Introduction: Ceramics are attractive alternative bearing materials because of their low wear rates articularating against ultra-high molecular weight polyethylene [1]. Alumina has been employed as a femoral head material since the 1970s, and zirconia ceramics were introduced in the 1980s with improved fracture toughness. However, concerns remain regarding rare clinical failure modes, including the potential for fracture and, in the case of zirconia ceramics, surface roughening caused by transformation from tetragonal to monoclinic phases in vivo. In 2001, zirconia femoral heads by one vendor presented high fracture rates because the manufacturing process triggered phase transformations in the material, resulting in the withdrawal from the market.

Recently, two alternative femoral head bearing materials, Oxinium® (Smith&Nephew Inc., Memphis, TN) and Biolox® Delta (CeramTec AG, Plochingen, Germany) have been clinically introduced to avoid in vivo fractures while preserving ultra-low wear rates. Oxinium® femoral heads are made of the metallic Zr-2.5Nb alloy, which is subsequently oxidized at high temperatures to promote a thin (5 microns) surface ceramic (monoclinic) layer of zirconia [2]. In contrast, Biolox® Delta ceramics consist of an alumina matrix and 17% volume of zirconia nanoparticles homogeneously dispersed [3]. Biolox® delta ceramics exploit the advantage of phase transformations in zirconia from tetragonal to monoclinic, which are expected to strengthen the matrix. The objective of this study was to document the clinical outcomes, wear performance and potential microstructure changes of Oxinium® and Biolox® Delta retrieved femoral heads. In this study we tested the hypothesis that the microstructure and surface roughness of Oxinium® and Biolox® Delta change over time in vivo.

Methods and Materials: Fifteen femoral heads were collected after revision surgery. After cleaning and detoxification, they were classified into three categories: historical zirconia (controls, n=5); Oxinium® (n=4); and Biolox® Delta (n=6). Patient information, reasons for revision, and implantation times were available in all cases. Femoral heads were visually inspected to identify and map superior (worn) and inferior (partially worn) sides, based on the presence of scratches, metal transfer, or pits (Figure 1). Then, the surface topography of the femoral heads was characterized by means of white light interferometry using a NewView 5000 Model 5032 equipped with advanced texture analysis software (MetroPro 7.7.0; Zygo, Middleton, CT). At least three roughness, Ra, and waviness, Wa, measurements were taken at each one of the different regions of interest: dome; worn (superior side); partially worn (inferior side); and control (near equator) areas. Material identification and potential phase transformations from tetragonal to monoclinic structures were monitored using Raman spectroscopy. Raman spectra were recorded at room temperature using a Microspectrometer (RM1000 VIS, Renishaw Inc., Chicago, IL). A short working distance objective (50x), and the green excitation line (514 nm) were used, while the laser power at the sample was 18 mW. To achieve a good signal-to-noise ratio, Raman spectra were obtained after 7 accumulations. At least two spectra were obtained at the same exact location where roughness measurements were taken. Monoclinic contents were calculated using the following relation [3]:

\[ C_m = \frac{I_{181}^{181}}{I_{31}^{181}} + \frac{I_{182}^{182}}{I_{31}^{182}} \times 0.97(\frac{I_{148}^{148}}{I_{31}^{148}} + \frac{I_{264}^{264}}{I_{31}^{264}}) \]

where \( I_{181}^{181} \), \( I_{182}^{182} \), \( I_{148}^{148} \), and \( I_{264}^{264} \) represent the intensity of bands associated to monoclinic phases, and \( I_{31}^{148} \) and \( I_{31}^{264} \) refer to the intensity of bands associated to tetragonal phases.

Results: Patient groups were statistically comparable regarding height, weight, and age (p>0.49). Implants with zirconia femoral heads were revised due to loosening (n=2), instability (n=1); malalignment (n=1); and fracture of the ceramic head (n=1). Patients with Biolox® Delta femoral heads were revised due to loosening (n=4), and infection (n=2), whereas all the implants with Oxinium® heads were revised due to instability (n=3), the only exception being an impingement. Zirconia femoral heads were implanted for an average of 8.5 years (range: 8.0 to 9.3y), whereas Oxinium® and Biolox® Delta heads were revised after an average of 1.2 (range: 0.2 to 2.8y) and 1.5 years (range: 0.3 to 3.5y), respectively. Consistent with visual inspections, average Ra results were significantly higher (p=0.01) in worn areas of zirconia (37±31 nm) than in Biolox® Delta femoral heads (2±1 nm). Similarly, Oxinium® heads had significantly higher roughness (average R, ranged from 15±13 to 23±6 nm at the dome and worn regions, respectively) than Biolox® Delta retrievals at all regions (p=0.01). Despite the typical higher roughness of worn regions with respect to unworn regions (29±26 nm) in zirconia heads, these regional differences were not significant (p=0.1). Similarly, there were no significant regional variations in the Oxinium® nor the Biolox® Delta groups, despite the fact that typically higher Ra values were found at worn and partially worn (25±7 nm, and 2±1 nm, respectively) regions compared to near equator areas (20±7 nm, and 3±1 nm, respectively). Higher average monoclinic contents typically characterized worn areas in zirconia (mean and range: 23%: 14 – 31%) and Biolox® Delta (24%: 10 - 46%) heads (Figure 3). As expected, for Oxinium® heads, all regions were purely monoclinic phase (99%).

Discussion: Oxinium® and Biolox® Delta have been widely used clinically for less than a decade, and consequently few data are available regarding their in vivo performance as new biomaterials. We found evidence of in vivo changes in the zirconia microstructure but not roughness of Biolox® Delta, whereas we observed changes in the surface roughness of Oxinium®, but not changes in its microstructure. It is important to note that the phase transformation in Biolox® Delta applies only to its 17% content of zirconia; the majority of the ceramic is composed of alumina, which has been shown to be stable for decades in vivo. It thus remains unclear whether increasing monoclinic contents will imply changes in roughness in Biolox® Delta femoral heads after longer-term implantation. As for zirconia heads, they demonstrated relatively high monoclinic contents, but mixed roughness results. These differences may stem from changes in manufacturing strategies, after high fracture rates experienced by one vendor. The evidence of in vivo changes in this study with only a limited number of retrievals provide motivation for longer term studies of these new ceramic biomaterials.

Acknowledgement: Supported by NIH R01 AR47904.