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# X-ray diffraction analysis of bone–cement interface in failed hip arthroplasties

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This study was focused on the bone tissue response to cement in failed hip joint prostheses. The investigation was carried out by means of micro-beam X-ray diffractometric (XRD) analysis of the bone–cement interface. Nine cemented prostheses retrieved because of loosening were studied. This research has demonstrated that the newly formed bone close to the cement in loosened prostheses showed a normal apatitic structure, though bone tissue was often found poorly mineralized. In contrast, in stable prostheses well-mineralized bone was observed. In both cases, however, the bone apatite lattice at the interface was shown not to be different from pre-existing bone. The authors conclude that the mineralization process close to the cement can be thoroughly evaluated by micro-beam XRD techniques.

## 1. Introduction

All materials used for orthopaedic implants must allow bone remodelling around the prosthesis. Cement is usually employed to fix the components of joint prostheses to the bone, though presenting mechanical and biological problems in the long term.

Bone cement is a self-hardening acrylic resin; polymerization is obtained by mixing a solid and a liquid component. The solid component contains mainly pre-synthesized polymethyl methacrylate (PMMA) and a polymerization initiator (benzoyl peroxide). The liquid component is mainly composed of methylmethacrylate monomer (MMA), a polymerization accelerator (N,N dimethyl-p-toluidine) and other substances inhibiting the spontaneous polymerization of MMA, such as hydroquinone. Polymerization reaction occurs about 15 min after mixing and is strongly exothermic.

The success of a cemented arthroplasty is closely related to the quality of fixation of the acrylic cement to bone. A large number of parameters are involved in the long-term maintenance of bone–cement bonding; toxic effects of cement against tissues occur, particularly before and during polymerization, and the interactions mainly occur at the prosthesis/tissue interface [1].

Histologic analysis at the interface between bone and cement often reveals the presence of a fibrous membrane: only rarely is living bone found in direct contact with the cement [2].

Depending on the assay techniques employed, different aspects of the interface can be studied. Molecular, microstructural, micro- and macroscopic information can be obtained using different instruments. The aim of this study was to analyse, by the X-ray diffraction technique, the bone mineral component at the interface with cement in hip prostheses replacement, as the cement can interfere with sequence of the bone-forming processes and, therefore, with the mineralization process.

The X-ray diffraction tests evaluated the microstructural characteristics of the newly formed bone, and particularly of the apatite crystallites at the interface, as this affects the correct load transfer from prosthesis to bone, namely the prosthesis stability [3].

Aspects of cement degradation or structural transformation and wear phenomena were also examined.

## 2. Materials and methods

Nine cemented prostheses retrieved following implant failure 2–10 years after surgery were studied; in four cases the bone cement contained added barium sulphate. One specimen of a stable prosthesis at autopsy, retrieved 2 years after surgery, was used as a control.

The mineralization of the newly formed bone in contact with the cement was examined. The specimens were fixed and embedded in epoxy resin. Slices about 100 μm thick were analysed using the Chesley Rx microcamera with micro-beam X-ray diffraction [4]. The sample is mounted in a hole in a metal plate with adhesive tape and transferred on a easy to handle sample holder. Using an X-ray, point-shaped collimated beam, the interface is thoroughly detailed because the X-ray beam strikes a 0.002 $mm^2$ area previously selected by microscopic examination [5].



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X-ray diffraction patterns were taken with Ni-filtered $CuK_\alpha$ radiation from a Philips PW/1840 X-ray generator. The following instrumental parameters were chosen: 25 kV, 25 mA, 100 μm diameter collimator, distance film–sample of 15.1 mm and 11 h of exposure. Kodak AA High Resolution films were used to record the diffractometric patterns.

Reflections of the crystalline phase of the perimplant newly formed bony trabeculae were analysed. The crystallographic pattern of the bone apatite was compared to the crystallographic identification file of HA published by the Joint Committee on Powder Diffraction Standards (File 9-432).

The X-ray diffractometric reflections were recorded onto film and converted into graphs which define the angles corresponding to such reflections. The microdensitographs were performed using a microdensitometer (Ital Structures); scanning operations were carried out by a stepper motor which moves the samples in radial directions. Each film was analysed with at least four radial scans using the following parameters: radial scanning from 8 to 45° 2θ and °2θ. The microdensitographs were analysed and the crystallographic lattice parameters, [a] and [c], of the bone apatite were calculated to obtain a semi-quantitative evaluation of the mineralization process. [6].

In addition, the wear particles observed in tissues were analysed and identified.

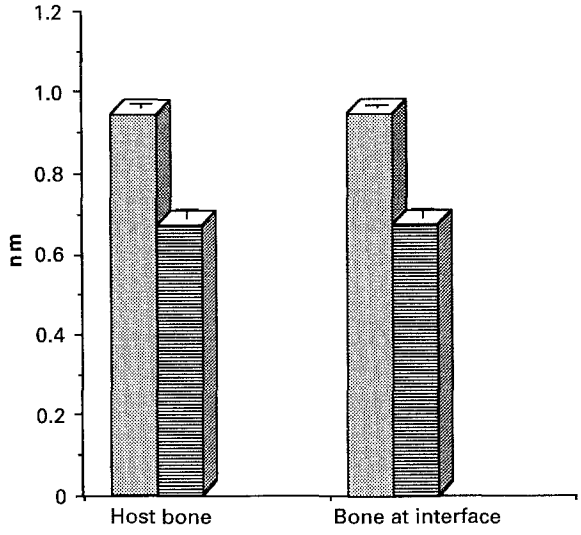


*Figure 1* (a) (▦) and (c) (▤) lattice parameters assay performed on the bone apatite in a stable prosthesis. Results are expressed as arithmetic mean ± standard deviation: lattice parameters show no statistically significant difference at the interface and far from the cement.

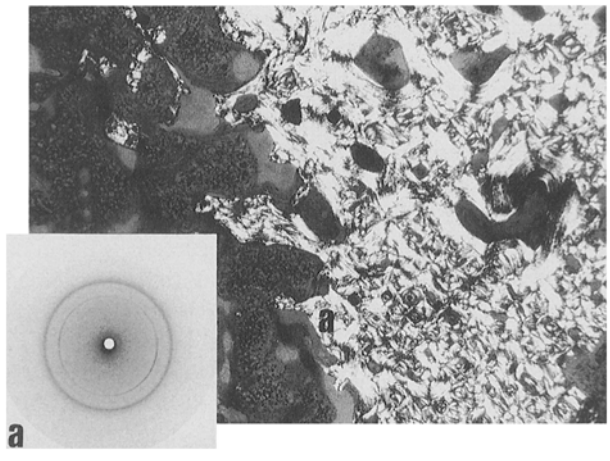


*Figure 2* Light microscopy of bone tissue adjacent to the cement of a retrieved loosened prosthesis (Paragon stain, ×25, pol.). Insert shows an XRD micrograph of bone tissue maintaining direct contact with cement, and shows a normal apatitic structure. The orientation effects of the (0 0 2) reflection are evident (Chesley microcamera, 25 kV, 25 mA, 11 h exposure).

## 3. Results

The XRD of the newly formed bone close to the cement in a stable prosthesis showed a ring pattern consistent with a polycrystalline structure. The recorded reflections expressed the *d*-values of a mineral with apatitic phase and matched those of the Joint Committee on Powder Diffraction Standards for HA (File 9-432).

Diffractograms varied, depending on the mineralization degree of the examined XRD-microarea: they showed numerous and increasingly resolved hydroxyapatite-specific reflections, whereas the amorphous component progressively decreased, until it disappeared.

Moreover it was noted that the (0 0 2) reflection of apatite crystallites was well resolved and showed a partial meridional orientation. Such orientation indicates the presence of longer crystallites regularly oriented along the *c*-axis, parallel to collagen fibres. The diffractometric pattern found in the newly formed tissue was therefore quite similar to that observed for the pre-existing bone.

Apatite lattice parameters at the interface and far from the cement showed no statistically significant difference (Fig. 1).

The bone–implant interface of the loosened prostheses showed the irregular interposition of a thin membrane of fibrous tissue. By X-ray diffraction, the trabeculae maintaining direct contact with cement showed a normal apatitic structure (Fig. 2). The orientation effects of the (0 0 2) reflection were evident. Nevertheless, in the loosened prostheses the bone was poorly mineralized and the trabeculae were lined by osteoid tissue, shown to be unmineralized by XRD.

Lattice parameters of the bone apatite at the interface with the cement did not show significant variations, compared to the bone of the stable prosthesis used as control (Fig. 3).

In the periprosthetic bone of the loosened prostheses with barium sulphate loaded cement, diffusion of cement particles sized 1–10 μm was observed. XRD of the bone revealed the barium sulphate reflections, in compliance with File 24-1035 of the JCPDS.

The apatite lattice parameters of the trabeculae containing barium sulphate were not modified.

## 4. Discussion

Bone cement is a polymer currently used in orthopaedics to fix prosthetic devices, and its wide-

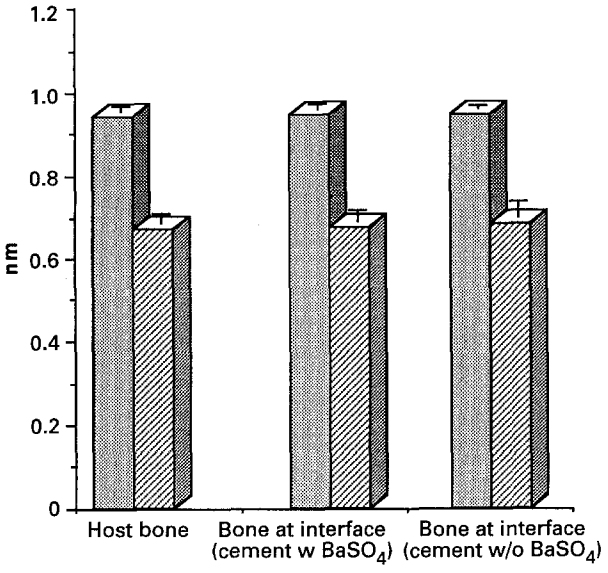


*Figure 3* (a) (▦) and (c) (▨) lattice parameters assay performed on the bone apatite in the loosened prosthesis. Results are expressed as arithmetic mean ± standard deviation: lattice parameters show no statistically significant difference at the interface and far from the cement.

spread use provides a very important aid to prosthesis stabilization.

It has long been known that the exothermic polymerization reaction is responsible for bone necrosis at the bone–cement interface, while the undesired persistence of methyl methacrylate monomer can induce both local cytotoxic effects and systemic effects. A fibrous tissue between bone and cement is normally formed. It has been demonstrated that the cement loses some resistance with ageing and can undergo microfractures.

X-ray diffraction analysis with specimen microfocusing was used to examine the mineral phase of bone at the interface with cement, and to evaluate the microstructural interactions between cement and apatite crystals in order to detect any damage to bone induced by cement during its polymerization or after ageing. This technique yields information on the apatite crystal texture and lattice parameters, and on the orientation level induced by collagen fibres. Using the diffractometric technique it is possible to determine whether wear phenomena have induced changes in the lattice parameters, which are strongly influenced by possible ion substitutions occurring in the bone apatite: therefore, the lattice parameters evaluation allows one to define possible modifications of the apatite lattice perfection at the interface with cement [7].

Microstructural characterization of the bone at the interface with cement has demonstrated that bony apatite undergoes no modification during the loosening processes, and it is substantially similar to that observed in stable prostheses.

In addition, in loosened prostheses with barium sulphate loaded cement, diffractometric analysis revealed the presence inside the bone trabeculae at the interface of sub-microscopic cement particles undetectable by histological analysis. The cell parameters of the this bone are not altered with respect to normal bone, showing that neither cement nor barium sulphate interfere with the mineralization process, even though this seems to slacken the osteoblast replication *in vitro* [8].

X-ray diffraction analyses allow one to conclude that, though the apatite lattice parameters appear unaltered at the interface with cement, an increase in the amorphous phase of the bone tissue during the loosening process has occurred. Such an increase, together with the release of cement particles in the surrounding bone tissue, leads to a weakening of the fixation of the prosthesis.

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