INTRODUCTION: Recent studies have reported measurable oxidation in highly crosslinked, re-melted UHMWPE components after retrieval [1-3]. This susceptibility to oxidation was unexpected due to the lack of measurable free radicals and the proven in-vitro oxidation resistance of these materials under aggressive aging conditions [4]. Virgin UHMWPE components sterilized with ethylene oxide (EtO) gas uniquely represent another type of orthopaedic components with no measurable free radicals and proven in-vitro oxidation resistance [5]. The primary purpose of this study was to determine if retrieved, virgin UHMWPE knee components are susceptible to either in-vivo or ex-vivo oxidation. Additional goals in this study included evaluations of (a) the distributions and qualitative amounts of lipids within the retrieved components, and (b) the relationship between the peak-height and peak-area oxidation indices.

METHODS: All of the retrieved components evaluated were fabricated from virgin UHMWPE that was subsequently sterilized with EtO (i.e., no exposure to radiation). Twelve Genesis I™ tibial inserts (Smith & Nephew, Memphis, TN) were evaluated after a mean (± SD) in-vivo time of 18.9 ± 19.9 months (Range = 0.6 – 66) and a mean (± SD) ex-vivo, shelf-aging time of 75.6 ± 42.9 months (Range = 37 – 168). Seven of these inserts were fabricated from ram-extruded GUR1050, and five were fabricated from compression-molded GUR1020. For each knee component, samples were removed from (a) the visible wear scar in the bearing region and (b) the central spine of the tibial insert (i.e., non-bearing region). A microtome was used to produce one through-thickness, thin film (~200 μm) thick) from each of these samples from each component. Three, through-thickness oxidation profiles were measured per film in the shelf-aged condition (i.e., no extraction) by FTIR spectroscopy. This analysis protocol was performed again with the same films after extraction. Extraction of the absorbed esterified fatty acids (EFAs) was conducted by refluxing the thin films in boiling hexanes for 16 hours [6]. Three metrics were calculated from the FTIR spectra:

- **Peak-area oxidation index** = PA-OI = A_{1718}/A_{1368} (ASTM F2102-06)
- **Peak-height oxidation index** = PH-OI = H_{1718}/H_{1368}
- **Ester index** = EI = I_{1738}/I_{1368} or I_{1738}/I_{1358}

Correlation was evaluated with the non-parametric Spearman’s rank correlation coefficient (ρ) with a 0.05 level of significance (α).

RESULTS: EFAs were present at all of the surfaces evaluated prior to extraction. In the bearing regions, the penetration depths of the EFAs ranged from 100 to 1900 μm on the proximal surfaces and from 100 to 700 μm on the distal surfaces. The mean (± standard deviation) EImax in the bearing region was 0.45 ± 0.17 with a range from 0.10 to 0.70.

In the non-bearing regions, the penetration depths were slightly lower and ranged from 100 to 1100 μm on the proximal surfaces and from 100 to 500 μm on the distal surfaces. The mean (± standard deviation) EImax in the bearing region was 0.30 ± 0.12 with a range of 0.10 to 0.58. Examination of the penetration of esters with time shows that the penetration depth was strongly associated with the in-vivo time.

After ex-vivo shelf aging and extraction, the ester indices were dramatically reduced by 43-97% in all of the samples. Extraction for an additional 16 hours resulted in few changes to the spectra, which suggests that 16 hours is sufficient. After extraction, measurable oxidation was observed in 10 of the 12 tibial inserts evaluated (Figure 1). In the bearing regions, the mean (± standard deviation) PA-OI was 0.28 ± 0.19 (Range = 0.02 – 0.56). The two inserts that did not exhibit any measurable oxidation (TI-10 and TI-11) were among the inserts that had experienced the shortest in-vivo and ex-vivo times. Six of these inserts had peaks in the PA-OI profiles at the bearing surface, and four of the inserts exhibited sub-surface peaks at depths of 300 to 500 μm. Measurable oxidation was also observed on the distal surfaces of four of these components. The penetration depth of the measurable oxidation ranged from 500 to 2100 μm at the bearing surface (i.e., proximal side) and from 300 to 1100 μm on the distal side of the bearing region.

In the non-bearing regions, measurable oxidation was observed in only one tibial insert (TI-1), which experienced one of the shortest in-vivo times, the longest ex-vivo time and exhibited one of the highest EImax. The measurable oxidation occurred on the proximal side of the insert to a depth of about 300 μm with the peak occurring at the surface. The correlation between the measured PH-OI before extraction and the peak PH-OI after extraction was strong and statistically significant (ρ=0.94, p<0.001) for the measurements in the bearing regions. More than 96% of the variation in the measured PH-OI before extraction was accounted for by the true PA-OI measured after extraction.

Correlation analyses for the PA-OI, the bearing regions after extraction did not exhibit strong, statistically significant correlations with any of these variables. The best correlation was with the total time since implantation (ρ=0.51, p=0.09), followed by the shelf-aging time (ρ=0.24, p=0.46) and the in-vivo time (ρ=0.20, p=0.54).

DISCUSSION: Esterified fatty acids (EFAs) were found at all of the surfaces examined with concentrations and penetration depths that appeared to be related to both mechanical loading and the exposure to synovial fluid. There was a strong, statistically significant correlation between the pre-extraction peak-height oxidation indices and the post-extraction peak-area oxidation indices, which suggests that measuring the ketone-peak height without conducting extraction might be a viable alternative for the analysis of oxidation in retrievals in limited circumstances.

Finally, relatively low but measurable oxidation was observed in 10 of the 12 tibial inserts after extraction. Unfortunately, the data generated in this small study did not provide conclusive evidence as to when the measured oxidation occurred. Despite the absence of strong correlations with this small data set, the combination of this study with the two previous studies of similar materials that reported no measurable oxidation [7-8] suggests that the oxidation occurred during shelf aging after retrieval.

SIGNIFICANCE: Recent reports of measurable oxidation in highly crosslinked, re-melted UHMWPE components after retrieval have raised questions regarding long-term stability. This study examines virgin UHMWPE, which has a longer clinical history, to shed light on the potential implications of oxidation in another material that has exhibited oxidative stability in vitro.

REFERENCES: