

HIGH TEMPERATURE OXIDATION OF ZIRCONIUM ALLOYS CLADDING MATERIAL IN SFP-LOCA CONDITIONS EXAMINED WITH MICRO RAMAN IMAGING AND ^{18}O TRACER TECHNIQUES

A. Kasperski^{1,2}, C. Duriez¹, M. Mermoux²,

1- IRSN/PSN-RES/SEREX/LE2M, Cadarache, 13115 Saint-Paul-lez-Durance, France

2- Université Grenoble Alpes, CNRS/LEPMI, 38402 Saint-Martin d'Hères cedex, France

HTCPM 2021, 28 March – 2 April 2021

Context : Study of nuclear spent fuel storage pool accidents

In case of a loss of water in a spent fuel pool, the Zr-based cladding tubes will oxidized at high temperature

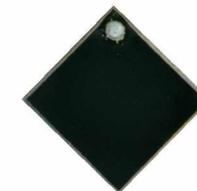
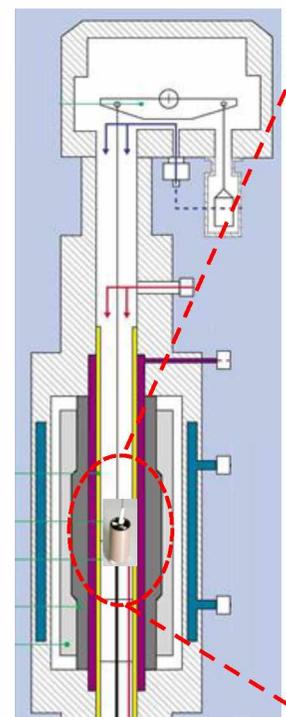
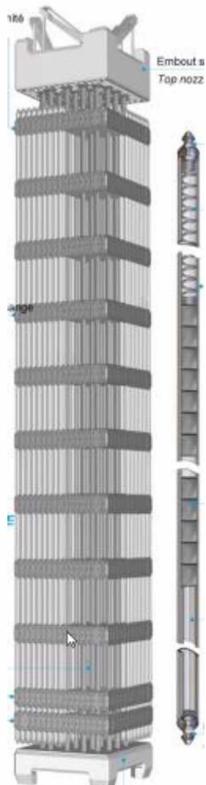
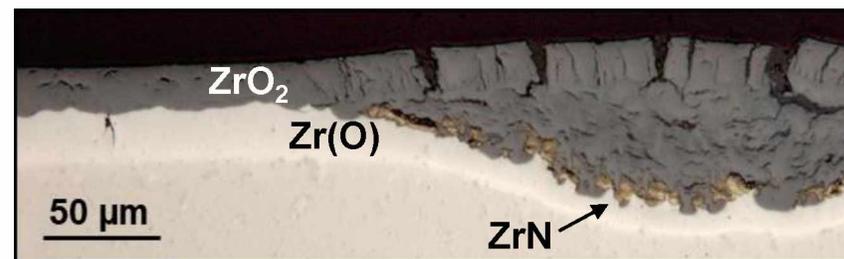
⇒ Temperature range of interest ~ 700-1000°C

⇒ Atmospheres considered $O_2 + N_2 + H_2O$ mixtures

- (1) $Zr + O \rightarrow Zr(O)$
- (2) $Zr + O_2 \rightarrow ZrO_2$ $\Delta G = - 787 \text{ kJ/mol Zr}$
- (3) $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$ $\Delta G = - 478 \text{ kJ/mol Zr}$ (at 850°C)
- (4) $Zr + \frac{1}{2} N_2 \rightarrow ZrN$ $\Delta G = - 260 \text{ kJ/mol Zr}$



Before breakaway After breakaway



C. Duriez et al., J. Nucl. Mat., vol. 380, pp. 30-45, 2008.
M. Lasserre, PhD Thesis, École des Mines de Saint-Étienne, 2013.
M. Gestin, PhD Thesis, École des Mines de Saint-Étienne, 2019.

Objective : An overview of **Raman microscopy** imaging capabilities for the study of thermally grown zirconia scales.

Content

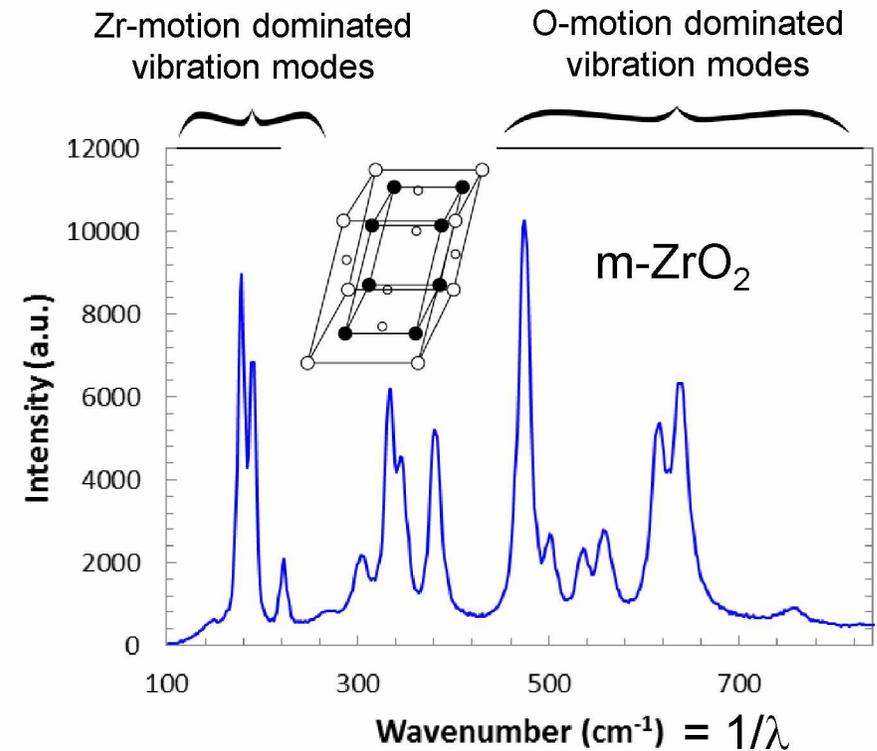
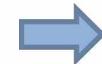
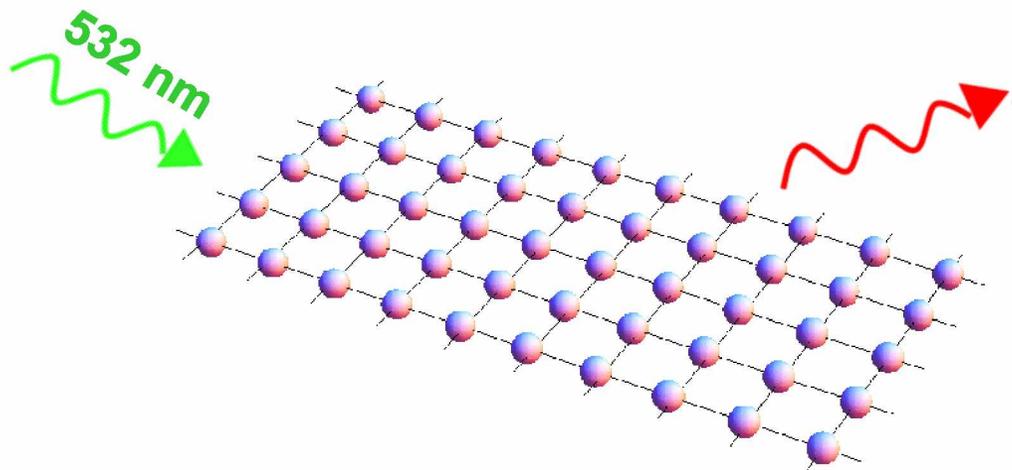
- Principle of Raman imaging
- Phases mapping
- Stoichiometry
- Stress mapping
- Oxygen 18 isotopic distributions
 - ❑ Two-stage diffusion experiments
 - ❑ HT oxidations tests in mixed $^{18}\text{O}_2 + \text{H}_2^{16}\text{O} + \text{N}_2$ atmospheres

Raman imaging system

laser + optical microscope + spectrometer



Lateral resolution $\leq 1 \mu\text{m}$
Probed depth $\sim 1\text{-}2 \mu\text{m}$ for ZrO_2

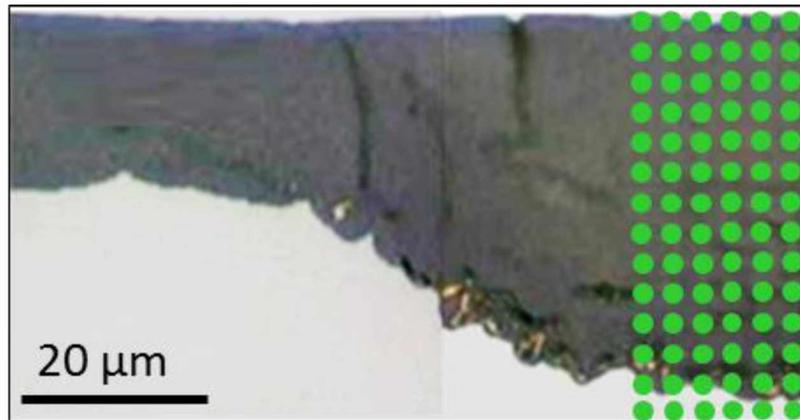


Raman scanning and phase identification

1- Scanning of a cross section → Dataset of experimental spectra

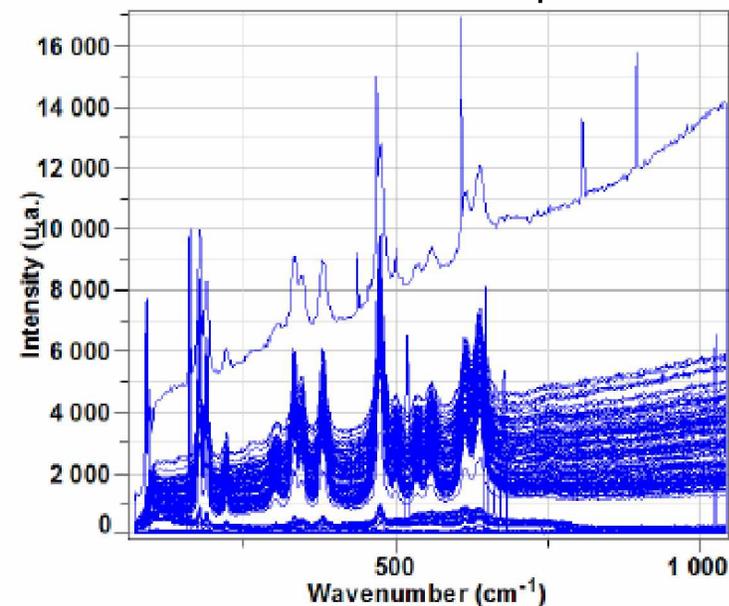
2- Comparison/subtraction of experimental spectra with reference spectra → 5 pure phase spectra identified : m-ZrO₂, t-ZrO₂, distorted t-ZrO₂, c-ZrO₂, ZrN + 1 broad-band signal due to high disorder (low crystal size, sub-stoichiometry, ...).

Zy-4 oxidized in air at 800°C

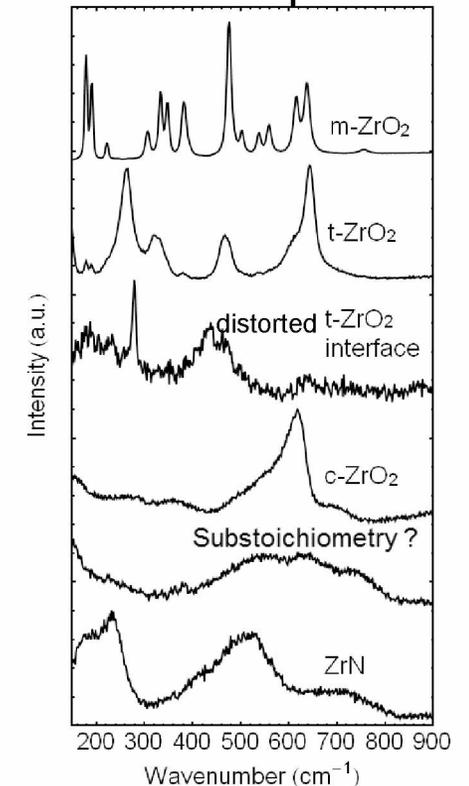


Scanned area 85 x 45 μm, step 0.7 μm

~8000 experimental spectra
several hours of acquisition



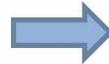
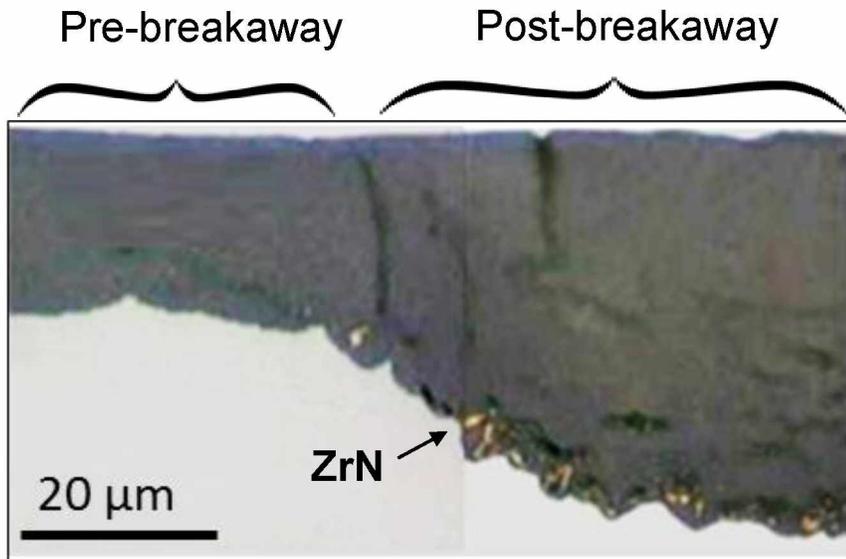
6 model spectra



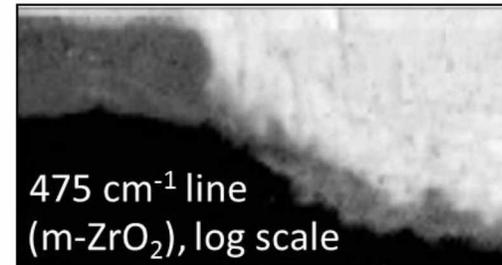
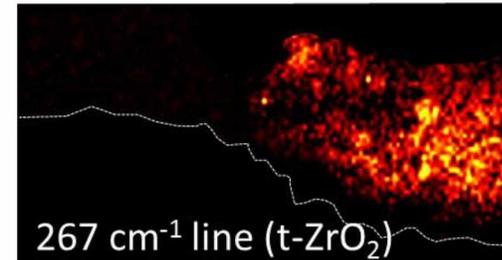
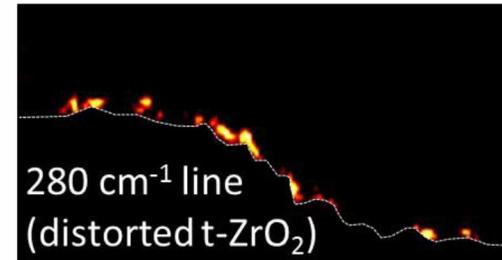
3- Phase maps construction

Method 1: Integrated intensity of a given line

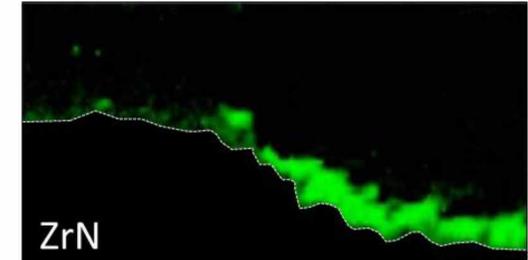
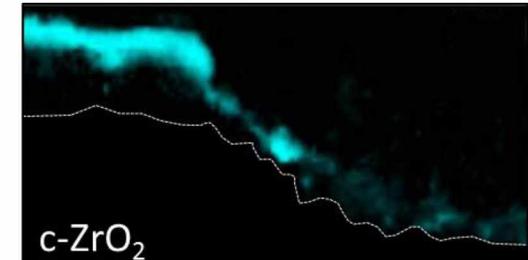
Method 2: Linear combinations of the model spectra



Method 1



Method 2 (not quantitative)

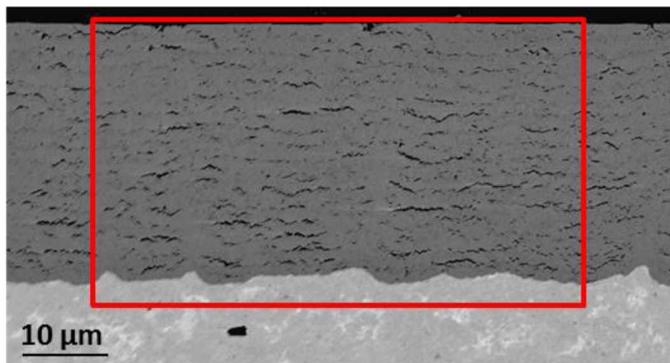


- Distorted t-ZrO₂ found at the M/O interface, for both pre and post-BA regions.
 - Significant amount of t-ZrO₂ in the post BA region
 - Cubic ZrO₂ detected (low amount)
 - Good sensitivity for ZrN detection.
 - m-ZrO₂ intensity likely linked to stoichiometry.
- } Stabilized by Nitrogen dissolved in ZrO₂ and/or by substoichiometry ?

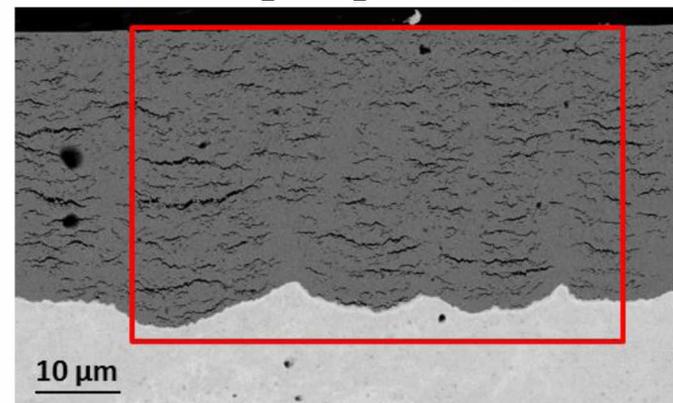
I. Idarraga et al, Oxid. Met. 79 (2013) pp. 289-302.

Zircaloy-4 oxidation at « low » temperature to simulate the corrosion in reactor → layered microstructure:

at 360°C in autoclave during 1265 days

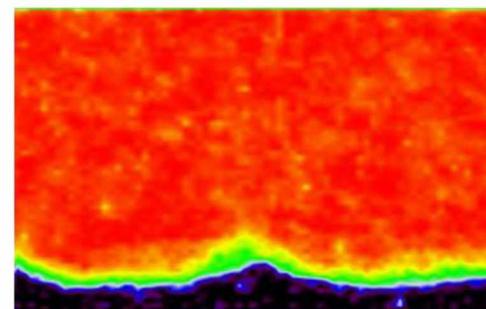
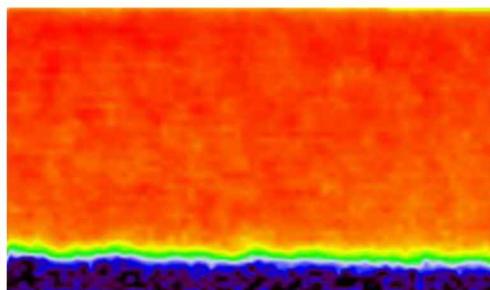


at 425°C in O₂ + H₂O during 250 days



SEM/BSE

Integrated intensity
of the 475 cm⁻¹ line
(m-ZrO₂), log scale

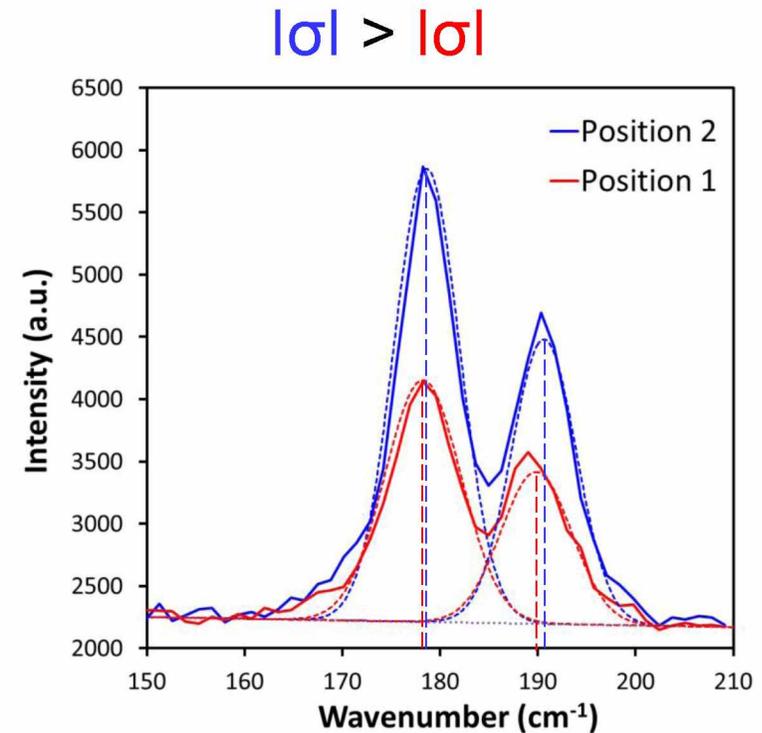
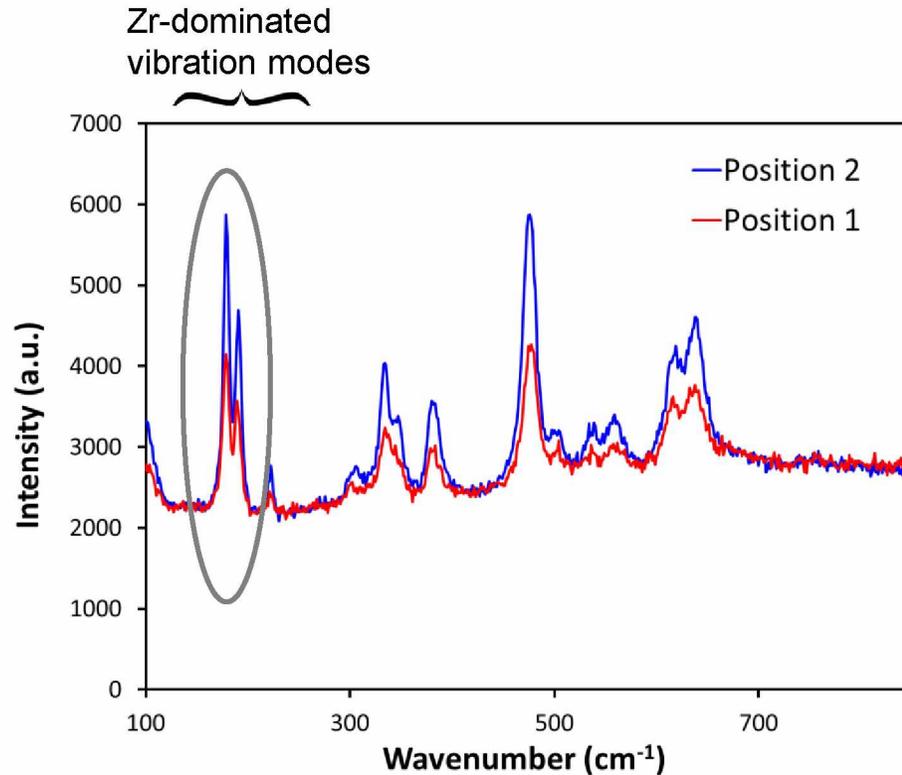


For both oxidation conditions :

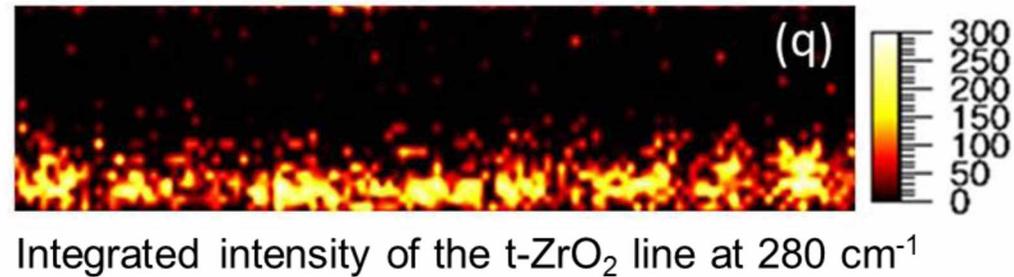
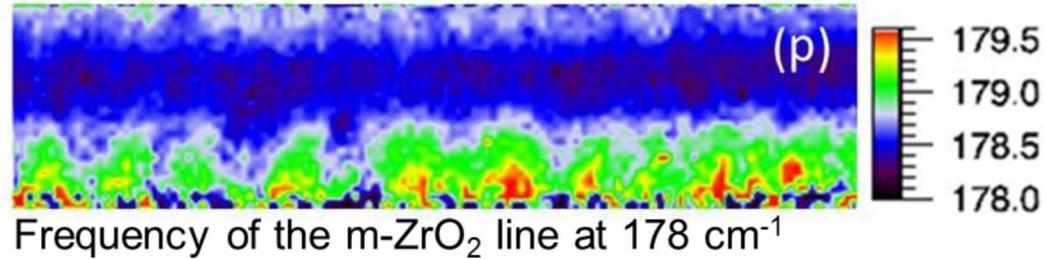
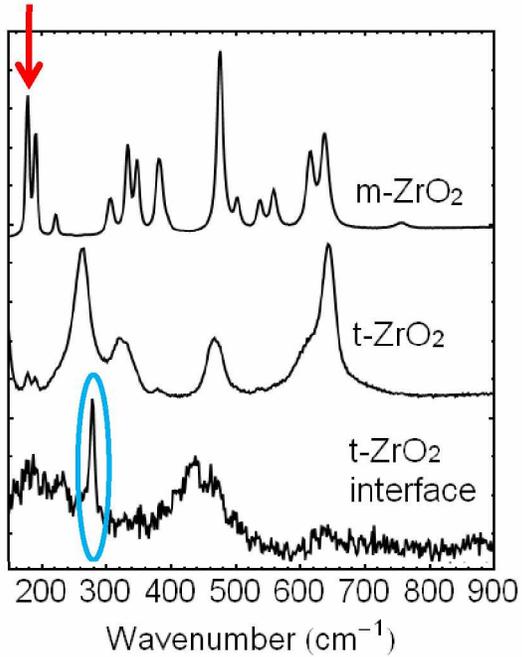
- The scales are mostly stoichiometric,
- Only the last formed layer at the M/O interface is sub-stoichiometric.

Stress mapping (1/2)

- Stress \rightarrow Lattice strain \rightarrow Slight shifts of Raman lines (few $\text{cm}^{-1}/\text{GPa}$).
- Calibrations through isostatic compression tests (diamond anvil-cell) **are not applicable**:
 - bi-axial stresses,
 - Strong texture + high anisotropy of the m-ZrO₂ Young modulus and thermal expansion coefficients.
- Stresses can be **qualitatively** mapped by measuring the shifts of the low-frequency lines (not influenced by stoichiometry) from a reference signal (relaxed sample).



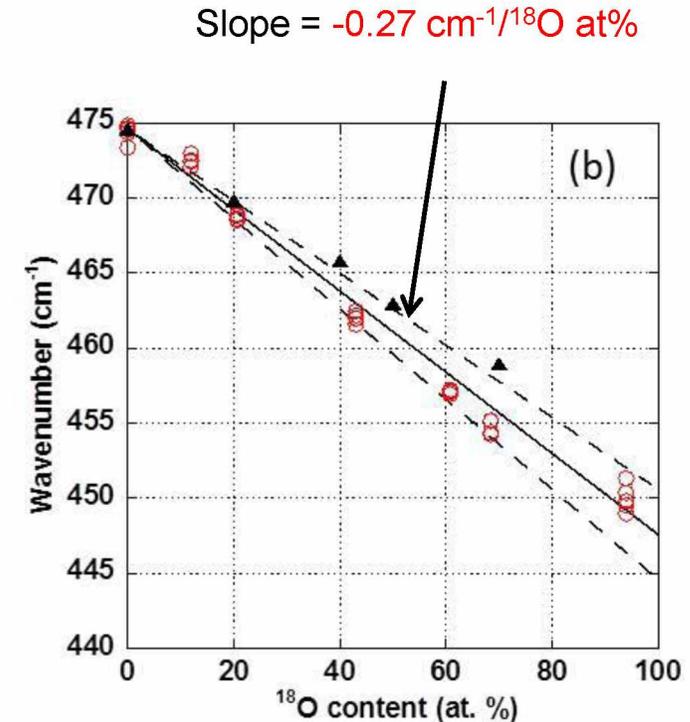
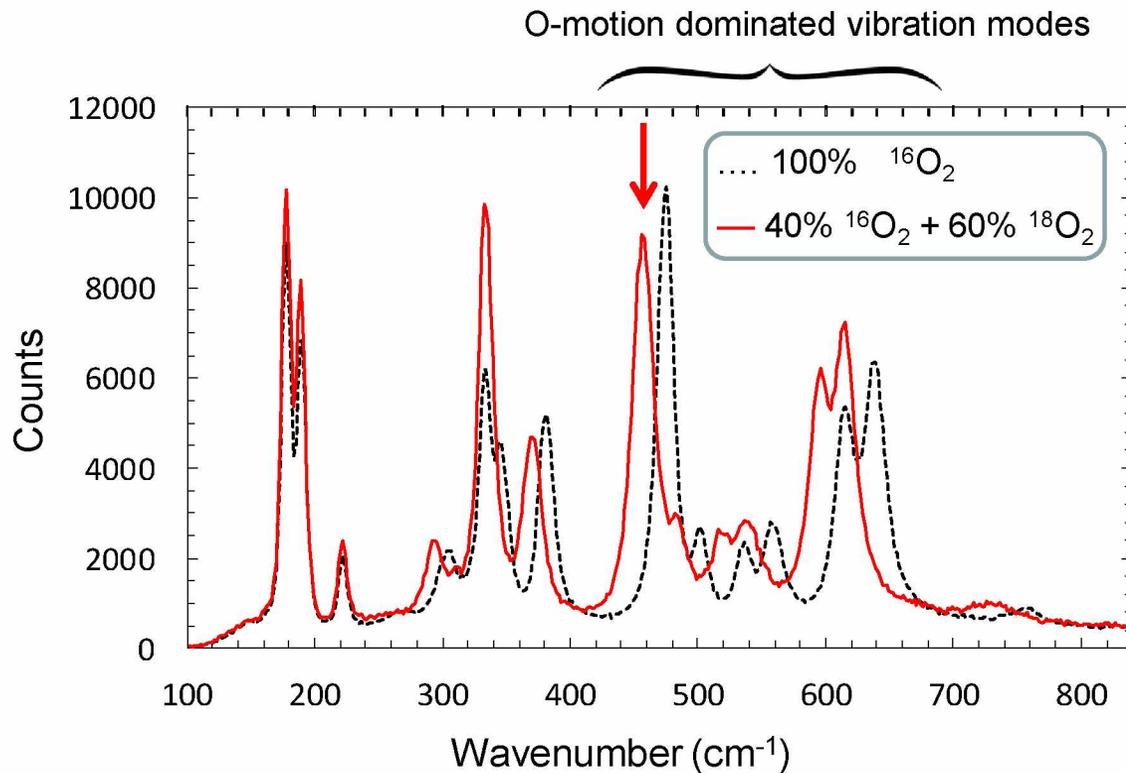
M5_{Framatome} oxidized in air at 800°C



- Compressive stresses close to the M/O interface.
- Compressive stresses stabilize t-ZrO₂ here.

Oxidation tests with isotopically-labeled oxygen

- $^{16}\text{O} \rightarrow ^{18}\text{O}$ substitution induces strong downward shifts of **O-dominated lines** of the m-ZrO₂ Raman spectrum.
- Zr(¹⁸O,¹⁶O)₂ standard powders prepared by Zy-4 total oxidation in $^{16}\text{O}_2 + ^{18}\text{O}_2$ atmospheres
→ Shifts are proportional to the ¹⁸O fraction.

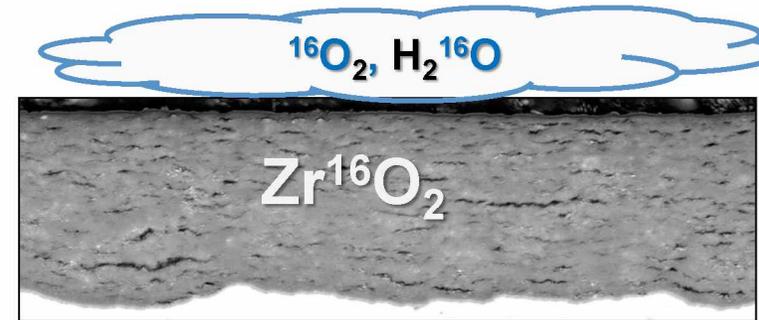


Raman imaging can be used to **quantitatively map** the ¹⁸O distribution in a zirconia scale by measuring the position of the 475 cm⁻¹ line.

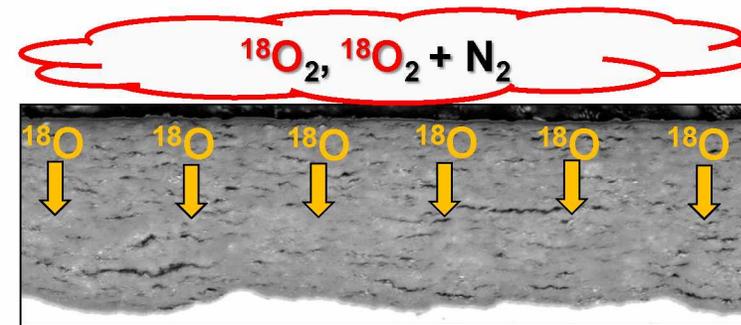
Two-stage oxidation experiments

Objective: Investigate oxygen ingress at high T through a low T pre-oxidation scale

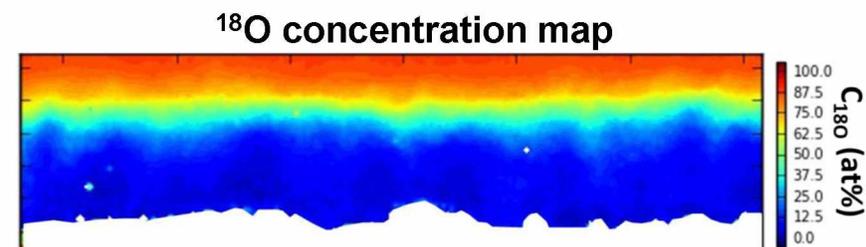
Stage 1: Pre-oxidation at 425°C in $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$



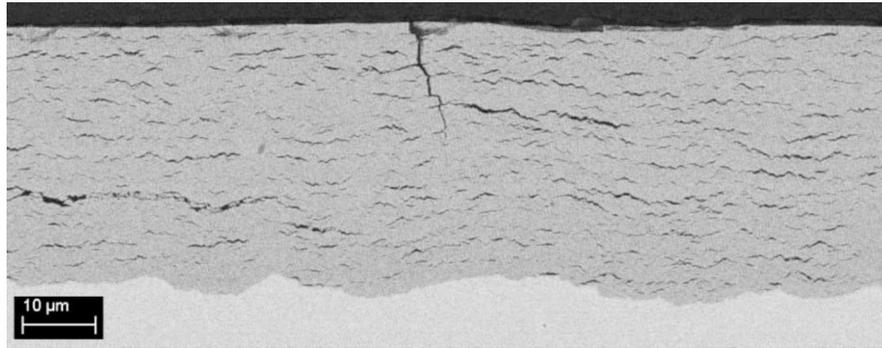
Stage 2: High T exposure in $^{18}\text{O}_2$ or $^{18}\text{O}_2 + \text{N}_2$
(at 700, 850 and 950°C)



^{18}O distribution by Raman imaging



Pre-oxidation at 425°C in $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$

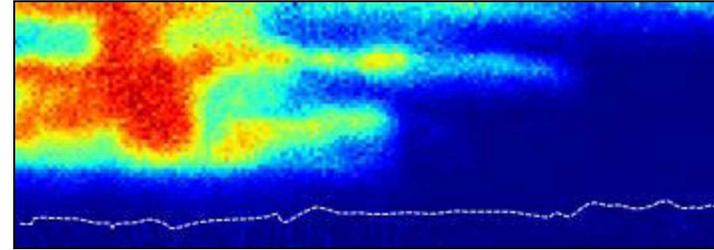


BSE-SEM image

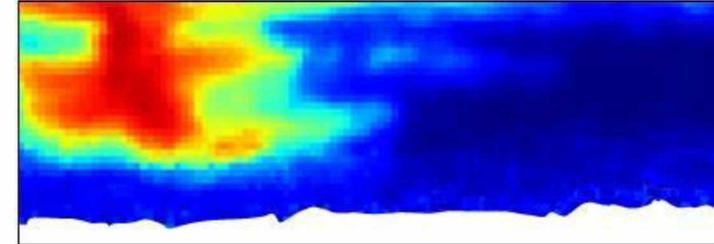


After 120 min at 850°C in $^{18}\text{O}_2 + \text{N}_2$

SIMS mapping



Raman mapping



$C_{^{18}\text{O}}$ (at. %)

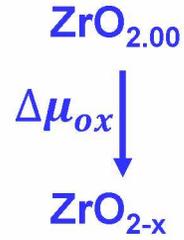
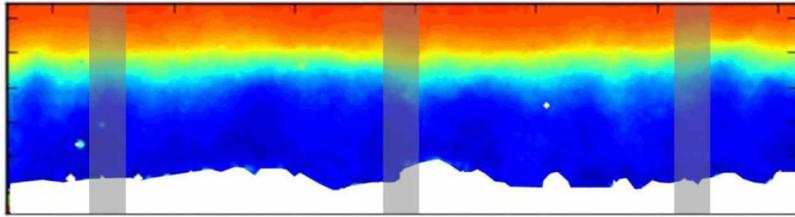
80
72
64
56
48
40
32
24
16
8
0



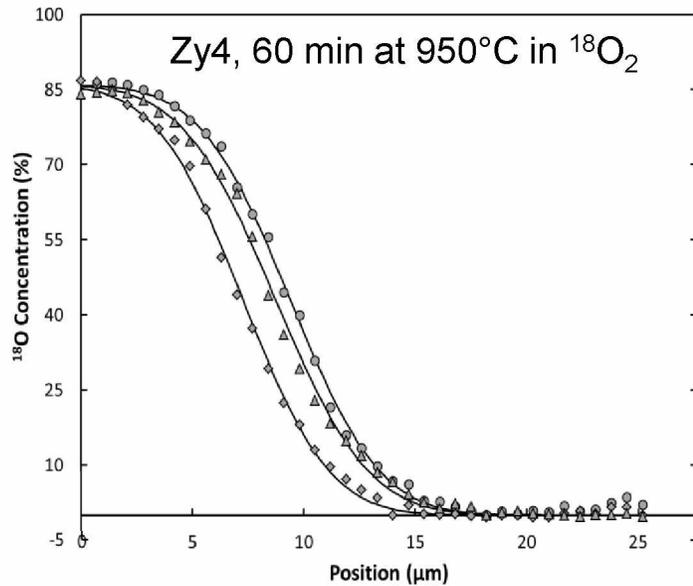
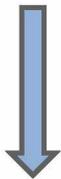
- Vertical cracks are preferential path for oxygen incorporation and circumferential cracks favor its lateral spreading.
- Comparison with SIMS imaging validates the ^{18}O Raman distribution.

Apparent oxygen diffusion coefficients

Surface



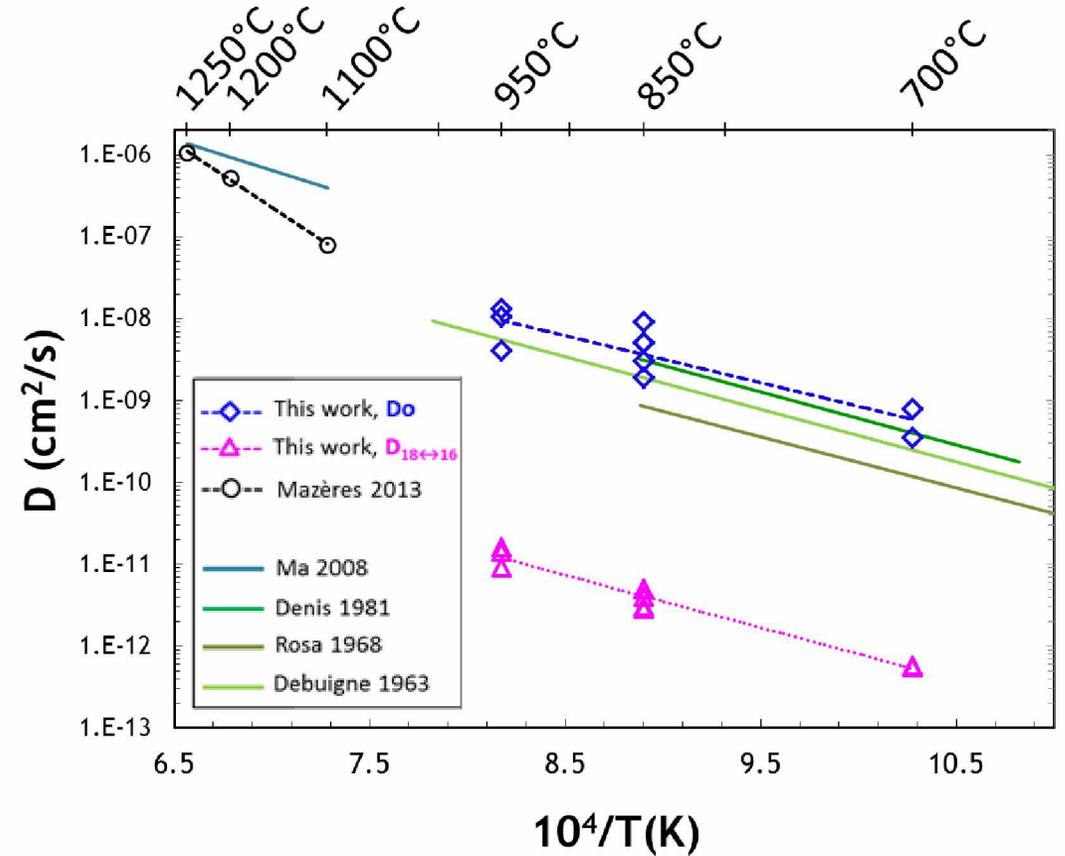
Metal



Surface

Metal

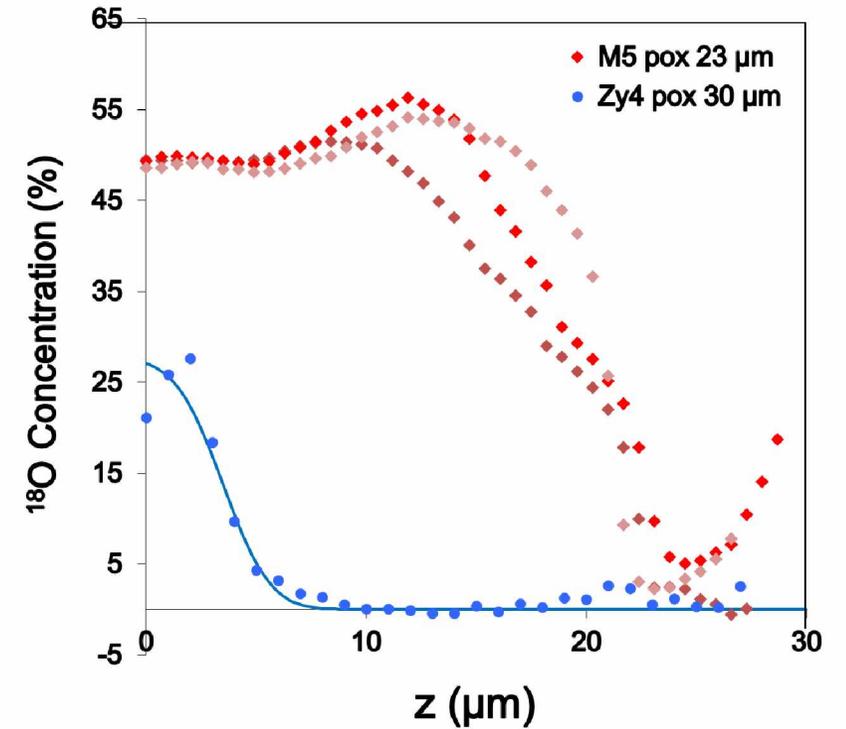
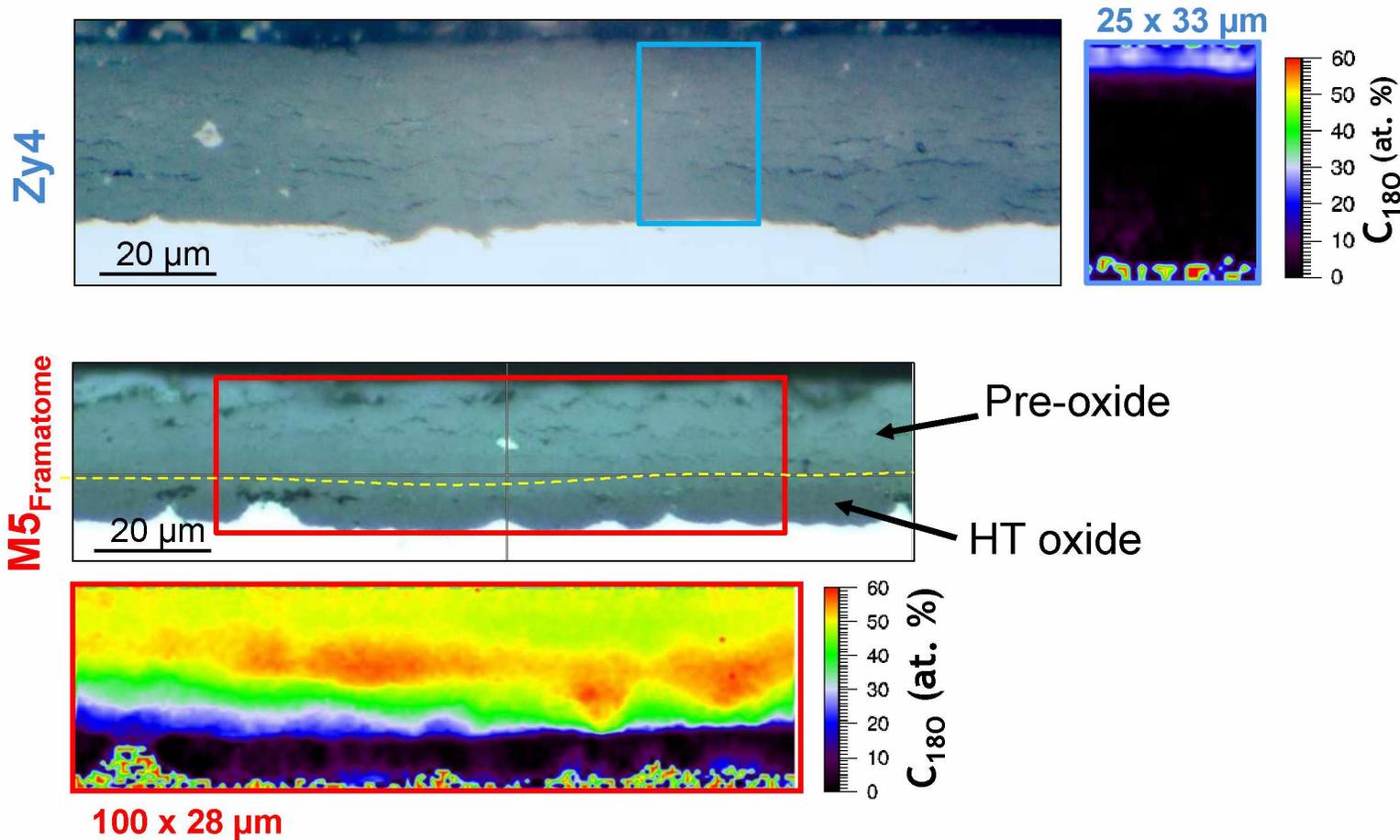
$$C_{18O}(x, t) = C_s \operatorname{erfc} \left(\frac{x + \frac{D_0 \Delta\mu_{ox} t}{RTe}}{2\sqrt{D_{16 \leftrightarrow 18} t}} \right)$$



- Our diffusion coefficients compare well with literature data.
- The pre-oxide scales grown at 425°C behave at 700-950°C as dense, protective scales.

Two-stage experiments: M5™ versus Zy-4

Pre-oxidation at 425°C in $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$, then 60 min at 850°C in $^{18}\text{O}_2$



Pre-oxide formed at 425°C is less protective against HT oxidation for M5_{Framatome} than for Zicaloy-4.

Objective:

Quantify, in mixed air + steam atmospheres, the **respective contributions** of the O_2 and H_2O to the oxidation process.

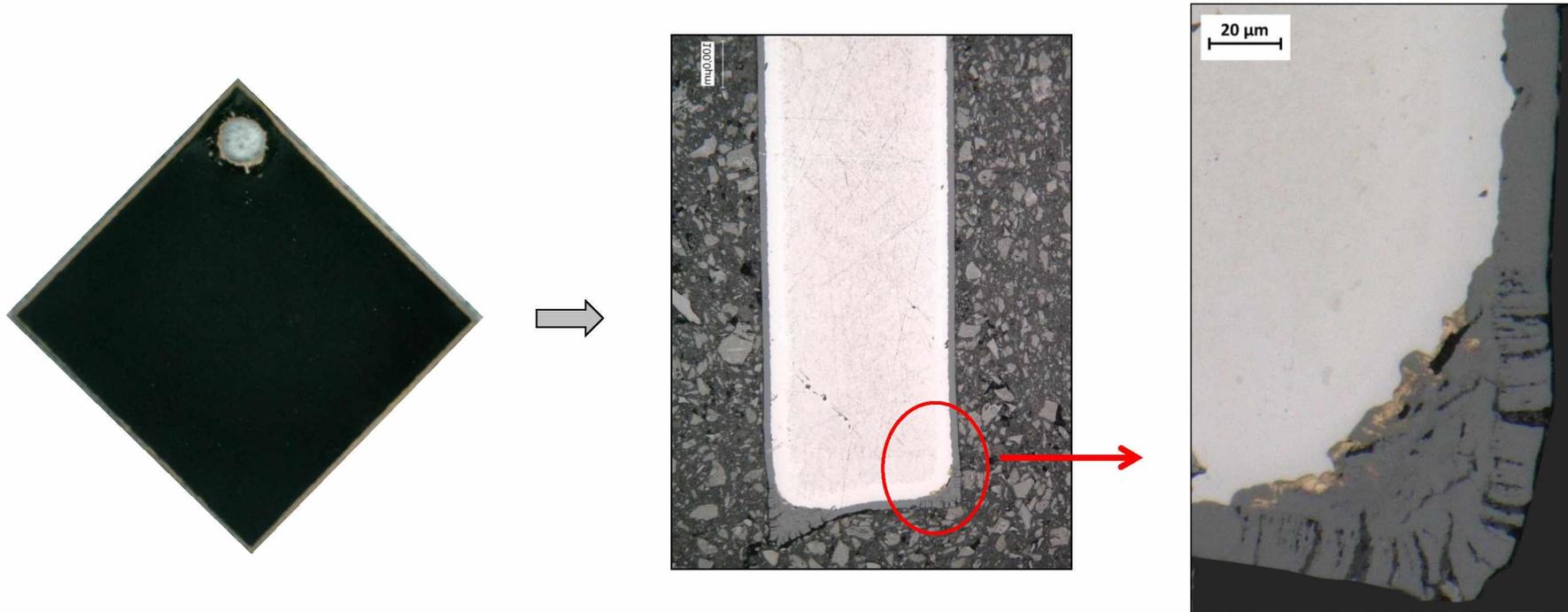


Principle:

1) Bare Zircaloy-4 plates oxidized at HT (700, 850 or 950°C) in flowing $^{18}\text{O}_2 + \text{H}_2^{16}\text{O} + \text{N}_2$ ($P_{^{18}\text{O}_2} / P_{\text{H}_2^{16}\text{O}} = 0.23$ or 0.93)

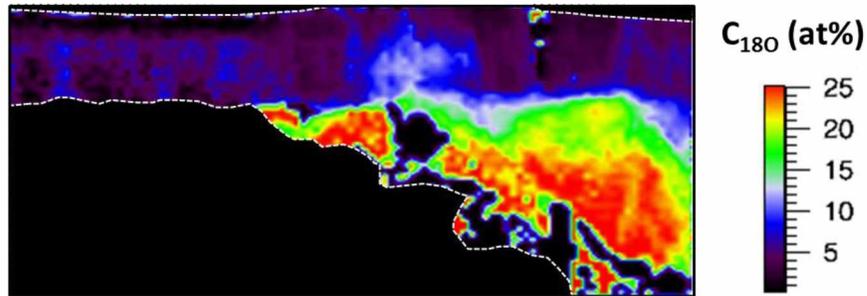
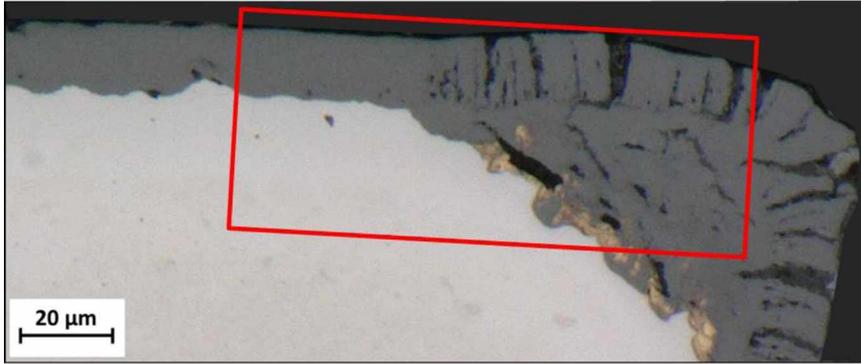
Short duration test to limit $^{18}\text{O}_2$ consumption and isotopic exchanges after oxide formation.

2) Raman mapping at the edges \Rightarrow isotopic composition of pre-BA and post-BA oxides.

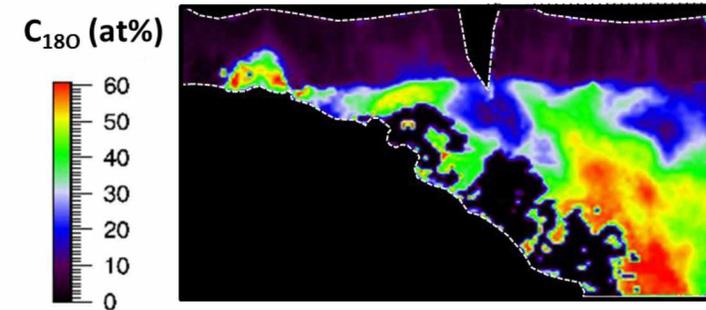
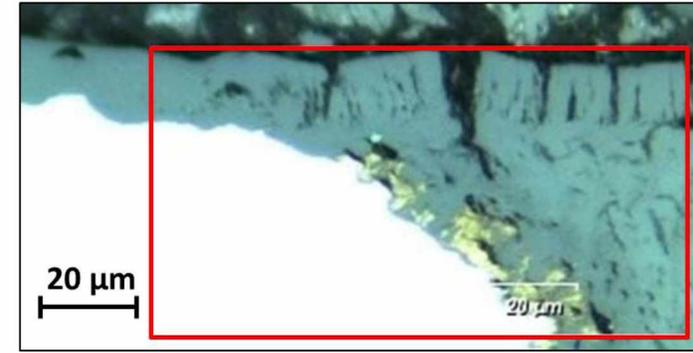


850°C, 60 min

$$P_{^{18}\text{O}_2}/P_{\text{H}_2^{16}\text{O}} = 0.23 \rightarrow ^{18}\text{O}/\text{O}_{\text{tot}} = 0.31$$



$$P_{^{18}\text{O}_2}/P_{\text{H}_2^{16}\text{O}} = 0.93 \rightarrow ^{18}\text{O}/\text{O}_{\text{tot}} = 0.63$$



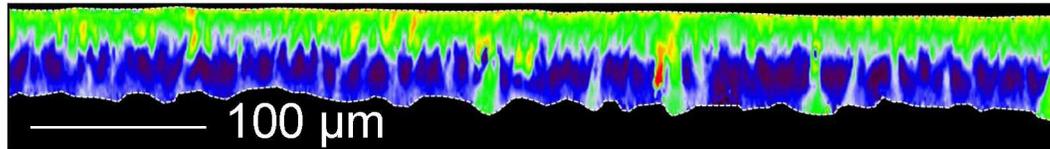
- The dense oxide grown during the diffusion-controlled pre-breakaway regime displays very low ^{18}O content \Rightarrow it forms mainly from H_2O .
- The post-breakaway porous oxide has roughly the same isotopic composition than the gas phase $\Rightarrow \text{H}_2\text{O}$ and O_2 contribute more or less proportionally to their partial pressure.

Two-stage oxidation tests at 850 °C

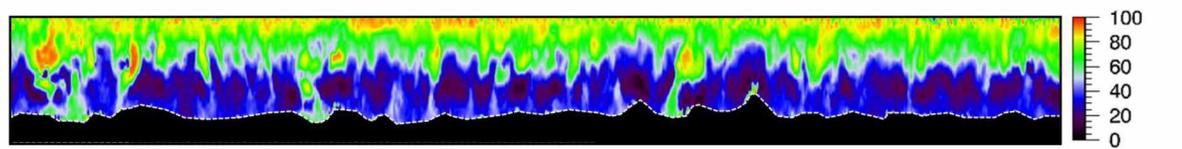
Objective: Compare the diffusion-controlled regime for O₂ atmosphere versus and H₂O atmosphere

Principle: 2-stage oxidation of Zircaloy-4 at 850°C : 1st stage in ¹⁸O₂ (30 min) then second stage in H₂¹⁶O or in ¹⁶O₂ (60 min)

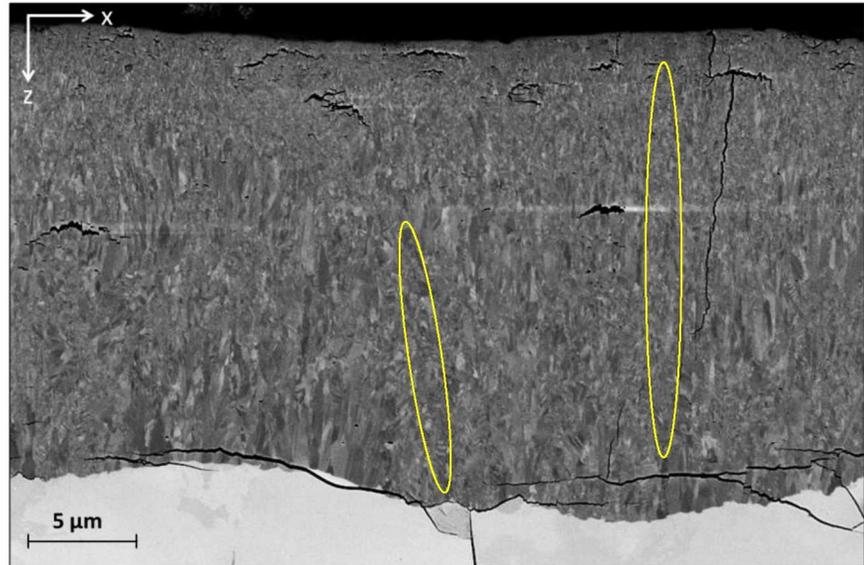
second step in H₂¹⁶O



second step in ¹⁶O₂



BSE-SEM image



- Spatially heterogeneous ¹⁶O distributions
→ Linked to the microstructure (veins of smaller grains)
 - **No significant difference between these two specimens**
→ Same diffusion process for O₂ and H₂O atmospheres.
- ⇒ Selectivity in mixed atmosphere may rather be explained by **competitive adsorption** at the zirconia surface, which favors the H₂O molecules.

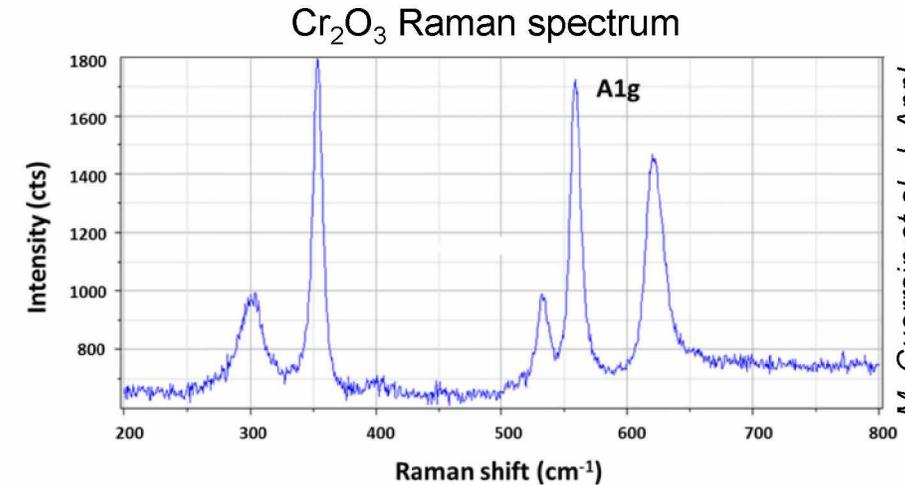
Raman imaging is a powerful tool for mapping thermally grown zirconia layers at μm scale

- ⇒ Phase distribution maps
 - ⇒ Stress distribution maps (not quantitative)
 - ⇒ Sub-stoichiometry
 - ⇒ ^{18}O isotopic distribution maps (quantitative)
- } After cool-down !

May be applied to other systems !

Prospect : Can Raman imaging be a **quantitative tool for local measurement of sub-stoichiometry** ?

Acknowledgments: Part of this work was performed in the frame of the DENOPI project, funded by the French government as part of the “Investment for the Future” Program reference ANR-11-RSNR-0006.



M. Guerrain et al. J. Appl. Phys. 122, 195105 (2017)



Thank you for your attention !