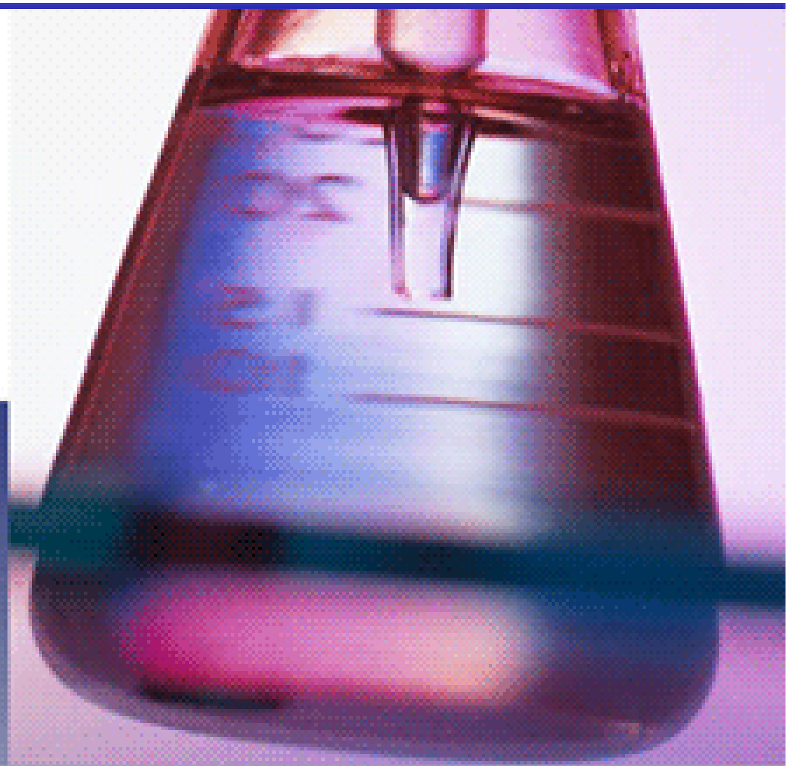

Isotopic and elemental data for tracing the origin of European olive oils

Federica Camin, Roberto Larcher, Giorgio Nicolini, Luana Bontempo, Daniela Bertoldi, Matteo Perini, Claus Schlicht, Antje Schellenberg, Freddy Thomas, Katharina Heinrich, Susanne Voerkelius, Micha Horacek, Henriette Ueckermann, Heinz Froeschl, Bernhard Wimmer, Gerhard, Heiss, Malcolm Baxter, Andreas Rossmann, Jurian Hoogerwerff

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EC Regulament n° 182/2009

↓

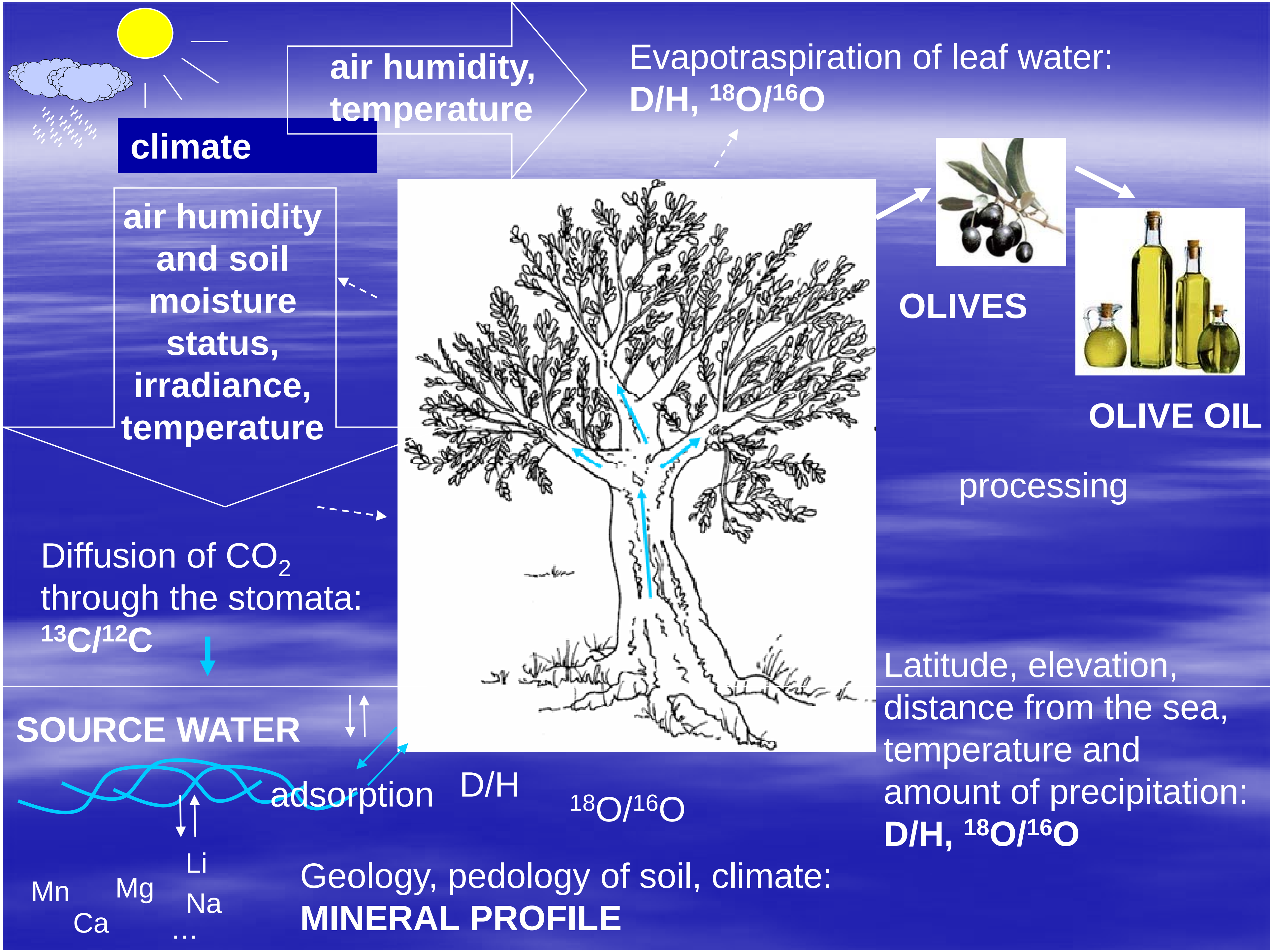
Compulsory origin labelling for virgin and extra-virgin olive oil

↓

Increasing demand for analytical methods and statistical tools to verify claims of origin

↓

Isotope ratios of bioelement and elemental profile


climate
air humidity, temperature
Evapotraspiration of leaf water:
D/H, $^{18}O/^{16}O$
air humidity and soil moisture status, irradiance, temperature
OLIVES
OLIVE OIL
processing
Diffusion of CO_2 through the stomata:
$^{13}C/^{12}C$
SOURCE WATER
adsorption
D/H
$^{18}O/^{16}O$
Latitude, elevation, distance from the sea, temperature and amount of precipitation:
D/H, $^{18}O/^{16}O$
Li
Mn
Mg
Na
Ca
…
Geology, pedology of soil, climate:
MINERAL PROFILE

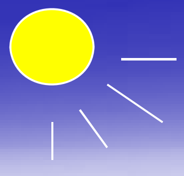
Sampling sites

267 olive oils
314 surface waters

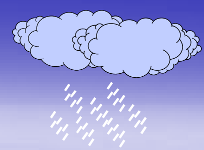
Geographical characteristics (latitude, longitude, distance from the sea, altitude)

Geological characteristics (shale/clay, limestone, acid magmatic)

Climatic characteristics (temperature, RH, amount of precipitation)



Climatic characteristics:



-mean values of 5 months temperature (°C),
-mean values of 5 months relative humidity (%)
-5 months total amount of rainfall (mm)

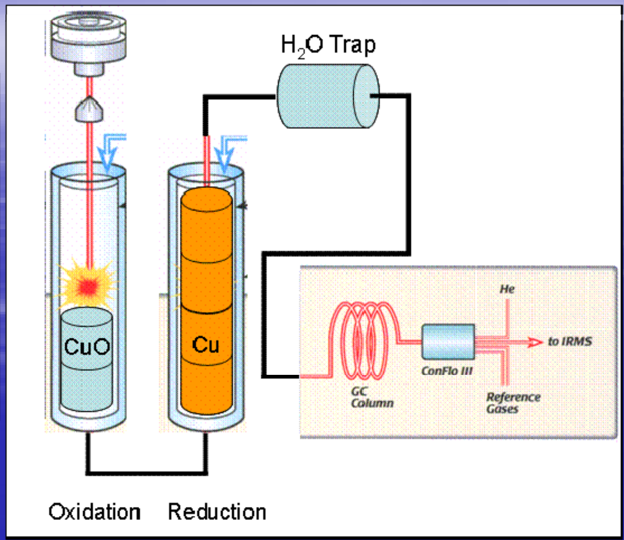
http://www.meteotrentino.it, Arco (TRE);
http://www.ilmeteo.it/, Sesto Fiorentino (TOS);
http://www.ilmeteo.it/, Assoro/Enna, (SIC);
http://www7.ncdc.noaa.gov/, Faro/Almanacil (ALG);
http://www7.ncdc.noaa.gov/, Carpentras (CAR);
the Servei Meteorològic de Catalunya, Barcelona (BAR);
the Hellenic National Meteorological Service, Mikra (CHA)*;
the Hellenic National Meteorological Service, Kalamata/Gythi (LAK)*;
http://www.wunderground.com.

*through prof. Michael Komaitis (Agricultural University of Athens, Greece)

Stable Isotope Ratio Analysis

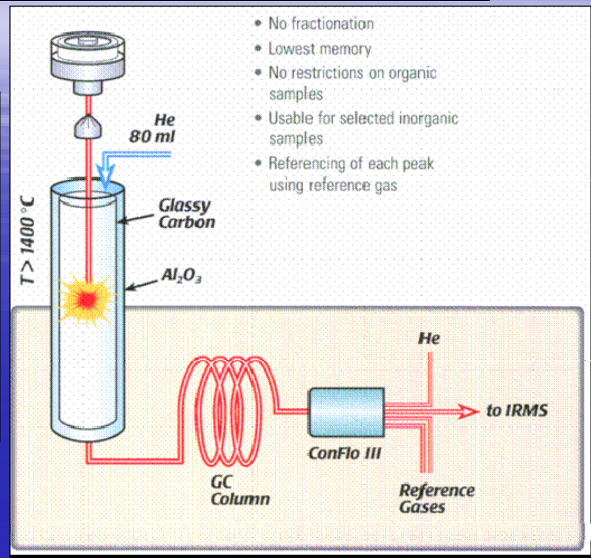
$^{13}C/^{12}C$, D/H, $^{18}O/^{16}O$
Olive Oil

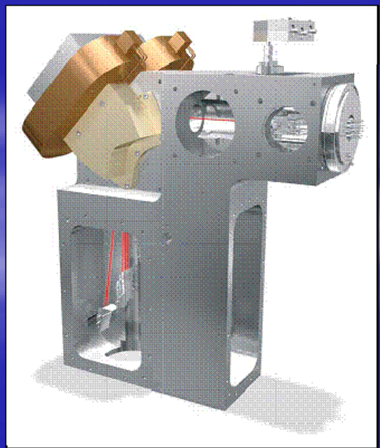
Elemental Analyzer



D/H, $^{18}O/^{16}O$,
Olive Oil, Water

Pyroliser





ISOTOPIC RATIO MASS SPECTROMETRY

	Commodity	Standard deviation of repeatability (‰)	Standard deviation of reproducibility (‰)
$\delta^{13}C$	oil	0,1	0,1
$\delta^{18}O$	oil	0,4	0,6*
	water	0,1	0,2
δD	oil	1	2
	water	1	2

*after normalization

TE analysis:

15 g oil + 15 ml
6.7% H_2O_2, 1% HNO_3 and 0.2% HCl

vortex

ultrasonic bath, 5 min

centrifugation 3500 rpm, 5 min.

Filtration of aqueous phase
with Polyvinylidene Fluoride (PVDF, 0.45 mm, 33mm) filter

ICP-MS

Method's performances

DETECTION LIMIT:

Calculated as 3 times the standard deviation of the signal of the blank samples, extracted and analysed ten times

ACCURACY:

Calculated as the mean recovery on a natural oil spiked with 1 g of NIST 2387 "Peanut butter" or of SPEX s-23 "Mineral oil"

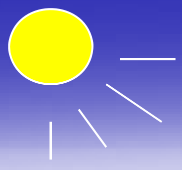
element / isotope	DL ug/kg	% sample >DL
Li / 7	0.008	6
B / 11	0.17	28
Na / 23	20	8
Mg / 26	4	92
Al / 27	3	4
K / 39	20	98
Ca / 40	25	100
V / 51	0.007	0
Mn / 55	0.2	64
Co / 59	0.002	34
Ni / 60	1	16
Cu / 63	0.10	68
Zn / 66	6	42
Ga / 71	0.001	0
Se / 78	0.014	0
Rb / 85	0.001	98
Sr / 88	0.3	32
Mo / 98	0.050	0
Cd / 111	0.005	0
Cs / 133	0.001	0
Ba / 137	0.12	34
La / 139	0.0020	48
Ce / 140	0.0050	34
Nd / 143	0.004	24
Sm / 147	0.0010	22
Eu / 151	0.0002	6
Yb / 171	0.0004	8
Lu / 175	0.0200	0
Tl / 205	0.0040	0
Pb / 208	0.1	38
U / 238	0.001	50

Certified Elements	R%
Zn	82
Mn	84
Ca	90
Mg	92
K	95
Na	101

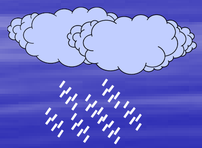
NIST 2387 "Peanut butter"

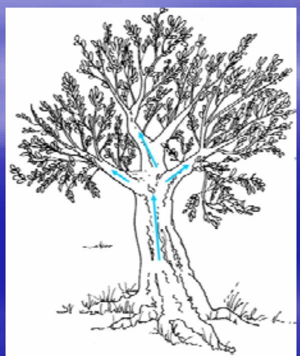
Certified Elements	R%
B	88
Na	80
Mg	67
Al	53
K	92
Ca	84
V	63
Mn	71
Ni	65
Cu	61
Zn	68
Mo	66
Cd	71
Ba	65
Pb	67

SPEX s-23 "Mineral oil"



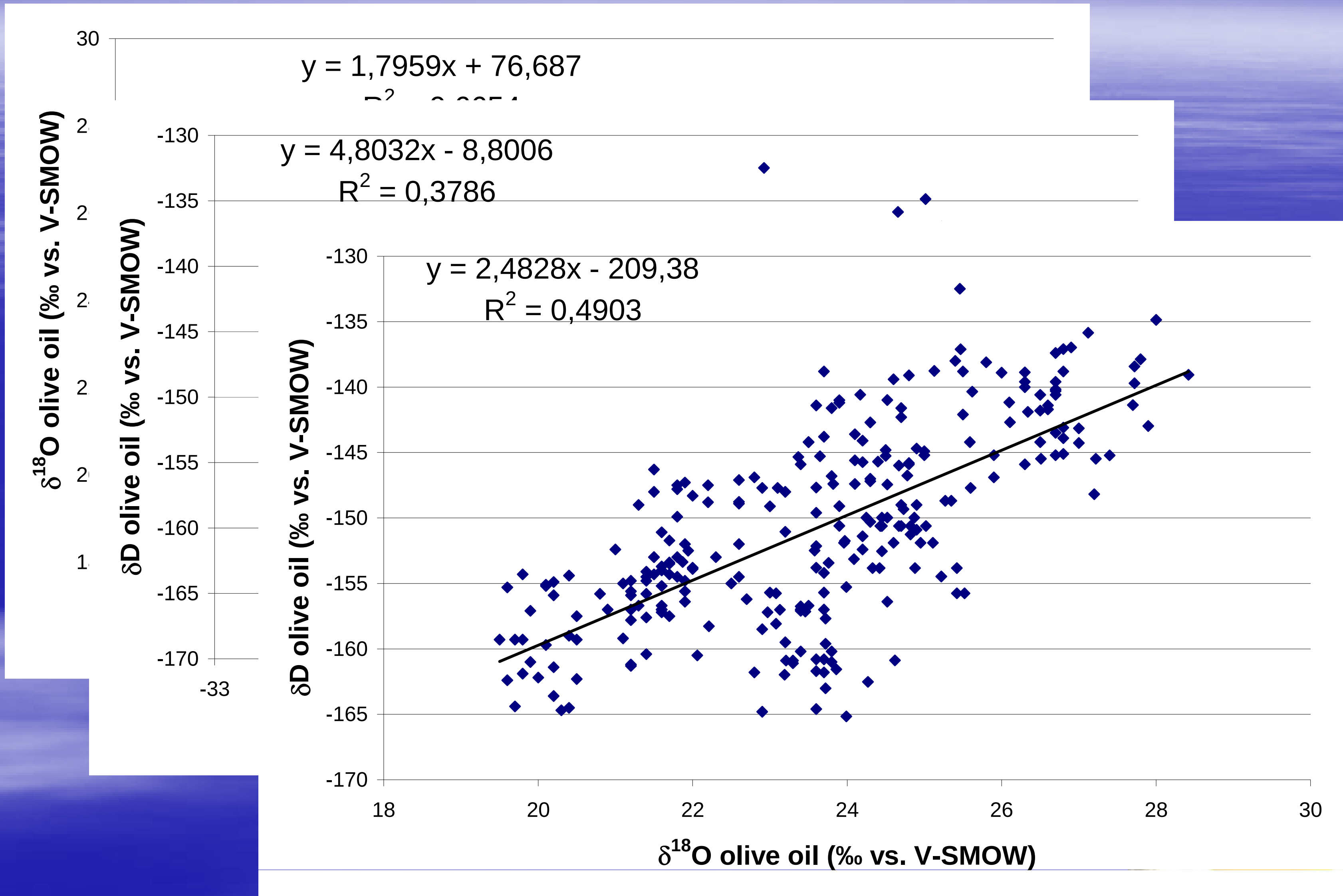
SIR correlations:



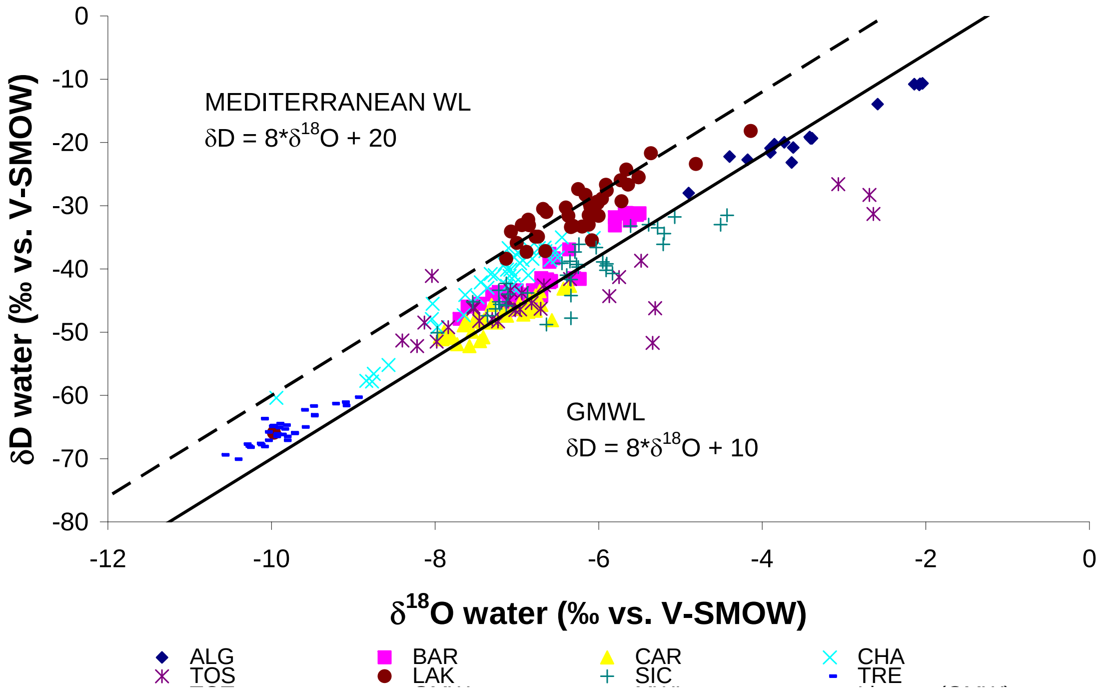


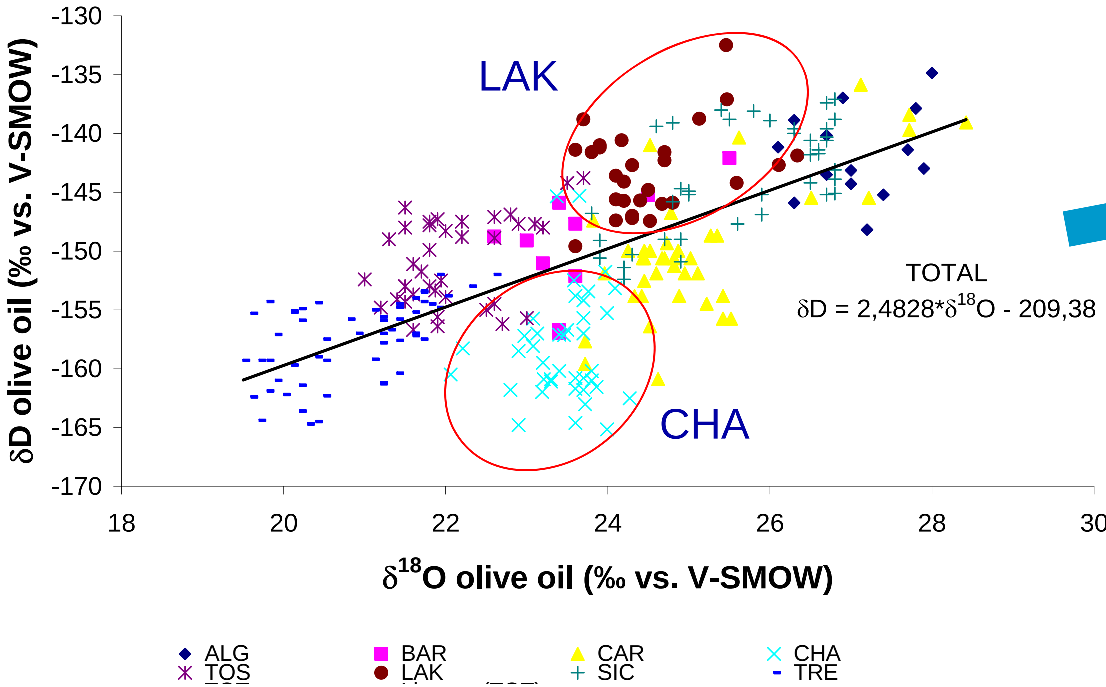
			$\delta^{13}C$	$\delta^{18}O$	δD	latitude DD	longitude DD	distance from the sea (km)	altitude m asl	temp. °C	relative humidity	mm rain
olive oil	$\delta^{13}C$	r		0,82	0,62	-0,80	0,13	-0,75	0,07	0,59	-0,61	-0,29
		r^2		0,67	0,38	0,64	0,02	0,56	$5*10^{-3}$	0,35	0,38	0,09
		signific.		<0.001	<0.001	<0.001	0,0377	<0.001	0,2687	<0.001	<0.001	<0.001
		intercept		-38,30	-17,67	-20,46	-29,75	-28,71	-29,63	-33,70	-22,20	-28,85
		slope		0,370	0,079	-0,218	0,015	-0,014	$3*10^{-4}$	0,273	-0,108	-0,002
	$\delta^{18}O$	r	0,82		0,70	-0,67	-0,16	-0,58	0,21	0,51	-0,41	-0,32
		r^2	0,67		0,49	0,45	0,03	0,34	0,04	0,26	0,17	0,10
		signific.	<0.001		<0.001	<0.001	0,0076	<0.001	0,001	<0.001	<0.001	<0.001
		intercept	76,69		53,38	40,50	24,13	25,05	23,09	15,84	34,41	25,31
		slope	1,796		0,197	-0,405	-0,042	-0,024	0,002	0,512	-0,159	-0,005
	δD	r	0,62	0,70		-0,56	-0,19	-0,37	0,27	0,43	-0,17	0,003
		r^2	0,38	0,49		0,31	0,03	0,13	0,08	0,18	0,03	$1*10^{-5}$
		signific.	<0.001	<0.001		<0.001	0,0023	<0.001	<0.001	<0.001	0,0047	0,9548
		intercept	-8,80	-209,38		-100,93	-148,63	-147,53	-153,20	-173,96	-134,61	-150,84
		slope	4,803	2,483		-1,196	-0,171	-0,054	0,009	1,530	-0,238	$2*10^{-4}$
water	$\delta^{18}O$	r			0,93	-0,62	-0,26	-0,55	-0,47	0,54	-0,30	-0,01
		r^2			0,87	0,39	0,07	0,30	0,22	0,29	0,09	0,0002
		sign.			<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0,8297
		intercept			-1,60	6,19	-6,35	-5,94	-5,96	-12,93	-1,15	-6,86
		slope			0,125	-0,319	-0,047	-0,022	-0,003	0,409	-0,085	-0,0001
	δD	r		0,93		-0,76	-0,07	-0,72	-0,54	0,70	-0,51	0,05
		r^2		0,87		0,58	0,01	0,52	0,29	0,49	0,26	0,002
		sign.		<0.001		<0.001	0,22	<0.001	<0.001	<0.001	<0.001	0,4292
		intercept		5,62		77,78	-41,40	-33,10	-34,37	-101,25	32,07	-43,91
		slope		6,982		-2,938	-0,102	-0,216	-0,023	3,984	-1,102	0,004

Correlations among SIR



Correlations $\delta^{18}O$ vs δD





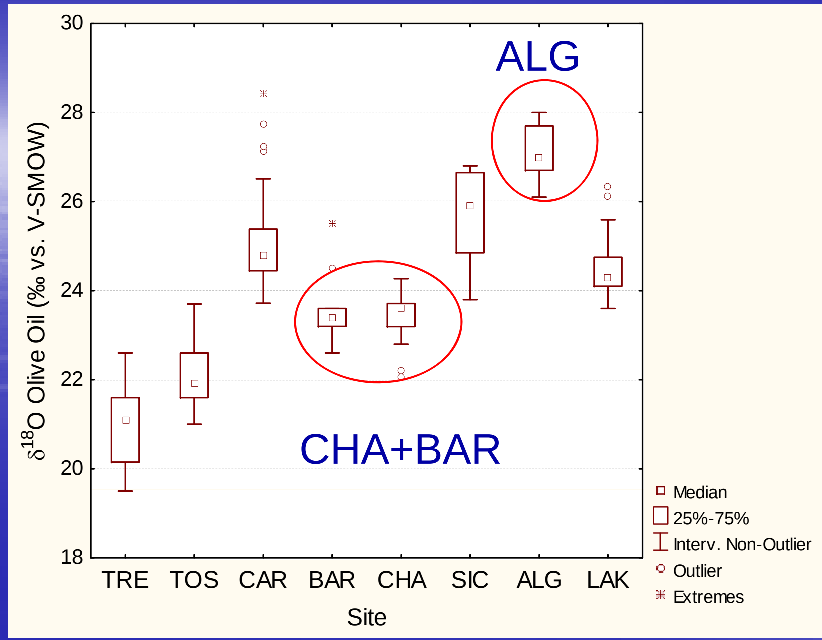
$\delta D = 2.5091\delta^{18}O - 208.1$*

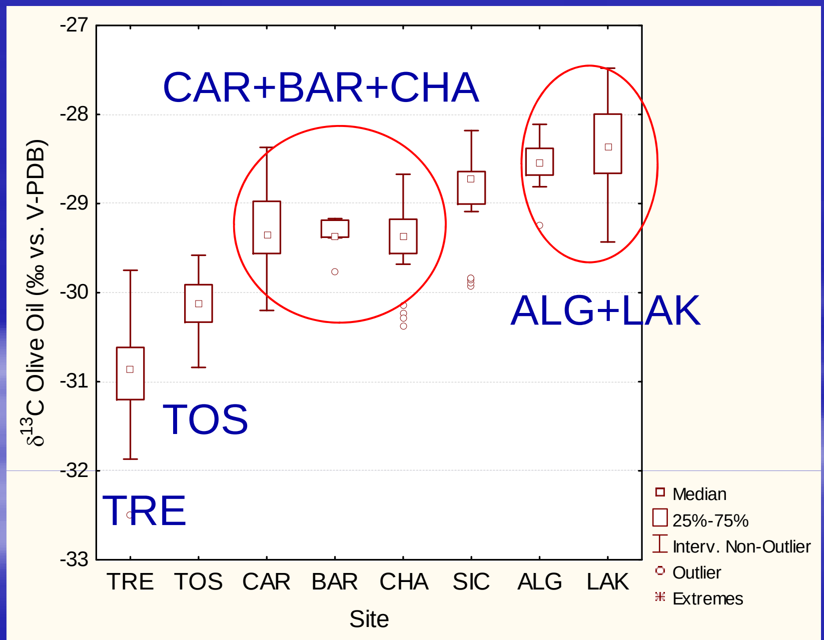
$\delta D = 2.663\delta^{18}O - 210.04$**

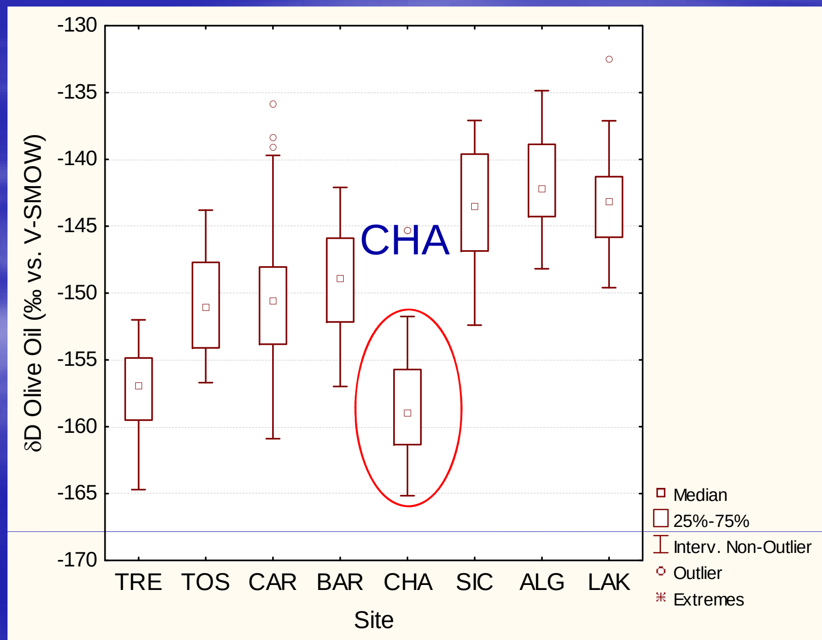
*Camin et al., Food Chem. (2010)

**Bontempo et al., RCM (2009)

SIRA Geographical discrimination of olive oils

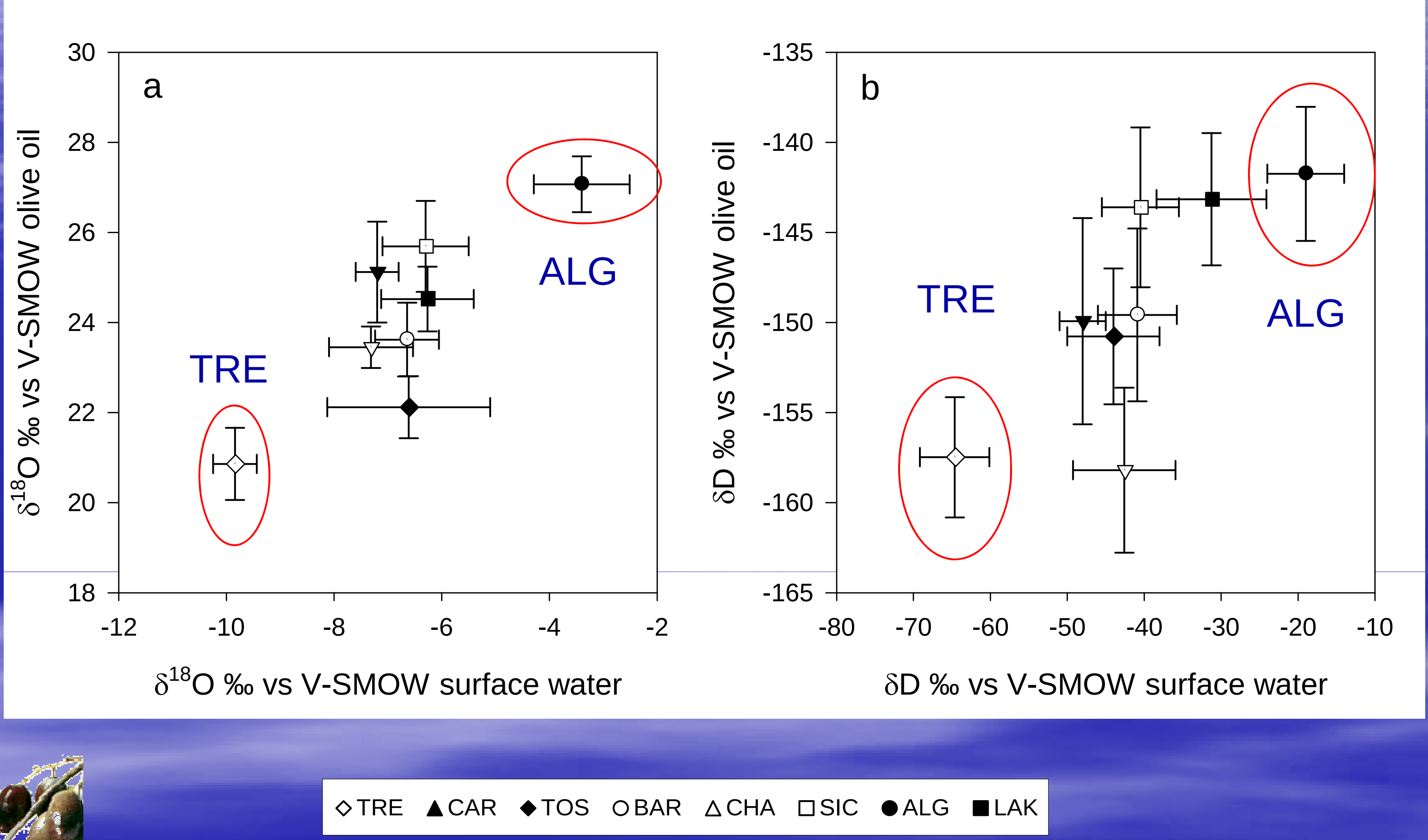






Latitude

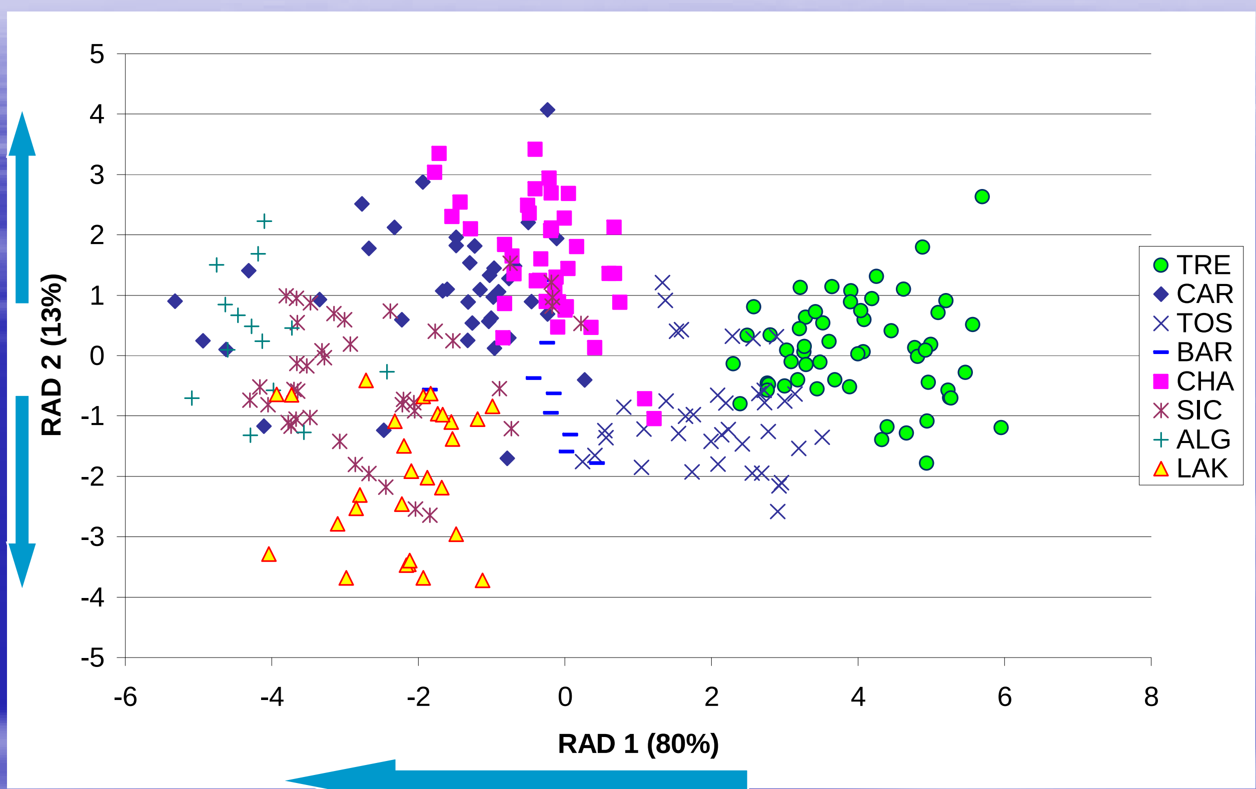
SIRA: olive oils versus surface waters



SIRA: geographical discrimination of olive oils – Canonical Multivariate Discriminant Analysis

$\delta^{18}O$

δD



RAD1+RAD2

93%

$\delta^{18}O$, $\delta^{13}C$

Re-classification

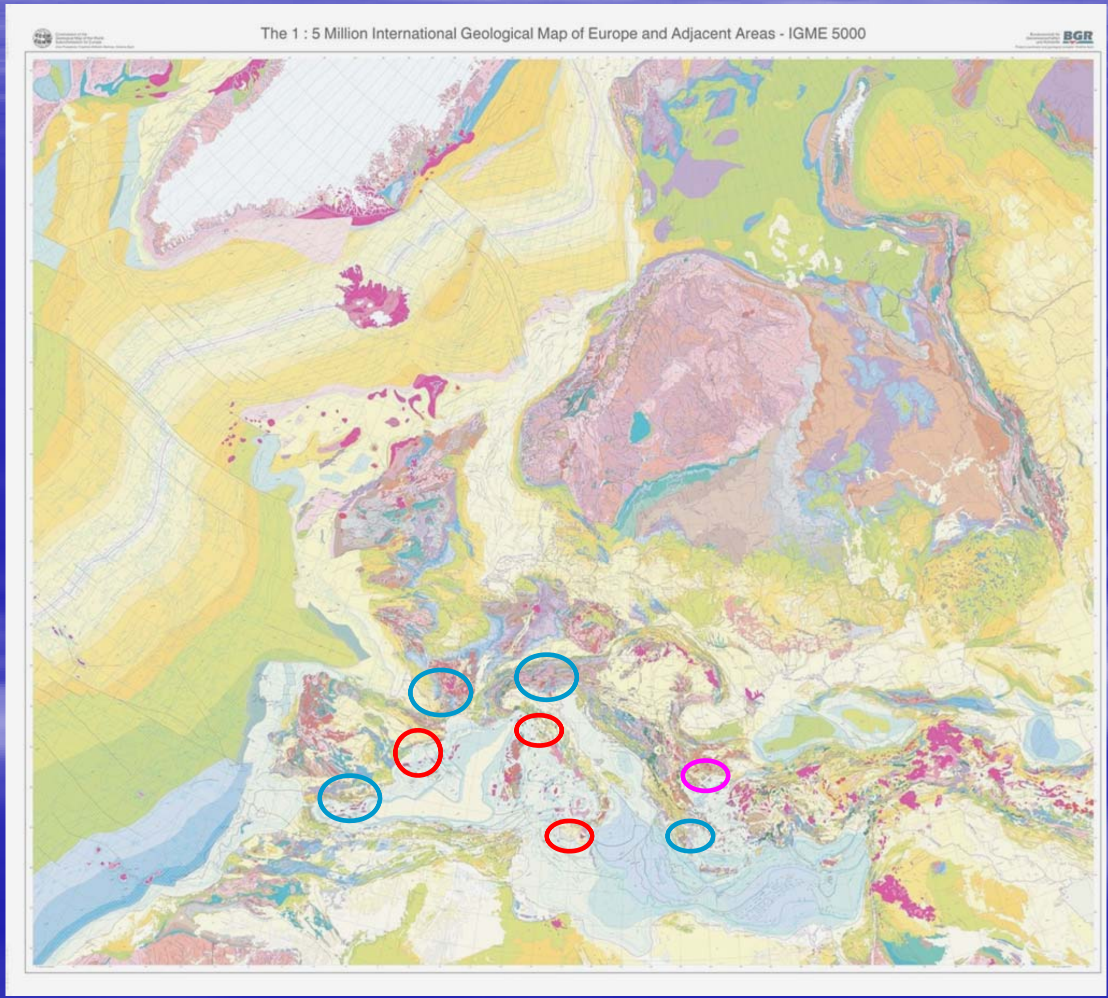
78%

	% correctly classified	TRE	CAR	TOS	BAR	CHA	SIC	ALG	LAK
TRE	91	51	0	5	0	0	0	0	0
CAR	70	0	28	1	0	3	4	4	0
TOS	87	5	0	34	0	0	0	0	0
BAR	40	0	1	1	4	3	1	0	0
CHA	90	0	1	3	0	36	0	0	0
SIC	63	0	8	0	2	0	25	3	2
ALG	57	0	0	0	0	0	6	8	0
LAK	79	0	0	0	0	0	6	0	22

TE: geological discrimination of olive oils

Significant differences between geological areas (limestone, shale/clay, acid magmatic) for:

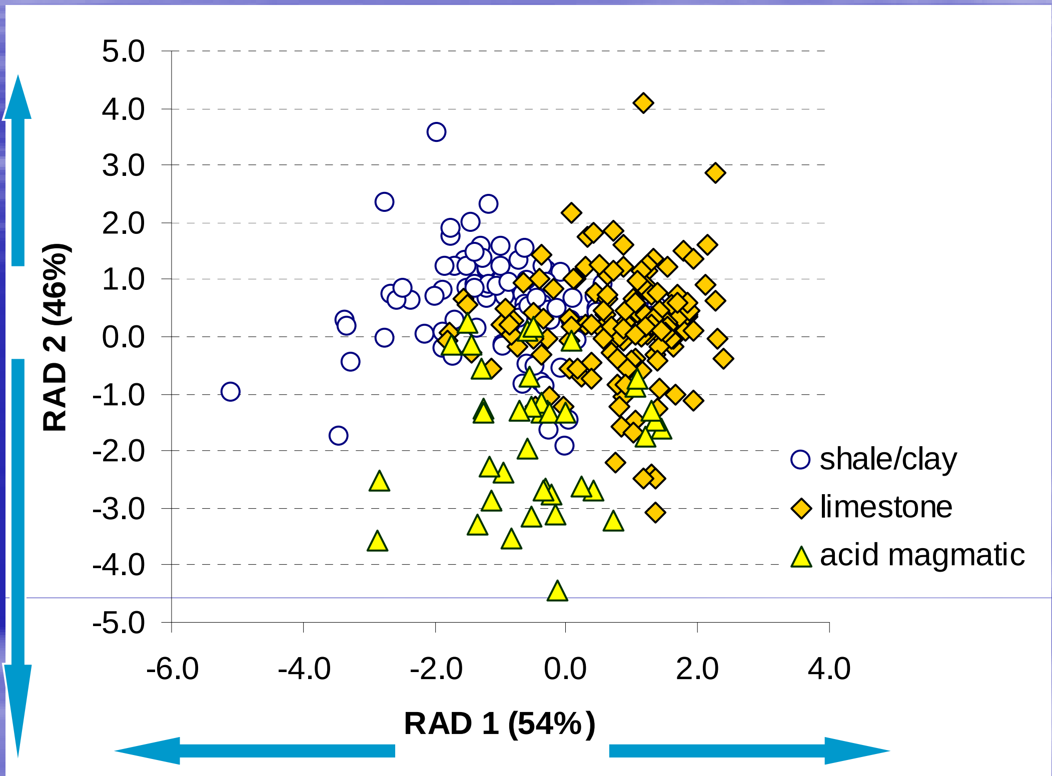
Mg, K, Ca, V, Mn, Zn, Rb, Sr, Ce, Sm, Cs, La, Eu, U



TE: geological discrimination of olive oils – Canonical Multivariate Discriminant Analysis

Ce

Sm, U, Ca, Rb



V, Rb

Cs

RAD1+RAD2

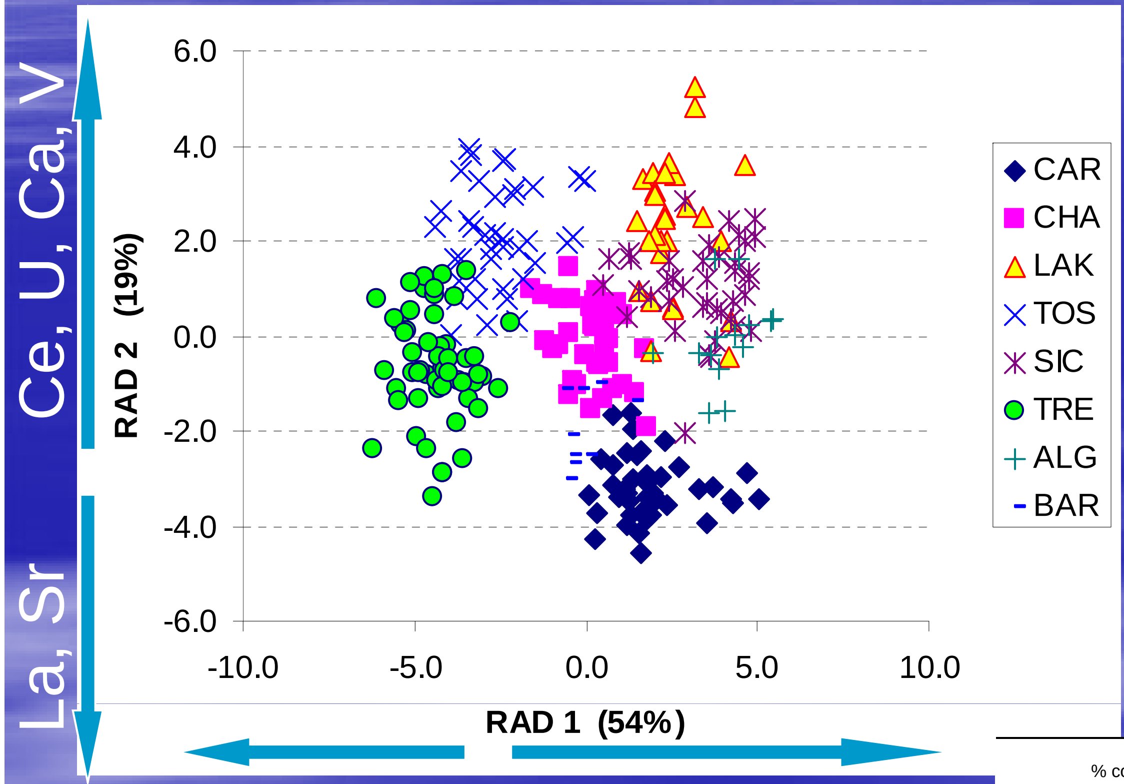
100%

Re-classification

76%

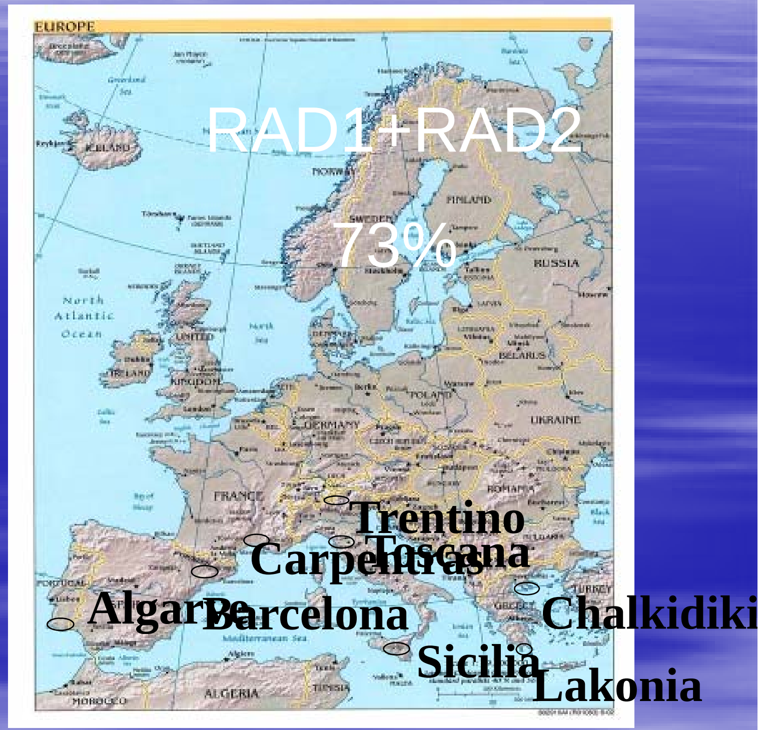
	% correctly classified	limestone	acid magmatic	shale/ clay
limestone	83	115	6	17
acid magmatic	63	9	25	6
shale/clay	72	20	5	64
Total	76	144	36	87

SIRA+TE: geographical discrimination of olive oils – Canonical Multivariate Discriminant Analysis



Ce

$\delta^{18}O$, $\delta^{13}C$, La



Re-classification 95%

	% correctly classified	TRE	CAR	TOS	BAR	CHA	SIC	ALG	LAK
TRE	95	53	0	2	0	1	0	0	0
CAR	98	0	39	0	1	0	0	0	0
TOS	97	1	0	38	0	0	0	0	0
BAR	100	0	0	0	10	0	0	0	0
CHA	98	0	0	1	0	39	0	0	0
SIC	95	0	0	0	0	0	38	0	2
ALG	100	0	0	0	0	0	0	14	0
LAK	86	0	0	0	0	0	3	1	24

Conclusions

- The stable isotope ratios of H, C and O of olive oils and the ratios of H and O of the relevant fresh surface waters correlated to the climatic (mainly temperature) and geographical (mainly latitude and distance from the coast) characteristics of the provenance sites.

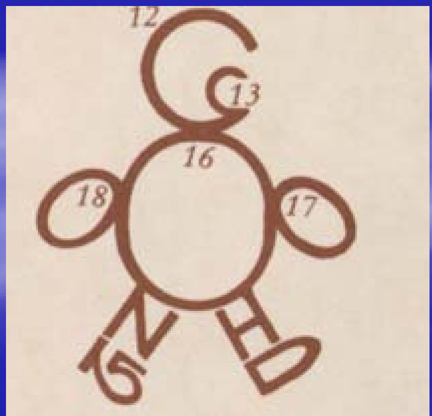
Conclusions

- It was possible to characterise the geological origin of the olive oils by using the content of 14 elements (Mg, K, Ca, V, Mn, Zn, Rb, Sr, Cs, La, Ce, Sm, Eu, U).

Conclusions

- By combining the 3 isotopic ratios with the 14 elements and applying a multivariate discriminant analysis, a good discrimination between olive oils from 8 European sites was achieved, with 95% of the samples correctly classified into the production site.

Thank you for your attention



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