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The Utilisation of Solid Carbon Dioxide in the Extraction of Extravirgin Olive Oil

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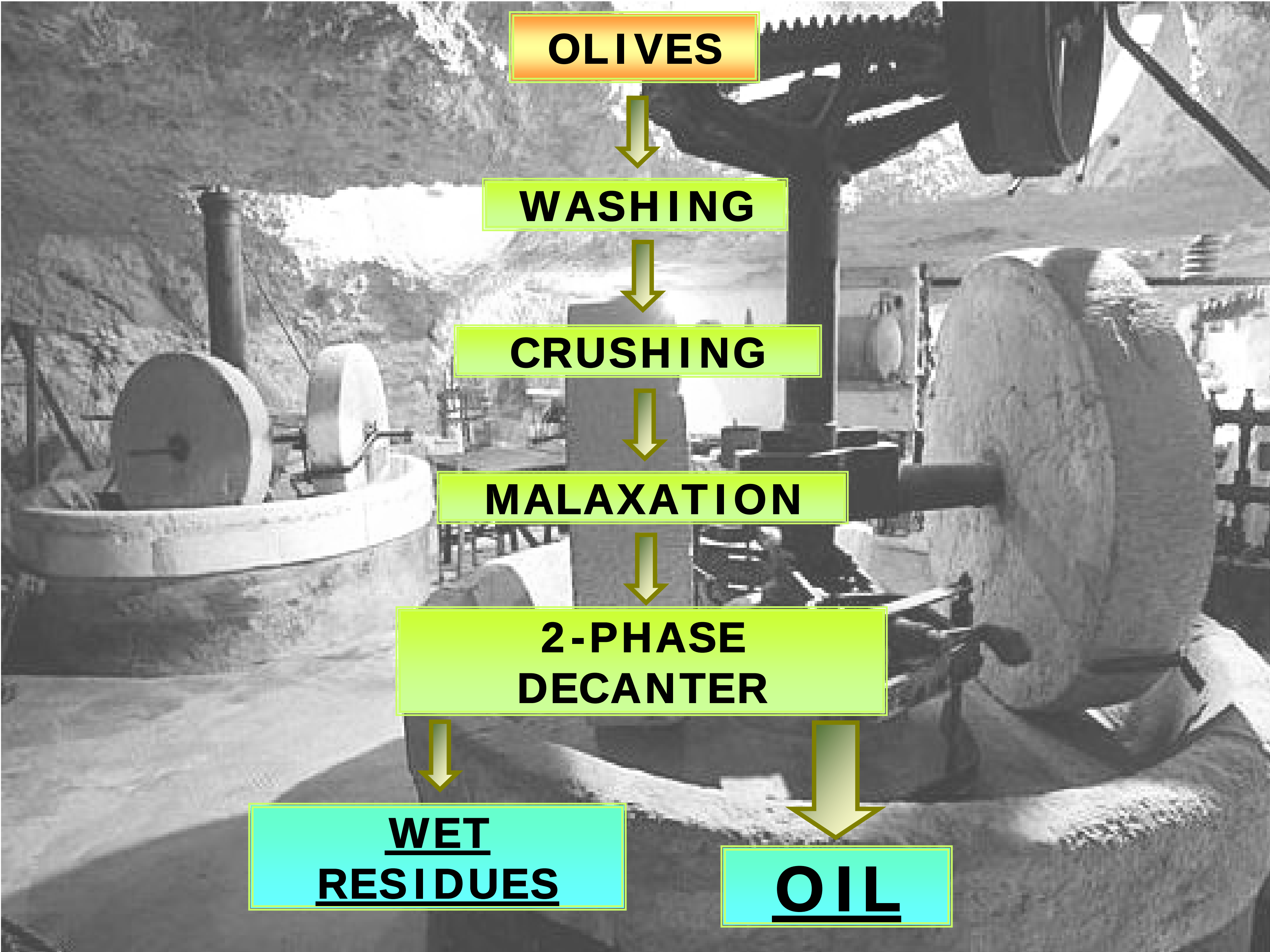
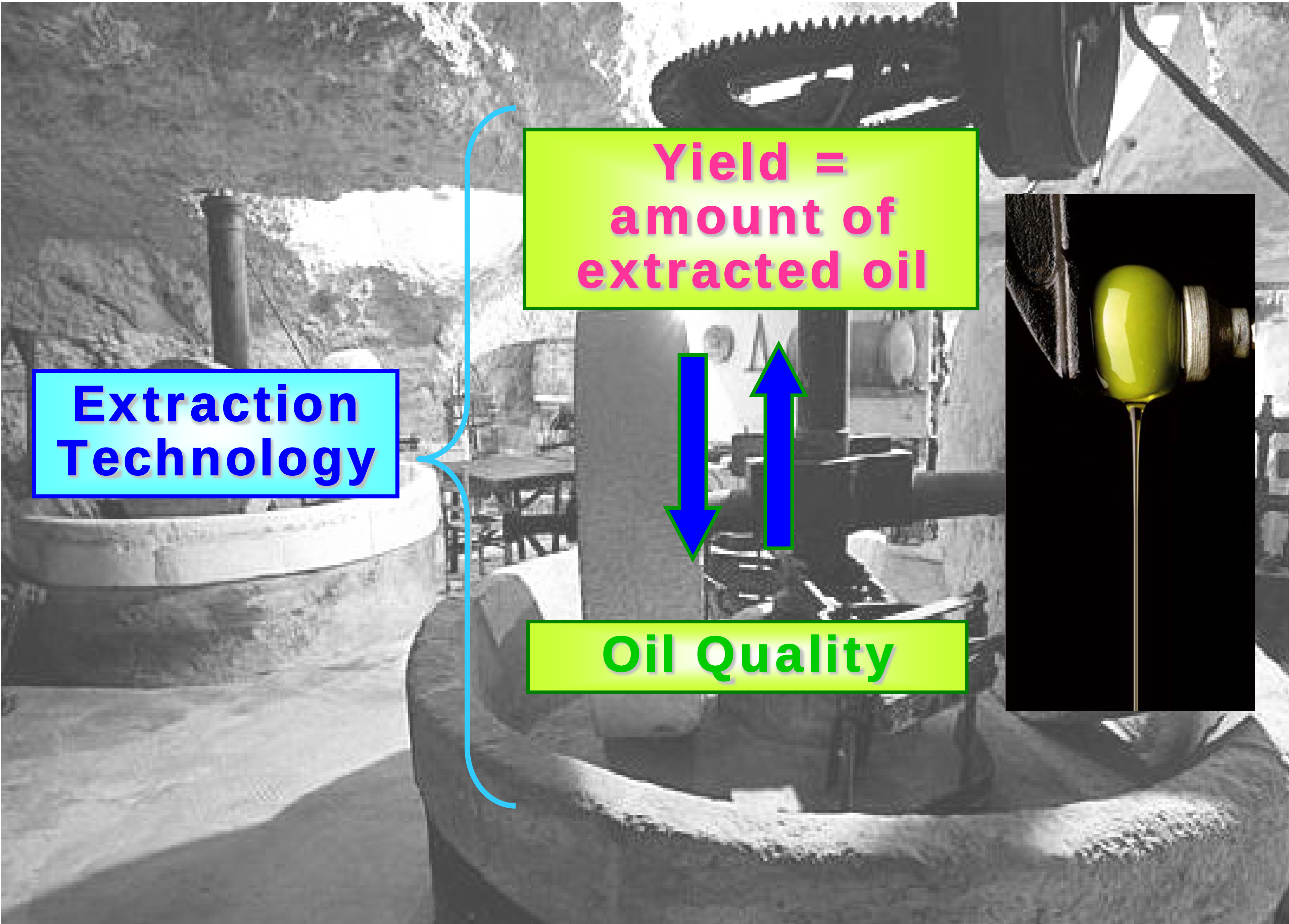
Health benefits of EVOO intake

EVOO is one of the main elements of the Mediterranean diet

- ✓ **Anti-inflammatory effect**
- ✓ **Cardiovascular protection**
- ✓ **Digestive health benefits**
- ✓ **Anti-cancer activity**

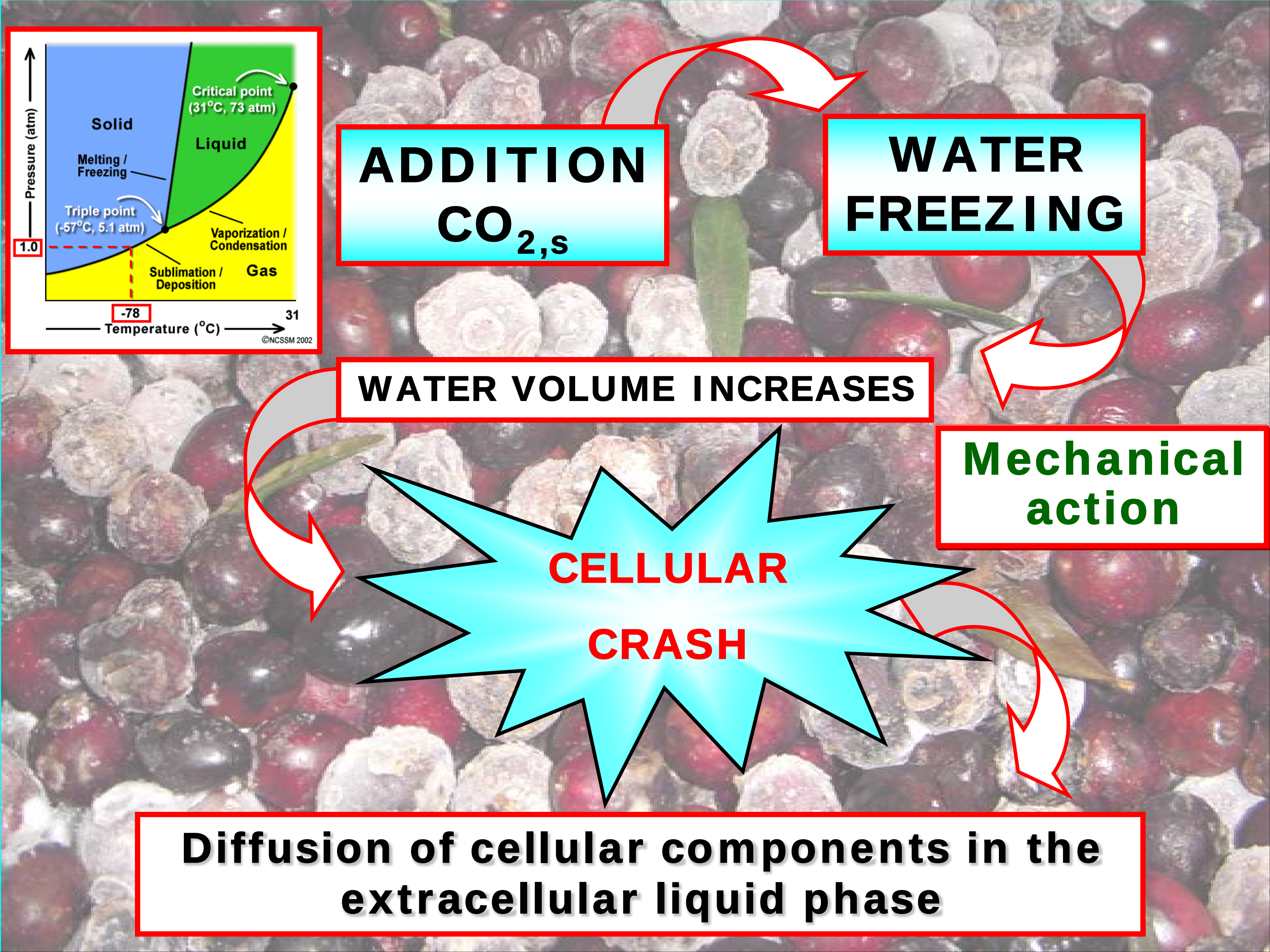

OLIVES
WASHING
CRUSHING
MALAXATION
2-PHASE DECANTER
WET RESIDUES
OIL


Extraction Technology
Yield = amount of extracted oil
Oil Quality

The addition of carbonic snow to grapes to produce high quality wines is a largely diffused oenological practice

Could this technology be usefully applied in extravirgin olive oil extraction

In order to advance in VOO technology, at DAFE of University of Pisa, an innovative EVOO extraction technology (Patent n° IT1405173-B) involving the addition of a cryogen (solid CO_2) to the olives were developed, in order to increase the extraction yield and to obtain an oil characterized by an higher concentration of phenolic compounds and a stronger link with the raw material and its production area.


Pressure (atm)
Solid
Liquid
Critical point
(31°C, 73 atm)
Melting /
Freezing
Triple point
(-57°C, 5.1 atm)
1.0
Vaporization /
Condensation
Sublimation /
Deposition
Gas
-78
31
Temperature (°C)
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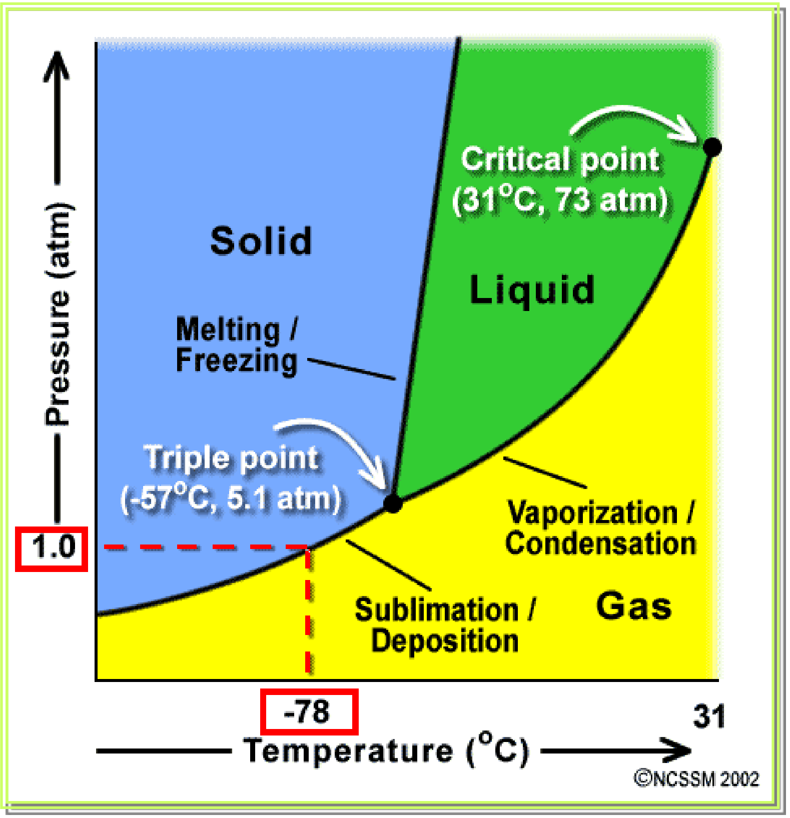
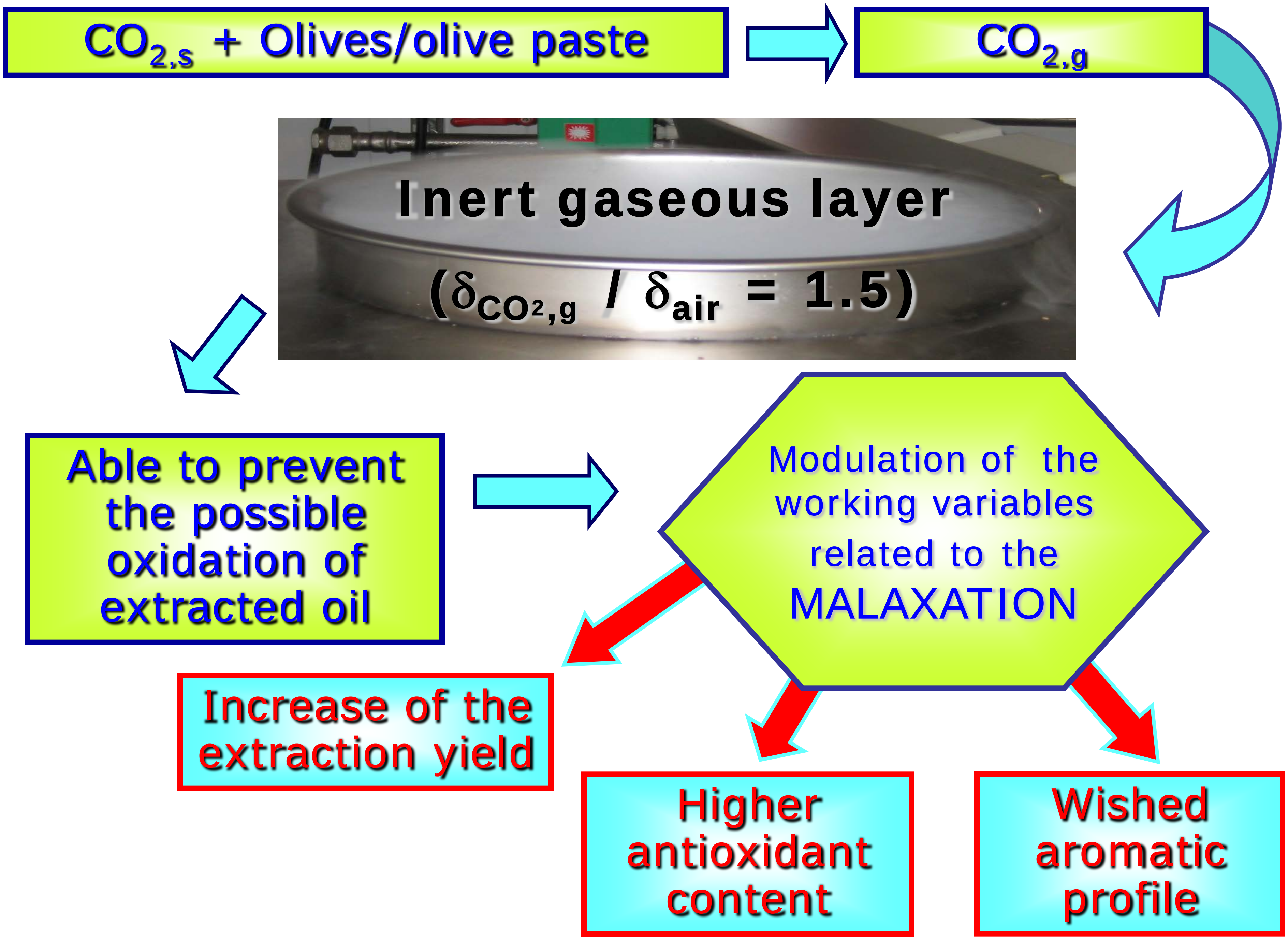
ADDITION
CO2,s
WATER
FREEZING
WATER VOLUME INCREASES
Mechanical
action
CELLULAR
CRASH
Diffusion of cellular components in the
extracellular liquid phase

Among all the possible cryogens suitable for food technology ($N_{2,L}$, He_L, Ar_L etc)

$CO_{2,s}$ (or carbonic snow) shows a lot of advantages



- *Nontoxic and does not leave residual*
- *Inflammable and less reactive*
- *Good solvent (non-polar)*
- *Inert by an organoleptic point of view*
- *Triple point easy to reach (-57.5°C; 5.1atm)*
- *Easy to find and to use*
- *Reduced costs*
- *Anti-microbial and anti-oxidant action*



$CO_{2,s}$ + Olives/olive paste
$CO_{2,g}$
Inert gaseous layer
$(\delta_{CO_2,g} / \delta_{air} = 1.5)$
Able to prevent the possible oxidation of extracted oil
Modulation of the working variables related to the MALAXATION
Increase of the extraction yield
Higher antioxidant content
Wished aromatic profile

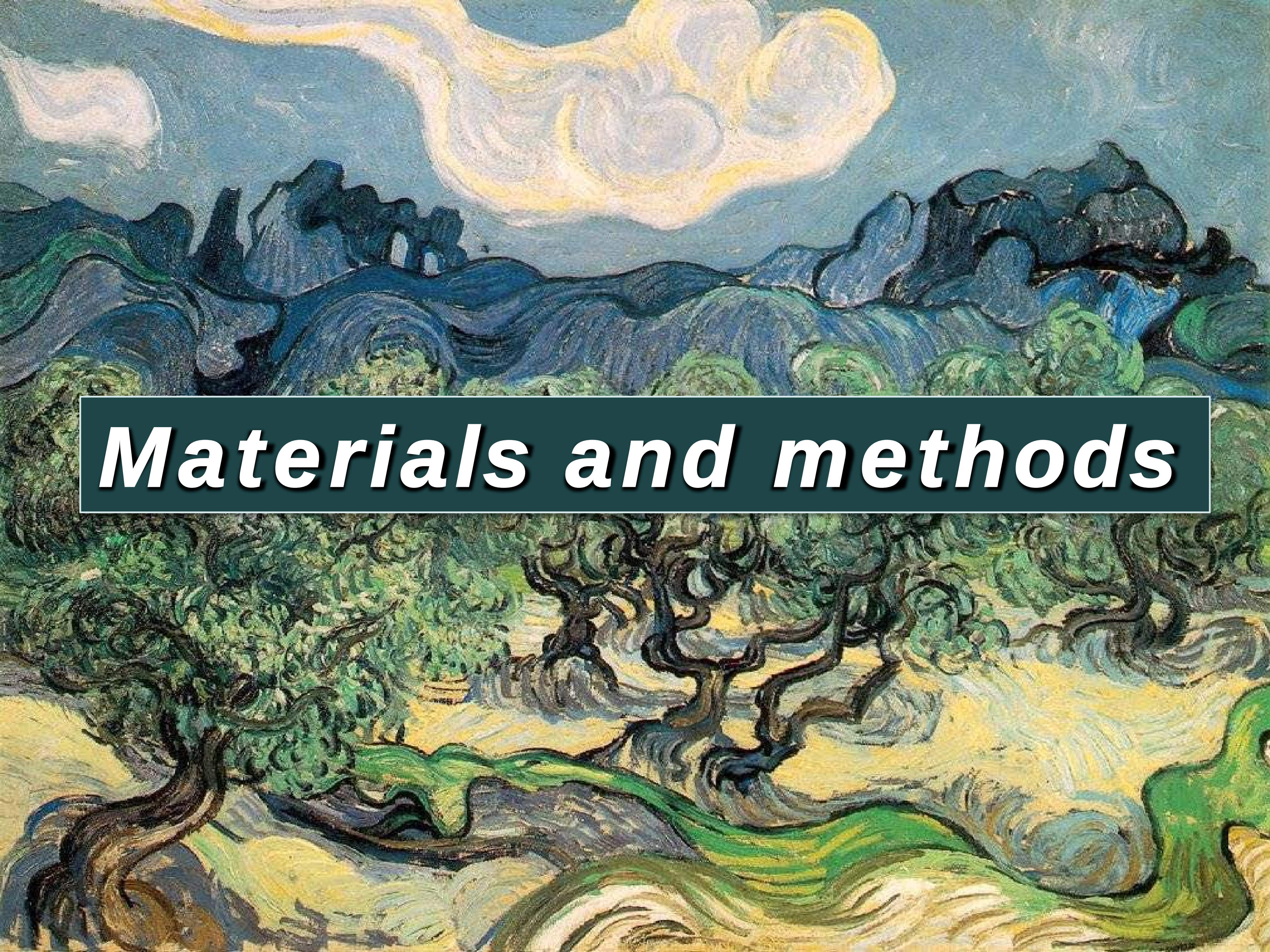
Aim of the work

The main object of this research work is twofold:

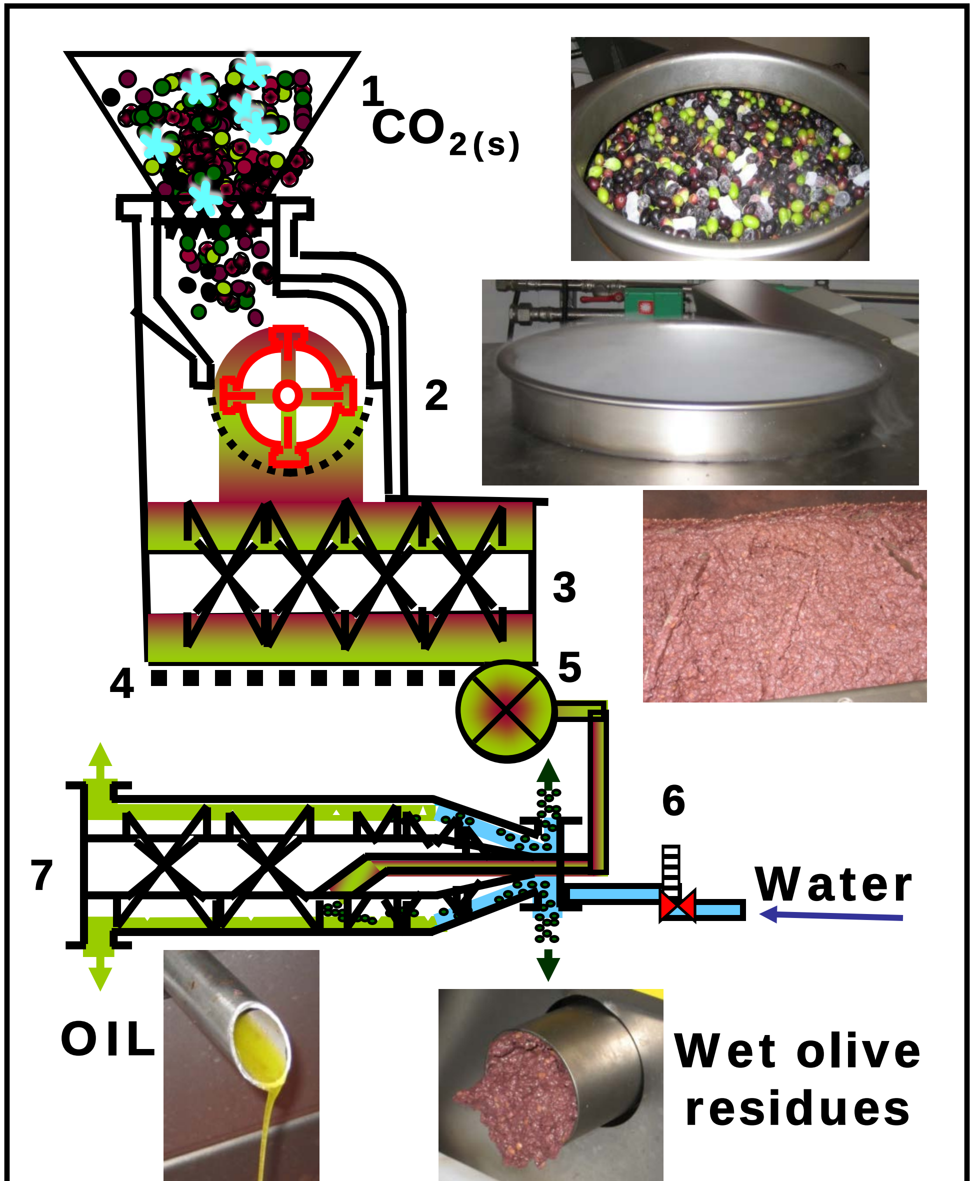
a) the first goal was to verify the influence of the addition of cryogen ($CO_{2,s}$), directly to olives during pre-milling phase, on the yield of the oil production, in order to obtain a preliminary evaluation of the suitability of the new proposed methodology for EVOO production.

b) the second goal was to develop specific analytical methods for evaluating the elemental profile of olive oil and to collect some preliminary data about the possibility to use these methods in order to put in evidence the possible influence of different process conditions (extraction with or ... f carbon ...) o ... ve o

Materials and methods



The olive crusher utilized: Oliomio Baby ® (T.E.M.)



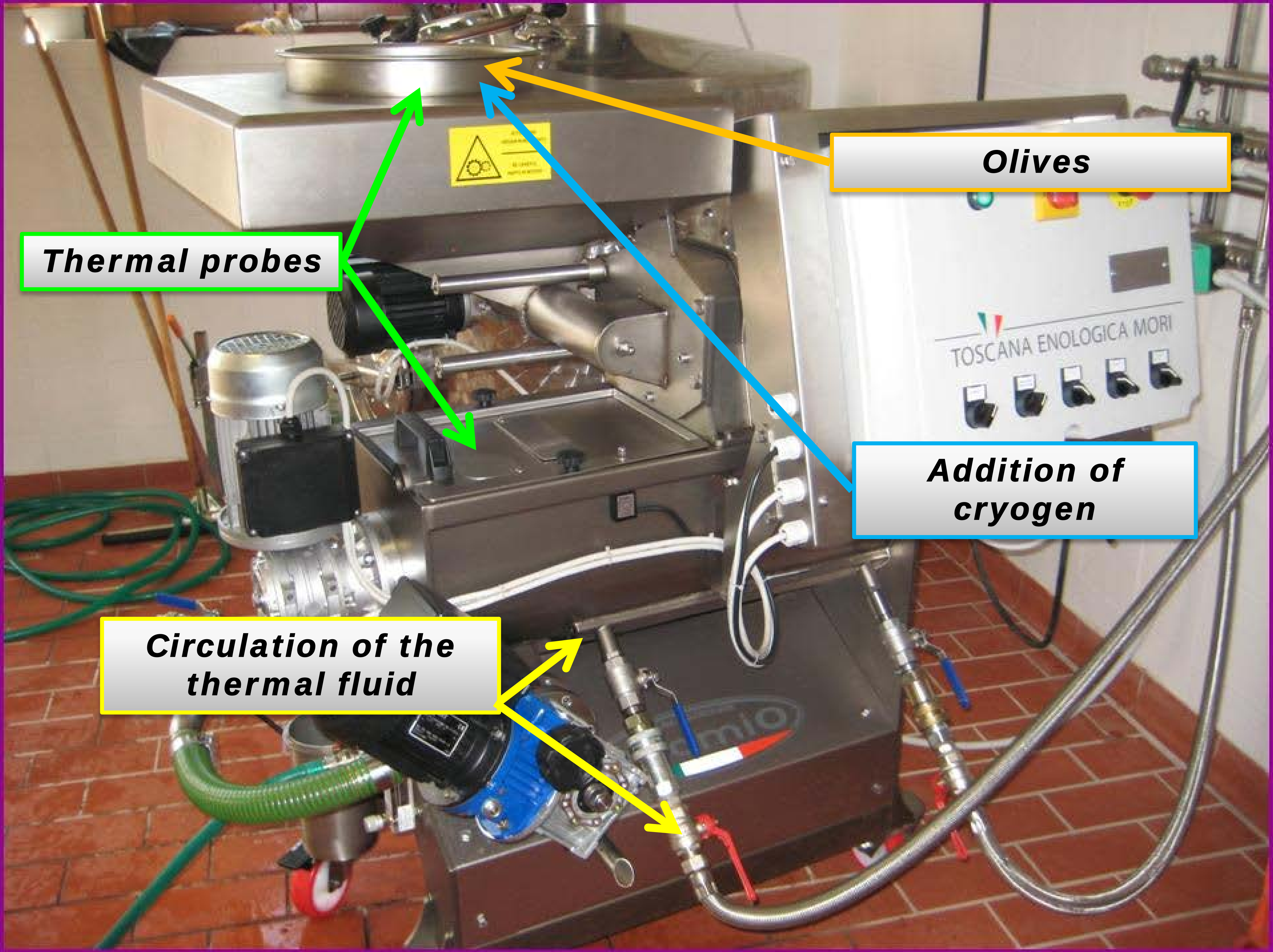
20-30 kg of olives/h

"mass cryogen"/"mass of fruits" ≅ 0,2

Knife crusher

Horizontal continuous malaxer

2-phase decanter


Olives
Thermal probes
Addition of cryogen
Circulation of the thermal fluid
TOSCANA ENOLOGICA MORI

The study were conducted on samples of olive oil produced from monovarietal and polyvarietal (*mix*) olives collected in two different Italian regions (from Tuscany and Basilicata) during the same season.

The olive f … d … rimental runs (~ 60 … e … suitably mixed to … o … s. Each sample w … (30 kg)

Traditional extraction process

Addition of $CO_{2,s}$

Origin and cultivar of the raw matter utilized

Sample ID		Geographical origin	Cultivar
Traditional	Cryo		
A	1	Tuscany (GR)	Frantoio
B	2	Tuscany (SI)	mix*
C	3	Tuscany (SI)	mix*
D	4	Tuscany (SI)	mix*
E	5	Basilicata (PZ)	Coratina
F	6	Basilicata (PZ)	Coratina
G	7	Basilicata (PZ)	Coratina

* Frantoio, Leccino, Correggiolo

Main operating variables adopted during the experimental runs

		Cryo	Traditional
Cryogen/olives (w/w)		*0.2*	*0*
Temperature of olives	*(°C)*	*~-2*	*11.5*
Temperature of paste	*(°C)*	*~24.0*	*~24.0*
Time of Malaxation	*(s)*	*2400*	*2400*
Time of Extraction	*(s)*	*4900*	*4300*
Water added/olives	*(%)*	*8.5*	*9.3*

MASS BALANCE during extraction process:

Total OIL entrance

(kg of crushed fruits x % of oil inside the olives)

=

Total OIL output

(kg of the olive residues x % of oil inside the olive residues)

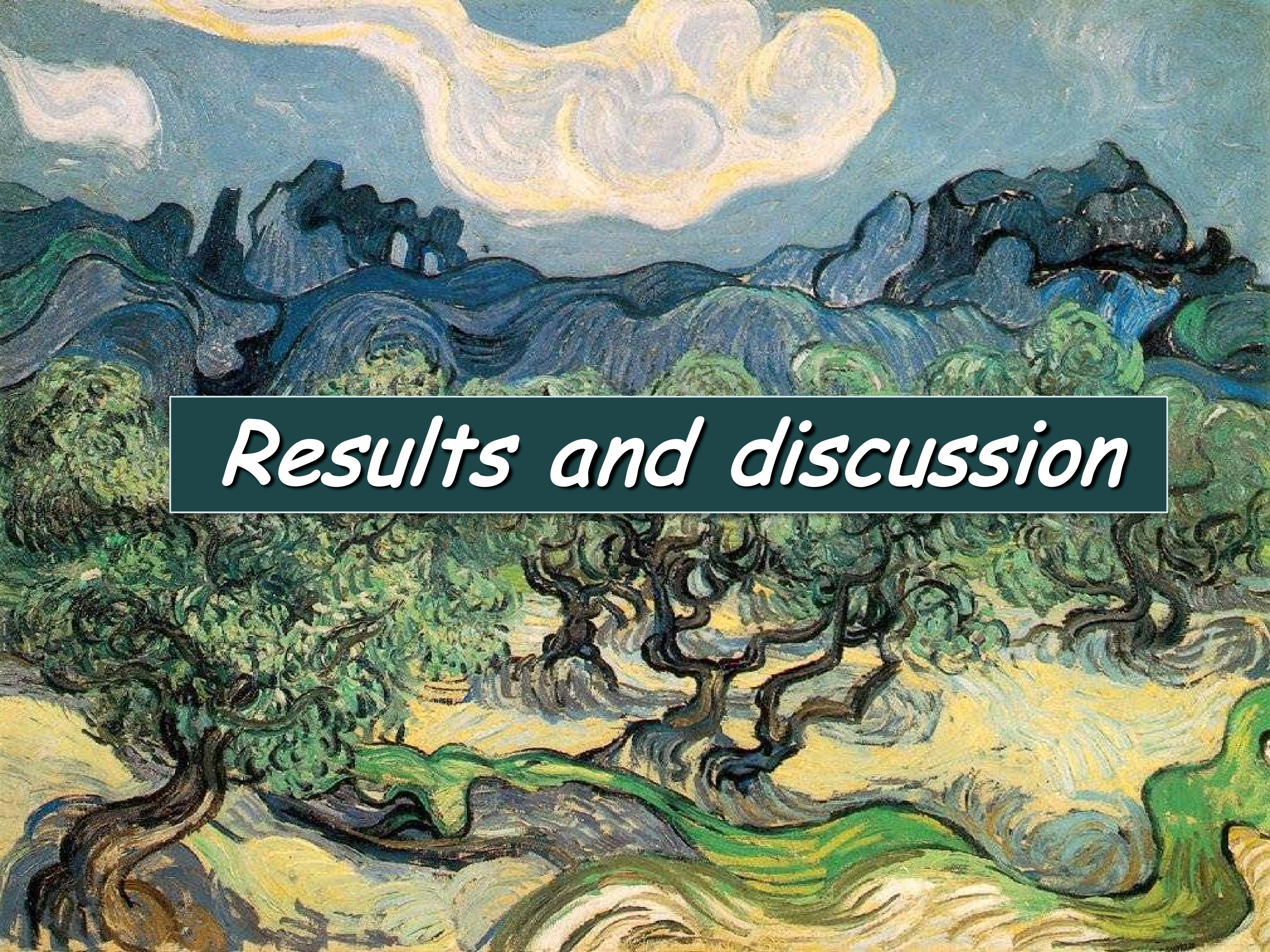
+

EXTRACTED OIL

In order to evaluate the effect induced by the addition of cryogen on the oil extraction yield, the Extractability Index Variation (EIV) was determined as the percentage of the variation of oil extractability using $CO_{2,s}$ compared with the same parameter obtained by a traditional extraction process

$$EIV = (EC-ET)/ET \cdot 100$$

Results and discussion



Oil extraction yield: preliminary results

Oil extraction yield: preliminary results.

Run	EC	ET	[(EC-ET)/ET]*100
1/A	85.8	82.5	4.0 %
2/B	85.5	77.2	10.8 %
3/C	91.2	82.7	10.3 %
4/D	84.1	74.8	12.4 %
5/E	80.8	79.3	1.9 %
6/F	73.6	68.9	6.8 %
7/G	84.4	77.4	9.0 %

The direct addition of cryogen to the olives during pre-milling phase could induce a general increase in the oil extraction yield, ranging from 2 to 12,4 %.

Preliminary results about oil extraction yield: discussion I

The number of the experimental runs carried out until now is quite reduced.

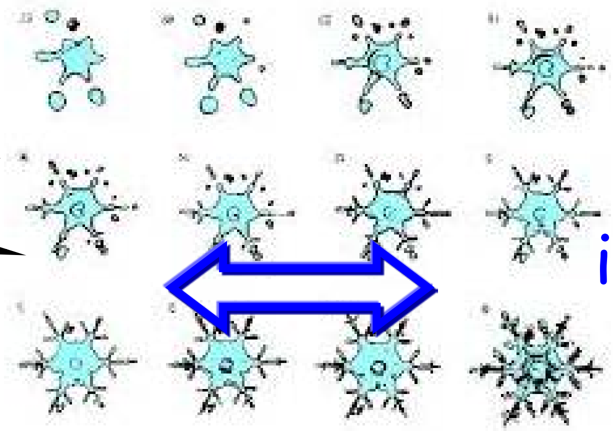
BUT

The results appear very encouraging and the new method seems very suitable for olive oil extraction

- During the next crop season we will increase the number of experimental runs adopting several combinations of the working parameters (i.e. amount of cryogen/amount of olives, fruit ripening stage, etc.).

Preliminary results about oil extraction yield: discussion II

CELLULAR CRASH



Water content inside the fruit

❖If necessary this method allows to move up the olive harvest time in order to greatly reduce the damages due to the third fly attack of *Bactrocera oleae* that can induce a significant loss in oil production (up to 60%) as well as a decrease in oil quality

We need 0.8 kg of CO_{2s} to lower 100 kg of olives temperature by 1°C.

Cost of 1 kg of CO_{2s} = €0.50 / $ 0,37

Cost to turn down the average temperature of 100 kg of olives by 10°C

(15°C → 5°C)

0.8kg/°C x 10°C x 0.37 $/kg

=

3 $

Considering an average oil yield of 15%,

The addition cost for a kg of extravirgin olive oil is

3 $/100 kg olives x 15/100kg oil/kg olives

< 0.2$/kg oil

Oil elemental profile: preliminary results

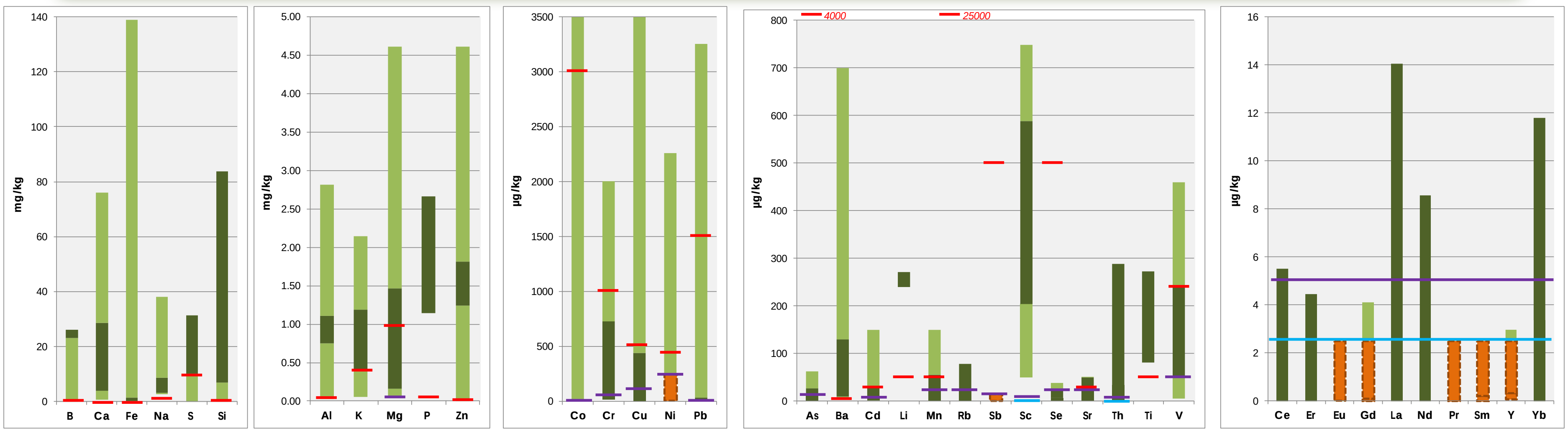
Preliminary results about oil elemental profile

- ICP-AES and ICP-MS techniques are particularly advantageous for the application in the definition of the elemental profiles of olive oil, since they allow simultaneous multi-elemental analysis and are characterized by wide linear ranges and (especially ICP-MS) very low Detection Limits

- Main analytical issues are related to the hard organic content of the oil matrix, which requires appropriate sample pre-treatments. Microwave-assisted digestion permitted to obtain a complete dissolution of olive oil samples, but resulted in the obtainment of highly acidic solutions not directly analyzable by ICP-MS, with a consequent reduction of sensitivity (due to the preliminary 1:10 dilution of the mineralized olive oil)

Preliminary results about oil elemental profile

- Preliminary results show a rather homogeneous elemental content among all the analyzed samples of olive oil
- For all elements, experimental concentrations fall within the ranges reported in literature. In respect to these ranges, analyzed samples show a high content of B, S and Si, while Fe, Na, Pb, Ba, Cr and Cu contents are quite low
- Samples of olive oil obtained by the "traditional“ process show - in general - a higher content of Ca, Cr, Mg, Si (except those originating from Basilicata) and Zn, compared to those obtained by the addition of “carbonic snow“



concentration range obtained from literature [2]
experimental concentration range

ICP-AES Detection Limit
ICP-MS Detection Limit - Normal Sensitivity mode
ICP-MS Detection Limit - High Sensitivity mode

S. B. Yasar, E. K. Baran, M. Alkan. *Metal determinations in olive oil.* In: Olive Oil – Constituents, Quality, Health Properties and Bioconversions. Ed by Boskou Dimitrios. 5; 89-108. 2012

For any further details about the second part of the research, you can contact our colleagues in ENEA

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Proceedings of EFFOST 2011, 9-11 November 2011, Berlino (D).

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C. Zoani, G. Zappa, A. Zinnai, F. Venturi, C. Sanmartin
11th Euro Fed Lipid Congress – Antalya (Turkey),
27-30 October 2013

Preliminary results on the influence of carbonic snow addition during the olive processing: oil extraction yield and elemental profile.
C. Zoani, G. Zappa, F. Venturi, C. Sanmartin, G. Andrich and A. Zinnai
Journal of Nutrition and Food Sciences 4: 277 (2014).
doi: 10.4172/2155-9600.1000277

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REGIONE TOSCANA

Research in progress….

Thank you for your attention!!!

Future developments

- It will be possible to apply matrix modification procedures (e.g. solvent extraction – also ultrasound assisted -, addition of organic solvents or emulsification) or to employ systems for direct oil sample introduction in torch (e.g.: Flow Injection Analysis systems)

- We are conducting experimental tests for evaluating the possibility to employ a Laser Ablation system or an ElectroThermal Vaporization system for direct sample introduction in ICP-AES and ICP-MS

Determination of oil elemental profile: sample pre-treatment

Different mixtures tested:
H_2O_2 30%$_{v/v}$ (1 ÷ 2 ml)+ HNO_3 69.9%$_{v/v}$ (2 ÷ 6 ml)

Total dissolution

2 ml H_2O_2 + 6 ml HNO_3

0.5 g olive oil

High Pressure Microwave Digestion

Milestone 1200 Mega

time	Power	Pressure
1 min	250 W	Free pressure race
1 min	0 W	
5 min	400 W	
5 min	650 W	
Vent = 5 min		

high-purity water (> 18 MΩ)

Mineralized oil sample (final V = 25 ml)

ICP-AES Analysis

Varian Vista MPX
(axial configuration,
simultaneous 1.12 Mpixel CCD detec

TQ mineralized olive oil solution

Analytical wavelengths (nm)		
Al - 396.152 nm	K - 766.491 nm	Rb - 780.026 nm
As - 188.980 nm	Li - 670.783 nm	S - 181.972 nm
B - 249.772 nm	Mg - 279.553 nm	Sb - 206.834 nm
Ba - 455.403 nm	Mn - 257.610 nm	Si - 251.611 nm
Ca - 396.847 nm	Na - 589.592 nm	Sr - 407.771 nm
Cr - 267.716 nm	Ni - 231.604 nm	Ti - 334.941 nm
Cu - 327.395 nm	P - 213.618 nm	V - 311.837 nm
Fe - 238.204 nm	Pb - 220.353 nm	Zn – 206.200 nm

Gas flows optimization ba
signal-to-background rati

		Auxiliary flow (l/min)		N
		1.0	**1.5**	0.9
S/B	Mg	3.296	11.720	13.948
	Mn	0.128	0.197	0.245
	Na	1.827	1.940	1.827

Operating parameters for ICP-AES quantitative analysis

Instrumental conditions	
RF Frequency	40 MHz (free running, air-cooled)
RF Power	1.2 kW
Gas (plasma, auxiliary, nebulizer)	Argon
Plasma flow	15.0 l/min
Auxiliary flow	1.5 l/min
Nebulizer flow	1.10 l/min
Replicates	5
Replicate read time	5 s

ICP-MS Analysis

Bruker Aurora M90 (90 degree ion mirror ion optics, Collision Reaction Interface)

1:10 diluted mineralized olive oil solution

Tuning with a 5 µg/l Be, Mg, Co, In, Ba, Ce, Ti, Pb and Th solution for sensitivity and resolution optimization and mass calibration

Check of the level of **oxide ions** by the CeO^+/Ce^+ ratio: < 2%

Monitoring of double charged ions by the signal $^{137}Ba^{++}/^{137}Ba^+$: < 3%

Check/Correction of isobaric interferences:

- examination of more isotopes of the same element(e.g.: Rb85, Rb 87; Sr88,Sr87; Nd142, Nd146, Nd144; Se77, Se78; Sn147, Sm148, Sm152; Gd157, Gd154; Er166, Er168; Yb170, Yb172)
- application of correction equations with respect to isotopes of other elements potentially interfering (e.g.: Nd142 corrected by analyzing Ce140, Nd144 by Sm147, Sm152 by Gd157, Rb87 by Sr88)
- use of the Collision Reaction Interface – CRI (for As and Se)

Normal Sensitivity Mode (without CRI), High Sensitivity Mode
As and Se – Normal mode with CRI

Working ranges:

•0.05 ÷ 5 µg/l -
As, Cd, Ce, Er, Eu, Gd, La, Mn, Nd, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sr, Th, V, Y, Yb

External calibration
5 standard solutions + blank
Curve Fit: Linear
Weighted Fit: No
Correlation coefficients:
R > 0.9999