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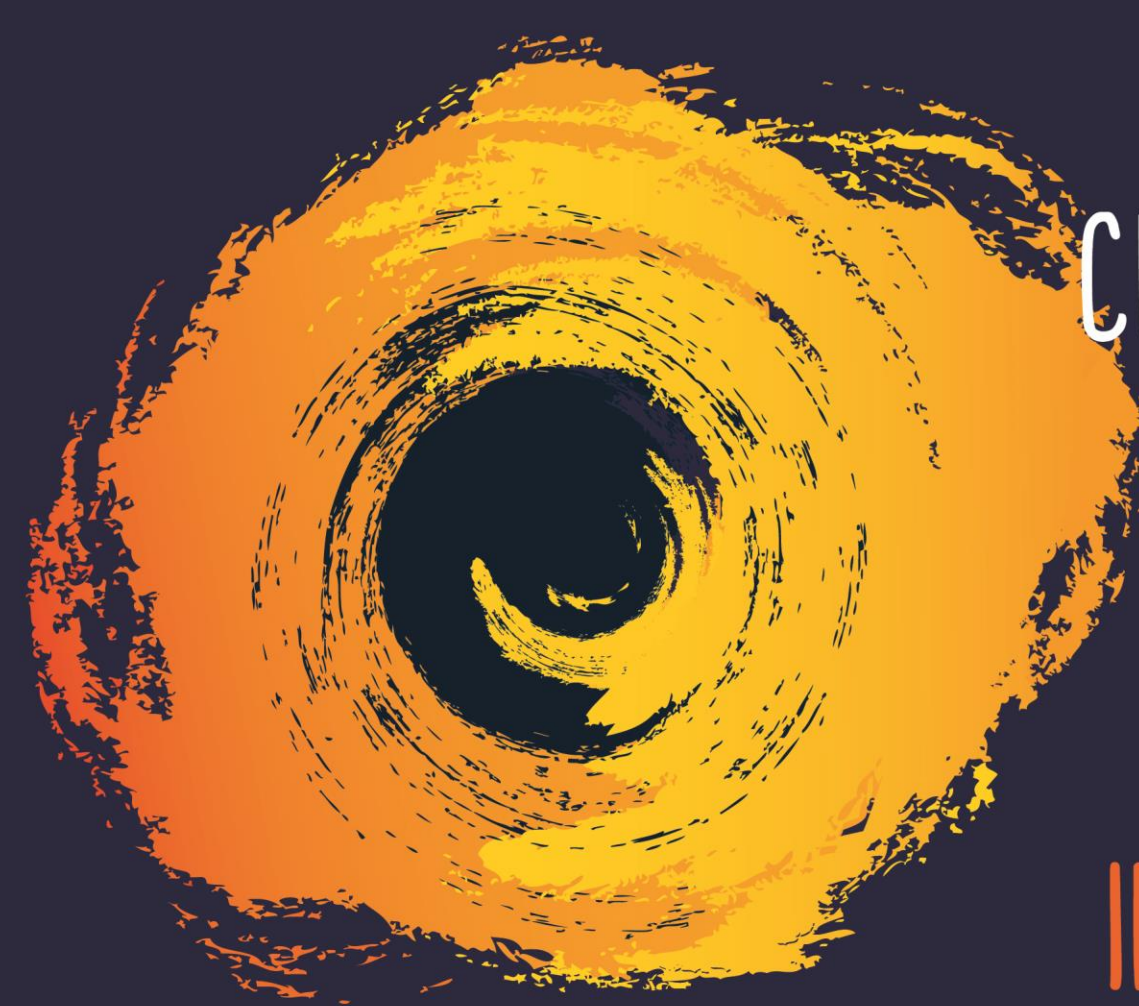
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CHARACTERIZATION OF THE EFFECT OF HEAT ON VEGETABLE TANNED LEATHER

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Introduction

Funded by the LabEx PATRIMA, this project combines the expertise of the CRCC laboratory, in physical chemistry and the ERRMECe laboratory in biology and biochemistry. The research aims to develop a new restoration approach for leather having lost its flexibility as a result of alteration, in particular after exposure to heat. This innovative method relies on the use of biological molecules to respect the nature of the object and preserve its past and future.

Our hypothesis is that exposure to heat causes a protein aggregation. To validate this hypothesis and develop the restoration method, the modifications taking place in the leather structure are examined at different scales.

Samples and artificial heating

Two vegetable (mimosa and sumac) tanned calf leather, prepared during the European STEP Project (1994) were used for the heat ageing trials. The leathers were exposed to dry heat in an oven at 160°C for 4 days to recreate extreme heat conditions caused by a fire [figure 1].

Analytical techniques

- **Thermal-mechanical:** Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Dynamic mechanical analysis (DMA)
- **Physical-chemical:** Contact angle measurement, Scanning electron microscopy (SEM), ATR-FTIR spectroscopy
- **Biochemical:** Protein extraction, Protein assays, Western Blot...

From the analysis of the unheated and artificially heated leathers the aim was to establish correlation between visual and structural modification at various scales.

Results

Heat induces leather browning, loss of mass (~17%), decrease in size (~10% in length and width), and stiffness increase [figure 1].

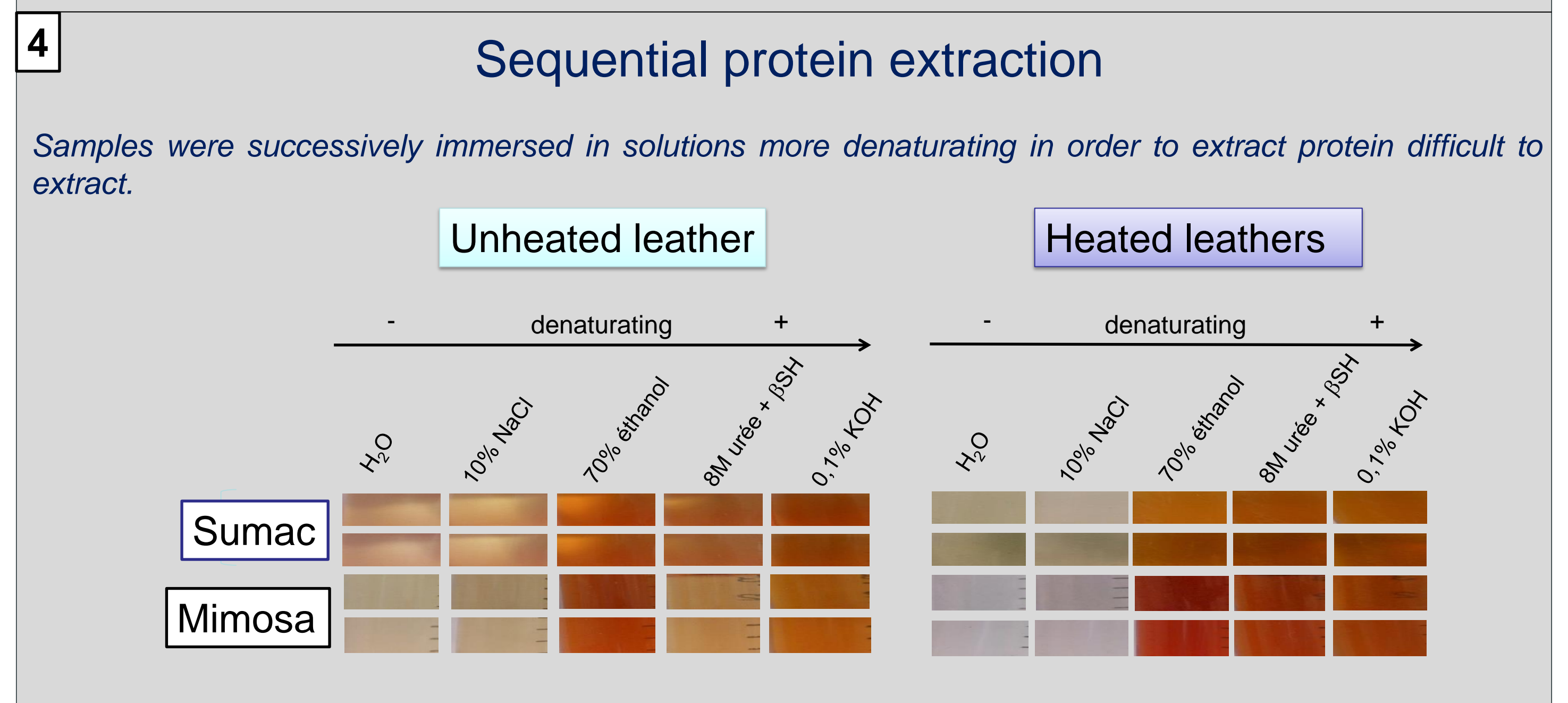
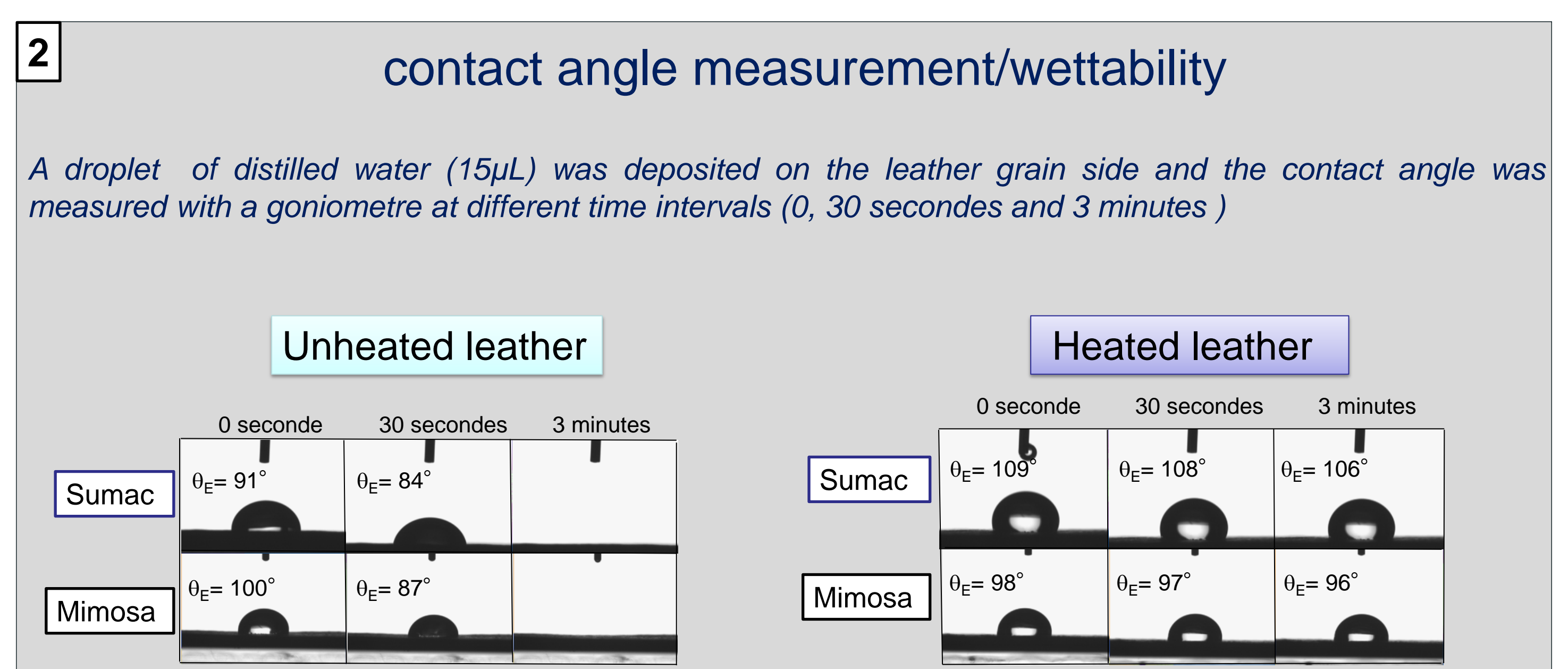
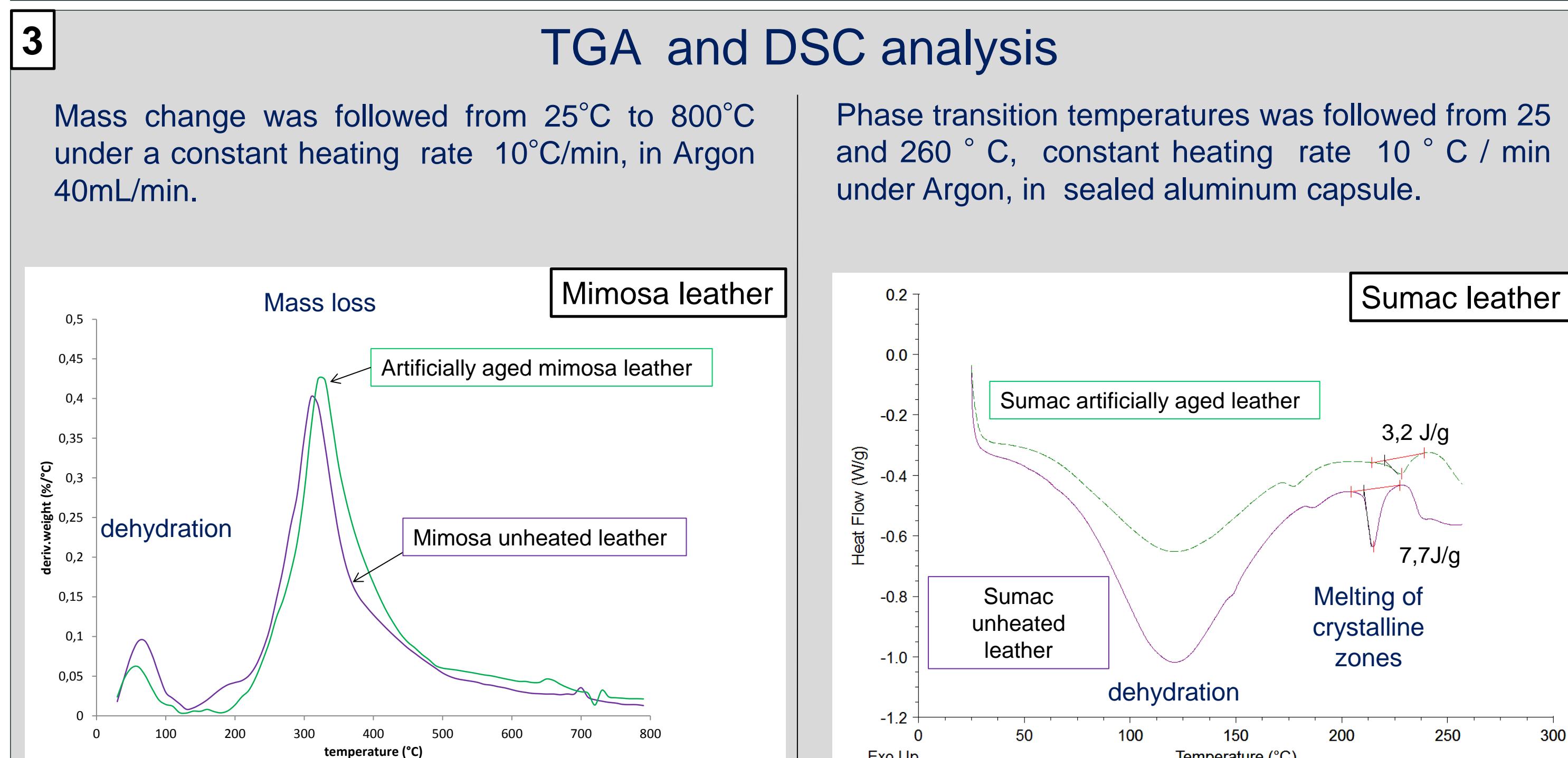
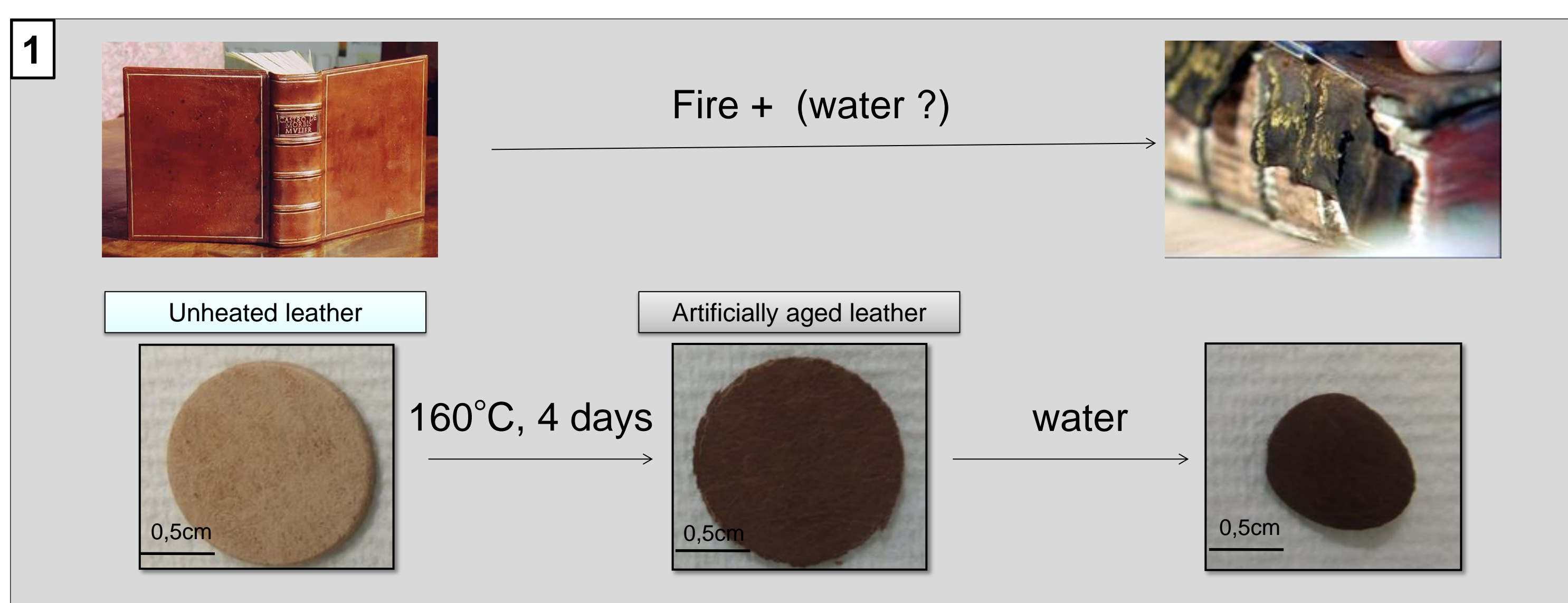
Heat modifies the surface properties of leather as shown by contact angle measurements: going from hydrophobic and wettable for the unheated sample to non wettable after heating [figure 2]. This change could be due to a rearrangement of leather proteins.

Mimosa and sumac leathers display similar TGA profiles for heated and unheated samples [figure 3]. Heat causes a peak shift to higher temperatures which could be due to the melting of crystalline zones as observed in DSC for sumac leather [figure 2 b]. This phenomenon could be correlated to protein aggregation.

Results of sequential protein extraction [figure 4], according to protein assay shows that after heating more denaturing solutions are required to extract proteins from the leather. This validates the protein aggregation hypothesis.

Conclusion

Heat induces similar modifications on sumac- (hydrolysable tannin) and mimosa (condensed tannin) leathers. Oxidation is known to be the main alteration process taking place in leather exposed to heat with degradation of both collagen and tannins. In this project, the combination of physical-chemical and biochemical characterization has evidenced a protein aggregation in leathers as a result of heat exposure. In the view of this new information, biochemical restoration approaches aiming to break the protein aggregates will be developed for heat damaged leather.



[Figure 1] New manuscript website "le fleuron du cuir", Virginie Gallon, picture of a book of the 17th century restored

[Figure 1] Damaged manuscript, le Nouvel Observateur, BibliObs "Weimar: une bibliothèque renaît de ses cendres" Sylvie Prioul, picture of a book exposed to heat during the fire of the Anna-Amalia library (Weimar).