DOI: 10.1017/S1431927603440968
Microsc Microanal 9(Suppl 2), 2003

A Comparative Analysis by LVSEM and DSC of Some Mineralized Biological Hard Tissues: Bone, Dentin and Ostrich Eggshell

L. Bucio, I. A. Belío*, A. Heredia, L. F. Lozano, M. A. Peña-Rico and A. Acosta-Romero

Instituto de Física, UNAM. Apartado Postal 20-364, 01000 México D.F., México
*Escuela de Odontología, Universidad Autónoma de Sinaloa, Blvd. de Las Américas y Universitarios, C.P. 80010 Culiacán, Sinaloa, México

Bone, teeth and eggshells as biological structures have been considered as some of the most exciting subjects in materials science, archaeology and medicine research. As *composite materials*, they contain both mineral and organic phases. In dentin in teeth and bone, we have hydroxyapatite carbonate $Ca_5(PO4, CO_3)_3OH$, (HA) and type I collagen. As for eggshells, they contain calcite ($CaCO_3$) along with unidentified biopolymers. Materials depend on structural stability of these interactions between both phases. The most important objective is the synthesis of new materials whose physical and chemical properties might find technological uses, for example as materials for implants and nanotechnology [1]. As is discussed everywhere in literature [1-4] molecular manipulation of materials implies the use of organic macromolecules or its monomers, even in very small amounts, to control the microstructure of the inorganic mineralizing phase. At this point, the question about how the biopolymer interacts with the structure of the crystal surface is the topic we want to discuss here in some representative cases: human bone, osteoid (from tumor), human dentin tissue and ostrich eggshell. The study of these biological hard tissues was carried out using Low Vacuum Scanning Electron Microscopy (LVSEM), Energy Dispersive X-ray Spectroscopy (EDS) and Differential Scanning Calorimetry (DSC).

In fig. 1 (LVSEM image of human bone) completely mineralized type I collagen fibers with hydroxyapatite nanocrystals show the typical fibrils arrangement. In fig. 2 an LVSEM image of osteoid tissue taken from a tumor is shown. In this case, an incipient mineralization is clearly observed. By EDS chemical mapping we have confirmed the presence of both calcium and phosphorus in the nodules observed in the image. In a previous work, we identified the mineral phase as calcium ultraphosphate, $Ca_2P_6O_{17}$, by X-ray powder diffraction measurements [5]. In figs. 3 and 4 we have LVSEM images of dentin tubules which under EDS results show poorly mineralized tissue (collagen) surrounding the apatite-mineralized tubules. The typical DSC plot of powdered human dentin (fig. 5) show two exothermic peaks (combustion) at $T \approx 340$ and 430°C (shoulder) as we have seen in human bones. The DSC plot for pure collagen show an exothermic peak at ≈ 550°C. Then the presence of a mineral phase reduces the thermal stability of the protein (the small crystallites act as fracture centres). For ostrich eggshell (fig. 6) the decomposition of calcite nanocrystallites into CaO becomes at lower temperatures (550°C) than in pure calcite. How mineralization changes the thermal and mechanical properties and how the surface interaction gives functionality to these mineralized *nanocomposite* tissues will be briefly discussed.

[1] Shenton, W., *et al*. Nature 389 (1997) 585-587
[2] Stupp, S.I. and Braun, P.V. Science 277 (1997) 1242-1248.
[3] Addadi, L. and Weiner, S. Proc. Natl. Sci. USA. 82 (1985) 4110-4114.
[4] Chernov, A. A. Soviet Phys. Usp. 4 (1) (1961) 116-148
[5] Acosta-Romero, A. Master Sci. Thesis (Medical Physics), Posgrado en Ciencias Físicas (Física Médica), UNAM (2002).
[6] Acknowledgments: project DGAPA PAPIIT IN-120801.

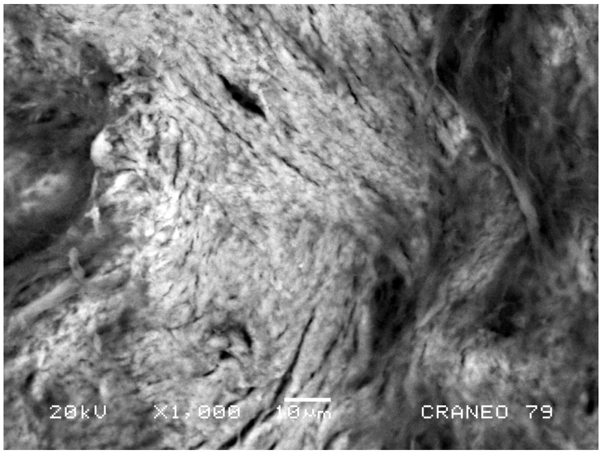

Figure 1: LVSEM photograph of human bone (skull) showing mineralized collagen fibers (mineral phase: hydroxyapatite).

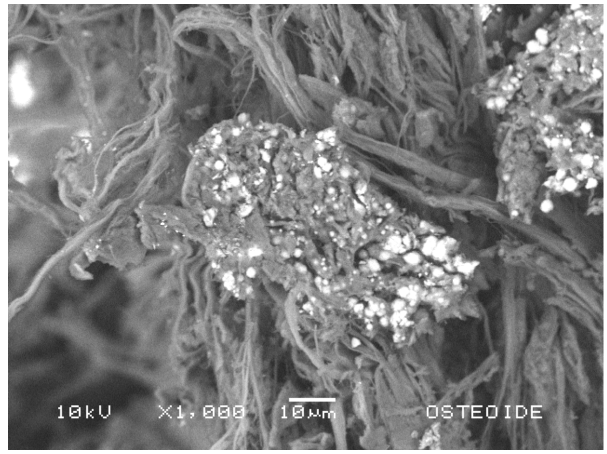

Figure 2: LVSEM image of osteoid tissue. The calcified nodules (in white) were identified as calcium ultraphosphate, $Ca_2P_6O_{17}$ (PDF 43-224).

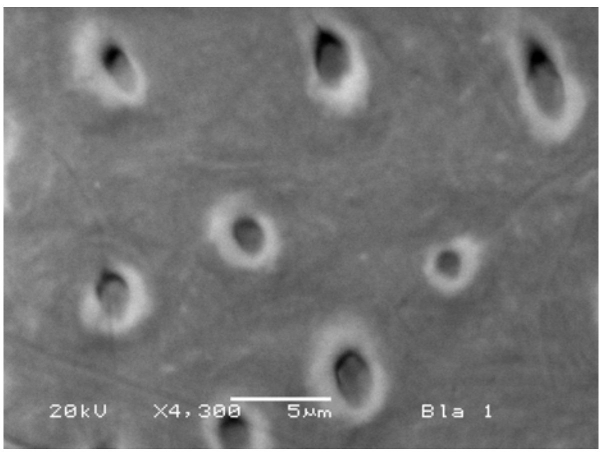

Figure 3: LVSEM image of human dentin tubules. Here, poorly mineralized fibers are surrounding the apatite-mineralized tubules.

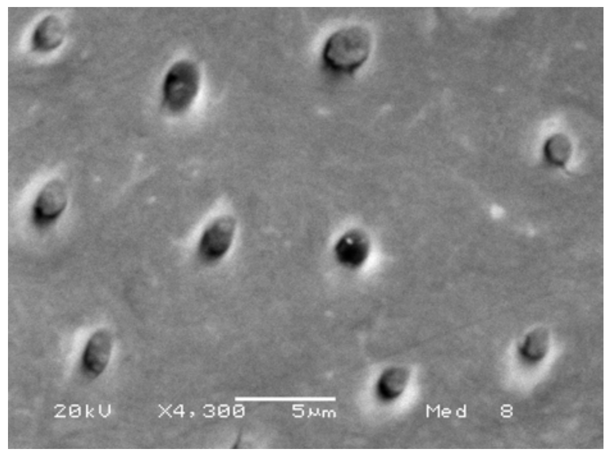

Figure 4: LVSEM image of human dentin tubules. In this sample a lower thickness of tubules than in figure 3 can be appreciated.

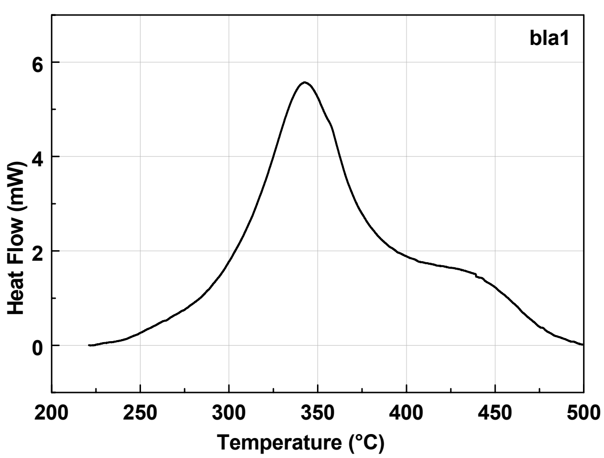

Figure 5: DSC plot of human dentin (powder) showing exothermic peaks at $T \approx 340$ and 430°C.

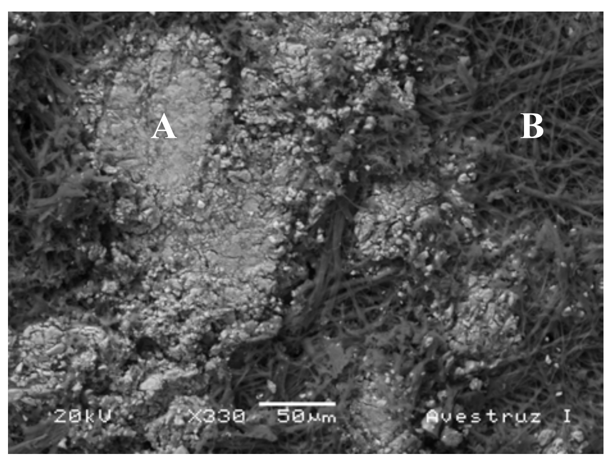

Figure 6: LVSEM image ostrich eggshell (inner side) in which calcite crystallites ($CaCO_3$) are mineralized in a biopolymer.

https://doi.org/10.1017/S1431927603440968 Published online by Cambridge University Press