Analytical Challenges in Determining the Origin of Olive Oil using $^{87}Sr/^{86}Sr$ isotope ratios

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2nd ISO-FOOD Symposium, April, 24th-26th,Portorož, Slovenia

Outline

- Introduction
  - Olive oil
  - Adulteration
  - Sr from soil to the oil
- Experimental work and discussion of results
- Linking Sr isotope ratio between oil and soil
- Conclusions

Olive oil

- important ingredient of the Mediterranean diet
- appreciation for nutritional and sensory properties
- low production and higher price compared to other oils

➔most adulterated food product

- PDO olive oil ➔ high price

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OLIVE OIL'S DARK SIDE

By Sally Errico February 7, 2012

In the August 13, 2007, issue of the magazine, Tom Mueller wrote about corruption in the olive-oil trade. By the late nineteen-nineties, olive oil—often cut with cheaper oils, such as hazelnut and sunflower seed—was the most adulterated agricultural product in the European Union. The E.U.'s anti-fraud office established an olive-oil task force, "yet fraud remains a major international problem," Mueller wrote. "Olive oil is far more valuable than most other vegetable oils, but it is costly and time-consuming to produce—and surprisingly easy to doctor."

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Olive-oil fraud continues today, though modern governments are often less thorough and effective than the Romans at preventing it. Olive oil has historically been one of the most frequently adulterated products in the European Union, whose profits, one E.U. anti-fraud investigator told me, have at times been "comparable to cocaine trafficking, with none of the risks." In America, olive-oil adulteration, sometimes with cut-rate soybean and seed oils, is widespread, but olive oil is not tested for by the F.D.A.—F.D.A. officials tell me their resources are far too limited, and the list of responsibilities far too long, to police the olive-oil trade.

Modern olive-oil production has changed since the Roman times, too. Where is its future headed?

Two diametrically opposed trends exist in the olive-oil business. In the first, toward high-quality olive oil, new milling technologies—stainless steel mills, high-speed centrifuges, temperature- and oxygen-controlled storage tanks—are making it possible to produce the best extra-virgin olive oils in history: fresh, complex, and every bit as varied as wine varietals. (There are about seven hundred different kinds of olives.) Consumer demand for high-quality olive

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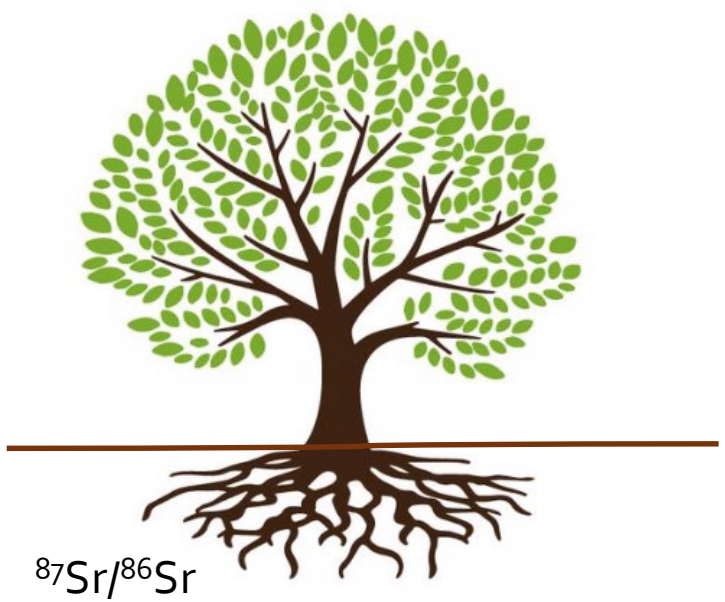
C, O, H, N, S and non-traditional elements - Sr

$^{87}Sr/^{86}Sr$ isotope ratio in olive oil



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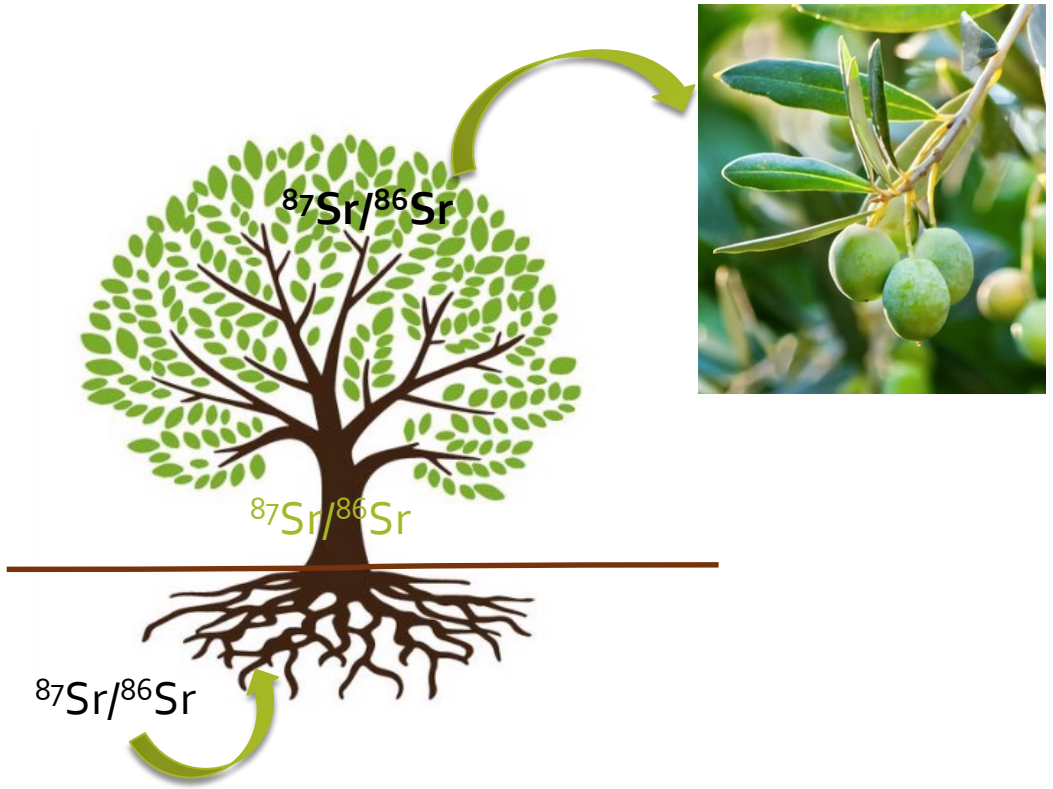

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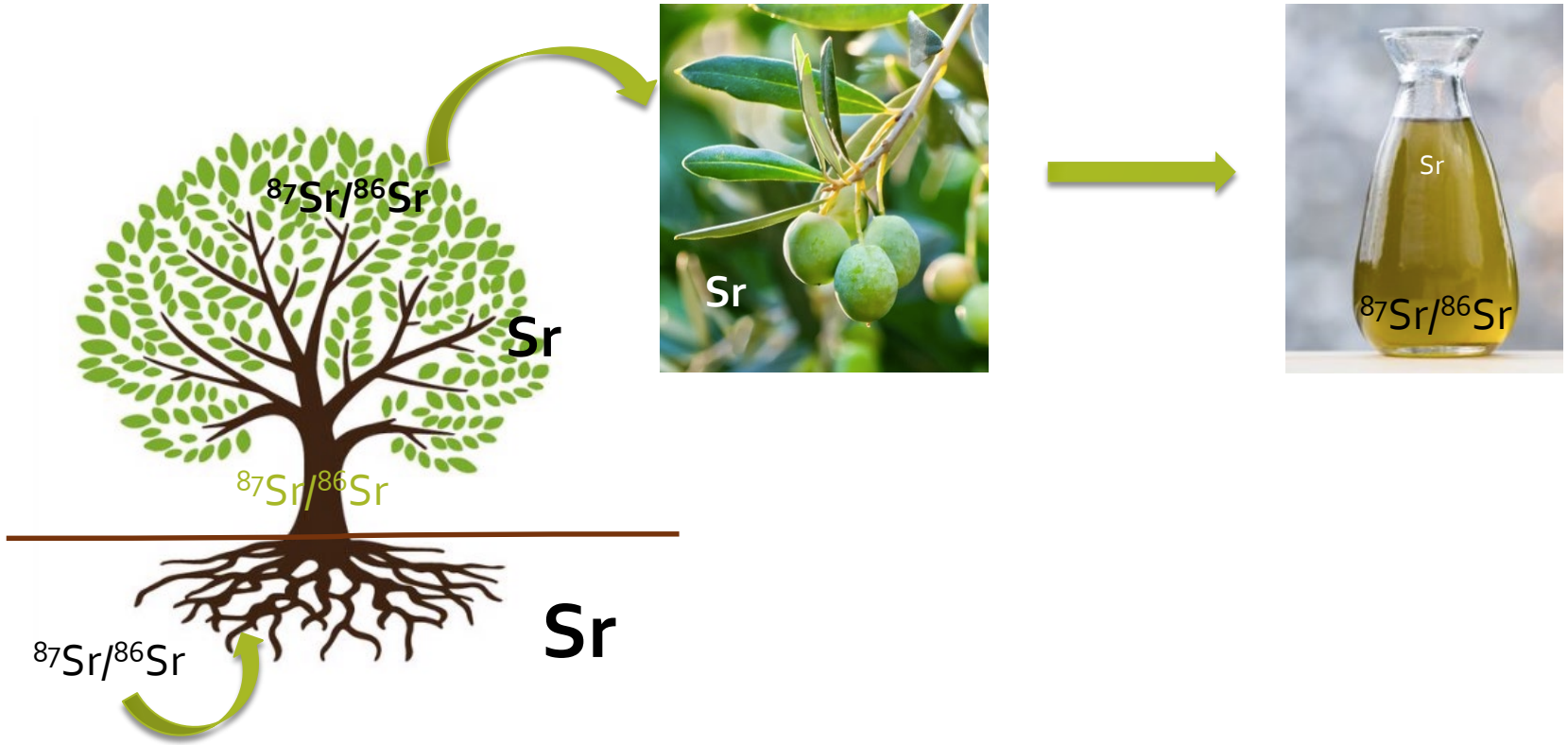

$^{87}Sr/^{86}Sr$ isotope ratio determination

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Reference	Benincasa et al., (2007)	Camin et al., (2010a)	Camin et al., (2010b)	Medini et al., (2015)	Damak et al., (2019)
Preparation method	MW digestion (HNO_3)	UAE (HNO_3 + HCl)	UAE (HNO_3 + HCl + H_2O_2)	MW digestion (HNO_3 + H_2O_2)	MW digestion (HNO_3 + H_2O_2)
Country	Italy	Italy	Italy	Morocco	Tunisia
Sr (µg kg^{-1})	< 9.6 – 48.9	0.049 – 13.4	< 0.3	2.0 – 13.9	30 - 37

- Sensitivity of the MC-ICP-MS (Nu II, dry plasma; optimum: 25 ppb Sr (0.001 %); min: 5 ppb (0.03 %); 1 ppb (0.08 %))

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- Complex matrix

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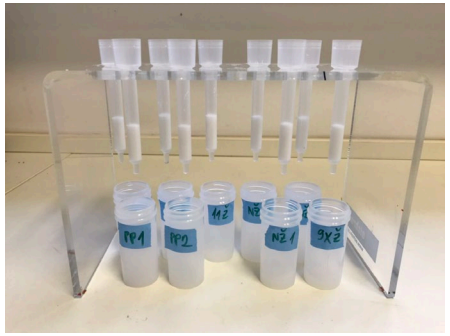


Sample pre-treatment

↓

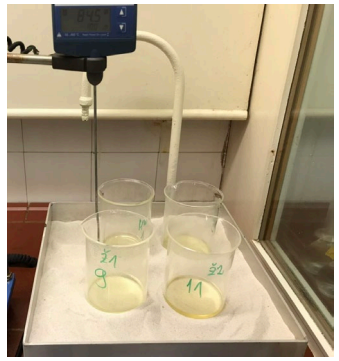
Evaporation and organic matter degradation

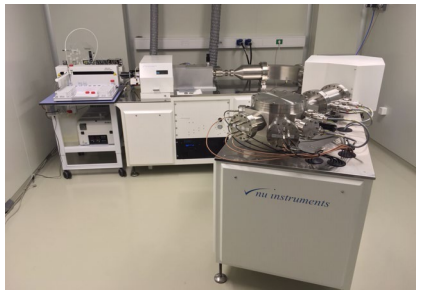
↓

Isolation of Sr
(Sr Resin, Eichrom)

↓

$^{87}Sr/^{86}Sr$ determination by MC-ICP-MS





Extraction of Sr from olive oil

Sample pre-treatment

Evaporation and organic matter degradation

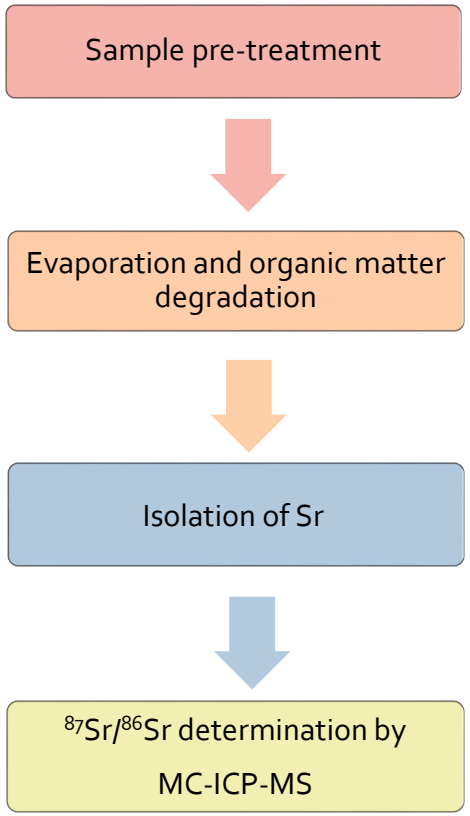
Isolation of Sr

$^{87}Sr/^{86}Sr$ determination by MC-ICP-MS

- Microwave digestion of the oil
- Digestion of the oil by H_2SO_4 at high T

- Large amounts of H_2SO_4 required;
- Contamination;
- Dangerous procedure.

Extraction of Sr from olive oil



- Microwave digestion of the oil
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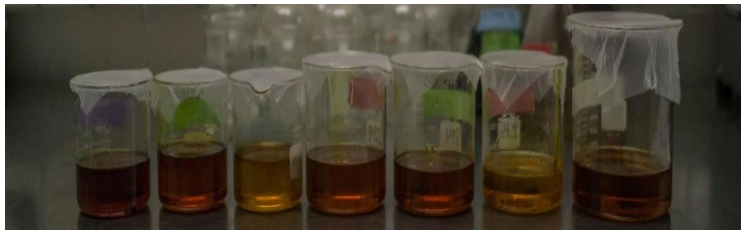
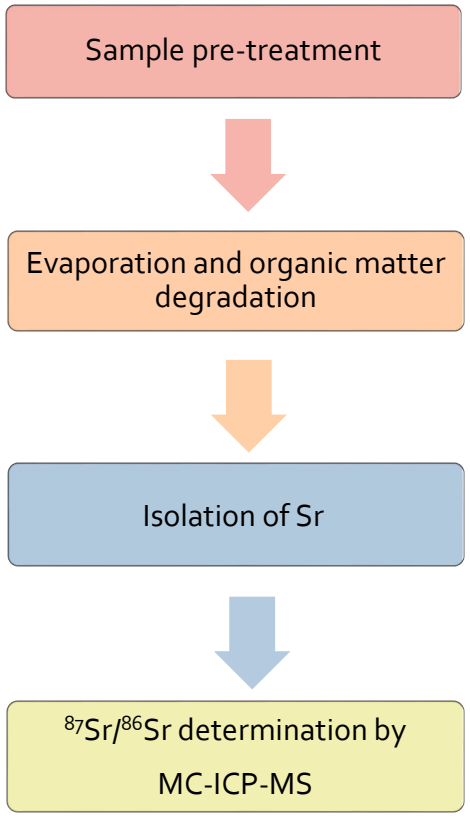


- Large amounts of H_2O_2 and HNO_3 required;
- After 14 days of „cooking" no change in oil quantity.

Extraction of Sr from olive oil



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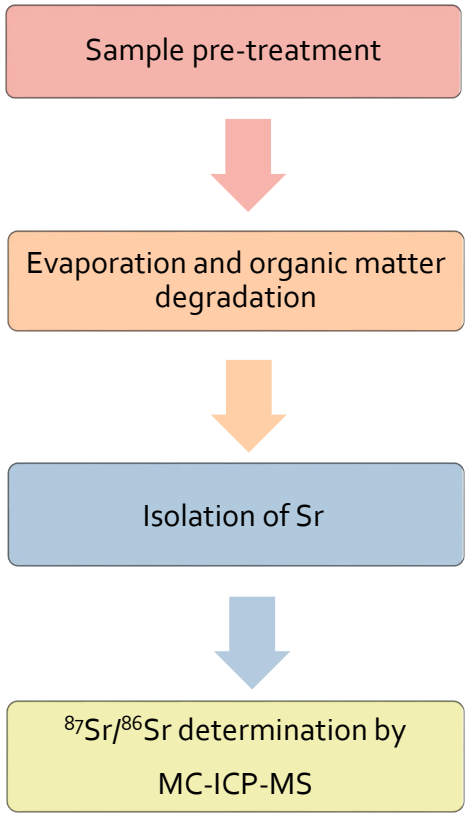

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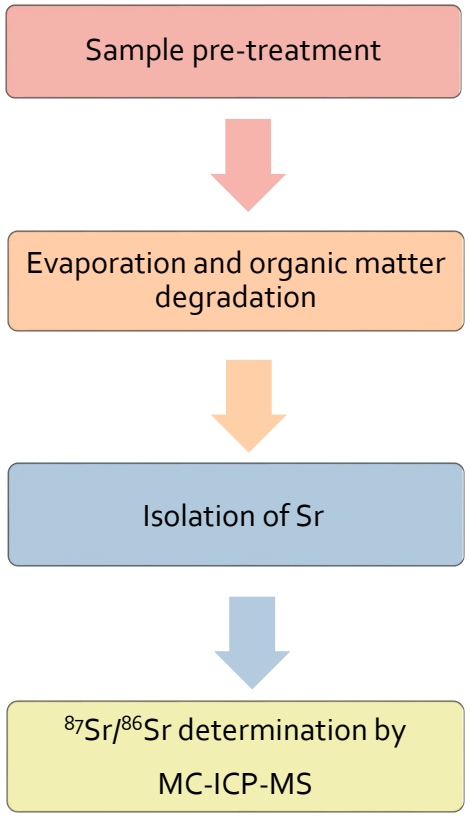
Extraction of Sr from olive oil



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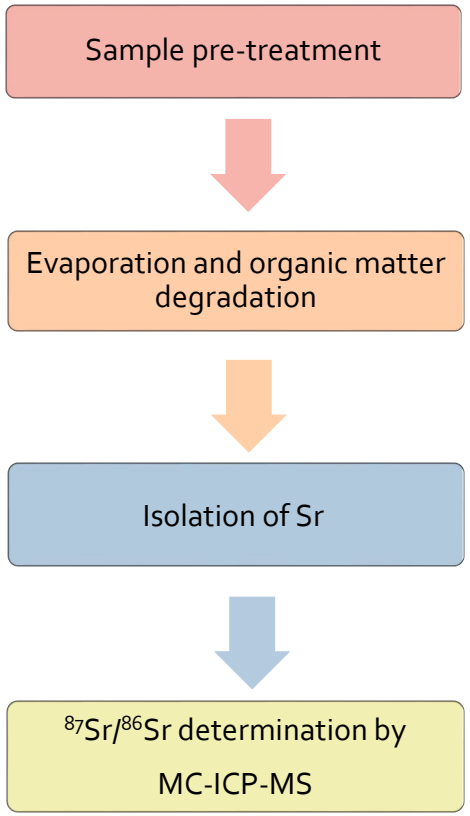

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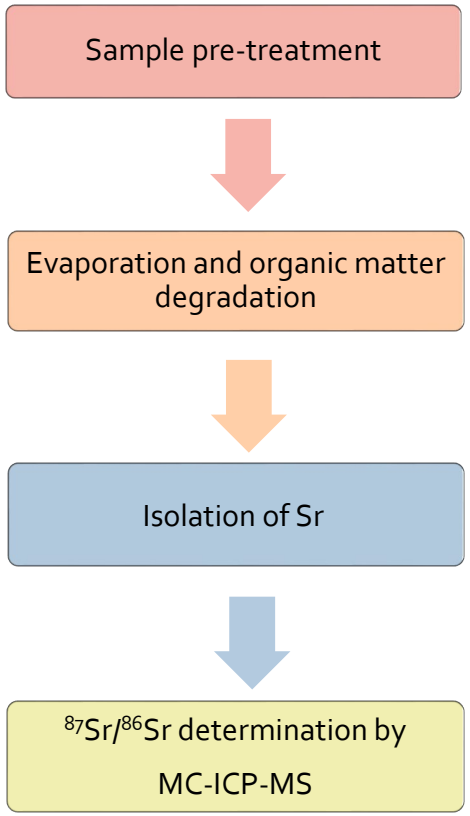

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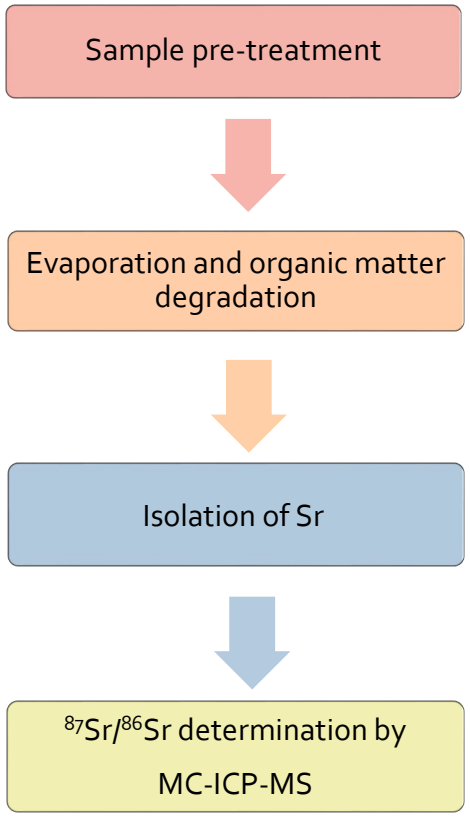

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  - Water → No Sr extracted
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  - 2 % HNO_3 + 0.1 % HCl (*ref.: Camin et al., 2010*)

Extraction of Sr from olive oil

Olive oil ➔ 1 ppb Sr
MC-ICP-MS ➔ > 10 ppb

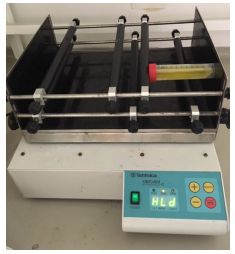
100 mL of oil

Microwave digestion

0.5 g olive oil
1 mL H_2O_2
5 mL HNO_3

Mechanical stirring

20 mL olive oil
20 mL 2 % HNO_3 + 0.1 % HCl
t = 2 h, 5 h, 16 h



Ultrasound assisted extraction

20 mL olive oil
20 mL 2 % HNO_3 + 0.1 % HCl
t = 1 h, 3 h

MS 16h + US 1h (40°C)

Elimination of organic matter

Sample pre-treatment

20 mL olive oil
20 mL mixture 2 % HNO_3 + 0.1 % HCl
MS 16h + US 1h (40°C)

Evaporation and organic matter degradation

Isolation of Sr

$^{87}Sr/^{86}Sr$ determination by MC-ICP-MS

Waste

Evaporation

Elimination of organic matter

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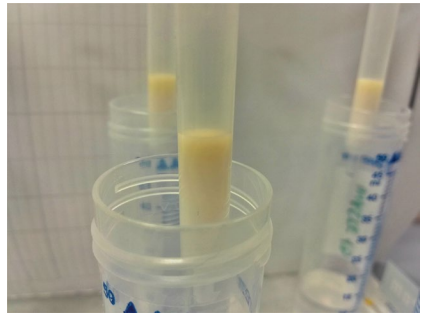

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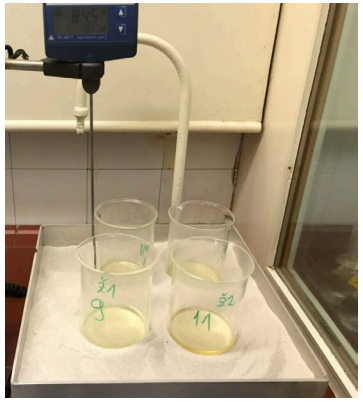
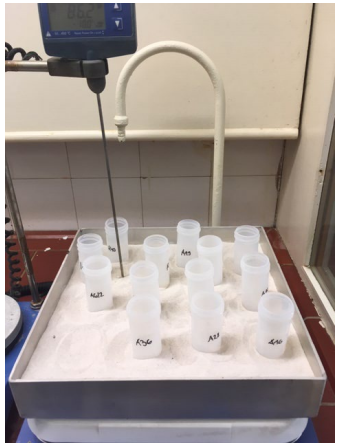


- evaporation of individual portions
  - destruction of residue with H_2O_2 and HNO_3; hot plate



- evaporation of merged portions
  - destruction of residue with H_2O_2 and HNO_3; hot plate
  - destruction of residue with MW digestion
  - destruction of residue with calcination

Sr/matrix separation on Sr specific resin (300mg)

Sr concentration determination by ICP-MS

$^{87}Sr/^{86}Sr$ isotope ratio determination by MC-ICP-MS

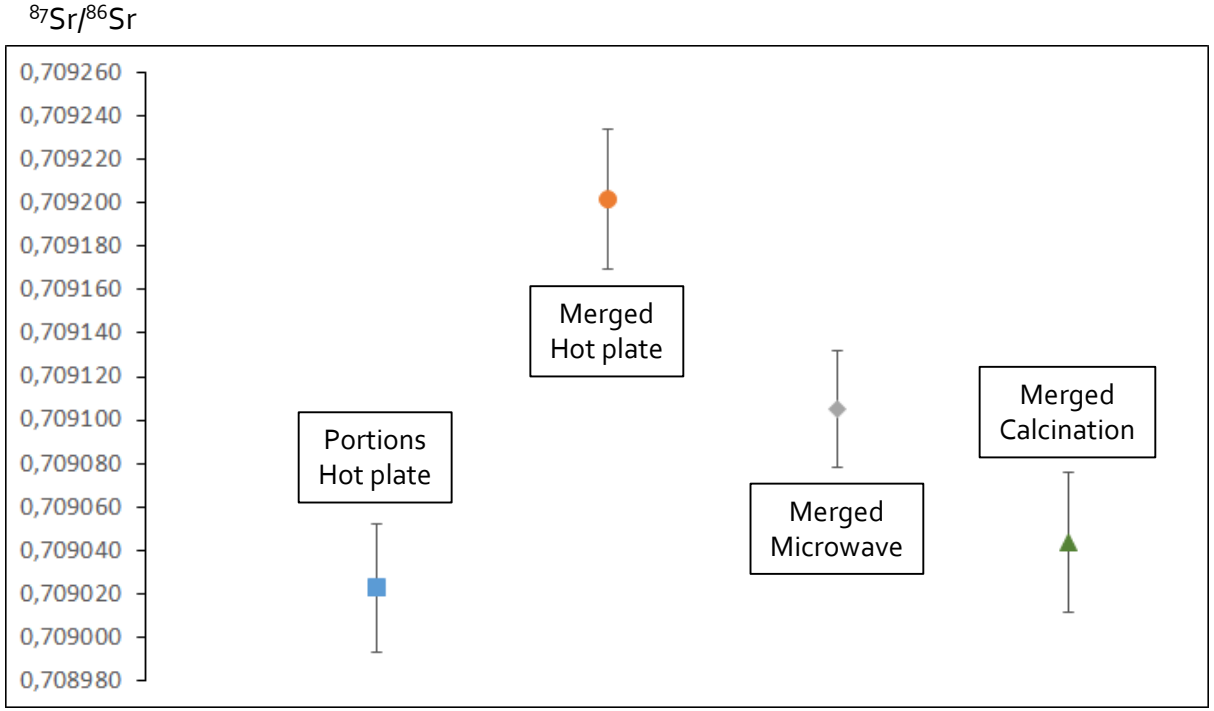
Elimination of organic matter

Individual portions:

- destruction of residue with H_2O_2 and HNO_3, hot plate – extraction recovery > 80 %

Merged portions:

- destruction of residue with H_2O_2 and HNO_3, hot plate – extraction recovery ~ 60 %
- destruction of residue with MW digestion – extraction recovery > 70 %
- destruction of residue with calcination – extraction recovery > 80 %



Method - overview

Sample pre-treatment

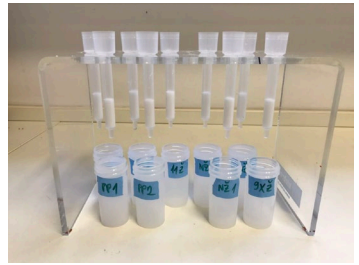
Evaporation and organic matter degradation

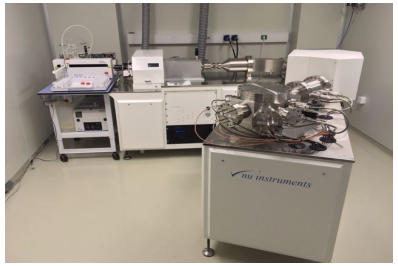
Isolation of Sr
(Sr Resin, Eichrom)

$^{87}Sr/^{86}Sr$ determination by
MC-ICP-MS

5 portions of 20 mL olive oil
20 mL mixture 2 % HNO_3 + 0.1 % HCl
MS 16h + US 1h (40°C)

genuine Tunisian olive oils





$^{87}Sr/^{86}Sr$ in Tunisian olive oil

Sample location	$^{87}Sr/^{86}Sr$	2xσ
Sfax	0.70897	0.00024
Kairouan	0.70820	0.00010
Zarzis	0.70920	0.00010

Linking $^{87}Sr/^{86}Sr$ in olive oil/pomace to the soil

- preliminary results
- oil-pomace and pomace-soil pairs from different locations (Izola, SI and Sfax, TN)

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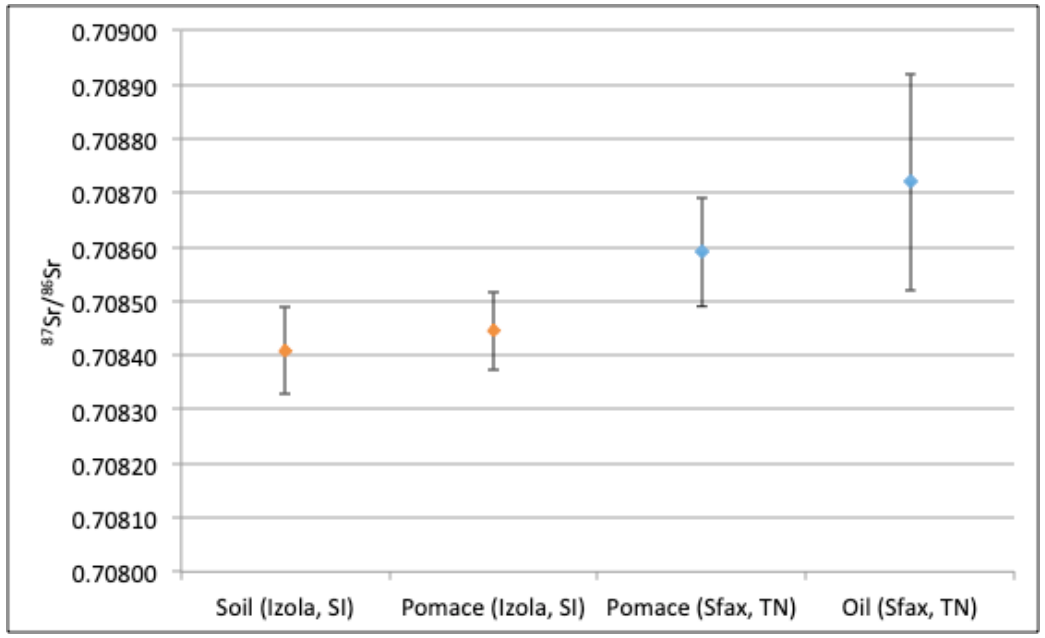

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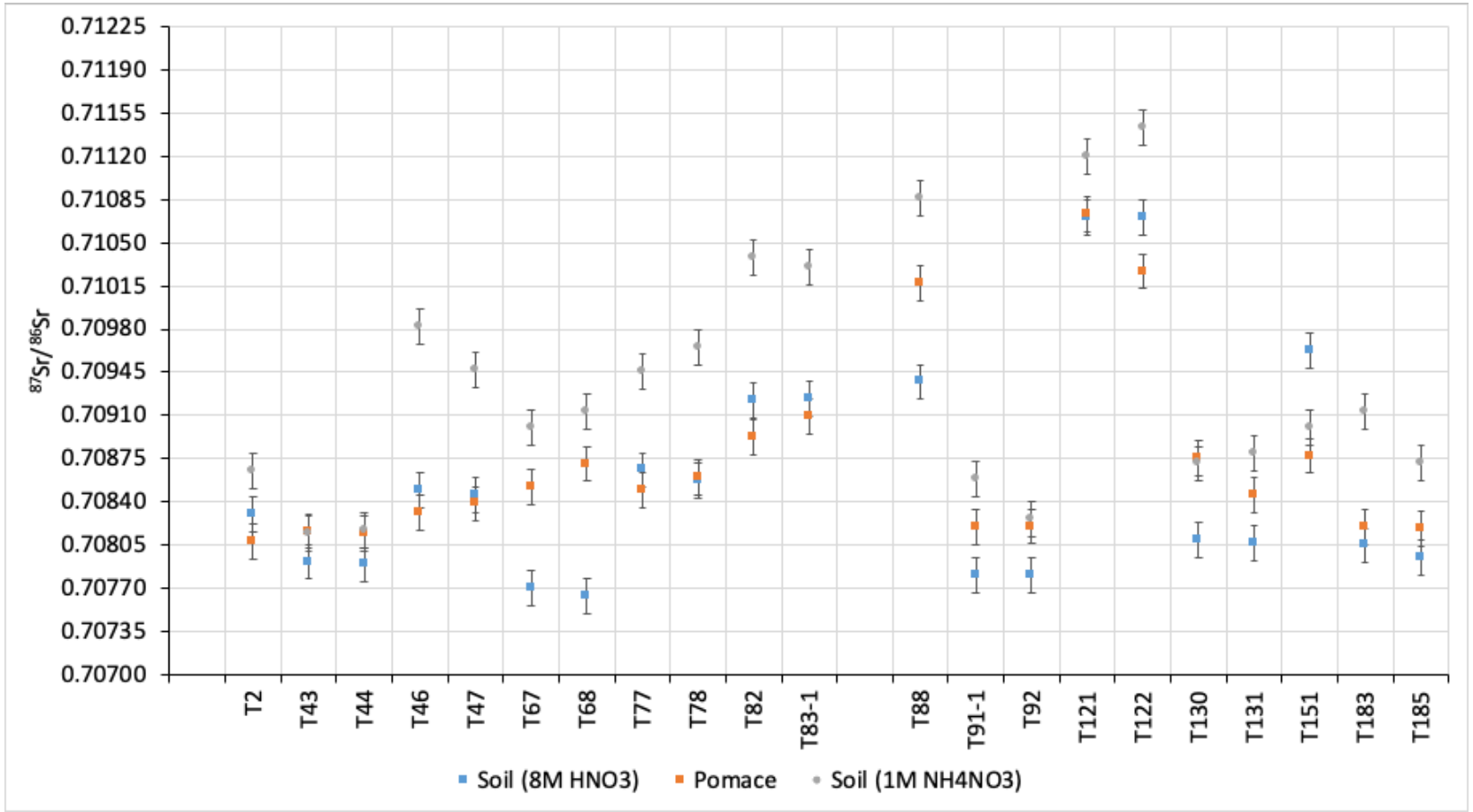
Samples from Croatia:
- Soil
- Pomace
- Oil



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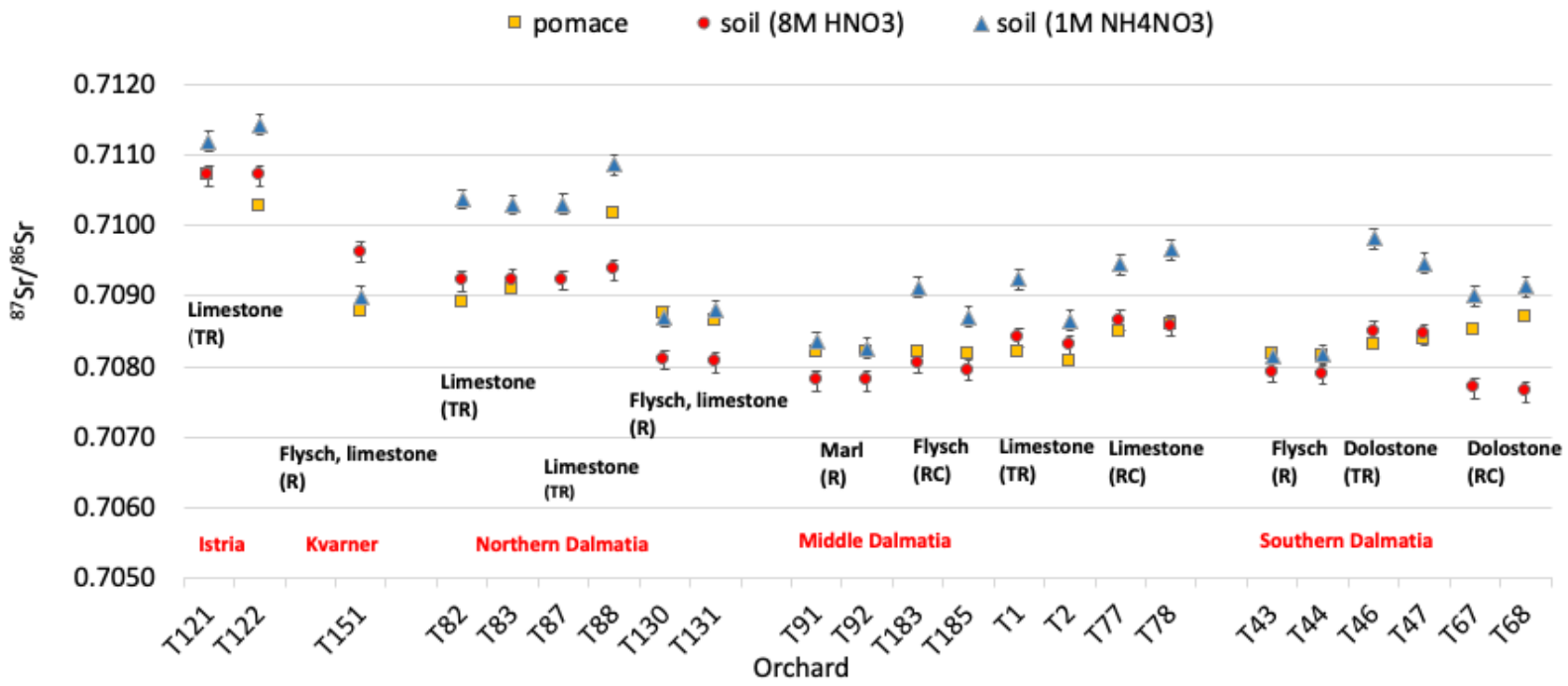

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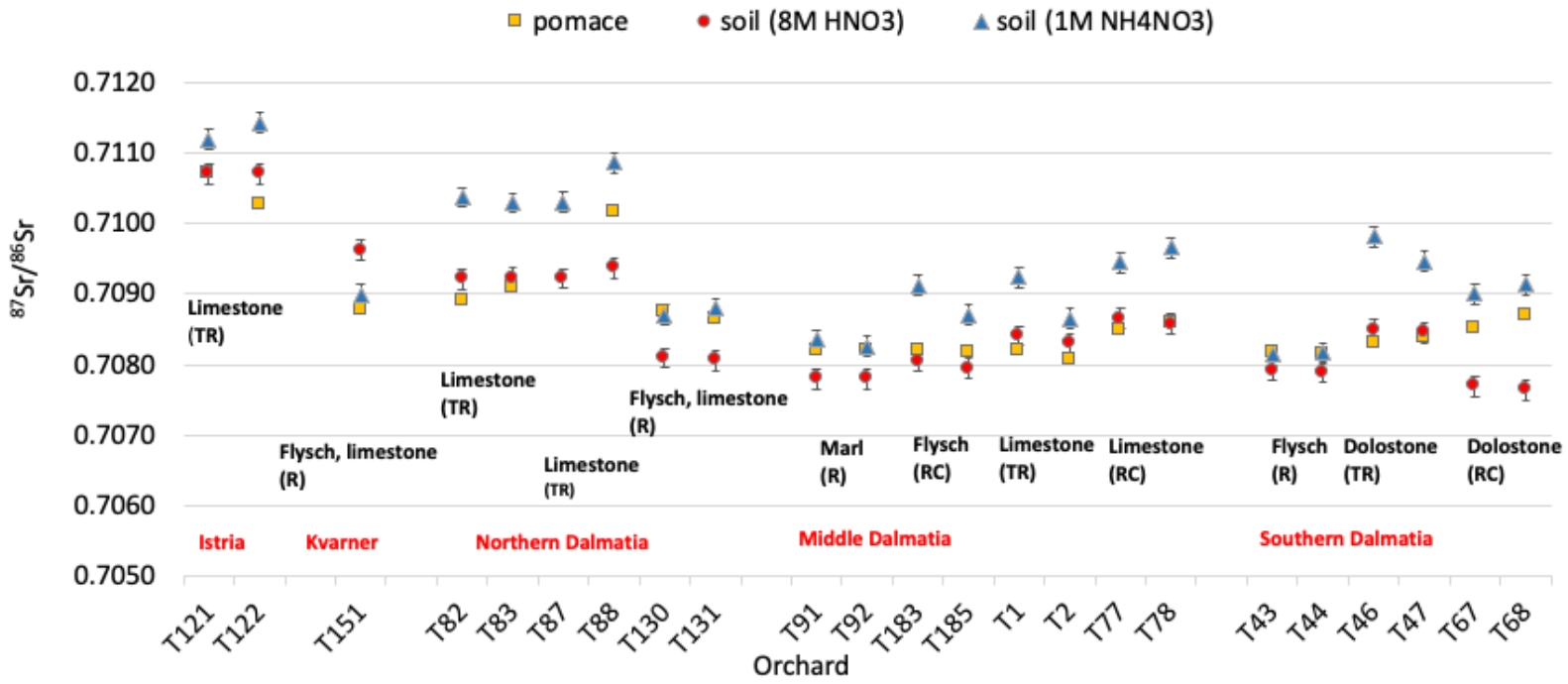

- Soil type and characteristics
- Bedrock
- Proximity to the sea
- Soil maintenance
- Orchard treatment

Conclusions

- recognition of olive oil authenticity – important issue regarding economic aspects and health risks
- the developed analytical method for $^{87}Sr/^{86}Sr$ determination in olive oil can be used for authenticity verifications
  - is limited by the amount of Sr present in the oil
  - reference materials – missing
  - validation of the method – intercomparison study
- Sr isotope composition in olive oil – additional information linking olive oil with the geological characteristics of the production area

Extra-Virgin Olive Oil
European oils, and especially Mediterranean supermarket brands like XXX, routinely fail purity tests (perhaps because of low-grade or stale oil). Try to sample olive oil before buying — real olive oil tastes and smells grassy, fruity, and ripe. One way to avoid fraud: Buy bottles from Chilean, Australian or Californian olive-growing regions. Ref.: www.mensjournal.com

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- proper selection of extraction methods from soil

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Thank you for your attention!