Lanthanides as Stabilizing Agents For UHMWPE

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Background

- Lanthanoids were tested *in vitro* as a tracer for wear of UHMWPE
- UHMWPE was doped with europium and gadolinium stearates
  - Tracing capabilities were demonstrated [1]
  - Doping does not interfere with wear [1]
  - Abundance of Lanthanides in humans is extremely small [2]
  - Cyto-compatibility results are promising [2]
- Eu(III) stearate doped UHMWPE was tested for oxidative stability and mechanical properties. [3]

1. Ngai, et al. Wear (2009)
2. Pennekamp, et al. ORS (2009)
3. Gallardo, et al. MoBT (2009)

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Hypothesis

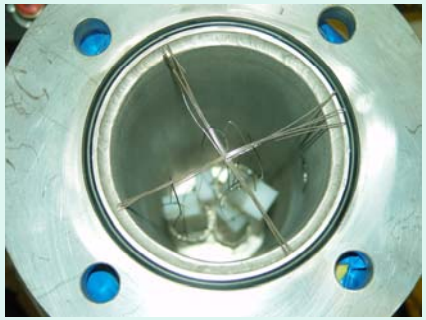
The addition of europium(II) will prevent oxidative degradation of compression molded UHMWPE.

Objectives

- Evaluate the oxidative stability of Eu(II)-stearate doped UHMWPE
  - Mechanical properties
  - Oxidation index
- Compare Eu(II) doped to conventional and Eu(III) doped UHMWPE

Materials and Methods

- GUR 1050 UHMWPE powder was doped with Eu(II) and Eu(III) stearates
- Compression molded into slabs, machined to 85x30x20 mm cuboids
- Gamma Irradiated (35 kGy)
- Accelerated Aging
  - ASTM Standard F2003-02
  - 70°C, 501 kPa, O_2 atmosphere, 14 days
- Final Dimensioning



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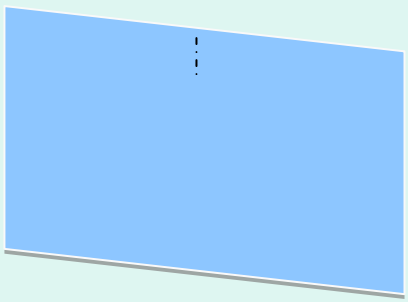
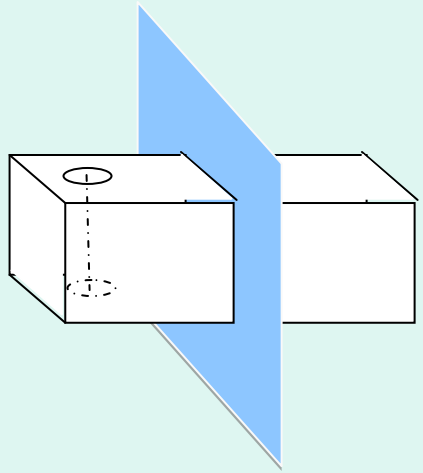
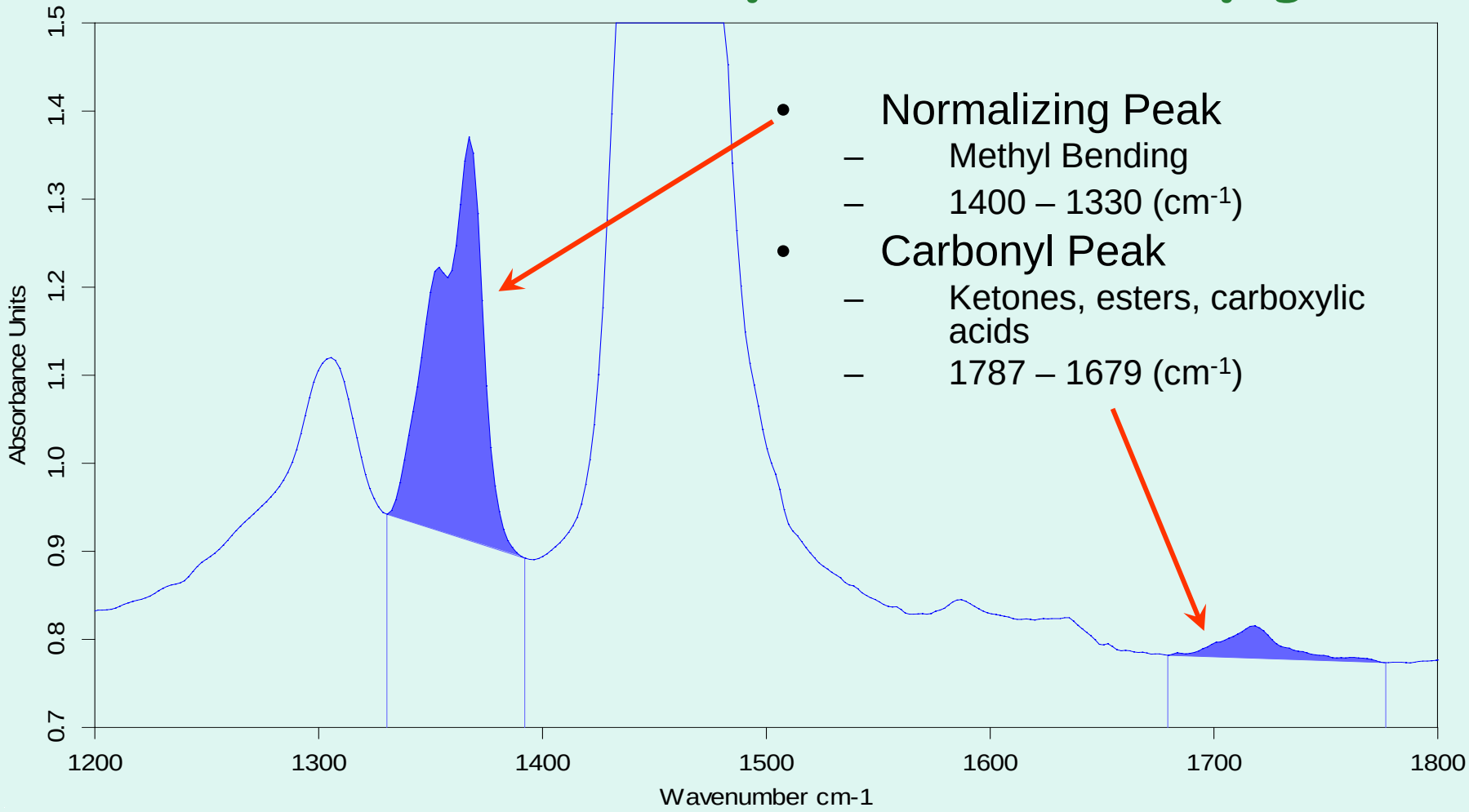
Materials and Methods

- 200 µm thin films
  - ASTM STD 2102-06
- FTIR spectra were collected
  - Line map along axis of SPT cores
  - From surface to 3 mm depth
  - 200 µm step intervals





FTIR Micro-Spectroscopy



- Normalizing Peak
  - Methyl Bending
  - 1400 – 1330 (cm^{-1})
- Carbonyl Peak
  - Ketones, esters, carboxylic acids
  - 1787 – 1679 (cm^{-1})

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Materials and Methods

- Morphology observations were made on each sample
  - 15x magnification
  - A visible light polarizer was used to observe the samples
  - Non-polarized light was used for snapshots

Sample Groups

Doping Conditions		
Non-Doped Control	Eu(III) Stearate	Eu(II) Stearate
0 ppm	375 ppm	375 ppm
	750 ppm	750 ppm

ORTHOPLASTICS GUR1050 UHMWPE		γ - Irradiated	
		Unaged	Aged
Surface	0.0-0.5 mm	5	5
Subsurface	0.5-1.0 mm	1	1
	1.0-1.5 mm	5	5
	1.5-2.0 mm	1	1
	2.0-2.5 mm	1	1

- Aged and non-aged conditions
- 130 small punch tests were performed in total

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Results

Small Punch Test

(Aged Relative to Non Aged)

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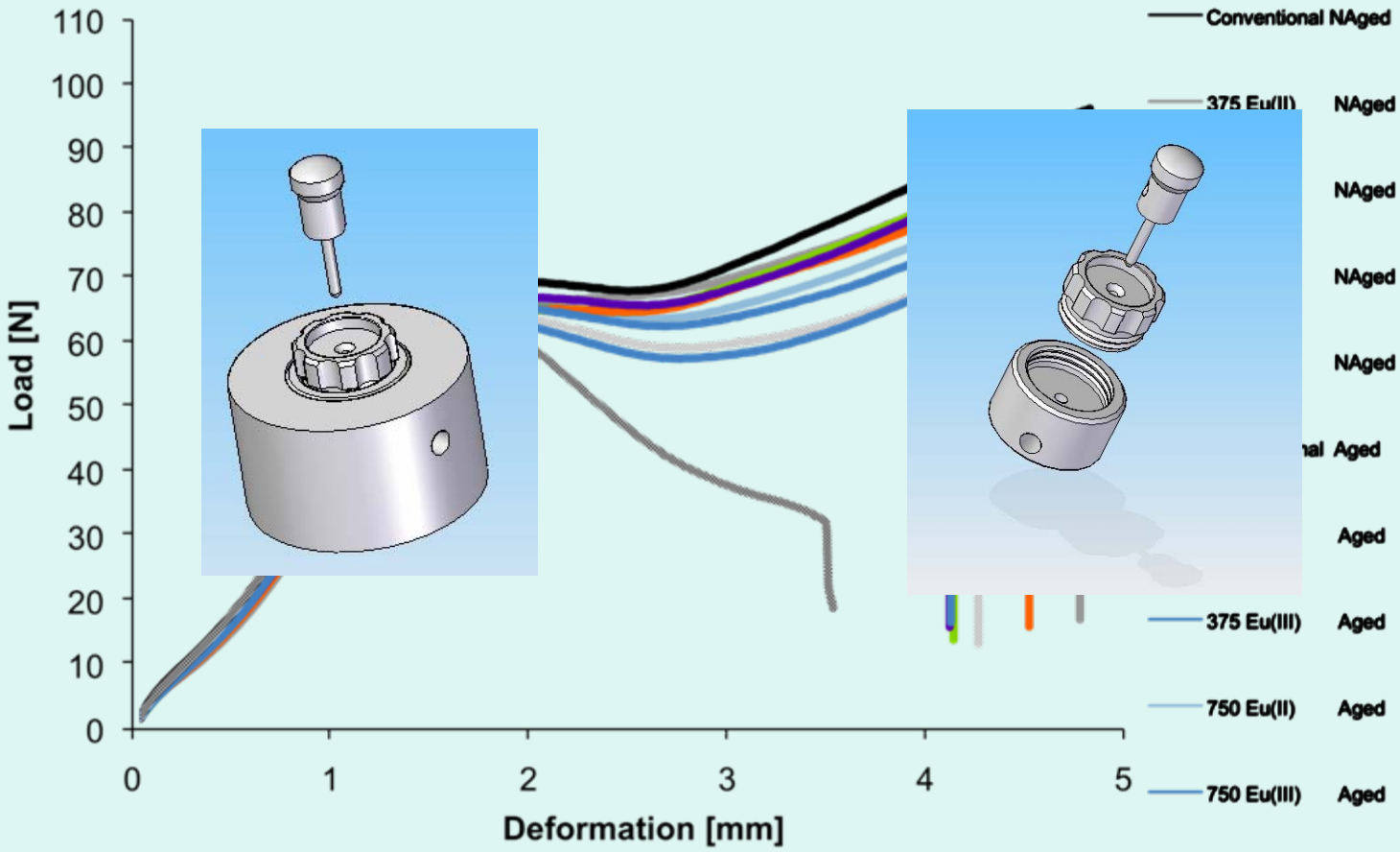
Load-Deformation Curves



* Single measurement curve trends

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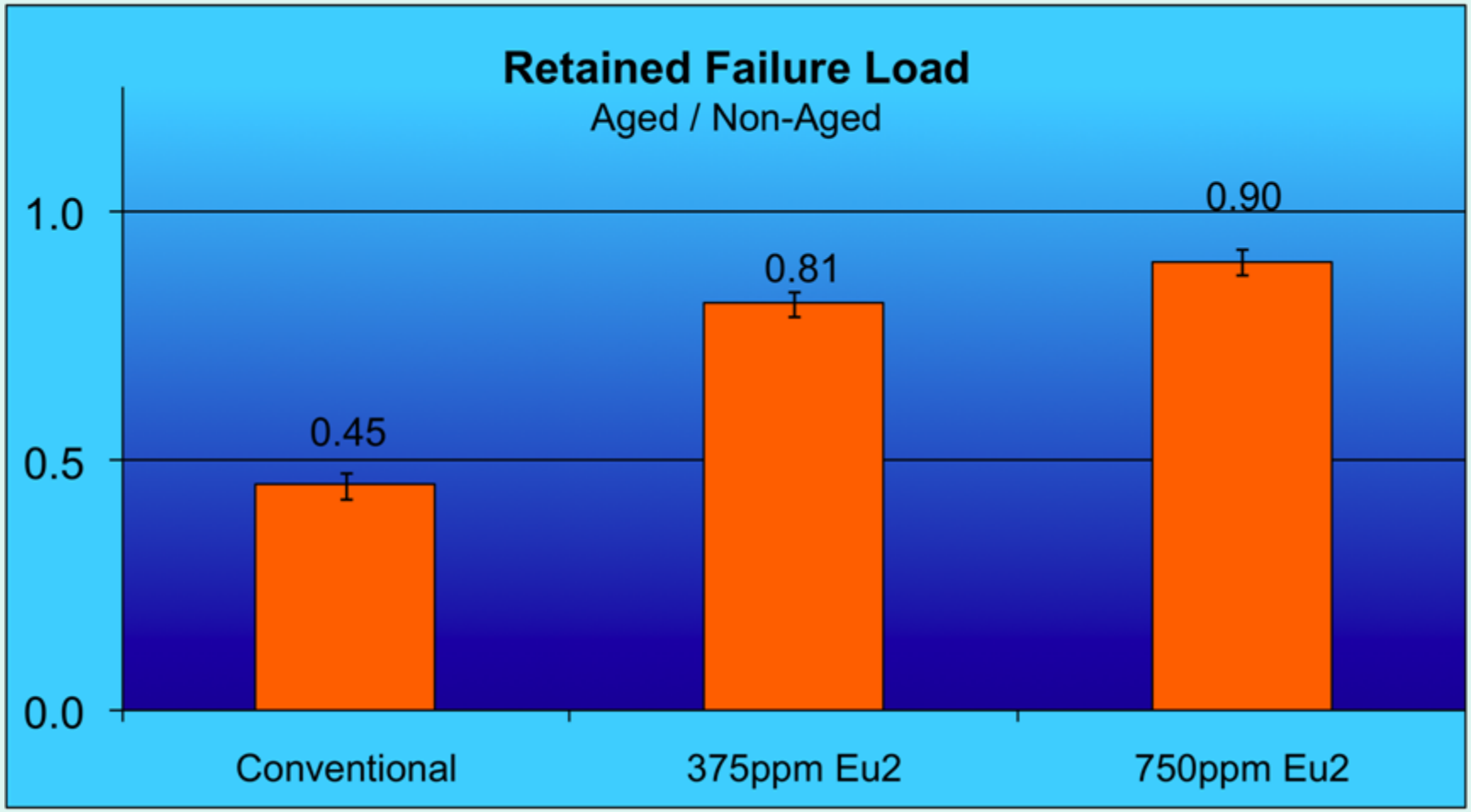
SPT Results



Note: Error bars represent Standard Error; Bars represent Mean where: n=10

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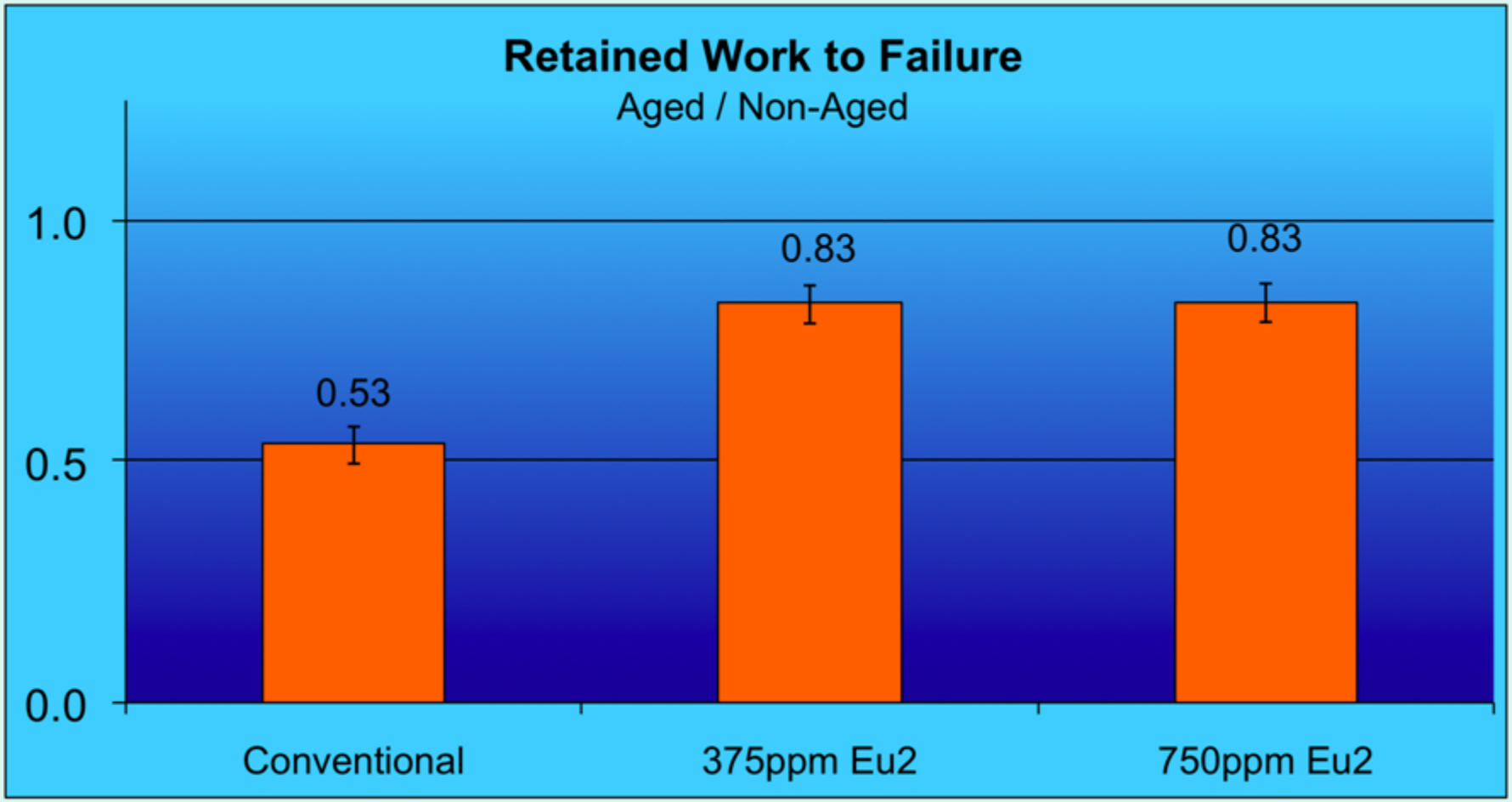
SPT Results



Note: Error bars represent Standard Error; Bars represent Mean where: n=10

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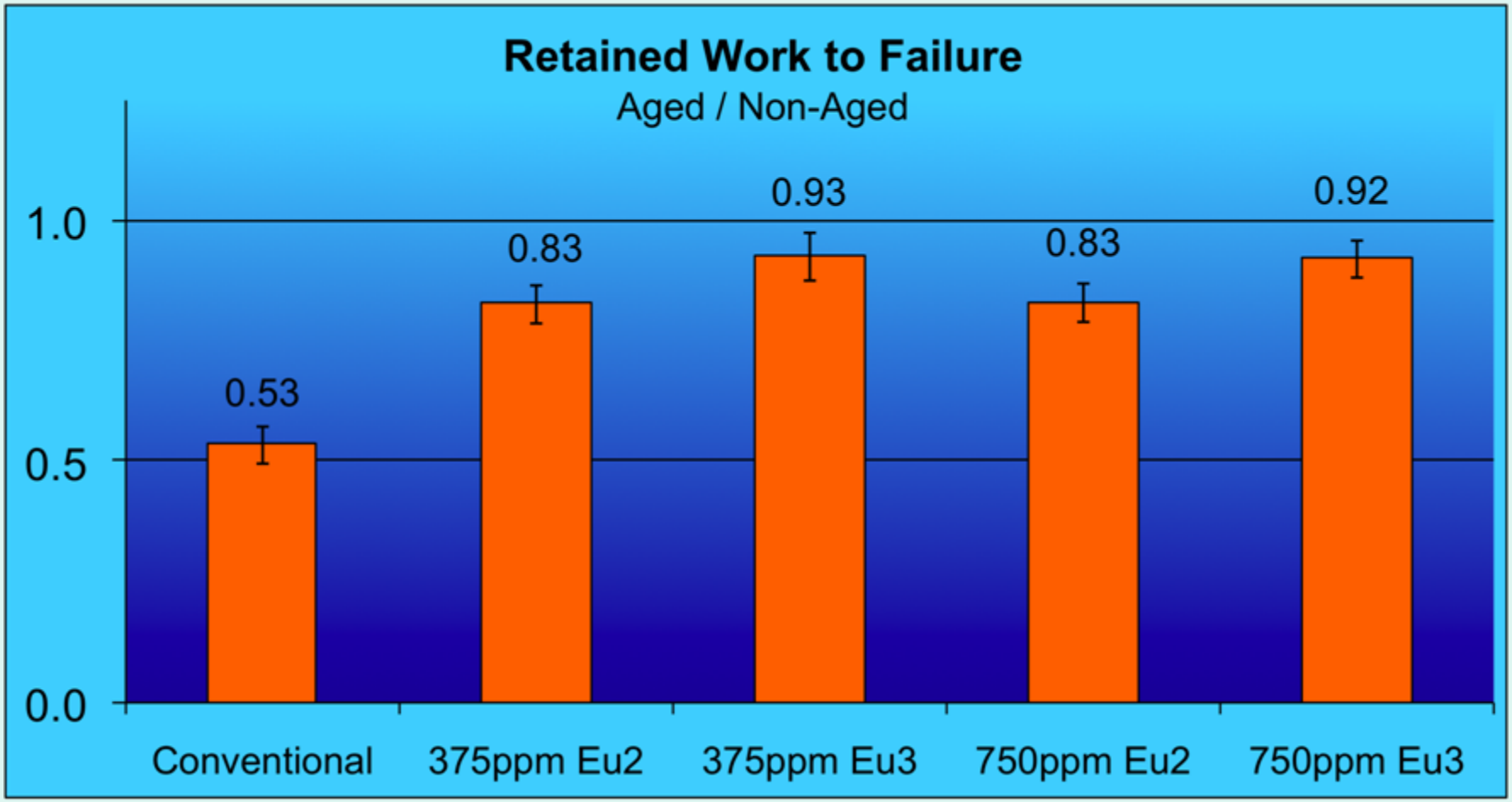
SPT Results



Note: Error bars represent Standard Error; Bars represent Mean where: n=10

Results

Surface Oxidation Index (SOI)

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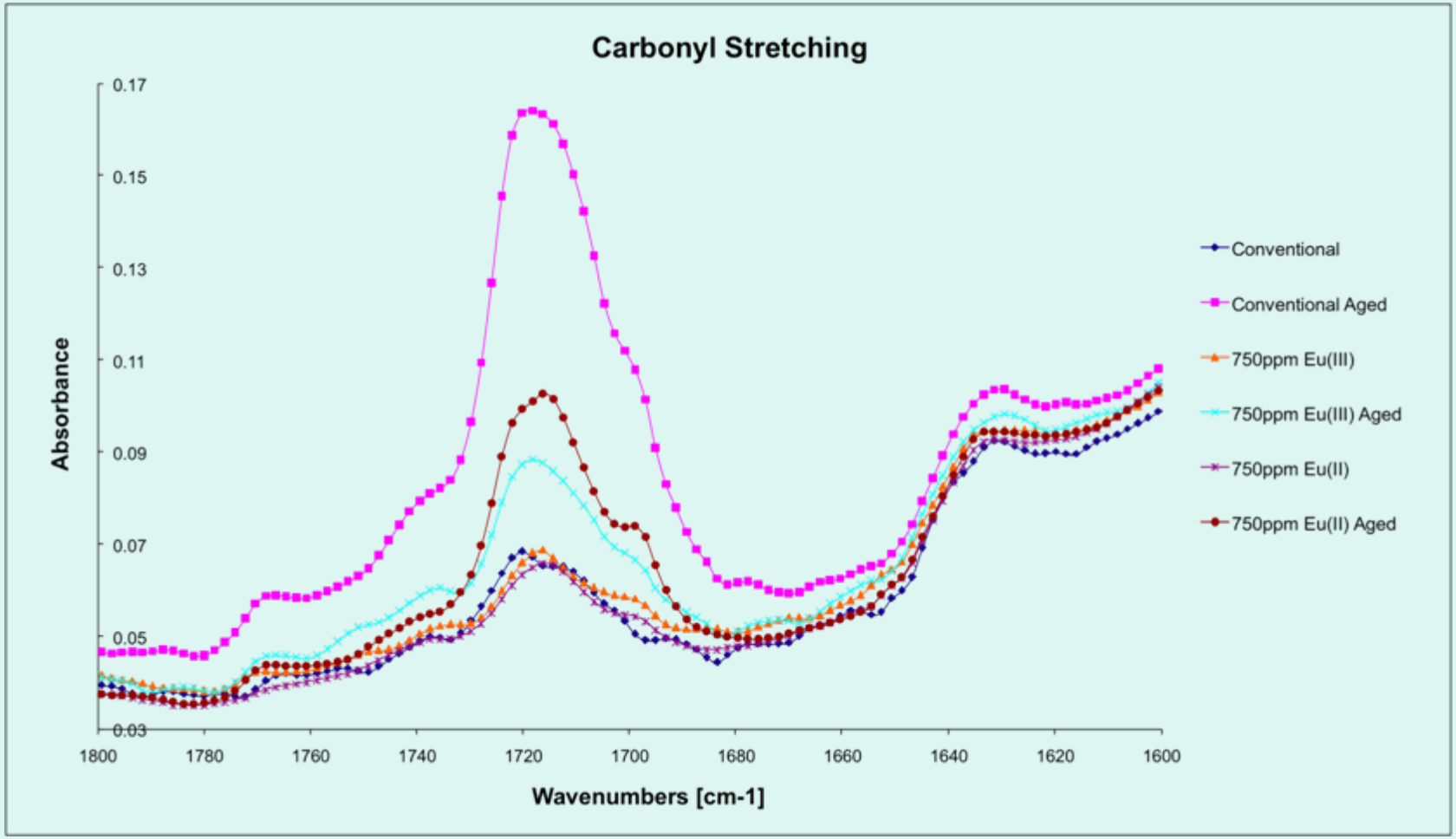
Results



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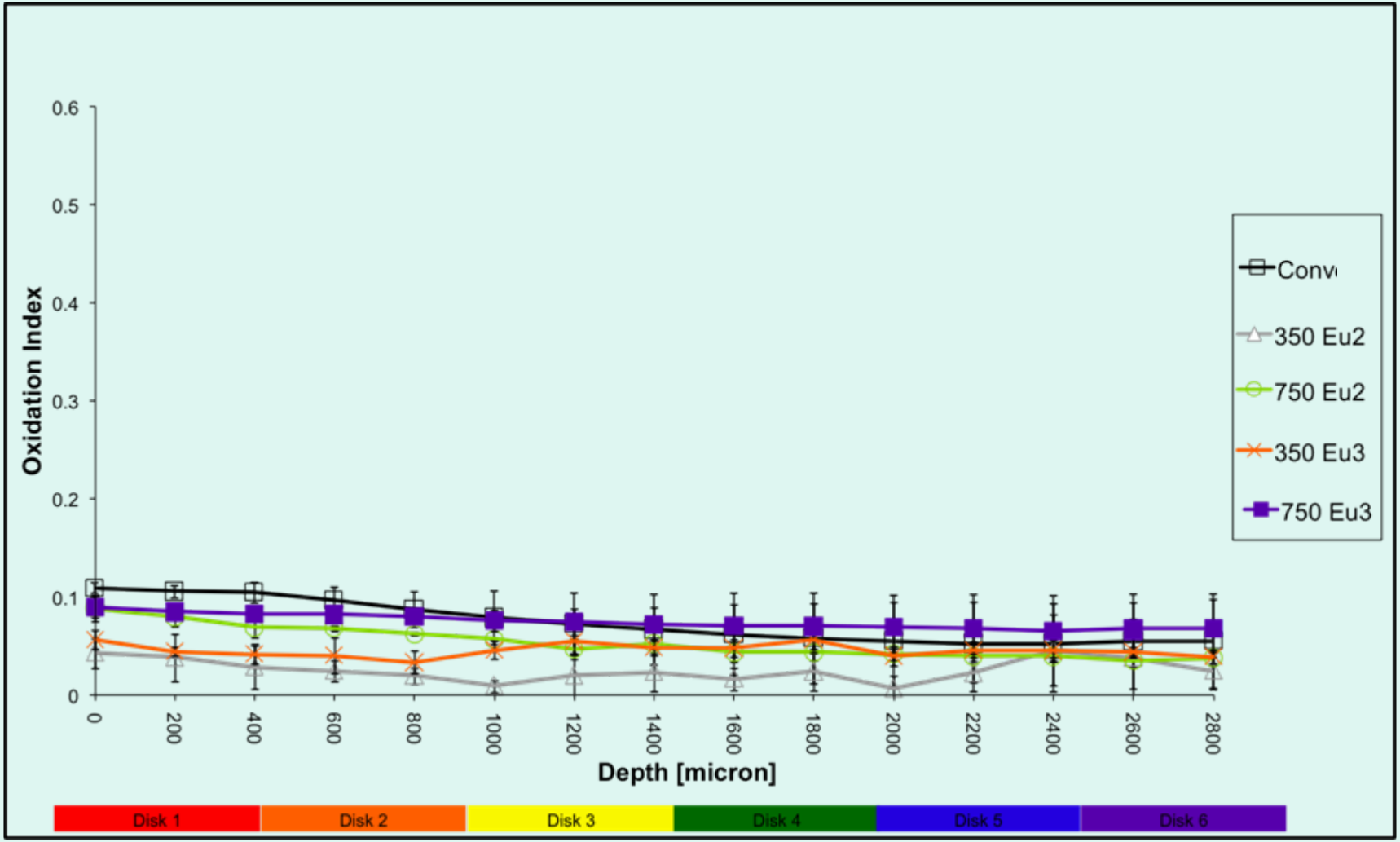
OI Before Aging



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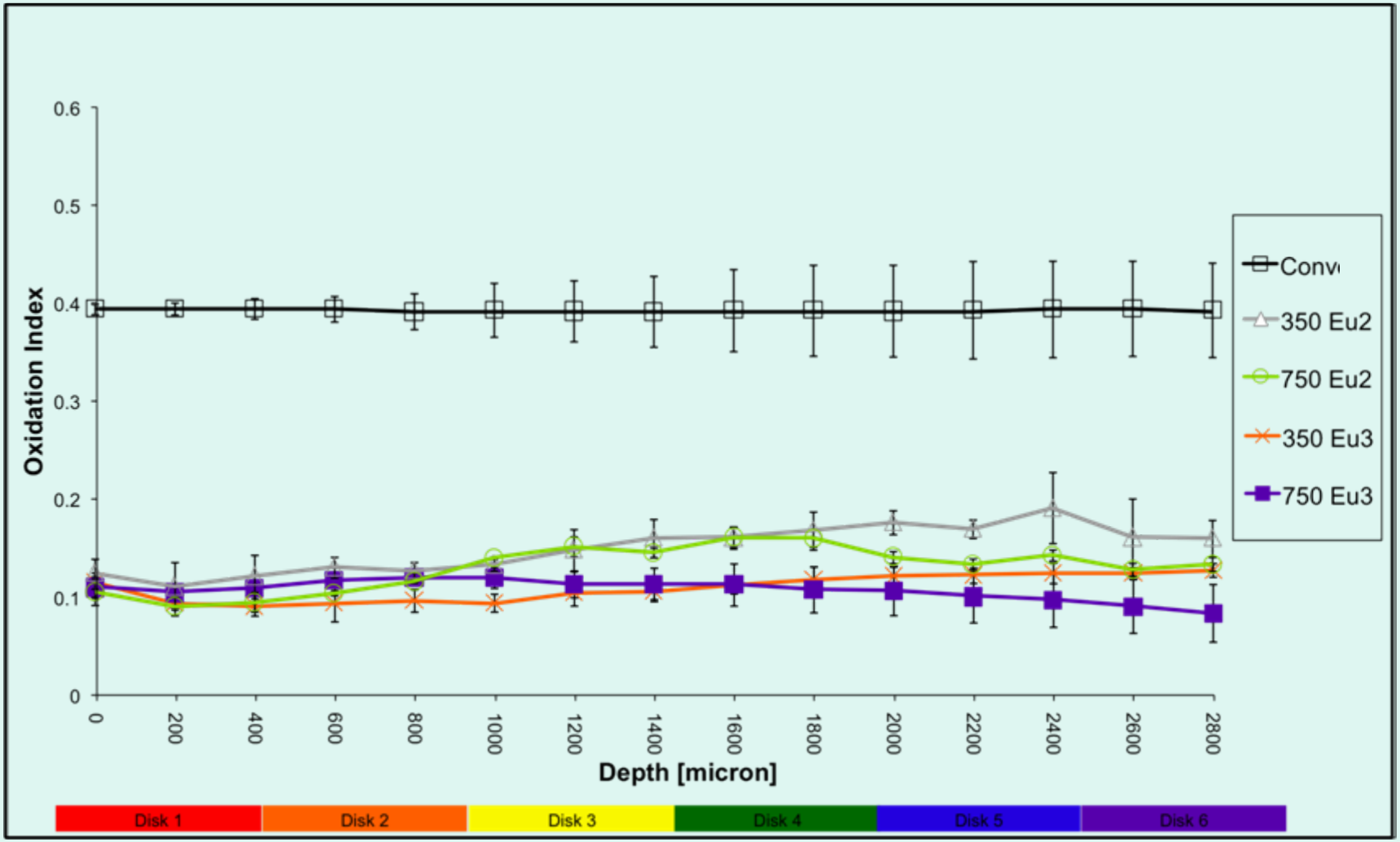
OI After Aging



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Results

Morphology

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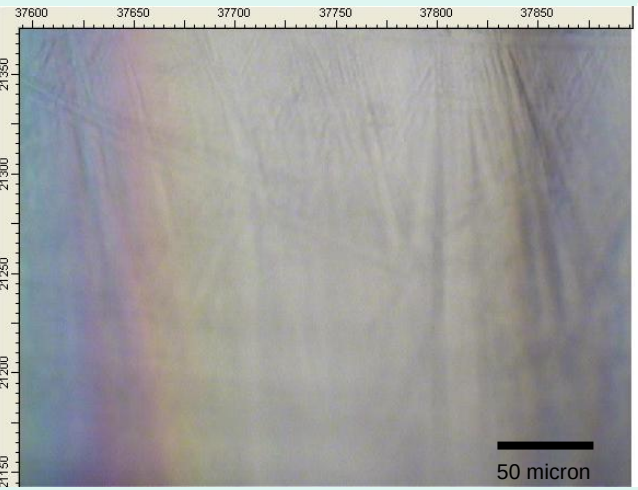
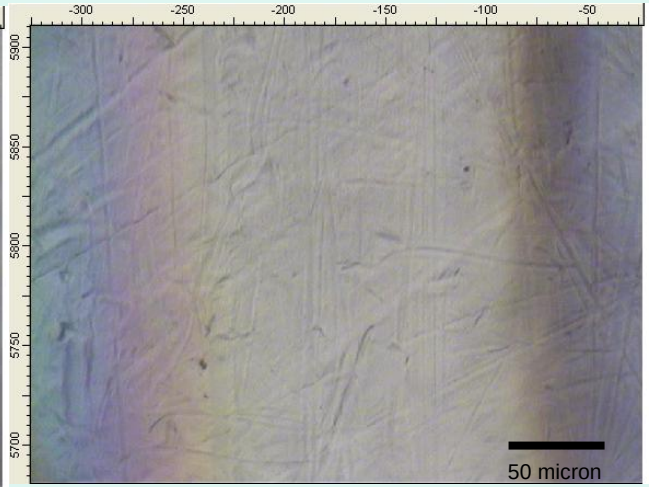
Microscopy Images



Non Doped



750 ppm Eu(III)

7500 ppm Eu(III)

- Europium stearate is accumulated along the grain boundaries (confirmed with FTIR)
- Noticeable only at high concentrations

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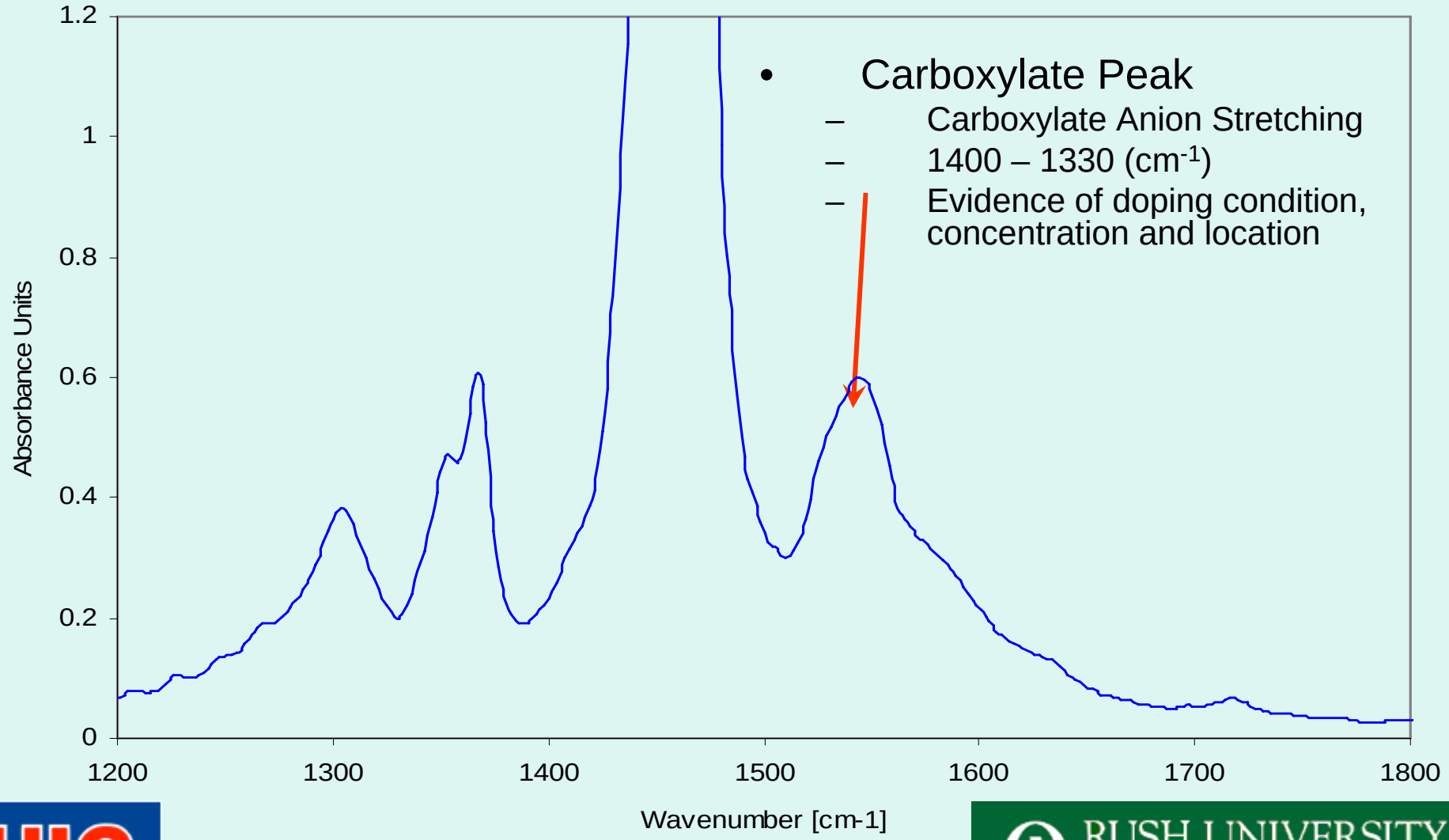
FTIR Micro-Spectroscopy



- Carboxylate Peak
  - Carboxylate Anion Stretching
  - 1400 – 1330 (cm^{-1})
  - Evidence of doping condition, concentration and location

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Conclusions

- Europium stearate shows strong evidence of preserving mechanical properties after aging in both ionic forms.
- FTIR indicates retention of original oxidation indexes in UHMWPE doped with this compound, suggesting stabilization is achieved for this material
  - The effect depends upon valence and concentration

Conclusions

- Yet, counter-intuitively, Eu(III) performed better than Eu(II) on both mechanical and oxidative properties
- There is a drop in initial mechanical properties after doping. It may be due to:
  - Solvent residues
  - Non optimized compression molding process for this material

Outlook

- Gain better understanding of the oxidation reaction dynamics and byproducts
- Optimize the compression molding process
- Determine the effect of doping on cross-linking
- Capitalize on other properties of Lanthanides that could make them attractive in orthopedics [1]:
  - Low toxic effects on osteogenic cells
  - Anti-proliferate effect on phagocytotic cells
  - Anti-inflammatory properties

1. Pennekamp, et al. ORS (2009)

Thank you

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