walker et al., 2009) well known for their impact on bone porosity. Furthermore, bone pores may be modified, also, by *postmortem* thermal treatments (Bosch et al., 2011).

In this work, we have chosen to study and compare bones which at first glance, *i.e.* by macroscopical criteria, are altered in their porosity at various degrees (Ortner, 2011). They correspond to Moorish Andalucía and Medieval Catalonia, in Spain. As bone evolves with age and pathology as well as with bone treatments, the characterization of bone texture is hard work, and no absolute values of specific surface area or porosity are acceptable.

A review of the anthropological and archeological references reveals that the results obtained with the current methodologies for the textural analysis of bone are often contradictory. It is difficult to understand

* Corresponding author. Tel.: +52 56 22 46 56.
E-mail address: croqcroq@hotmail.com (P. Bosch).

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measurements as they depend not only on bone condition (taphonomy, diagenesis or washing) but also on characterization methods, which *see* different features. Although experiments with SAXS (Hiller and Wess, 2006; Pijoan et al., 2007) or nuclear magnetic resonance, NMR, have been fruitful (Wang and Ni, 2003), the most direct technique to evaluate texture should be gas adsorption as it happens with other materials (Sing, 2001; Fairén-Jiménez et al., 2006; Smith et al., 2008). Indeed, when a gas or vapor phase is brought into contact with a solid, part of it is taken up and remains on the outside attached to the surface, this phenomenon is known as adsorption. In physisorption (*i.e.* physical adsorption), there is a weak attraction (through Van der Waals forces) between the gas and the solid surface. The technique based on those principles is a useful tool to determine specific surface area, pore size distribution, and porosity (Rouquerol et al., 1999).

In this work, results obtained from N_2 adsorption–desorption isotherms at −196 °C are compared to those provided by scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS). The studied materials, mainly tibias (*i.e.* cortical tissue) and skulls (*i.e.* trabecular tissue), are human archeological bones from Spain which present different types of pathology and various degrees of diagenesis. The ultimate purpose is to discuss bone texture and the methods to evaluate it, macro, micro or nano-scopically. The discussion of porosity and cavities is meaningful as the extent of cavities and increased porosity play an important role in the physicochemical dissolution process of calcium phosphates. The larger the exposed surface to the environment, the faster the biomaterial dissolves, simply because larger quantities of exchanges can take place (Barrère et al., 2006).

2. Experimental

2.1. Archeological context

All bones were found in Granada, except for one which comes from the monastery of Poblet. During the Arabic period, in the actual gardens

Fig. 1. Location of Granada and Poblet in Spain.