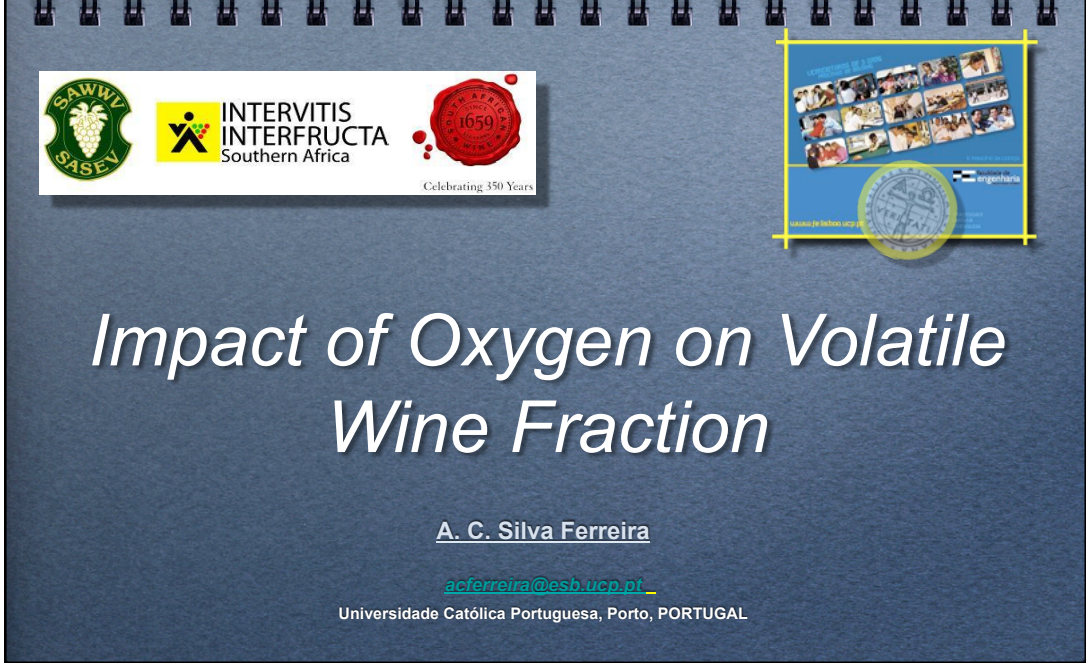

Impact of Oxygen on Volatile Wine Fraction

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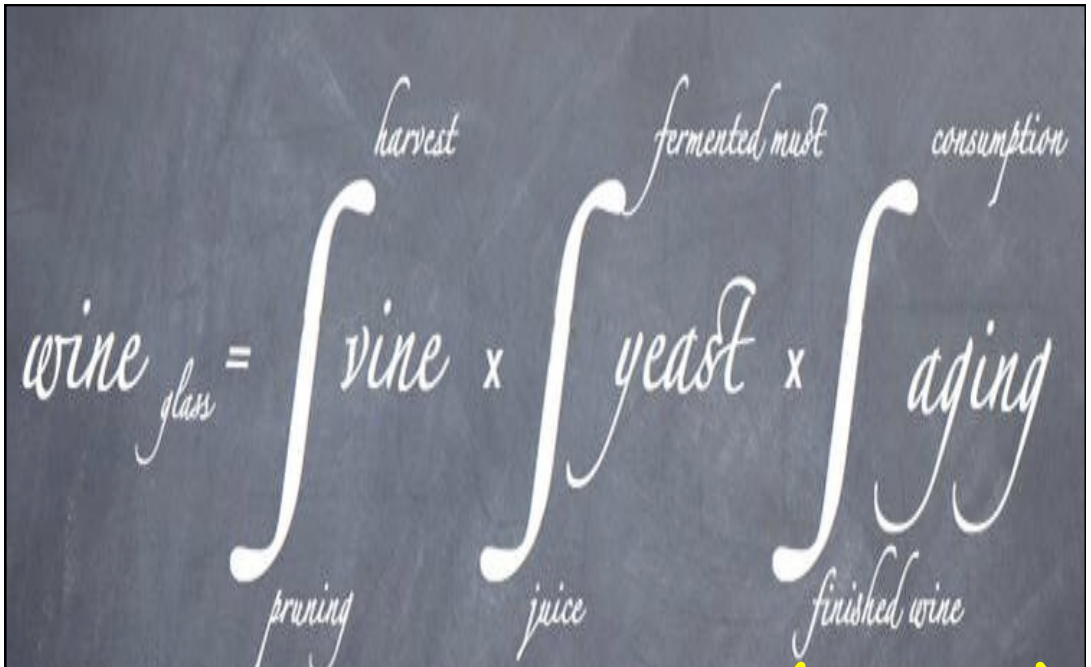
Universidade Católica Portuguesa, Porto, PORTUGAL



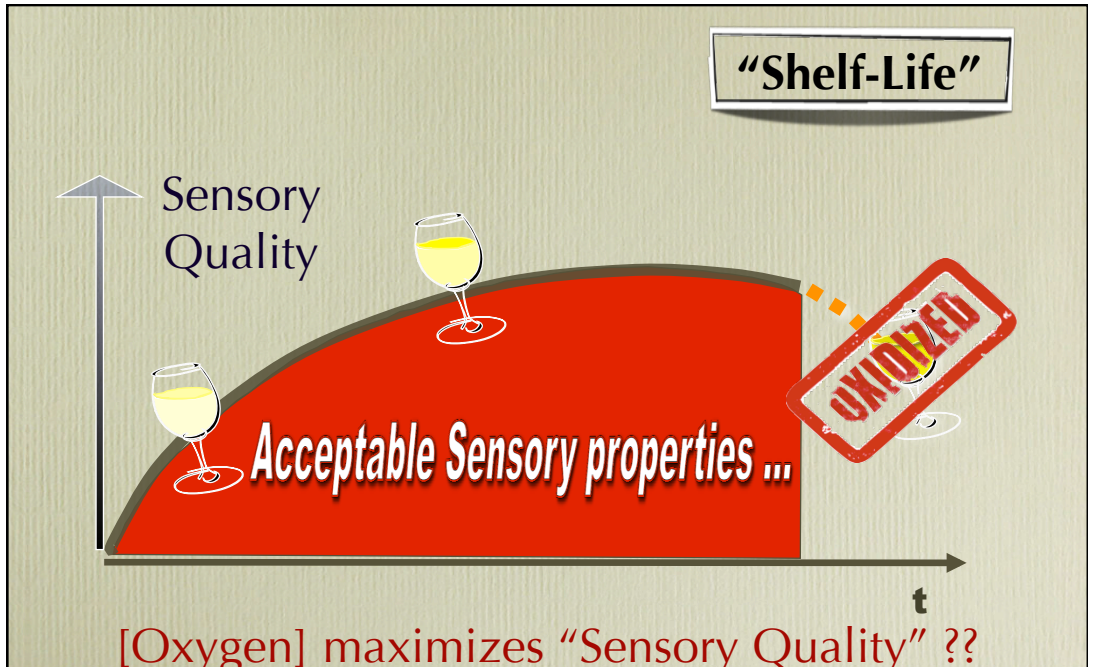
Objectives

Oxygen : A management tool for "Sensory Quality"

i) Applying empirical kinetic models of the key-compounds to monitor the impact of O_2 and Temperature;

ii) Building a "wine feature database" from the target compounds in order to predict/classify the effect of temperature and O_2 using the kinetic models

iii) Highlighting other correlated compounds through a non target approach to allow better understanding of mechanisms "interfaces";

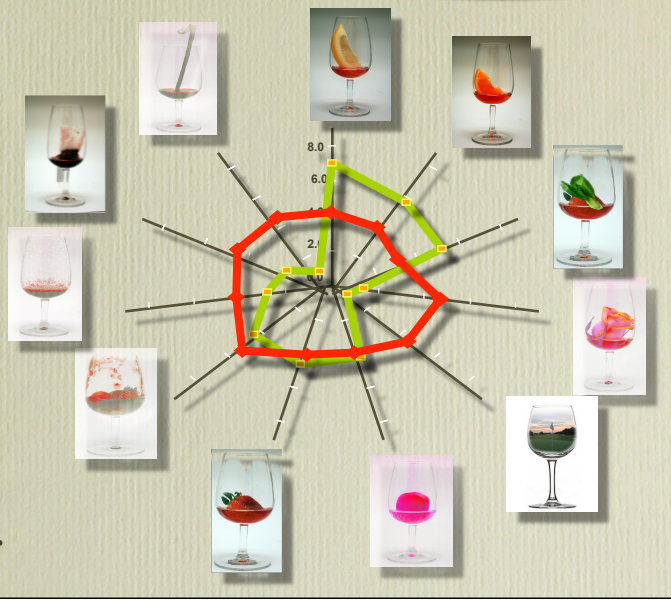


"Brand-Key"

High O_2 levels

Low O_2 levels

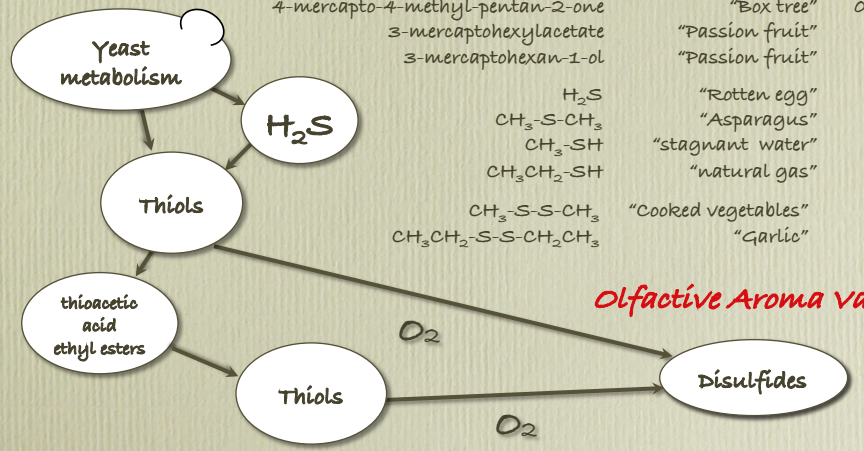
Defining the "Brand Key" Oxygen Dependency ...



"Managing the Paradox Family"

Sauvignon Blanc

Potent Odorants		Sensory Threshold (µg/L)
4-mercapto-4-methyl-pentan-2-one	"Box tree"	0,0008
3-mercaptohexylacetate	"Passion fruit"	0,004
3-mercaptohexan-1-ol	"Passion fruit"	0,060
H_2S	"Rotten egg"	0,5
CH_3-S-CH_3	"Asparagus"	10,0
CH_3-SH	"stagnant water"	1,5
CH_3CH_2-SH	"natural gas"	1,1
CH_3-S-S-CH_3	"Cooked vegetables"	15,0
CH_3CH_2-S-S-CH_2CH_3	"Garlic"	4,3



Olfactive Aroma Value ... ???

Formation of Sulfur compounds during wine making and

"Workflow"

1. Sensory Information

2. Key-Molecules Identification

3. Mechanisms of Formation

4. Kinetic Measurements

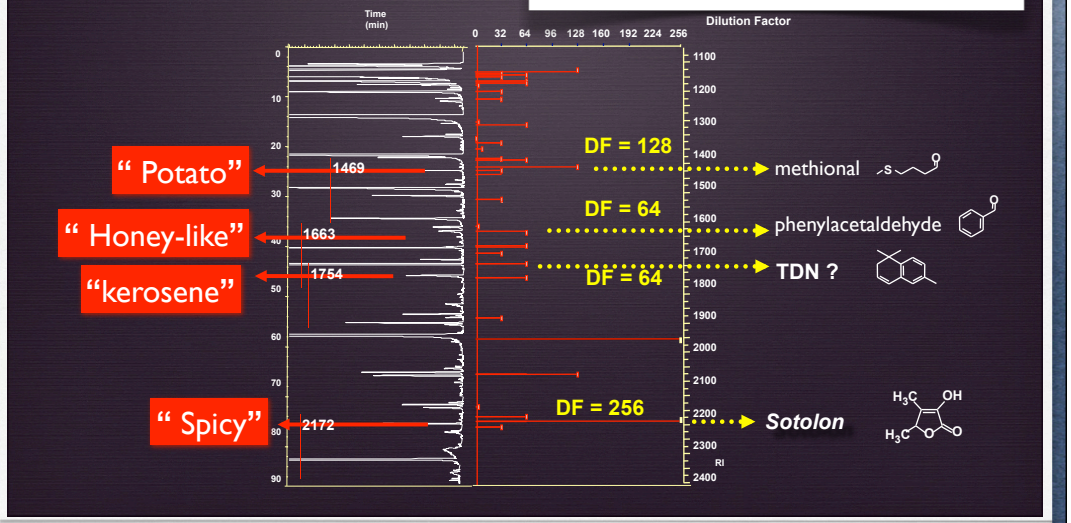
"Correlate Sensory & Chemical Data"

Sensory Analysis

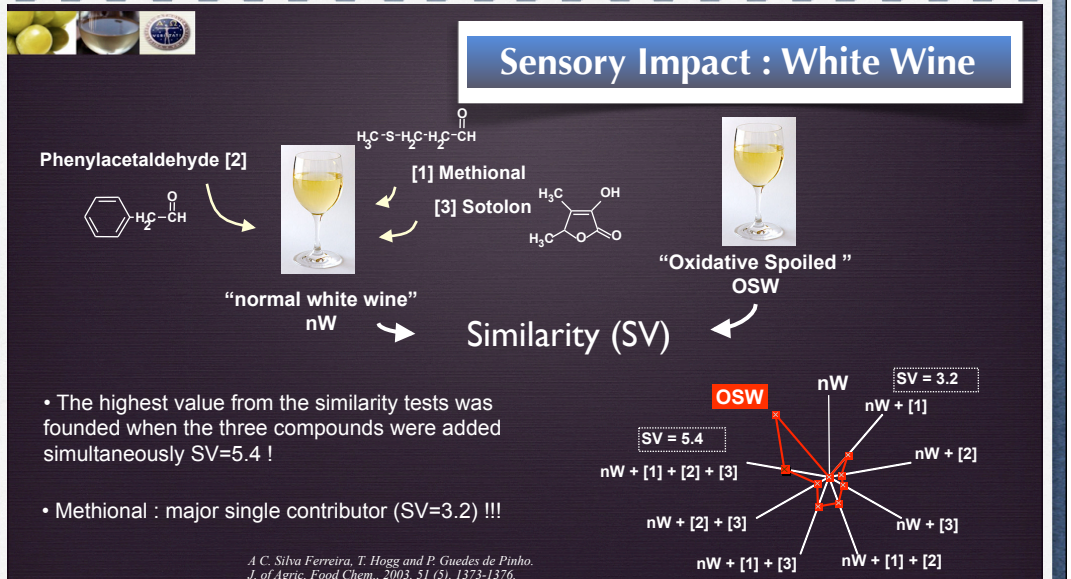
Instrumental Analysis

Hybrid techniques

Ranking "OZ's" : AEDA



Sensory Impact : White Wine



A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho. J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Sensory Impact : Port Wine

4 years Old : "Ruby"
(R) [Sotolon] < 2 μg/L

40 %

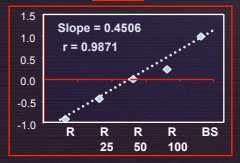
"Blended Sample"
(BS) [Sotolon] =58 μg/L

60%

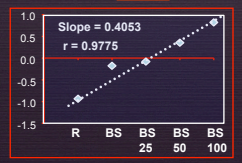
10 years Old : "10 Anos"
(10 Y) [Sotolon] = 91 μg/L

added : NO | added : 25 μg/L | added : 50 μg/L | added : 100 μg/L

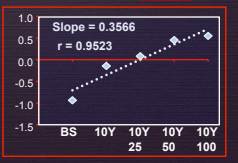
Set 1



Set 2



Set 3



"Perceived as Older ..."

A C. Silva Ferreira, Barbe J.C and Bertrand A.B.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

" Key-Odorants"

Phenylacetaldehyde

Methional

Sotolon

White Wine

***off* - Flavor**

A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Escudero, A.; Hernandez-Orte, P.; Cacho, J. E.; Ferreira, V. J.

Sotolon

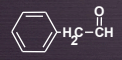
Porto, Sherry Madeira Wines

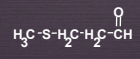
***positive* - Flavor**

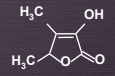
A C. Silva Ferreira, Barbe J.C and Bertrand A.B.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Background: Mechanisms …

Major flavor impact compounds …







Rate of Formation Highly Dependent

Oxygen Levels !!!

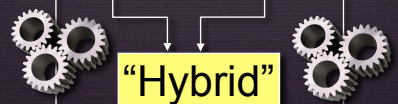
A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho. J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

A C. Silva Ferreira, Barbe J.C and Bertrand A.B. J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Background: Mechanisms …

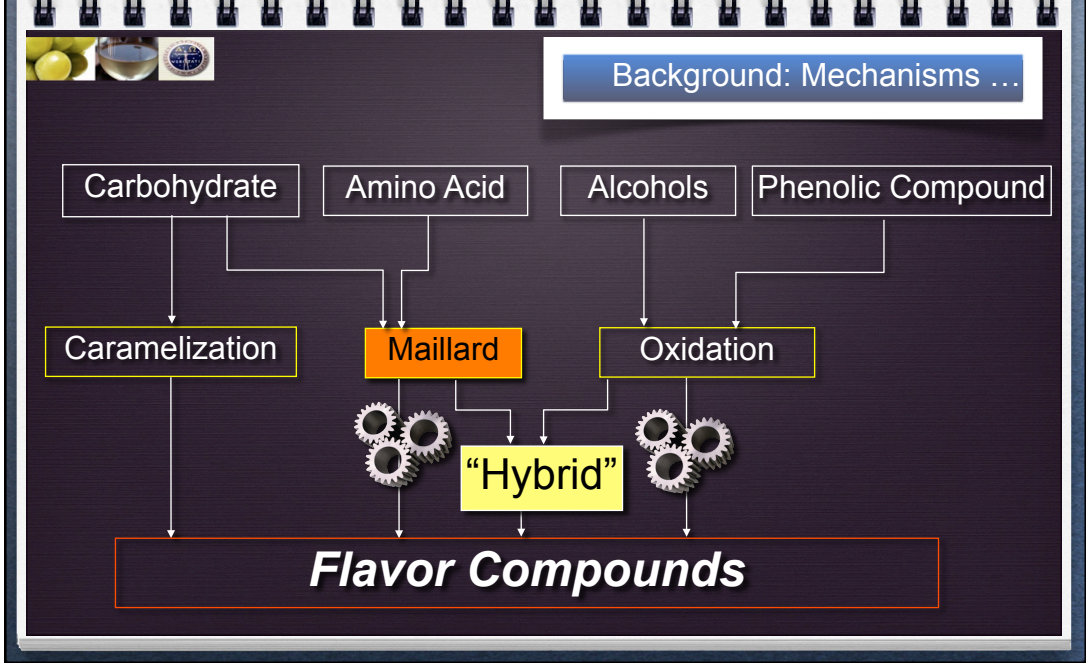
Carbohydrate | Amino Acid | Alcohols | Phenolic Compound

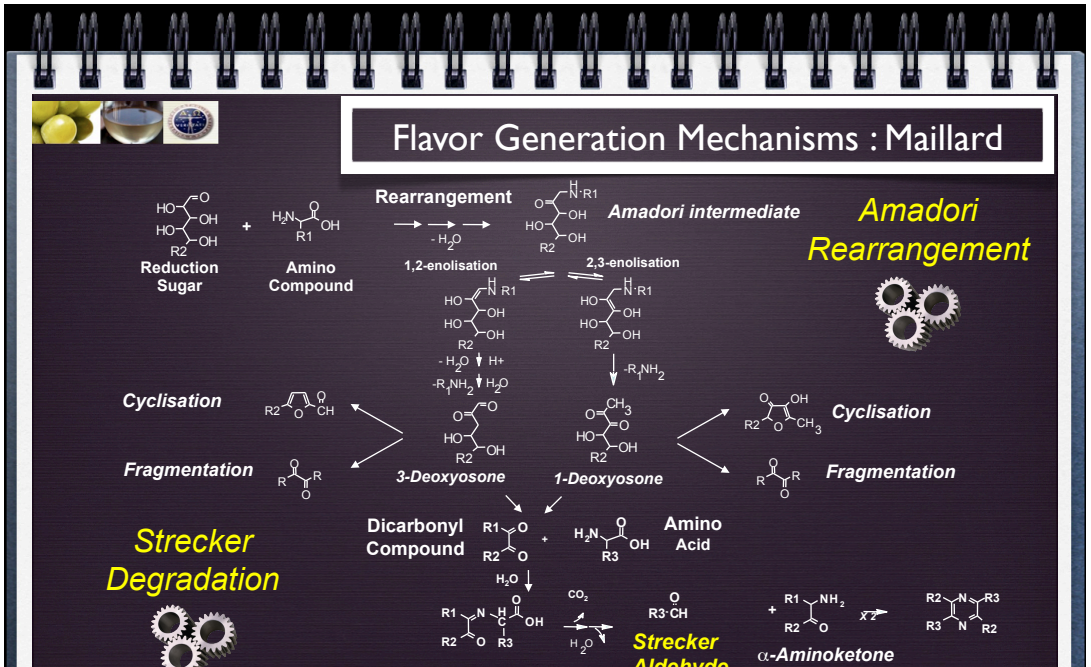
Caramelization | Maillard | Oxidation

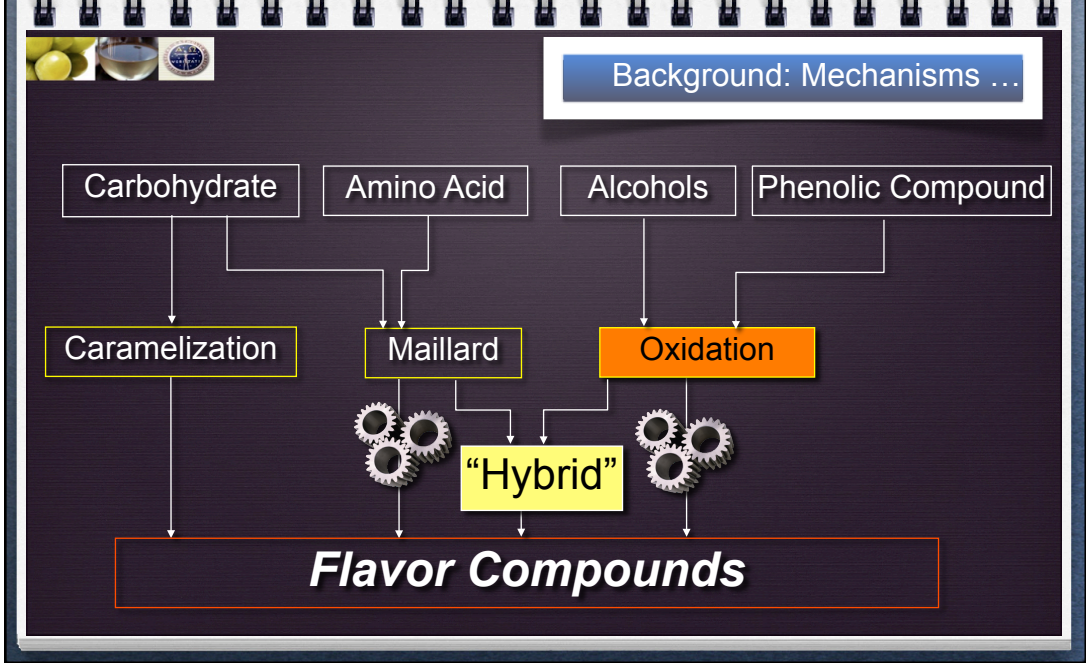


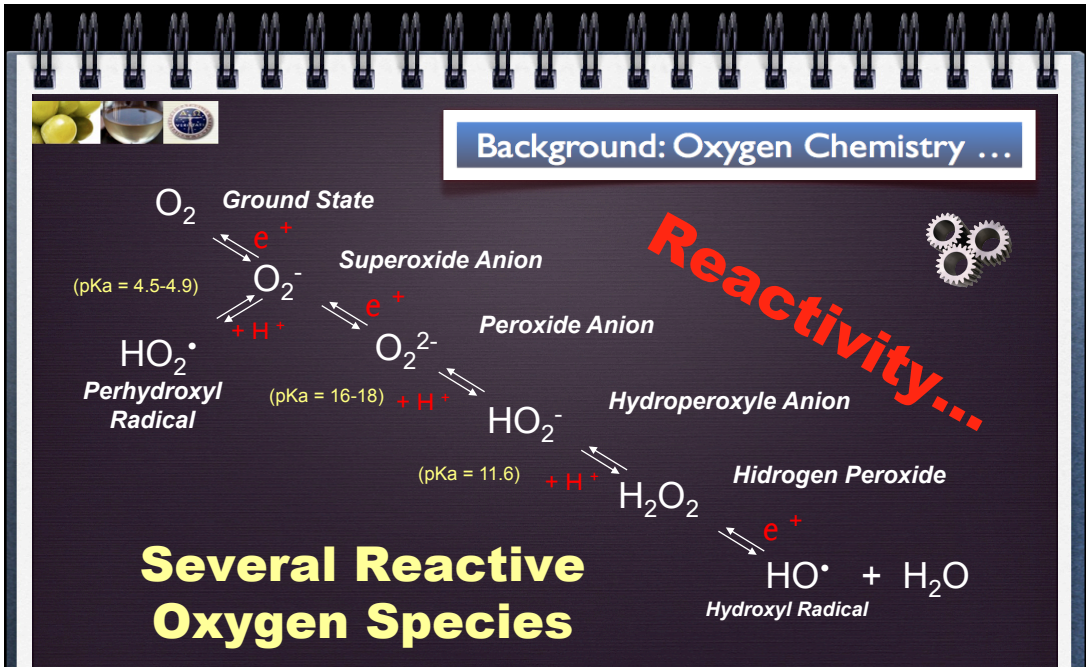
"Hybrid"

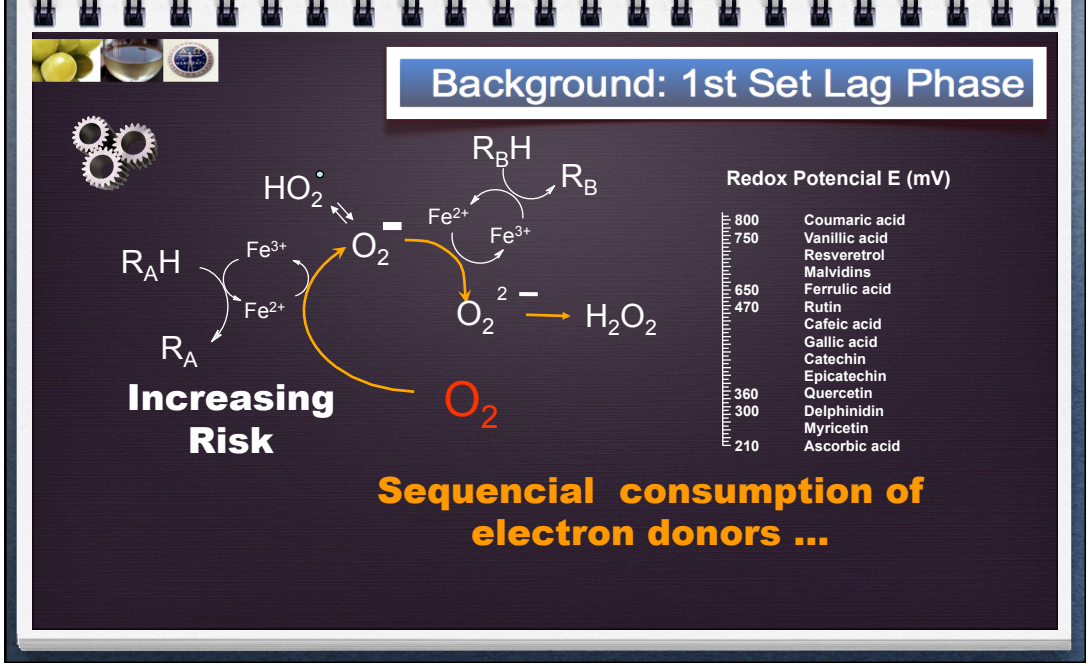
Flavor Compounds

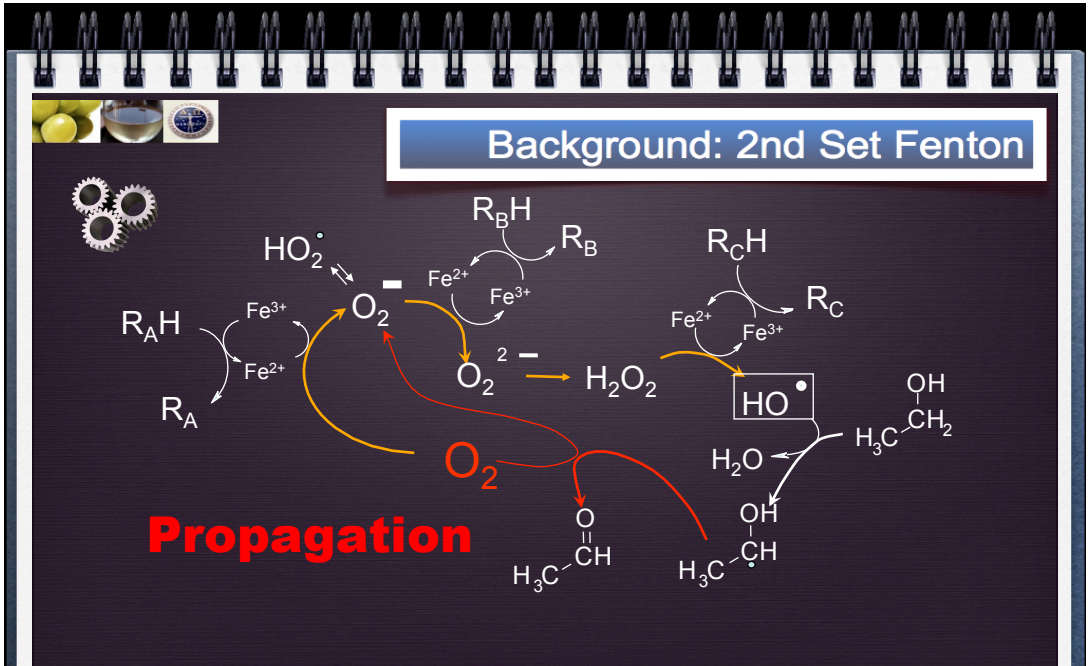

Background: Mechanisms …
Carbohydrate
Amino Acid
Alcohols
Phenolic Compound
Caramelization
Maillard
Oxidation
"Hybrid"
Flavor Compounds


Flavor Generation Mechanisms : Maillard
Reduction Sugar
Amino Compound
Rearrangement
Amadori intermediate
Amadori Rearrangement
1,2-enolisation
2,3-enolisation
Cyclisation
Fragmentation
3-Deoxyosone
1-Deoxyosone
Cyclisation
Fragmentation
Strecker Degradation
Dicarbonyl Compound
Amino Acid
Strecker Aldehyde
α-Aminoketone

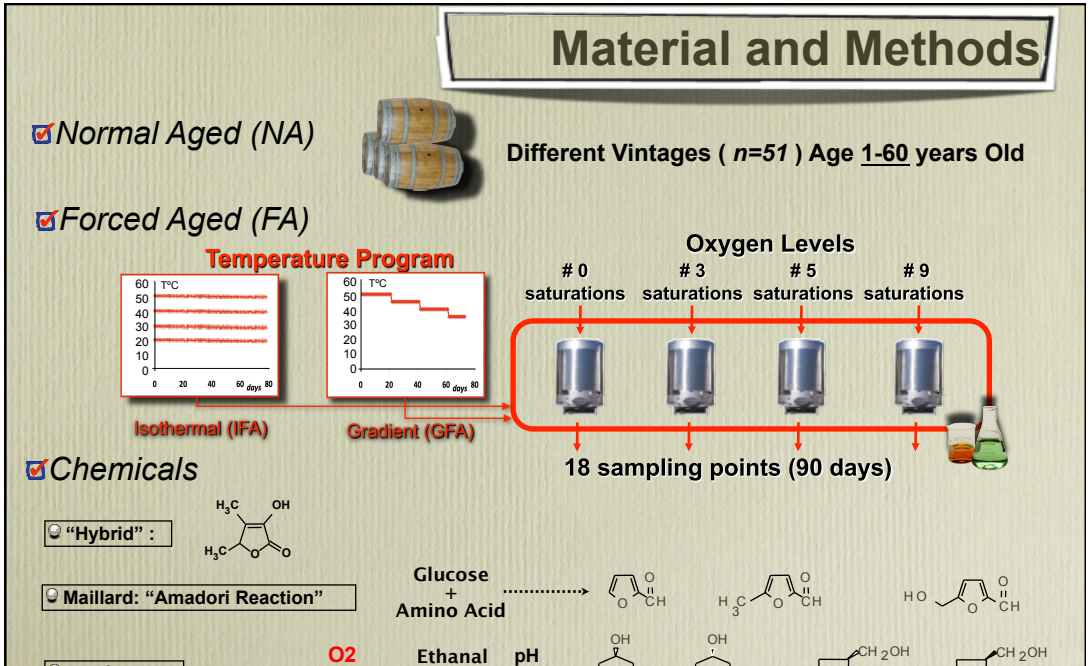

Background: Mechanisms …
Carbohydrate
Amino Acid
Alcohols
Phenolic Compound
Caramelization
Maillard
Oxidation
"Hybrid"
Flavor Compounds

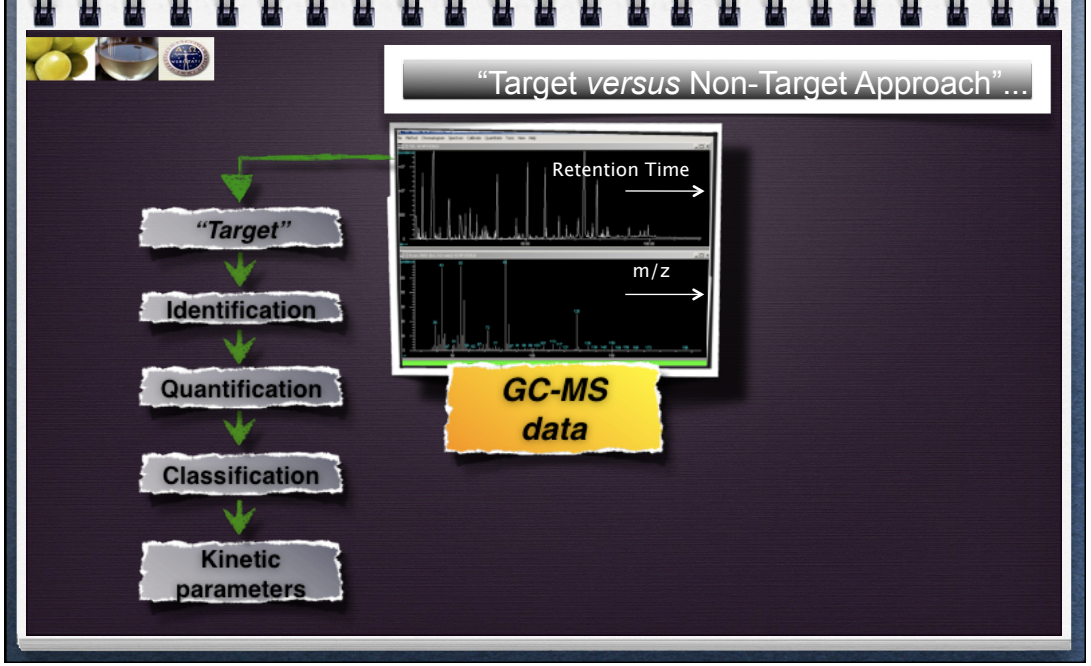

Background: Oxygen Chemistry …
O_2 Ground State
e^+
O_2^- Superoxide Anion
(pKa = 4.5-4.9)
$+ H^+$
$HO_2^\bullet$ Perhydroxyl Radical
e^+
O_2^{2-} Peroxide Anion
(pKa = 16-18) $+ H^+$
HO_2^- Hydroperoxyle Anion
(pKa = 11.6) $+ H^+$
H_2O_2 Hidrogen Peroxide
e^+
$HO^\bullet + H_2O$ Hydroxyl Radical
Reactivity…
Several Reactive Oxygen Species

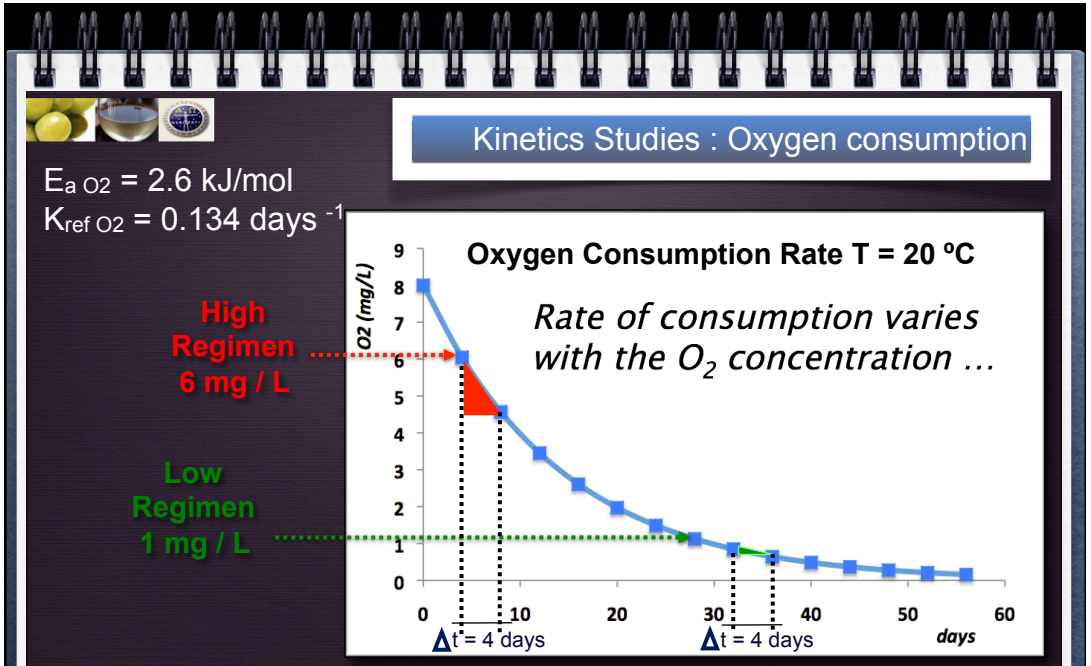

Background: 1st Set Lag Phase
$HO_2^{\bullet}$
$O_2^{\bullet-}$
R_BH
R_B
Fe^{2+}
Fe^{3+}
R_AH
R_A
O_2^{2-}
H_2O_2
O_2
Increasing Risk
Redox Potencial E (mV)
800 Coumaric acid
750 Vanillic acid
Resveretrol
Malvidins
650 Ferrulic acid
470 Rutin
Cafeic acid
Gallic acid
Catechin
Epicatechin
360 Quercetin
300 Delphinidin
Myricetin
210 Ascorbic acid
Sequencial consumption of electron donors ...


Background: 2nd Set Fenton
$HO_2^{\bullet}$
$O_2^{\bullet-}$
R_BH
R_B
R_CH
R_C
Fe^{2+}
Fe^{3+}
R_AH
R_A
O_2^{2-}
H_2O_2
HO•
H_2O
O_2
Propagation


?
?
Antioxidants
Dissolved


Material and Methods
Normal Aged (NA)
Different Vintages (n=51) Age 1-60 years Old
Forced Aged (FA)
Temperature Program
Oxygen Levels
0 saturations
3 saturations
5 saturations
9 saturations
Isothermal (IFA)
Gradient (GFA)
18 sampling points (90 days)
Chemicals
"Hybrid" :
Maillard: "Amadori Reaction"
Glucose + Amino Acid
O2
Ethanal
pH

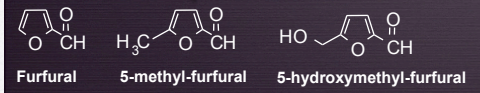

"Target *versus* Non-Target Approach"...
"Target"
Identification
Quantification
Classification
Kinetic parameters
Retention Time
m/z
GC-MS data


Kinetics Studies : Oxygen consumption
$E_{a\ O2}$ = 2.6 kJ/mol
$K_{ref\ O2}$ = 0.134 days $^{-1}$
High Regimen 6 mg / L
Low Regimen 1 mg / L
Oxygen Consumption Rate T = 20 ºC
Rate of consumption varies with the O_2 concentration ...
O2 (mg/L)
days
Δt = 4 days
Δt = 4 days

Kinetics Studies : Furfurals & Acetals

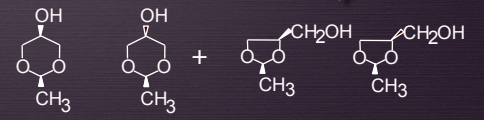
Maillard : Amadori Reaction

Glucose + Amino Acid



Oxidation

Ethanol $\xrightarrow{O_2}$ Ethanal + Glycerol $\xrightarrow{pH}$



$$C(t) = C_{eq} - (C_{eq} - C_0)\, e^{-\int_0^t k_{app} dt}$$

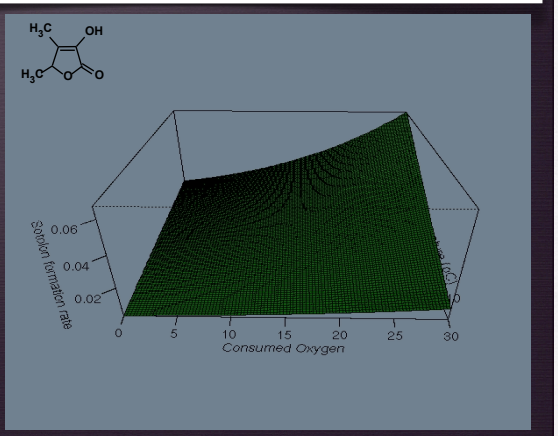
Ea; k - First Order reversible with Temperature

$E_{a\ furfural}$ = 143.1 kJ/mol
$K_{ref\ furfural}$ = 0.0009 days $^{-1}$

$E_{a\ dioxane}$ = 32.5 kJ/mol
$K_{ref\ dioxane}$ = 0.0011 days $^{-1}$

Kinetics Studies : Sotolon Rate of Formation

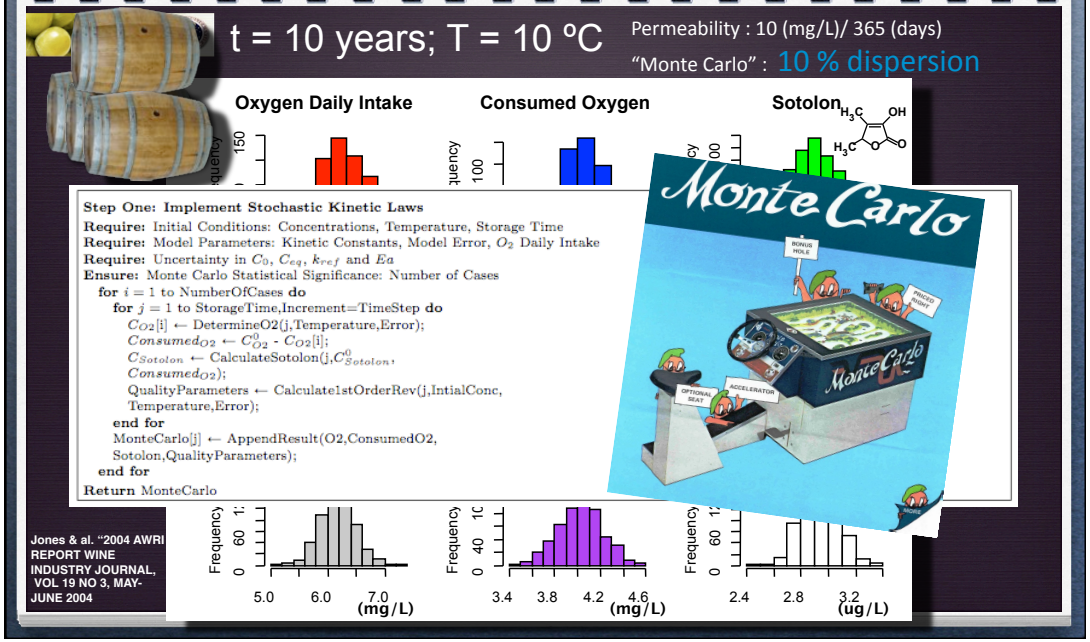
$$r_{Sot} = C_{O_2}^{Cons} \cdot k_{ref}^{Sot} \cdot \exp\left[\frac{E_a^{Sot}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

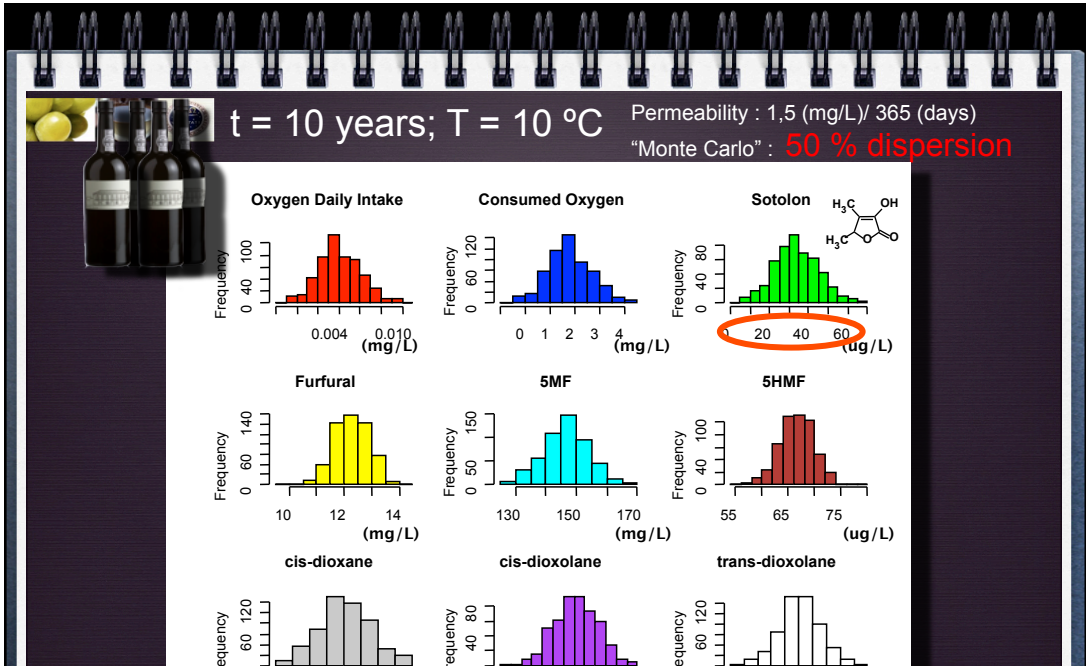


$E_{a\ sot}$ = 38 kJ/mol
$K_{ref\ sot}$ = 0.012 days $^{-1}$

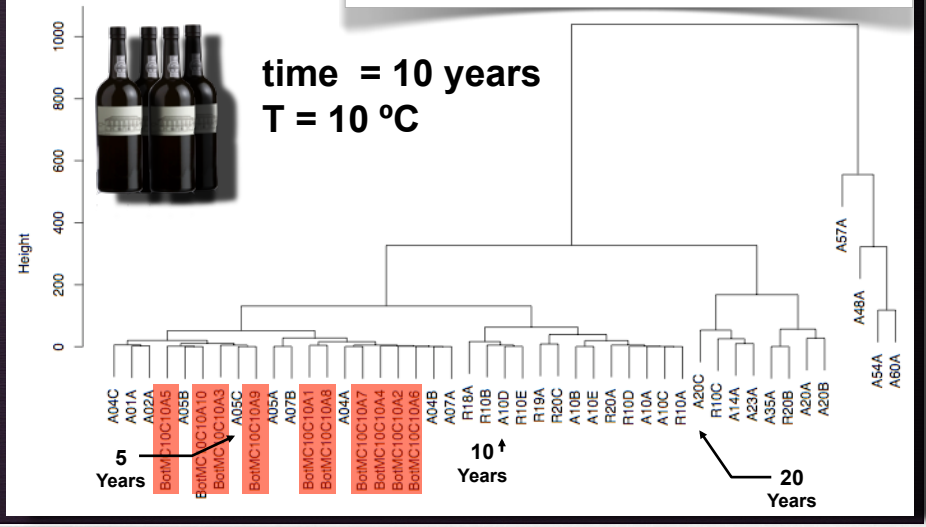
Sotolon Rate of Formation

- directly proportional to oxygen consumption rate;


t = 10 years; T = 10 ºC
Permeability : 10 (mg/L)/ 365 (days)
"Monte Carlo" : 10 % dispersion
Oxygen Daily Intake
Consumed Oxygen
Sotolon
Step One: Implement Stochastic Kinetic Laws
Require: Initial Conditions: Concentrations, Temperature, Storage Time
Require: Model Parameters: Kinetic Constants, Model Error, O_2 Daily Intake
Require: Uncertainty in C_0, C_{eq}, k_{ref} and Ea
Ensure: Monte Carlo Statistical Significance: Number of Cases
for $i = 1$ to NumberOfCases do
for $j = 1$ to StorageTime,Increment=TimeStep do
C_{O2}[i] ← DetermineO2(j,Temperature,Error);
$Consumed_{O2} \leftarrow C^0_{O2}$ - C_{O2}[i];
$C_{Sotolon}$ ← CalculateSotolon(j,$C^0_{Sotolon}$, $Consumed_{O2}$);
QualityParameters ← Calculate1stOrderRev(j,IntialConc, Temperature,Error);
end for
MonteCarlo[j] ← AppendResult(O2,ConsumedO2, Sotolon,QualityParameters);
end for
Return MonteCarlo
Monte Carlo
Jones & al. "2004 AWRI REPORT WINE INDUSTRY JOURNAL, VOL 19 NO 3, MAY-JUNE 2004
Frequency
(mg/L)
(ug/L)

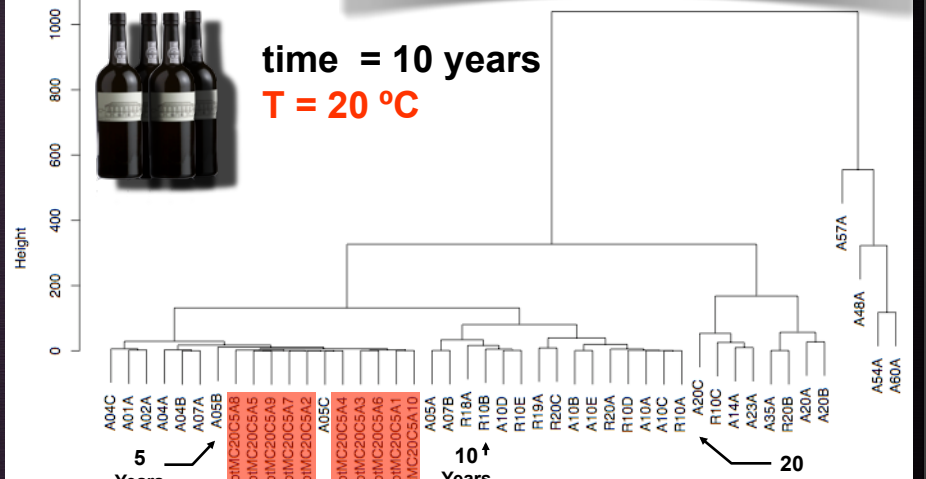

t = 10 years; T = 10 ºC
Permeability : 1,5 (mg/L)/ 365 (days)
"Monte Carlo" : 50 % dispersion
Oxygen Daily Intake
Consumed Oxygen
Sotolon
Furfural
5MF
5HMF
cis-dioxane
cis-dioxolane
trans-dioxolane
Frequency
(mg/L)
(ug/L)

“Clustering” : 10 years “Vintage”

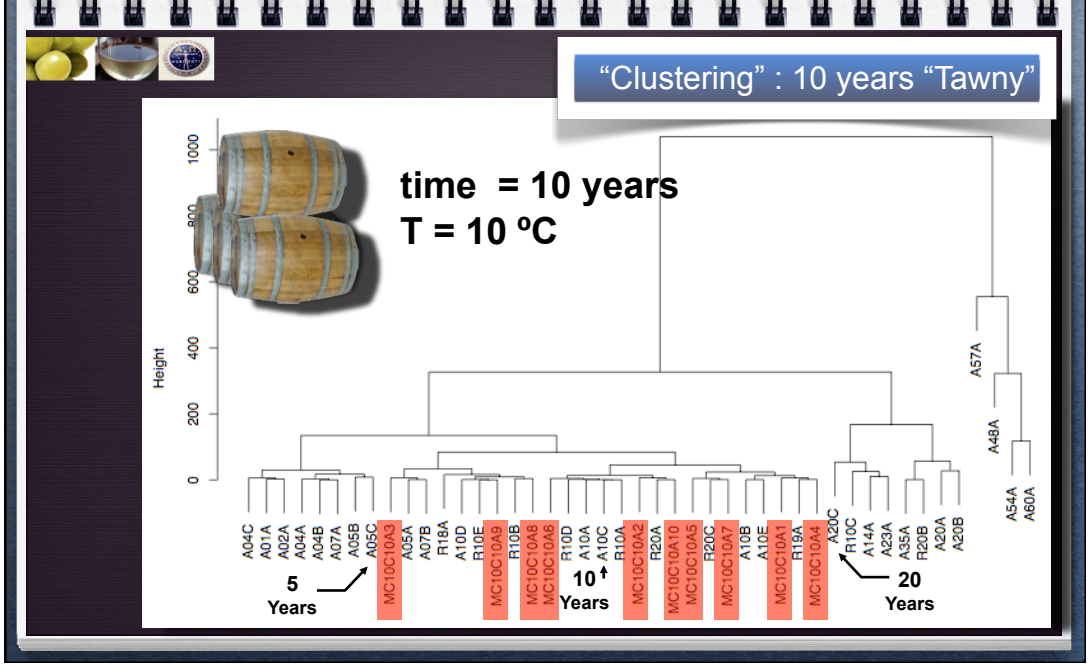


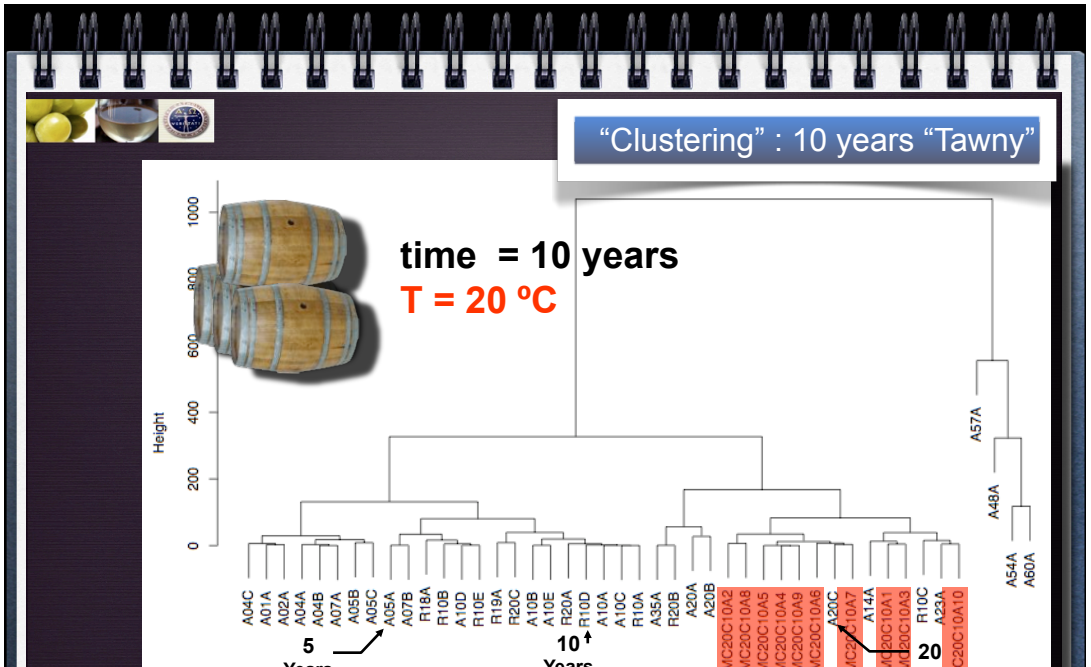
time = 10 years
T = 10 ºC

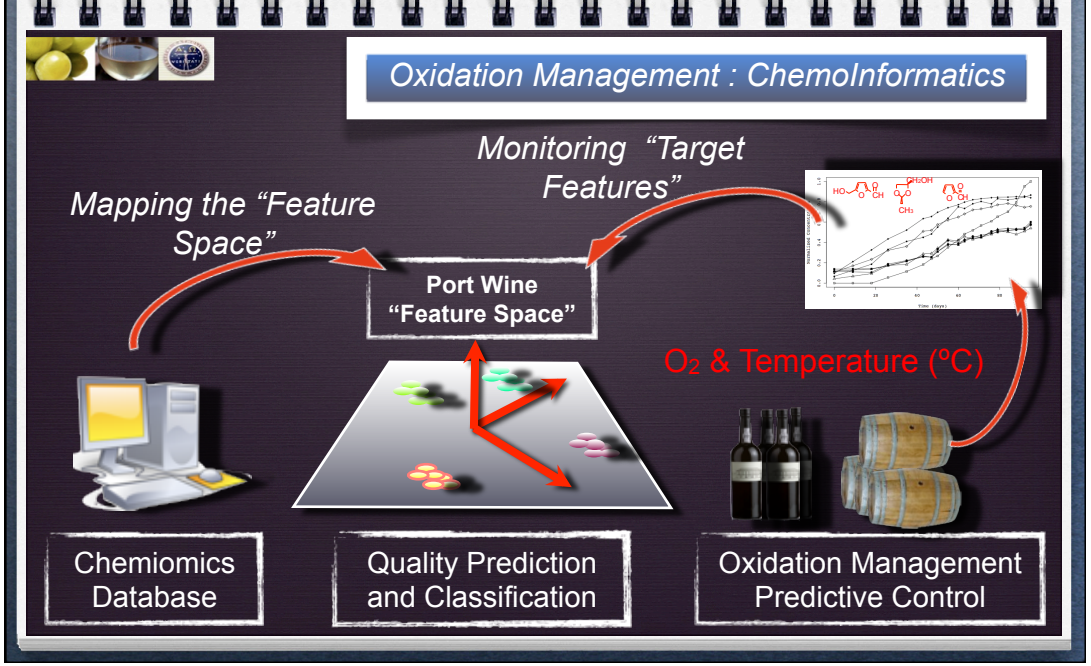
“Clustering” : 10 years “Vintage”

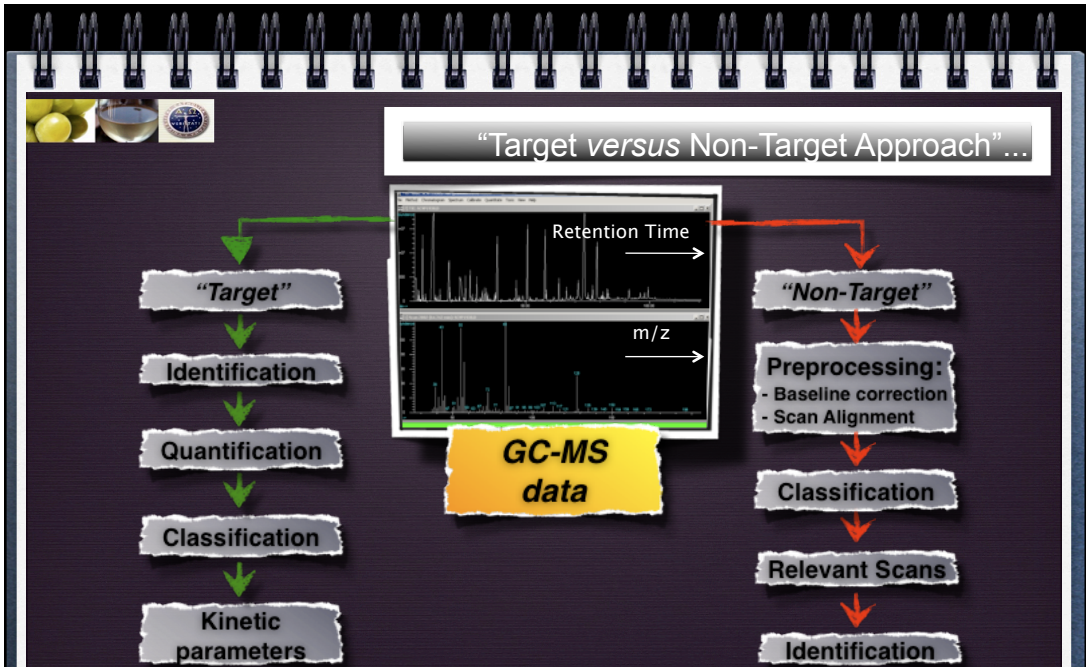


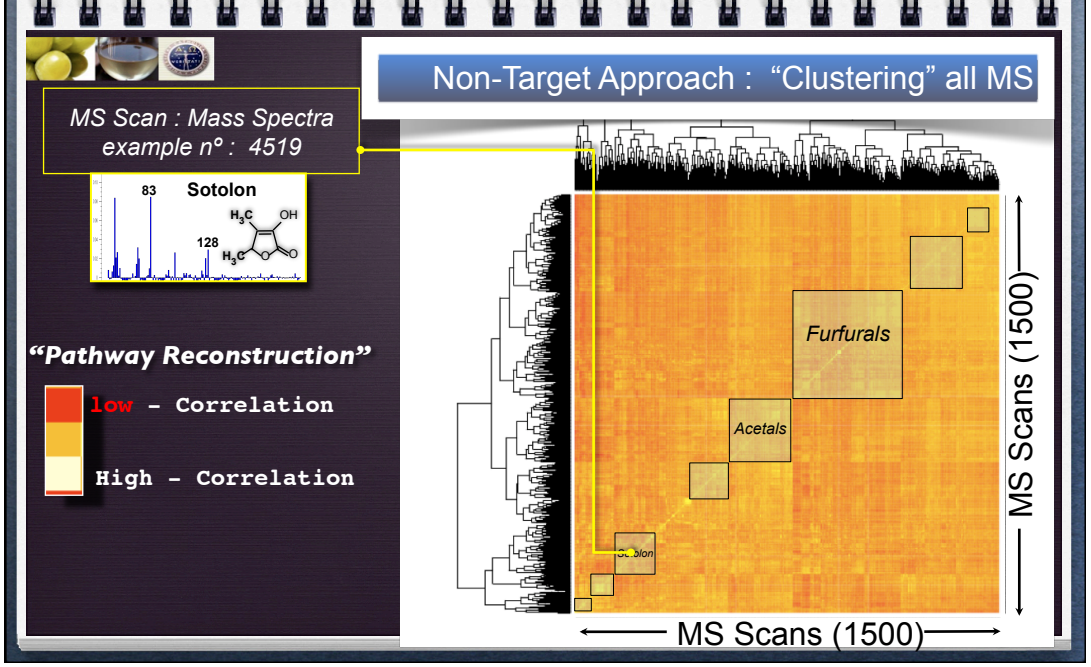
time = 10 years
T = 20 ºC

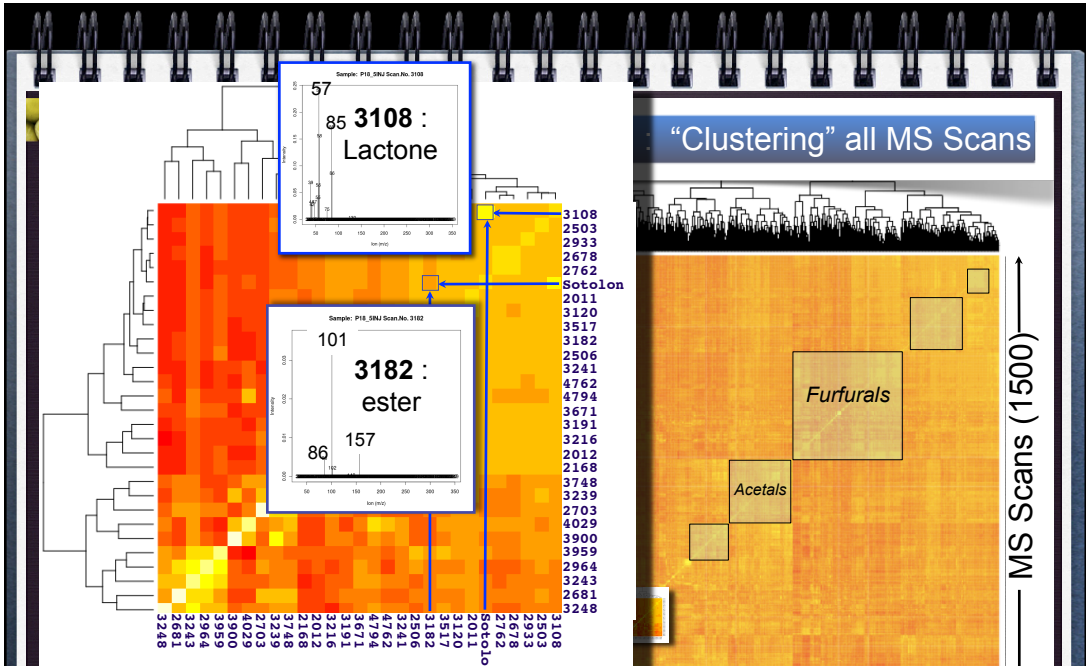

"Clustering" : 10 years "Tawny"
time = 10 years
T = 10 ºC
Height
0
200
400
600
800
1000
5 Years
10 Years
20 Years

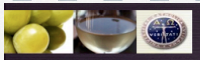

"Clustering" : 10 years "Tawny"
time = 10 years
T = 20 ºC
Height
0
200
400
600
800
1000
5
10
20


Oxidation Management : ChemoInformatics
Monitoring "Target Features"
Mapping the "Feature Space"
Port Wine "Feature Space"
O2 & Temperature (ºC)
Chemiomics Database
Quality Prediction and Classification
Oxidation Management Predictive Control


"Target versus Non-Target Approach"...
Retention Time
m/z
GC-MS data
"Target"
Identification
Quantification
Classification
Kinetic parameters
"Non-Target"
Preprocessing:
- Baseline correction
- Scan Alignment
Classification
Relevant Scans
Identification


Non-Target Approach : "Clustering" all MS
MS Scan : Mass Spectra
example nº : 4519
83
Sotolon
128
"Pathway Reconstruction"
low - Correlation
High - Correlation
Furfurals
Acetals
MS Scans (1500)
MS Scans (1500)


57
85
3108 :
Lactone
101
3182 :
ester
86
157
3108
2503
2933
2678
2762
Sotolon
2011
3120
3517
3182
2506
3241
4762
4794
3671
3191
3216
2012
2168
3748
3239
2703
4029
3900
3959
2964
3243
2681
3248
"Clustering" all MS Scans
Furfurals
Acetals
MS Scans (1500)
MS Scans (1500)



Conclusions

In order to optimize “Sensory Quality” three conditions must be addressed :

1. “Brand Key” Oxygen dependence;

2. Kinetic studies are indispensables to establish temporal relationships between wine constituents and infer the chemical network of reactions - the “chemiomics”.

3. Oxygen regimes of the container need to be provided.

Appling high-throughput data mining methodologies will allow the understanding of the complexity of wine aging : i) identifying the compounds; ii) their reaction network; iii) kinetics and thermodynamics.