IN VIVO OXIDATION IN TKA COMPONENTS: A SPECTROSCOPIC AND NANOINDENTATION STUDY

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INTRODUCTION

- *In vivo* oxidation confirmed for traceable THA polyethylene components. This phenomenon may be more relevant in TKA.

- FTIR is commonly used to characterize oxidation in medical polyethylene.

- Raman spectroscopy and Nanoindentation provide microstructure and mechanical information, respectively.

OBJECTIVE AND HYPOTHESIS

- Global
  - Compare the utility of FTIR, Raman spc., and nanoindentation to characterize mechanical and microstructure changes due to in vivo oxidation of historical TKA polyethylene tibial inserts.
- Secondary
  - These techniques would allow us to detect regional differences in the physical, chemical, and mechanical properties

Knee Retrievals Information (n = 8)

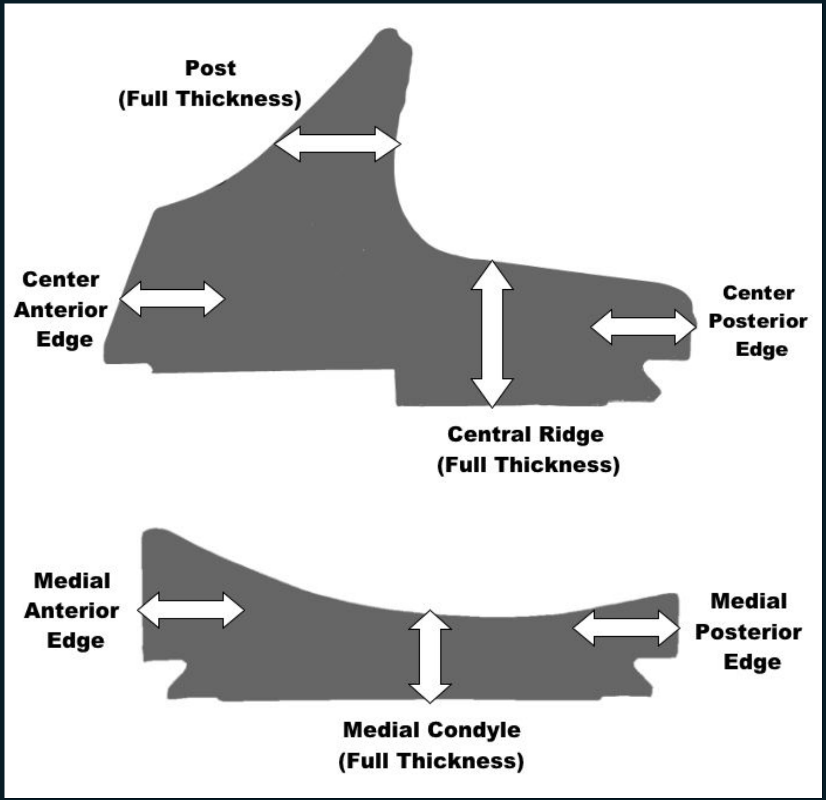
- Processing route&resin:
  - Molded 1900H/Extruded GUR 415
- Implant designs:
  - Miller-Gallante I and II, Insall-Burstein II, AGC
- **Gamma-air sterilization**
- **Average Shelf Life: 0.6 years (0.2-1.0 y)**
- **Average Implantation Time: 11.5 years (8.3-13.0 y)**

Clinical information

- Gender: 6F/2M
- Age at revision: 54-84 years
- Diagnosis at revision:
  - Loosening, PE Wear, Instability, Failed Patella, Metallosis

FTIR spectroscopy

- **Method**
  - 200 mm thick sections:
    - Medial Condyle
    - Unloaded central spine
  - Boiled in heptane for 6 hours
  - Scanned at 0.1 mm increments
  - **Max OI** (ASTM F2102-01)
  - **Max TVI** (ASTM F2381)
  - $$\%C = \frac{A_{1897}/A_{1303}}{A_{1897}/A_{1303} + 1}$$



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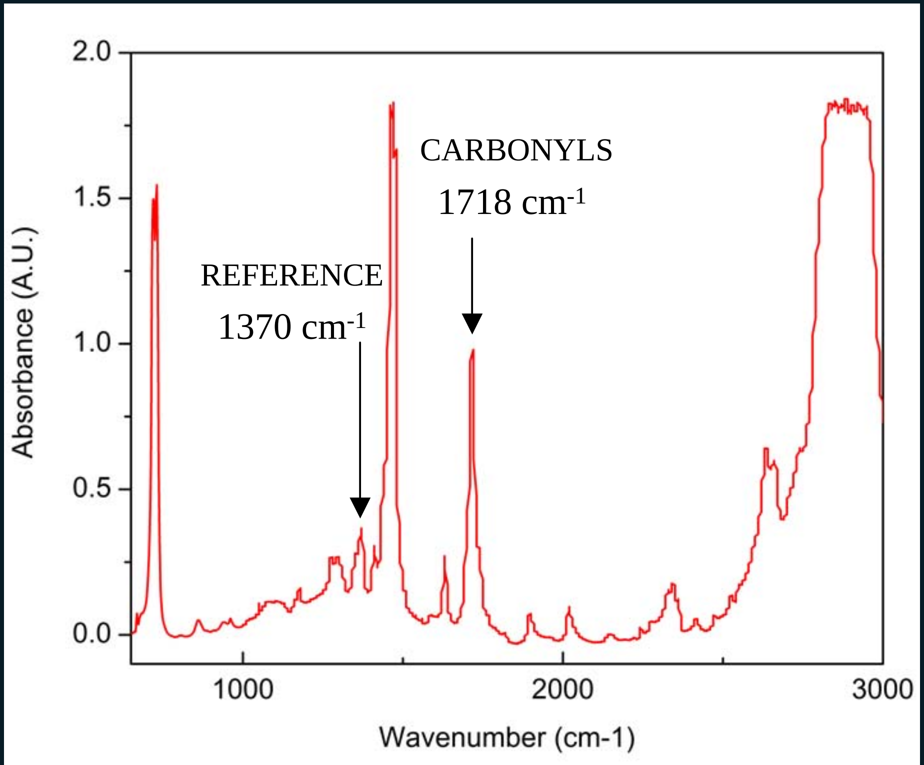

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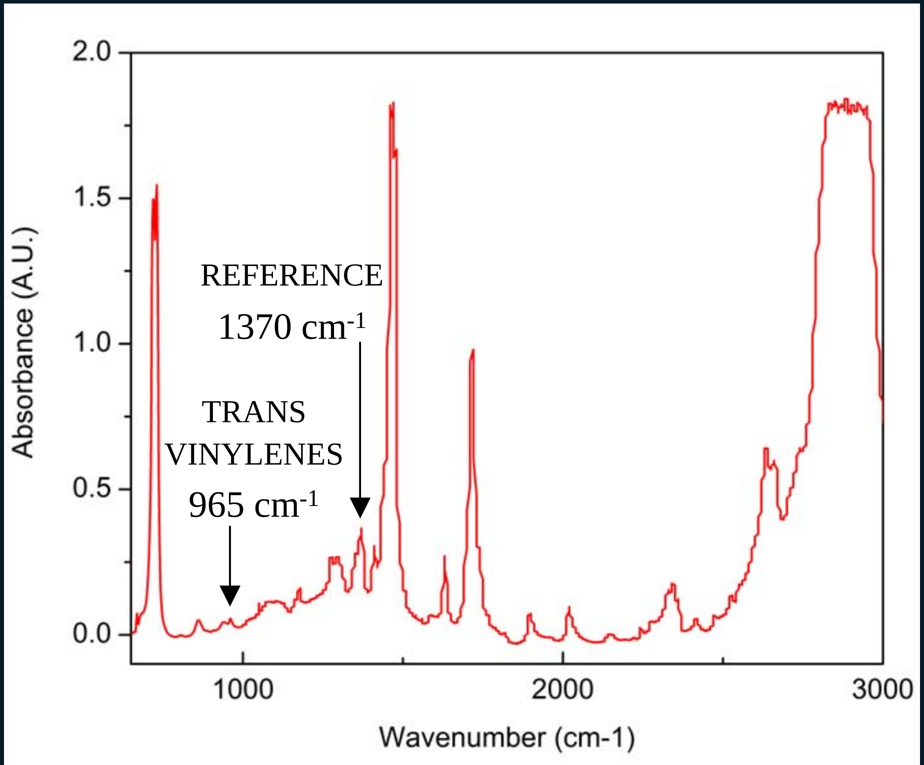

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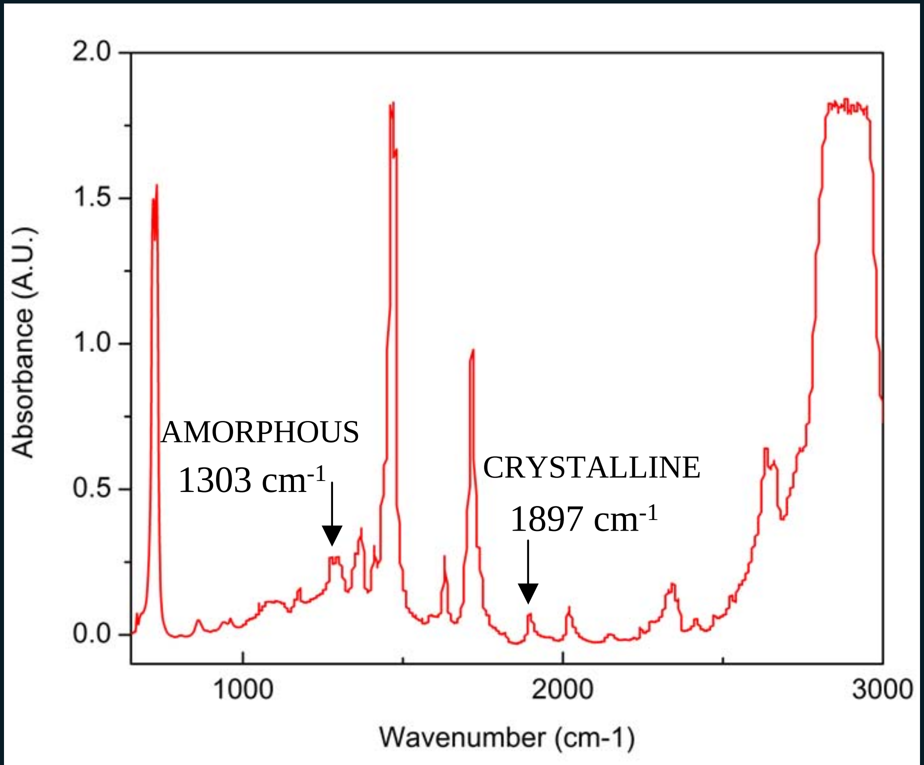
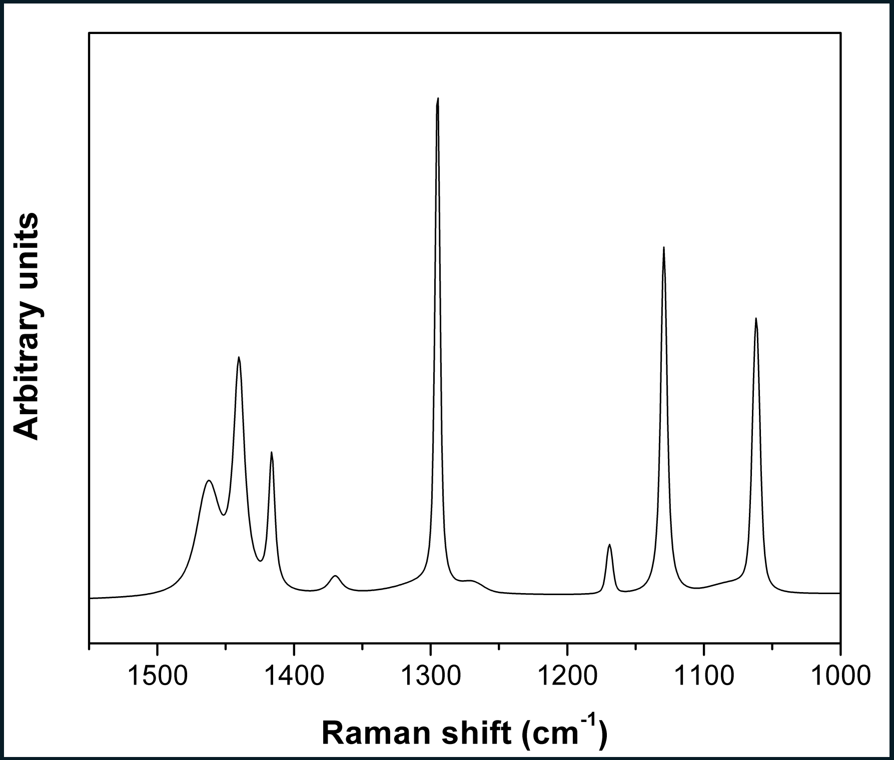


Raman spectroscopy

- **Method**
  - Regions probed:
    - Surface, Subsurface and Bulk
  - Green laser line (514 nm)
    Initial power 25 mW
  - 1800 mm^{-1} gratings.
    2cm^{-1} spectral resolution
  - Integration time (~ 420 s)
  - Properties measured
    - **Orthorhombic Crystallinity**
    - Amorphous fraction
    - Intermediate fraction
    - Overall Crystallinity



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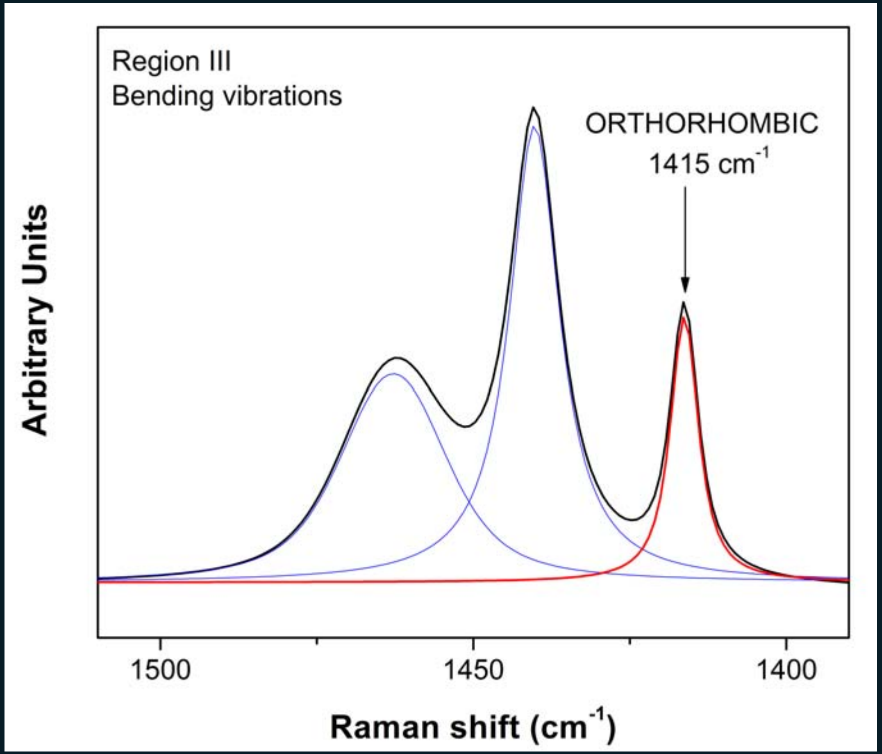

$$\alpha_c = \frac{I_{1415}}{\left(I_{1295+1305+1269}\right) x 0.45}$$

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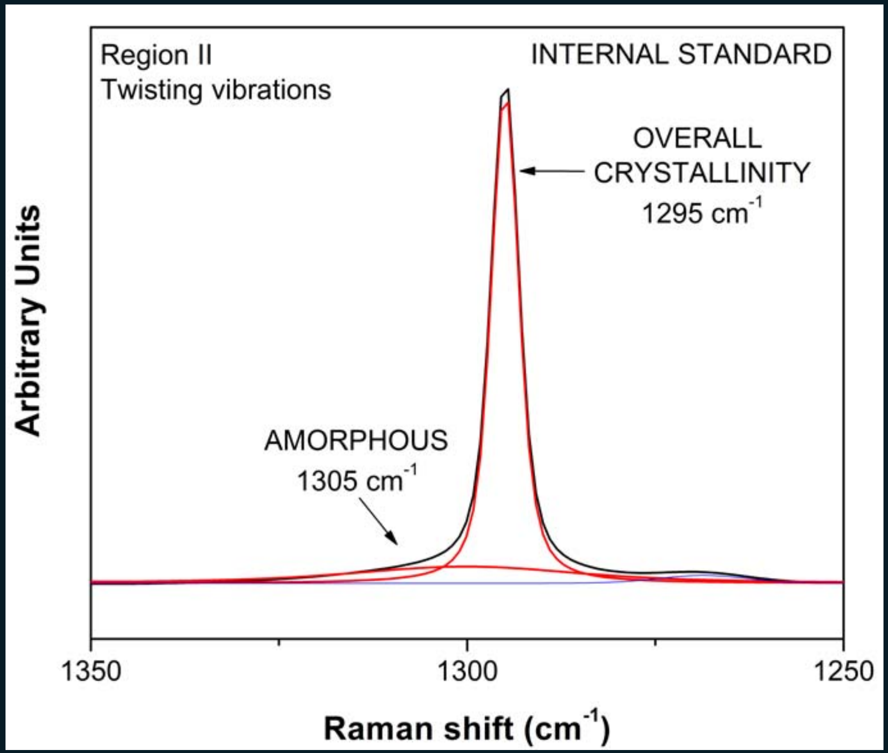

$$\alpha_a = \frac{I_{1305}}{\left(I_{1295+1305+1269}\right)}$$

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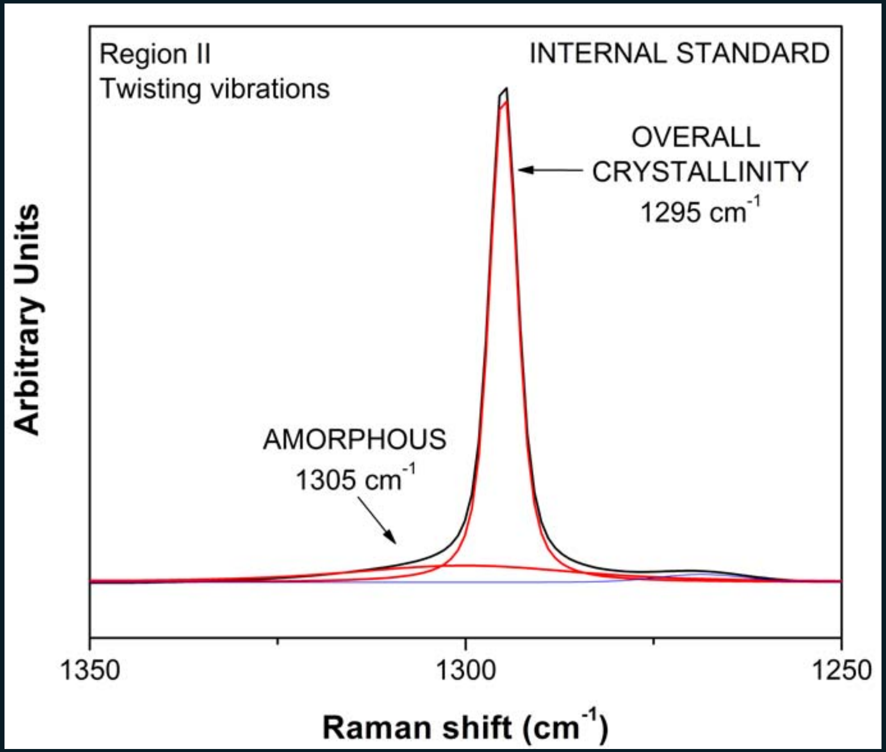

$$\alpha_d = \frac{I_{1295}}{(I_{1295+1305+1269})}$$

Raman spectroscopy

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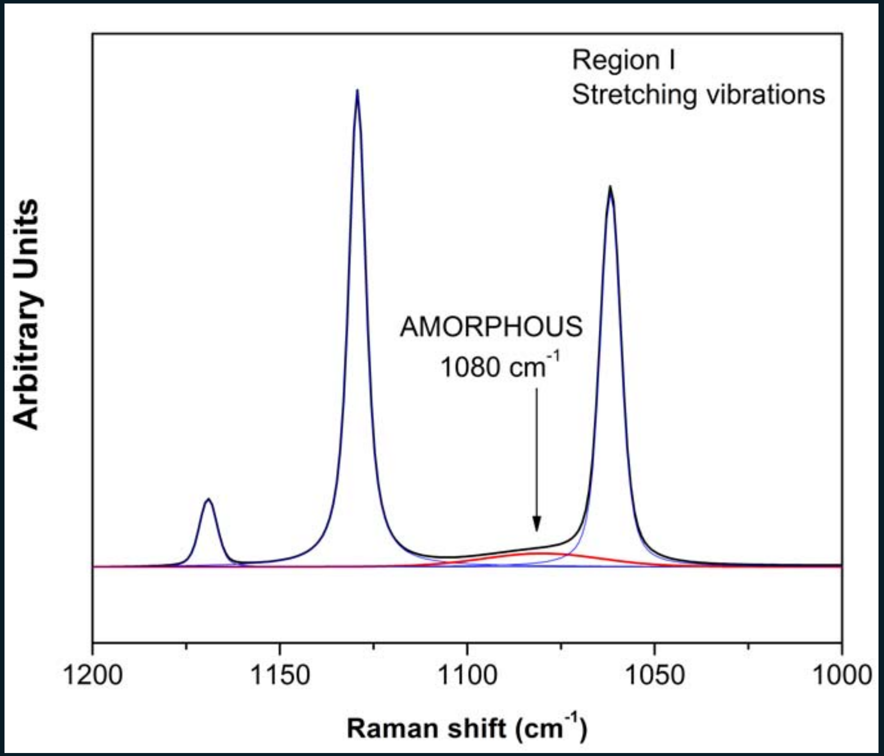

$$\alpha_a = \frac{I_{1080}}{\left(I_{1295+1305+1269}\right) x 0.80}$$

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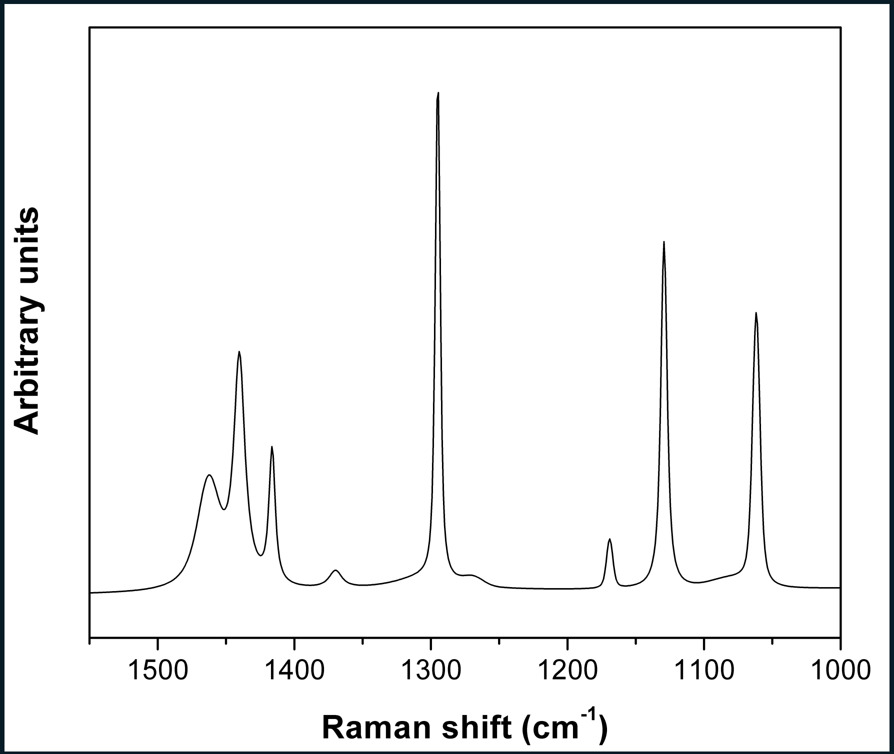
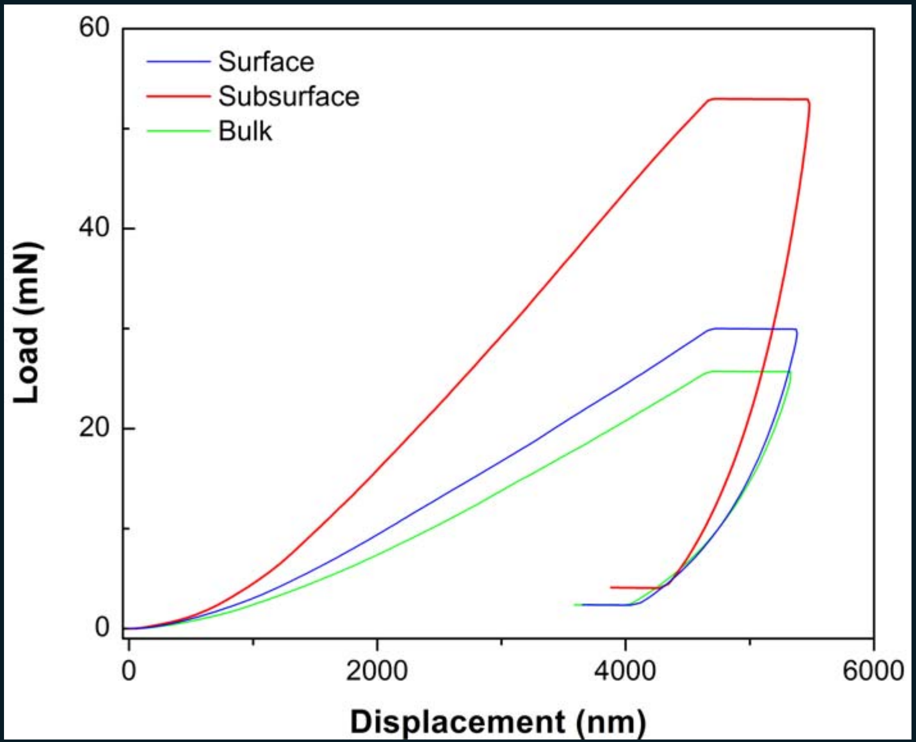


$$\alpha_b = 1 - (\alpha_c + \alpha_a)$$

Nanoindentation

- **Method**
  - Hemispherical tip (ø 13.5 µm)
  - Indentation depth 4.5 µm
  - 0.2 mm steps
  - **Hardness**
    (Oliver and Pharr method)
  - **Elastic Modulus**
    (Sneddon equation)



$$H = \frac{L_{\max}}{A} = \frac{L_{\max}}{\pi\left(\frac{h_{\max} + h_r}{2}\right)\left[2R - \left(\frac{h_{\max} + h_r}{2}\right)\right]}$$

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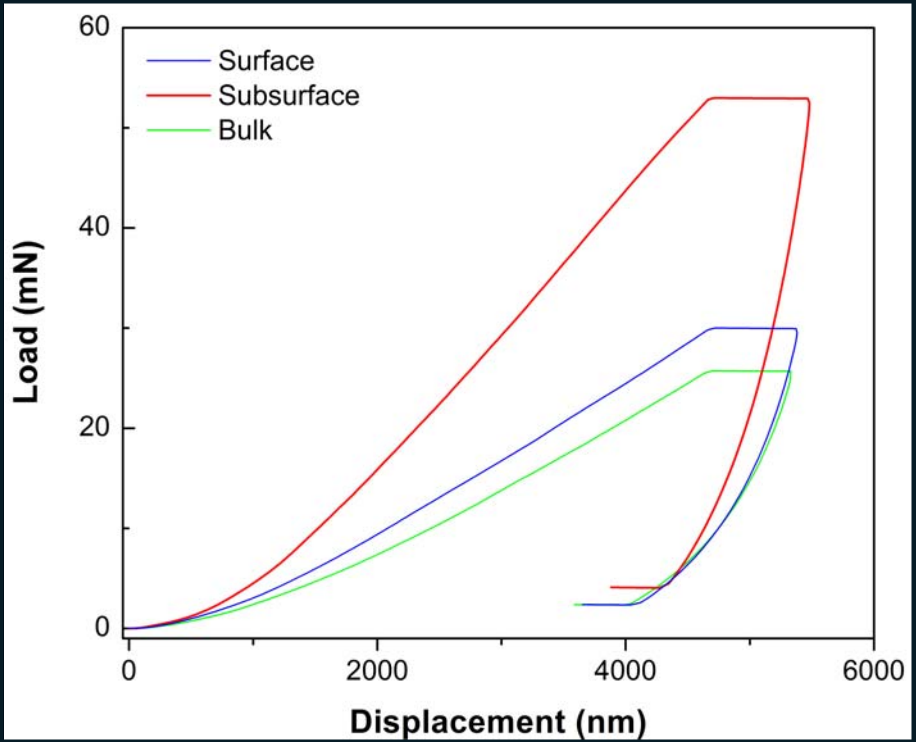
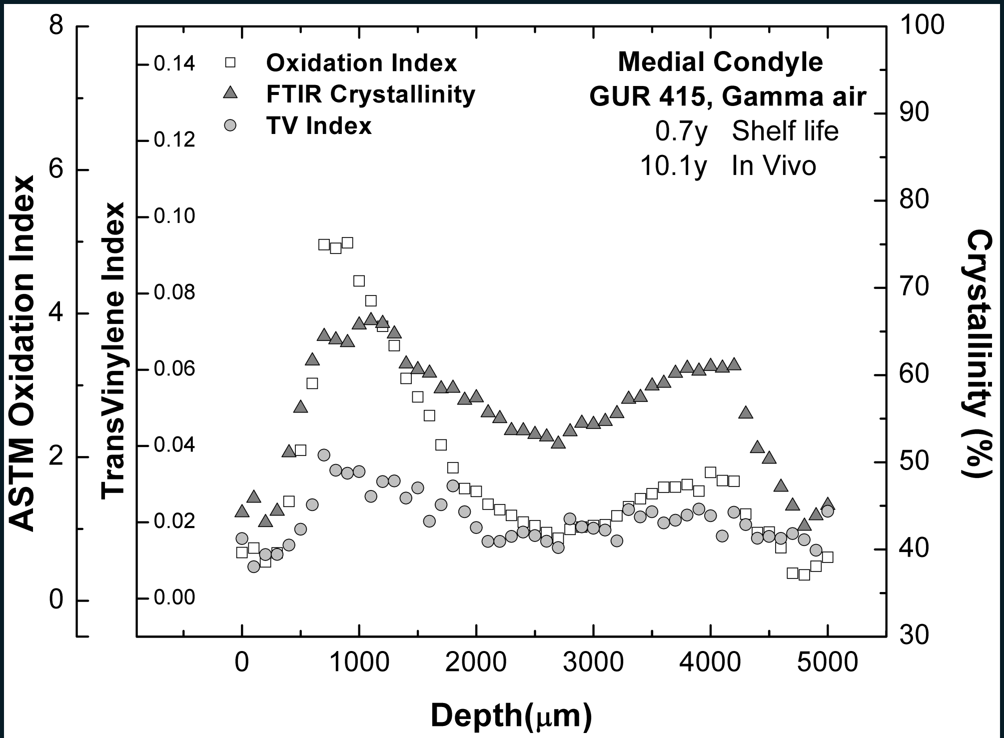


$$E = \frac{(1-\nu^2)\sqrt{\pi}}{2\sqrt{A}}\frac{dl}{dx} = \frac{(1-\nu^2)\sqrt{\pi}}{2\sqrt{A}}\frac{2L_{\max}}{h_{\max}-h_r}$$

RESULTS

OI, TVI and %C

- Property profiles showed **subsurface maxima** (~ 1 mm)
- **Backside less degraded** than the superior surface ($p \leq 0.03$*)
- **Antero-posterior faces more degraded** than bearing surfaces ($p < 0.05$*)



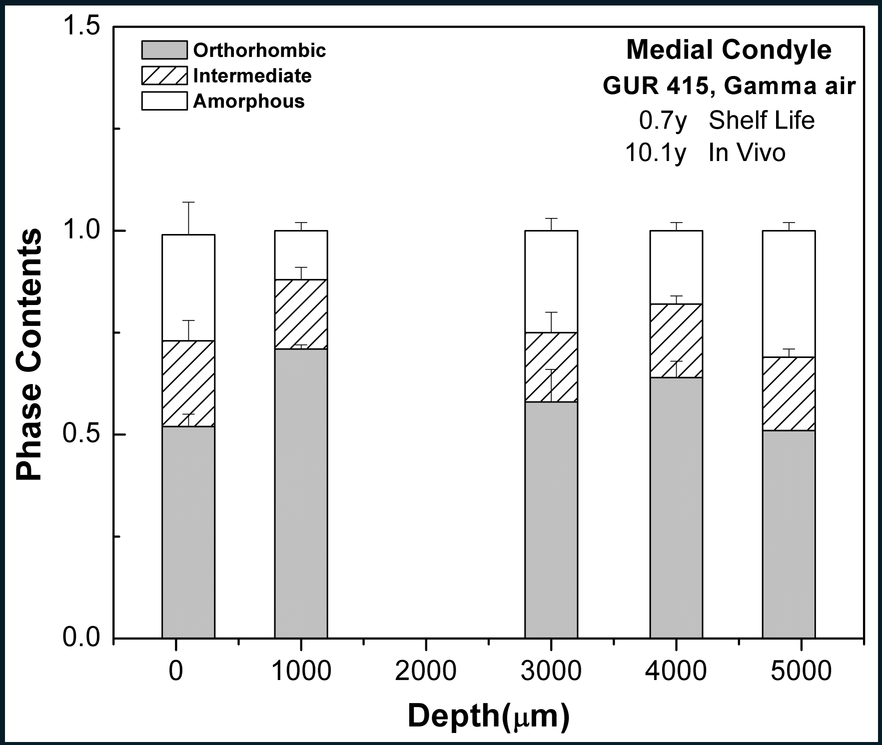
*** Paired t-tests**

RESULTS

Raman spectroscopy

- **Subsurface extrema** (~ 1 mm)
  - ✓ **Orthorhombic crystallinity (α_c)**
  - ✓ **Overall crystallinity (α_d)**
  - ✓ **Amorphous content (α_a)**
  - ✓ **Intermediate fraction (α_b) (Anomalous)**
- **Phase fractions higher/lower at the superior surface** **($p \leq 0.04$*)**
- **Higher %C and α_c in the antero-posterior faces** **($p < 0.03$*)**
- α_c and α_d higher than %C (†)

THREE PHASE MODEL



*Paired t-tests

†Student t-test

RESULTS

Crystallinity contents

Region \ Property	% C	α_c	α_d
M. Anterior	$0.64 \pm 0.17^*$	0.68 ± 0.16	0.73 ± 0.07
M. Condyle	0.55 ± 0.10	$0.74 \pm 0.14^\dagger$	$0.71 \pm 0.07^\dagger$
M. Posterior	$0.70 \pm 0.20^*$	$0.79 \pm 0.07^*$	0.74 ± 0.06
C. Anterior	0.62 ± 0.16	0.68 ± 0.16	0.73 ± 0.08
Ridge	0.55 ± 0.09	$0.67 \pm 0.14^\dagger$	$0.71 \pm 0.04^\dagger$
Post	0.53 ± 0.14	0.53 ± 0.08	0.71 ± 0.01
C. Posterior	0.59 ± 0.11	$0.69 \pm 0.09^\dagger$	$0.73 \pm 0.04^\dagger$

Antero-posterior faces: **Higher %C and α_c (Paired t-tests; $p < 0.03^*$)**

α_c and α_d higher than %C (Student t-test†)

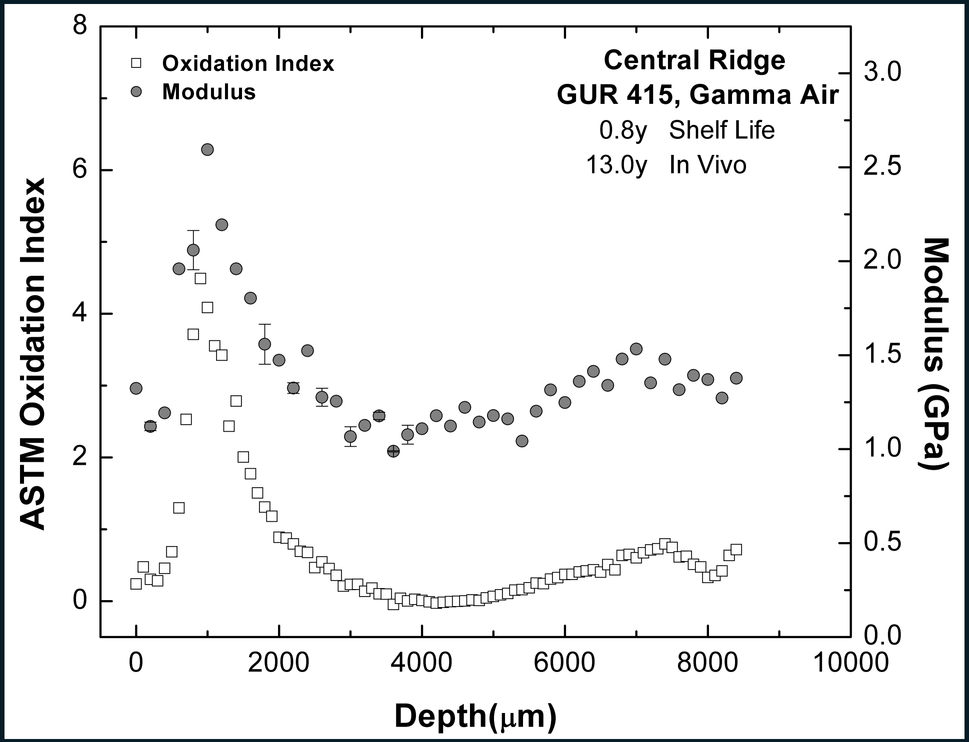
RESULTS

Hardness and Modulus

• Harder and stiffer material: **subsurface maxima** (~ 1 mm)

• No significant differences between superior and inferior surfaces (p = 0. 3*)

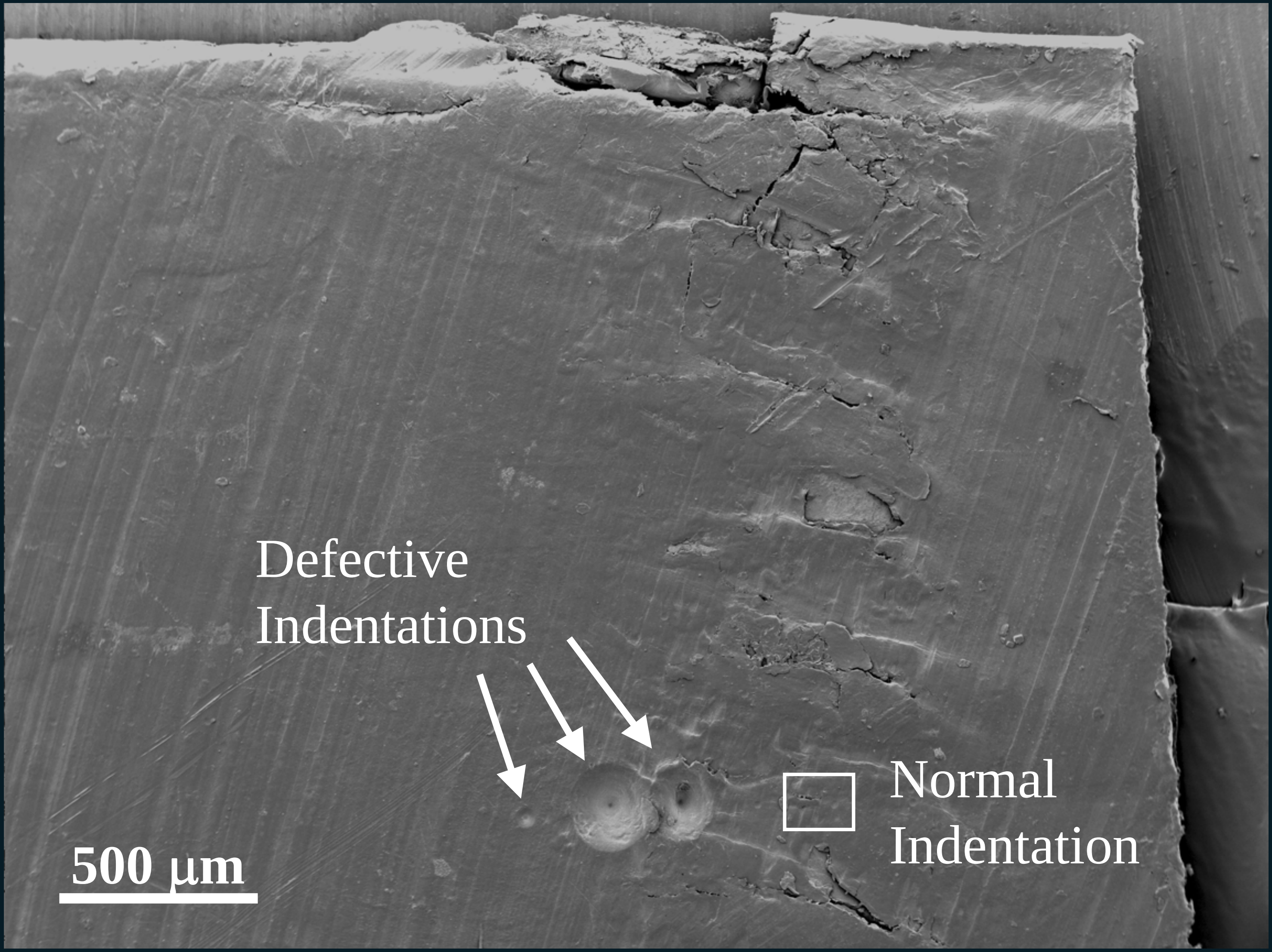
• Lower hardness and modulus at **the medial condyle** (p ≤ 0.02*)



*** Paired t-tests**

RESULTS

Nanoindentation



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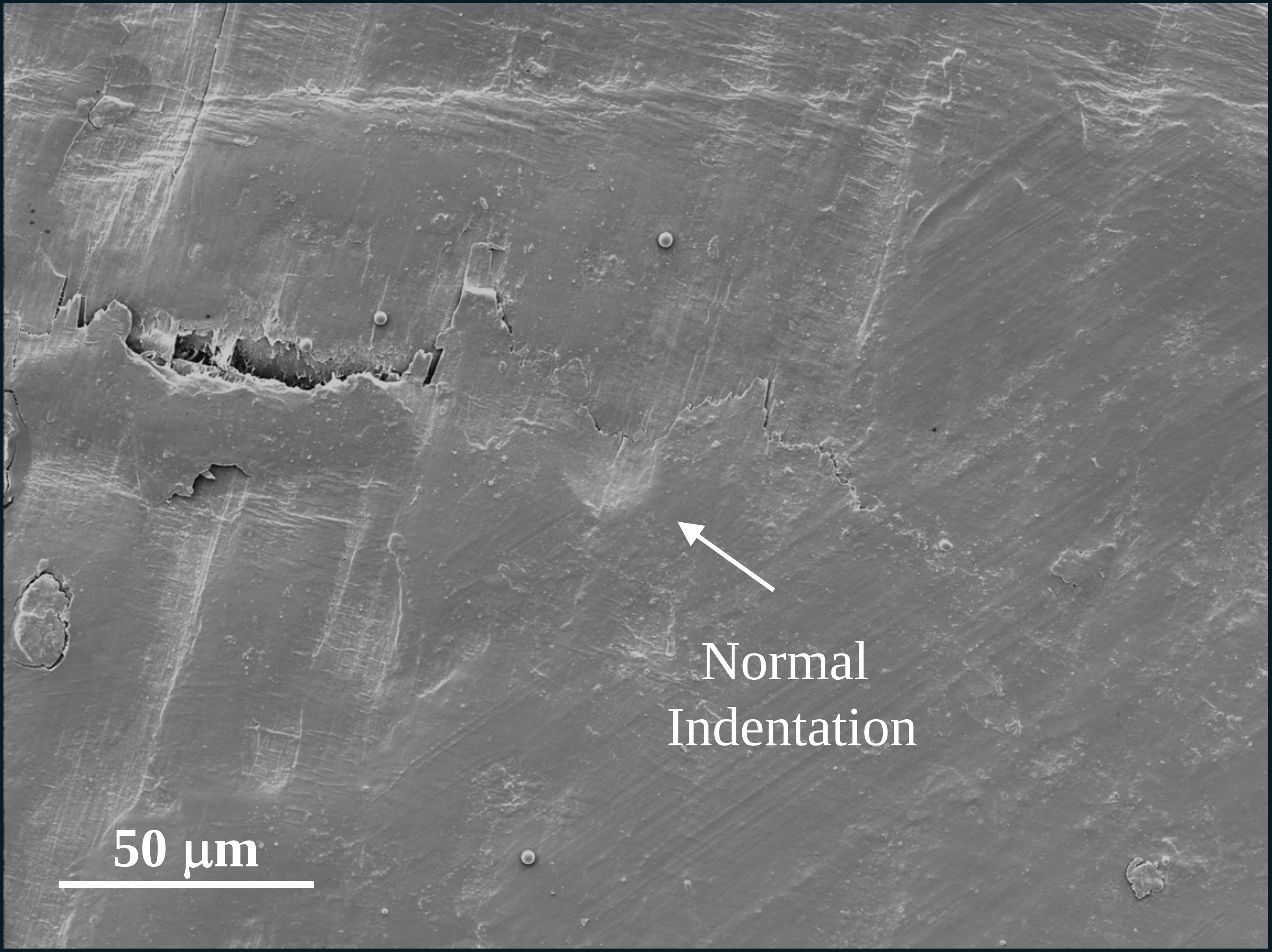

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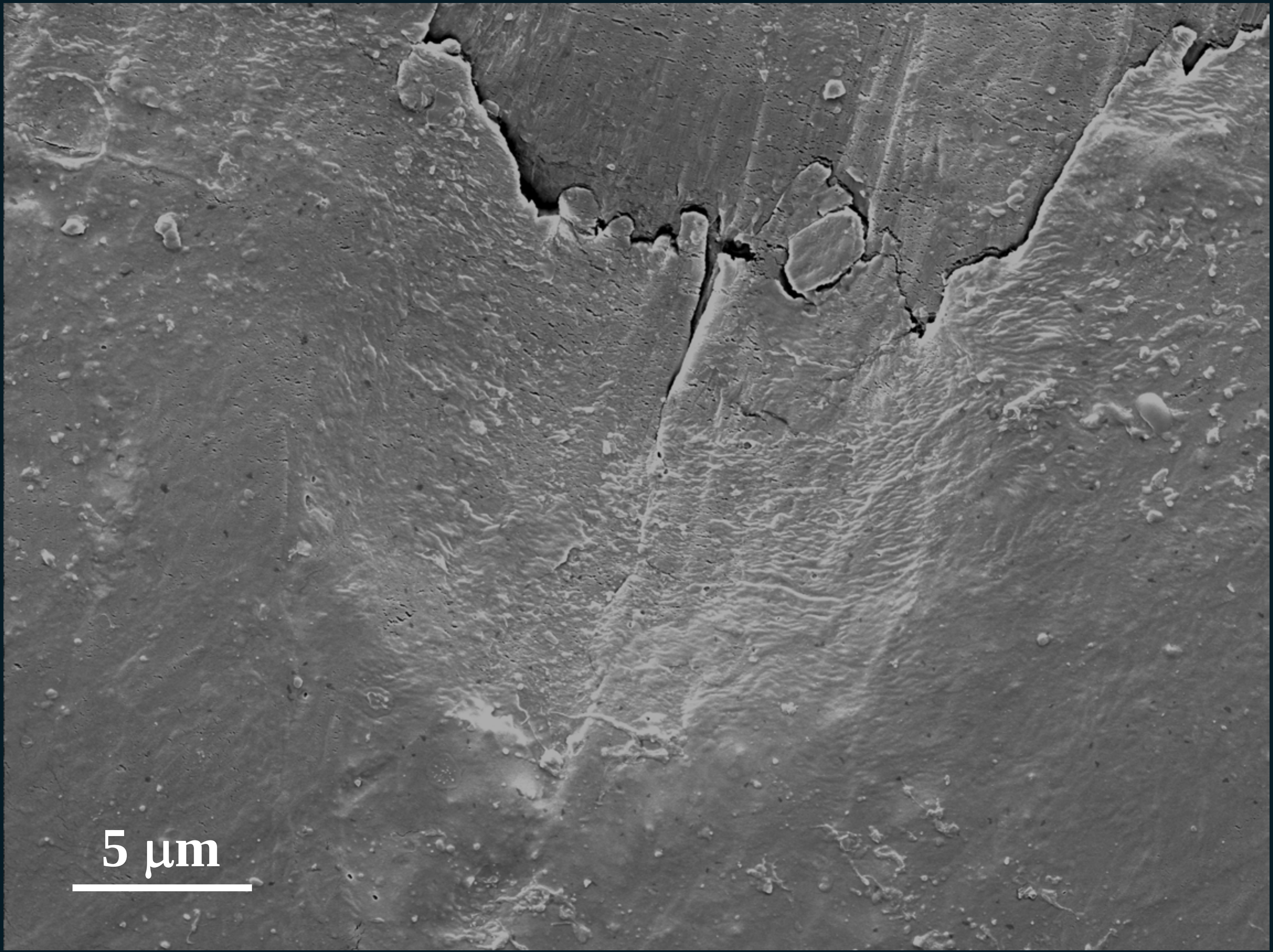

DISCUSSION

- **Historical TKA tibial inserts undergo oxidative, microstructural and mechanical degradation *in vivo:* access to body fluids is a key mechanism.**

- **FTIR and Raman spectroscopies confirm *in vivo* oxidation induces crystallinity changes**
  - **Qualitative estimations (dependence with density)**
  - **3-Phase model not valid for highly oxidized PE**

- **Nanoindentation confirms evolution to a harder and stiffer PE, in spite of the high sensitivity to surface defects.**

ACKNOWLEDGEMENTS

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