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Control of geographic origin of saffron using stable isotope analysis

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ELEA/TIF

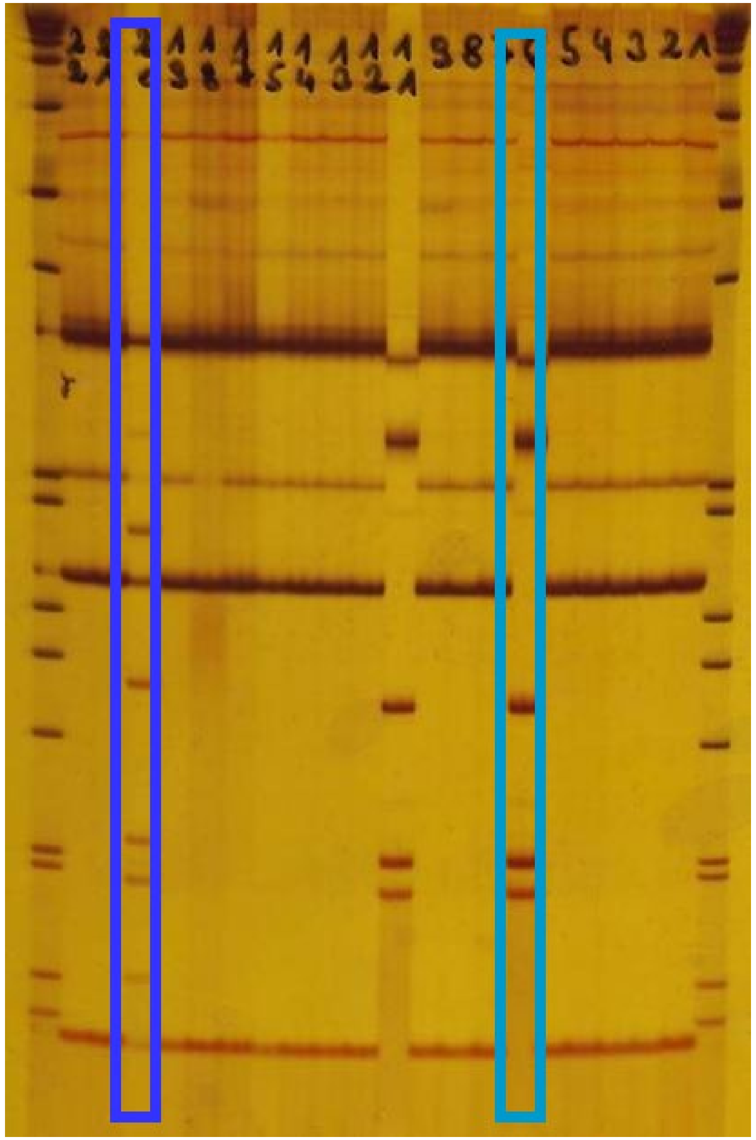
Saffron Geographic Origin

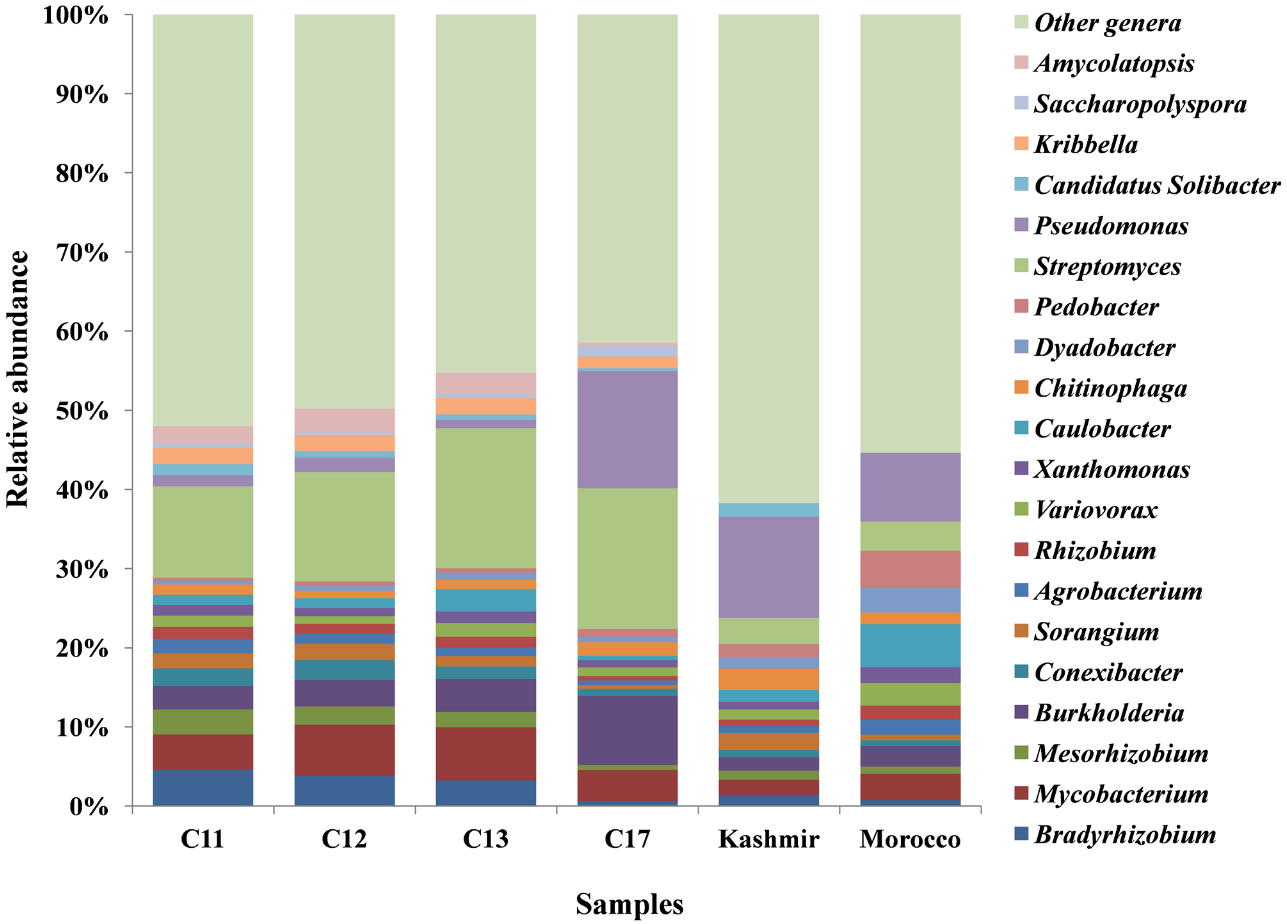
- Most expensive spice, common target of adulteration and mislabeling
- Iran largest producing country. Other big producers: Morocco, India, Greece, Spain
- Spanish saffron wonder: Annual probuction of ca. 2tons, export of Spanish saffron of ca. 20tons

Crocus sativus cartwrightii

- Saffron are the dried stigmata of the *crocus sativus* plant.
- Crocus plant remains dormant in its bulb/onion called corm for a significant ime of the year.
- No genetic heterogeneity

Molecular markers & Microbiome





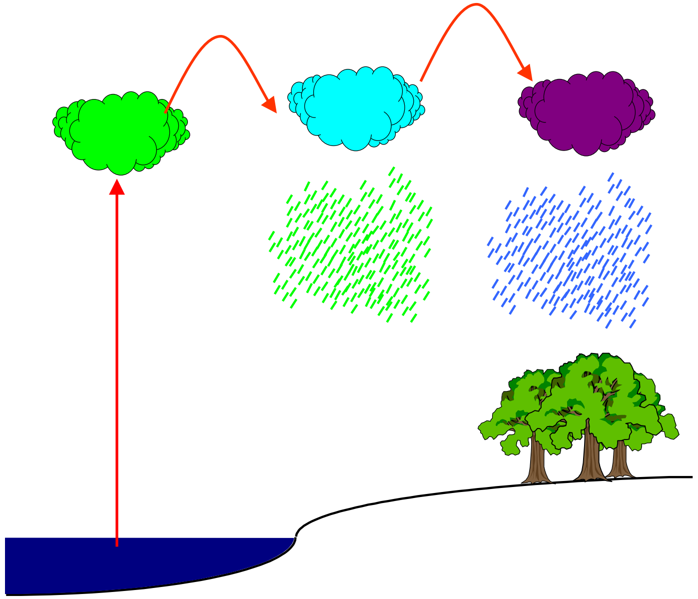
Bhagat et al., 2021

SAFFRON PROJECT:

- Samples from Morocco, Spain, Kashmir/India, Switzerland, Slovenia, Greece, Italy, Iran, Egypt, Saudi Arabia, Argentina.
- Harvest 2011 – 2014

Reasons for isotopic fractionation (H and O): water cycle

Hydrological cycle



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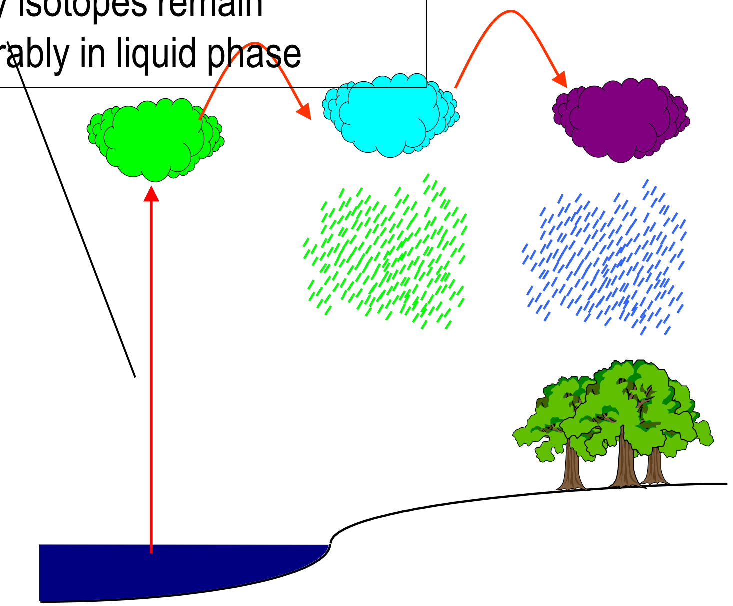
Hydrological cycle

Evaporation:
heavy isotopes remain preferably in liquid phase



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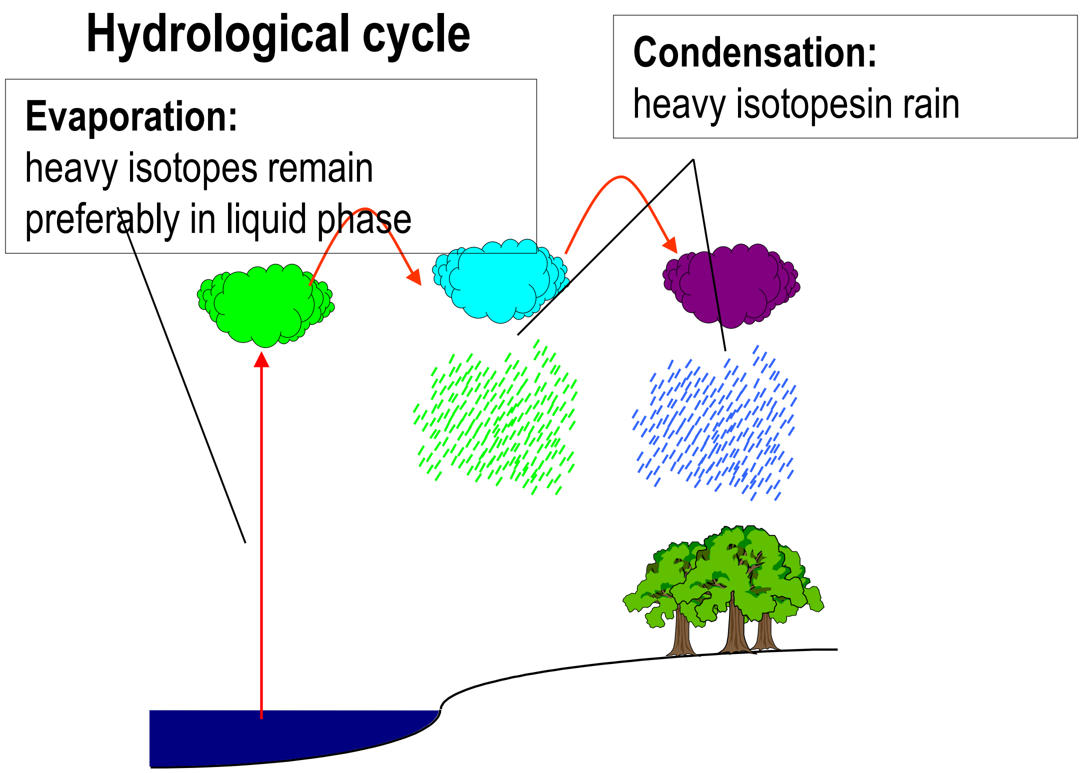

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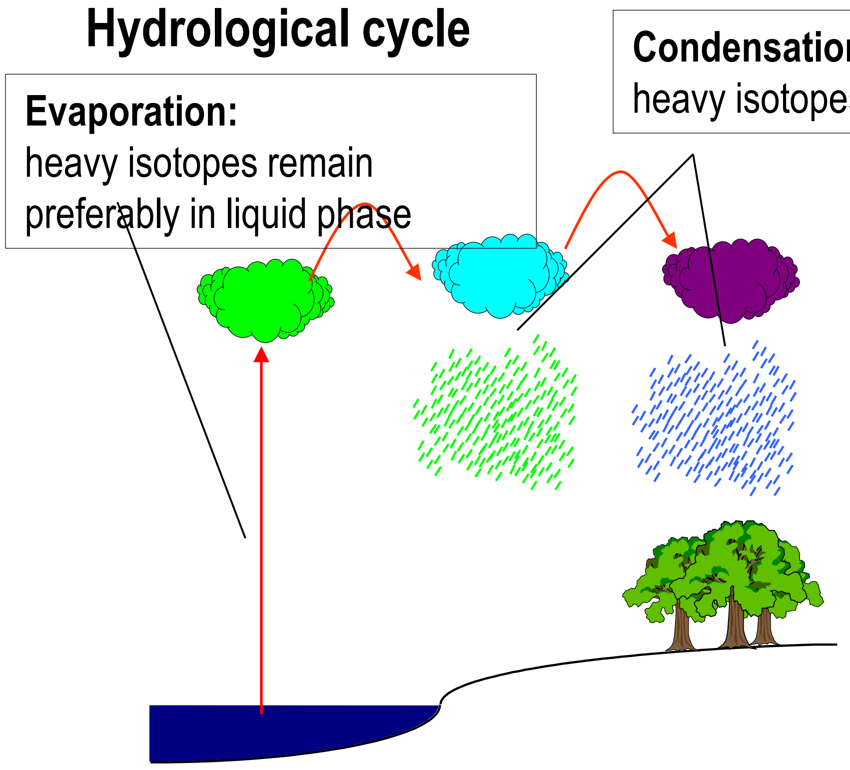

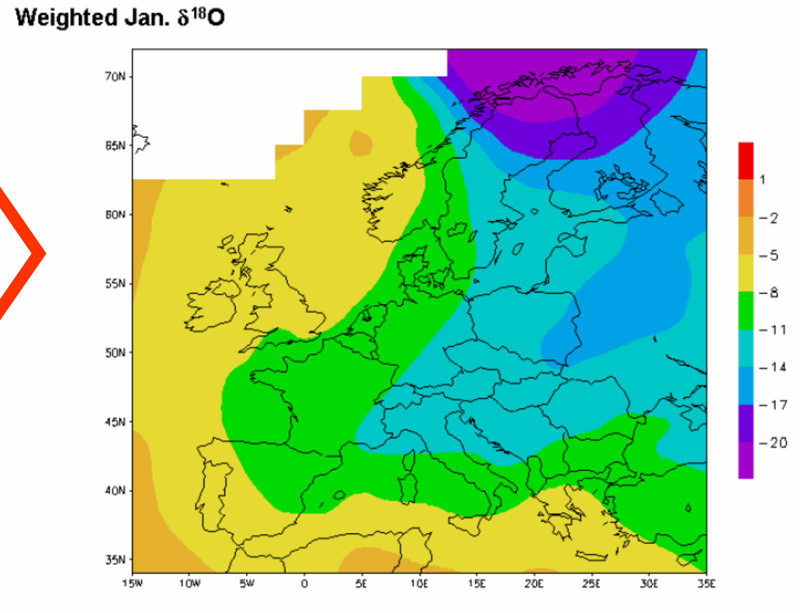

Reasons for isotopic fractionation (C): metabolism/photosynthesis

C_3-plants (Calvin-cycle)

$\delta^{13}C$ = -20 ... -30

C_4-plants (Calvin-Z. + Hatch-Slack-Pathway)
e.g. corn, cane

$\delta^{13}C$ = -10 ... -15

water availability,
drought stress

Reasons for isotopic fractionation (N): origin of N

- $\delta^{15}N$ ratio in plants depends on nitrogen isotope ratio of the bio-available N in the soil. Fertilizers influence and often dominate the $\delta^{15}N$ signal of the soil.
- N_{air} and N fixed by leguminoses may have a different isotopic composition than N fixed in soil.

Sulfur isotopes ($\delta^{34}S$), Strontium isotopes ($^{87}Sr/^{86}Sr$)

Reasons for isotopic fractionation: geogenic parameter

- S, Sr is incorporated into biological material without significant fractionation. Thus the isotopic composition of S, Sr is determined by the soil $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ composition, which is determined by the sulfur and strontium isotopic composition of the rock weathered to soil plus immissions from the atmosphere, sea, volcanoes or anthropogenic sources (e.g. fertilizer).

Determination and Control of Geographic Origin

Differentiation of geographic origin due to the respective environmental conditions

Influences on isotope ratios in plant products

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Biological

- Species
- Photosynthesis rate
- Genetic variability
- Age
- State of development

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Biological

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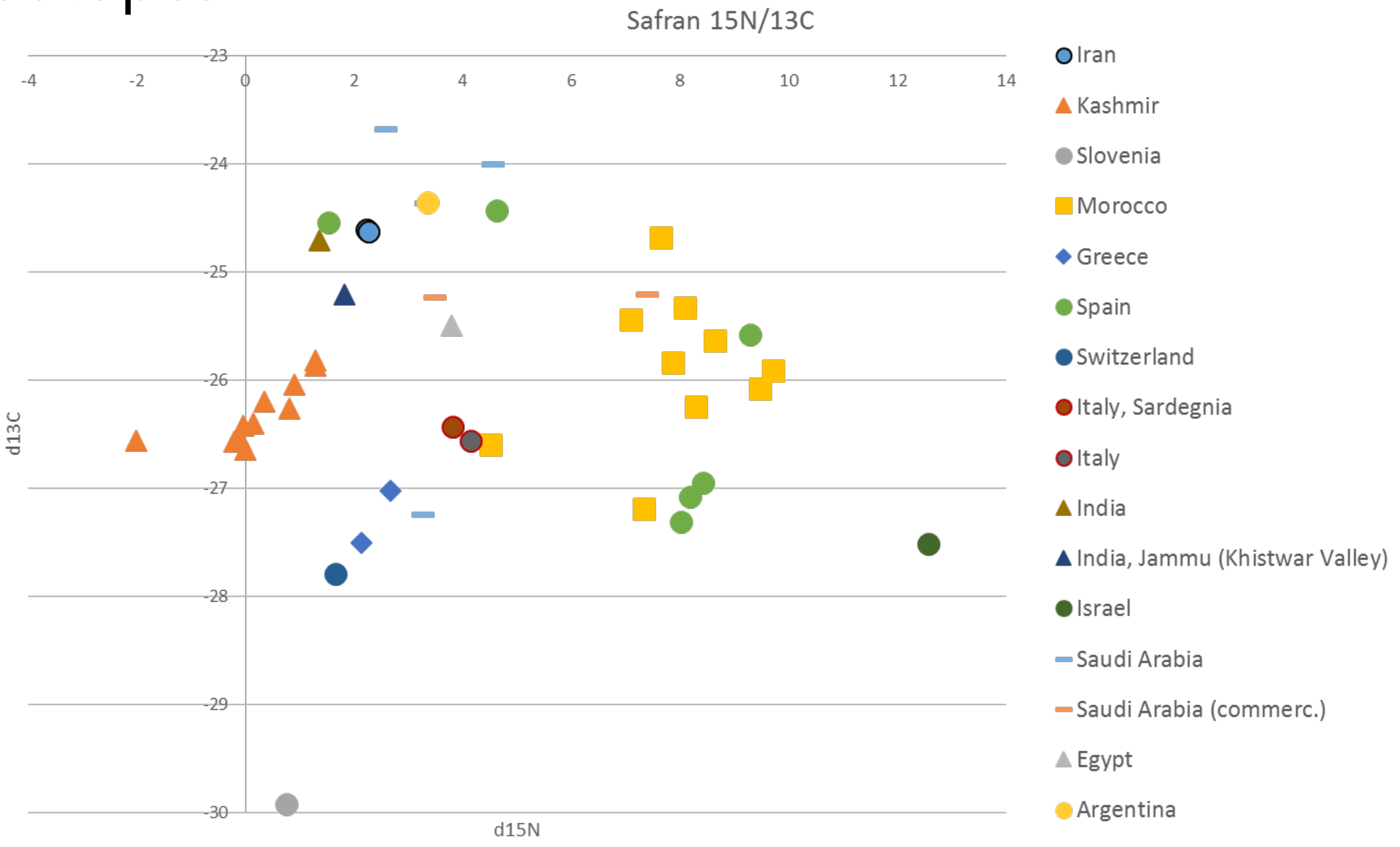
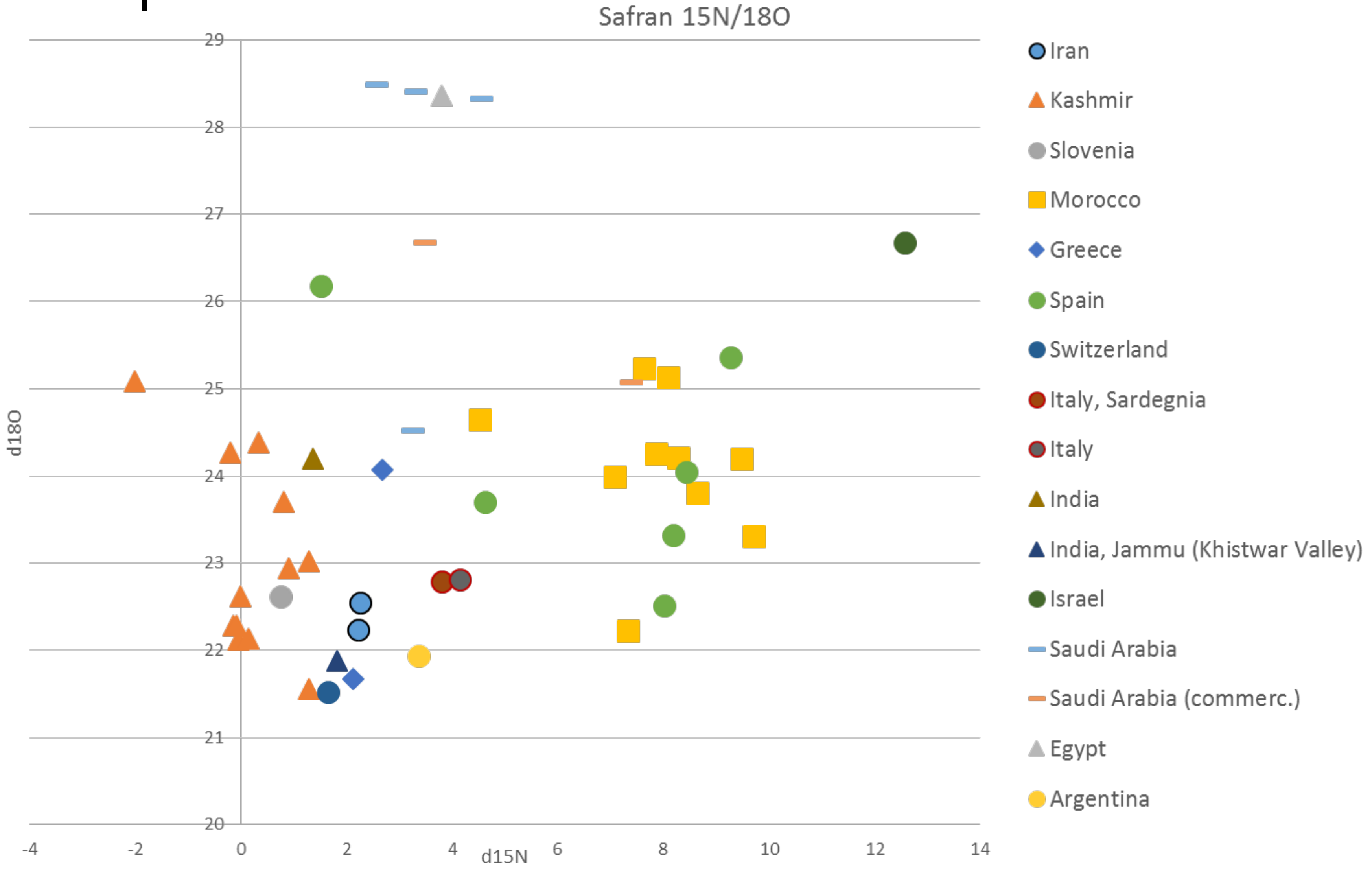
Environmental

- Water availability
- Salinity
- CO_2-Concentration
- Altitude
- Geology
- Weather
- Air pollution

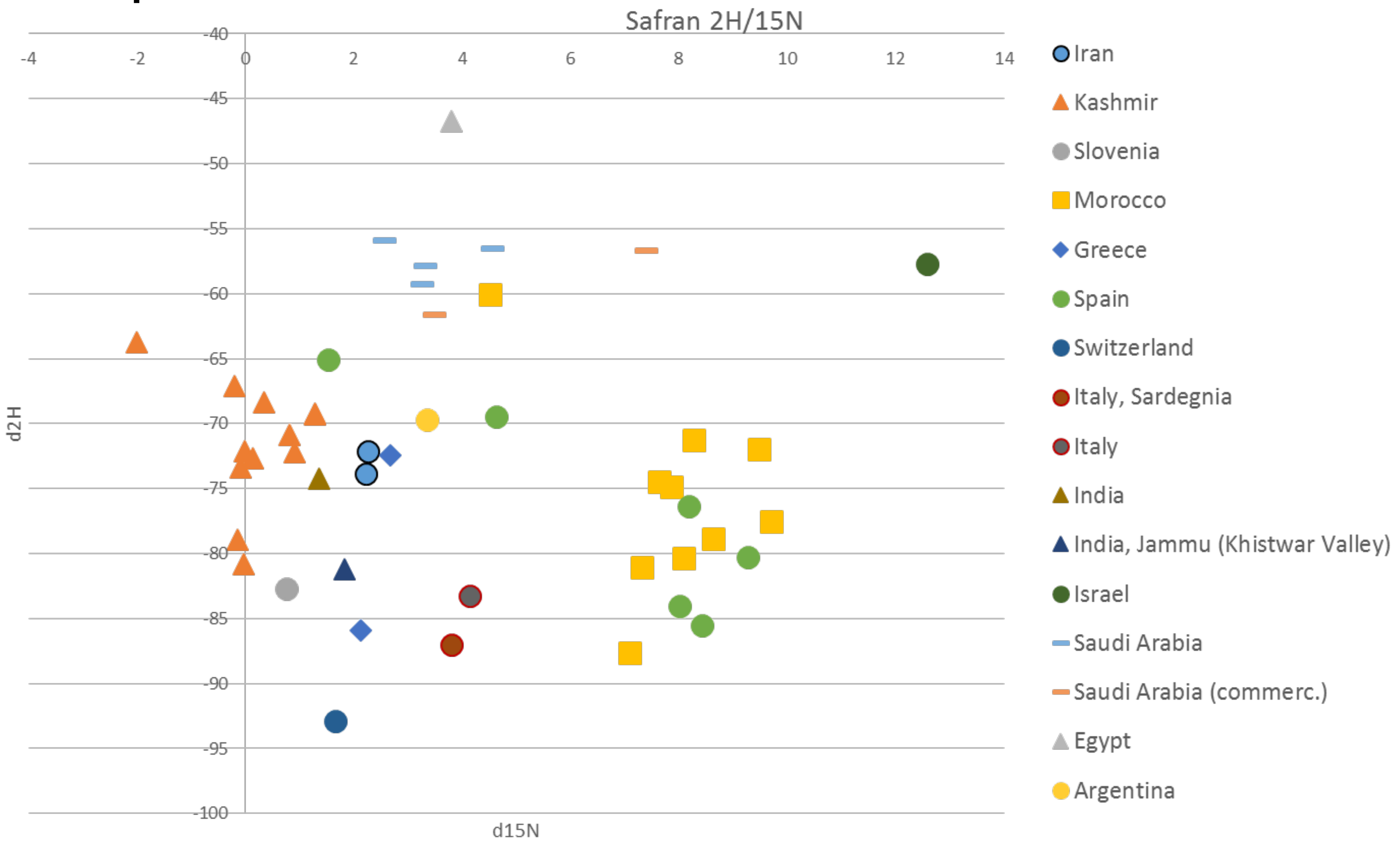
C-/N-isotopes


Safran 15N/13C
-23
-24
-25
-26
-27
-28
-29
-30
-4
-2
0
2
4
6
8
10
12
14
d13C
d15N
Iran
Kashmir
Slovenia
Morocco
Greece
Spain
Switzerland
Italy, Sardegnia
Italy
India
India, Jammu (Khistwar Valley)
Israel
Saudi Arabia
Saudi Arabia (commerc.)
Egypt
Argentina

N-/O- isotopes


Safran 15N/18O
d18O
d15N
29
28
27
26
25
24
23
22
21
20
-4
-2
0
2
4
6
8
10
12
14
Iran
Kashmir
Slovenia
Morocco
Greece
Spain
Switzerland
Italy, Sardegnia
Italy
India
India, Jammu (Khistwar Valley)
Israel
Saudi Arabia
Saudi Arabia (commerc.)
Egypt
Argentina

H-/N-isotopes



Safran 2H/15N
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-4
-2
0
2
4
6
8
10
12
14
d2H
d15N
Iran
Kashmir
Slovenia
Morocco
Greece
Spain
Switzerland
Italy, Sardegnia
Italy
India
India, Jammu (Khistwar Valley)
Israel
Saudi Arabia
Saudi Arabia (commerc.)
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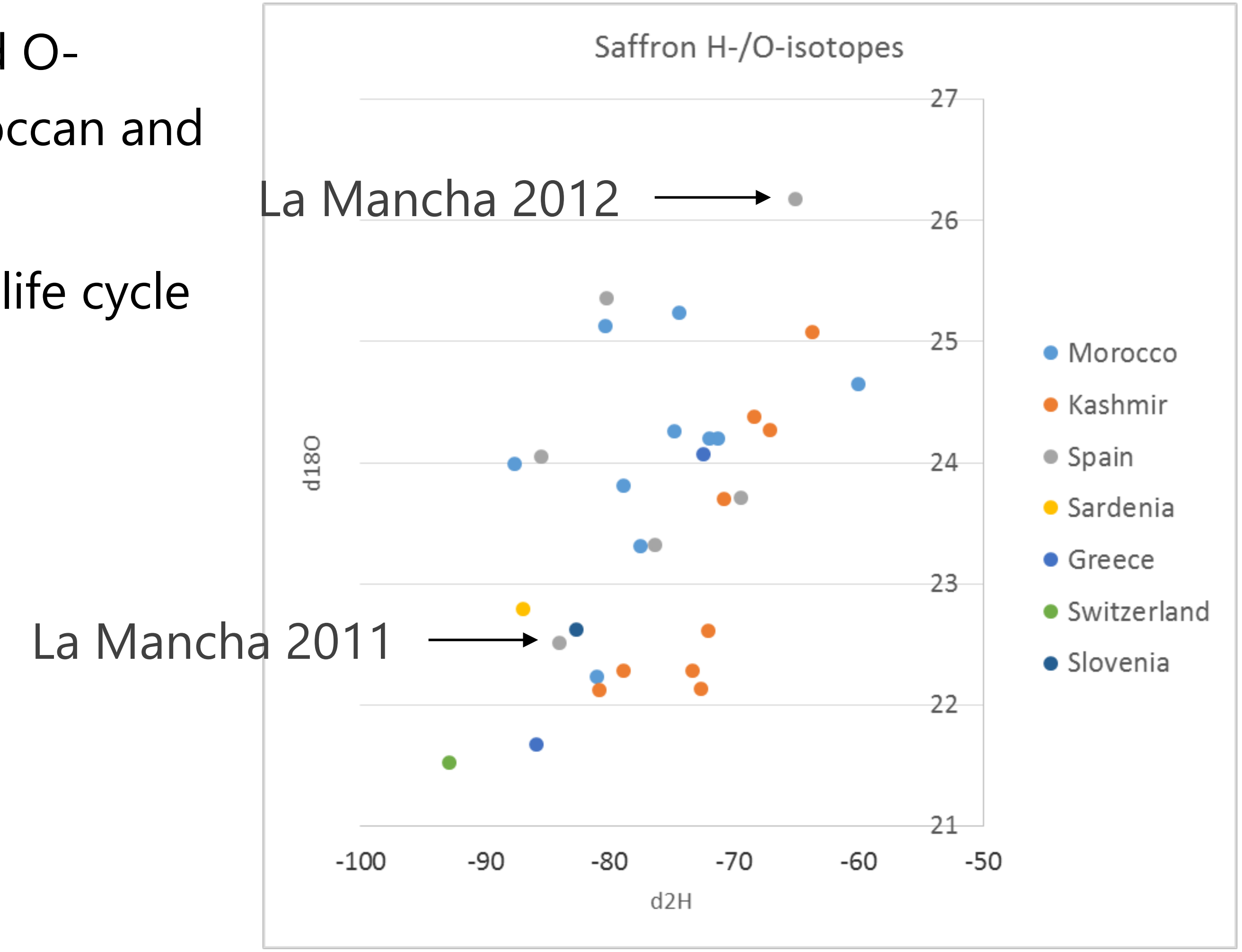
H-/O-isotopes

- Large variation of H- and O-isotopes for Spanish, Moroccan and Kashmir saffron.
- Reason might be crocus life cycle



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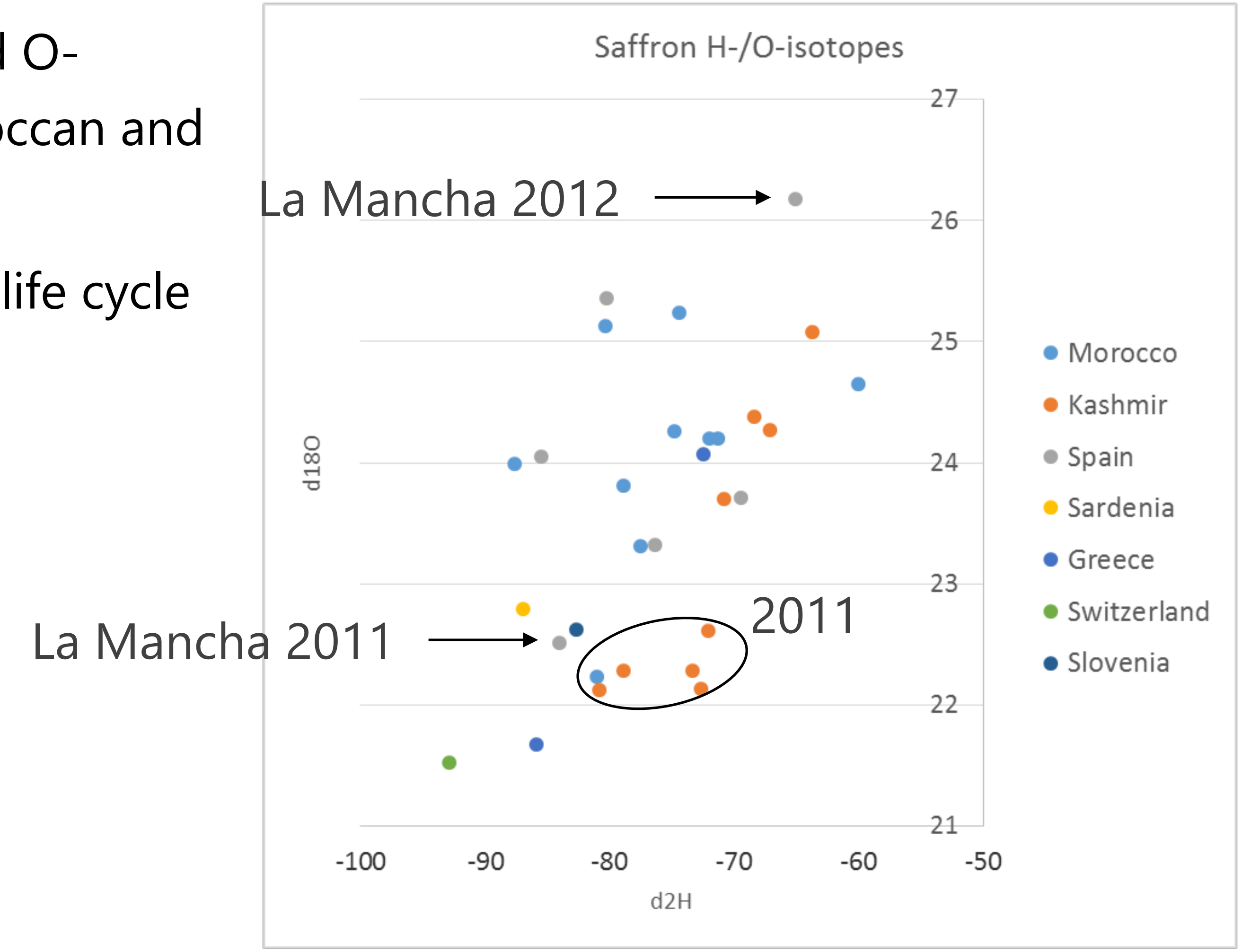

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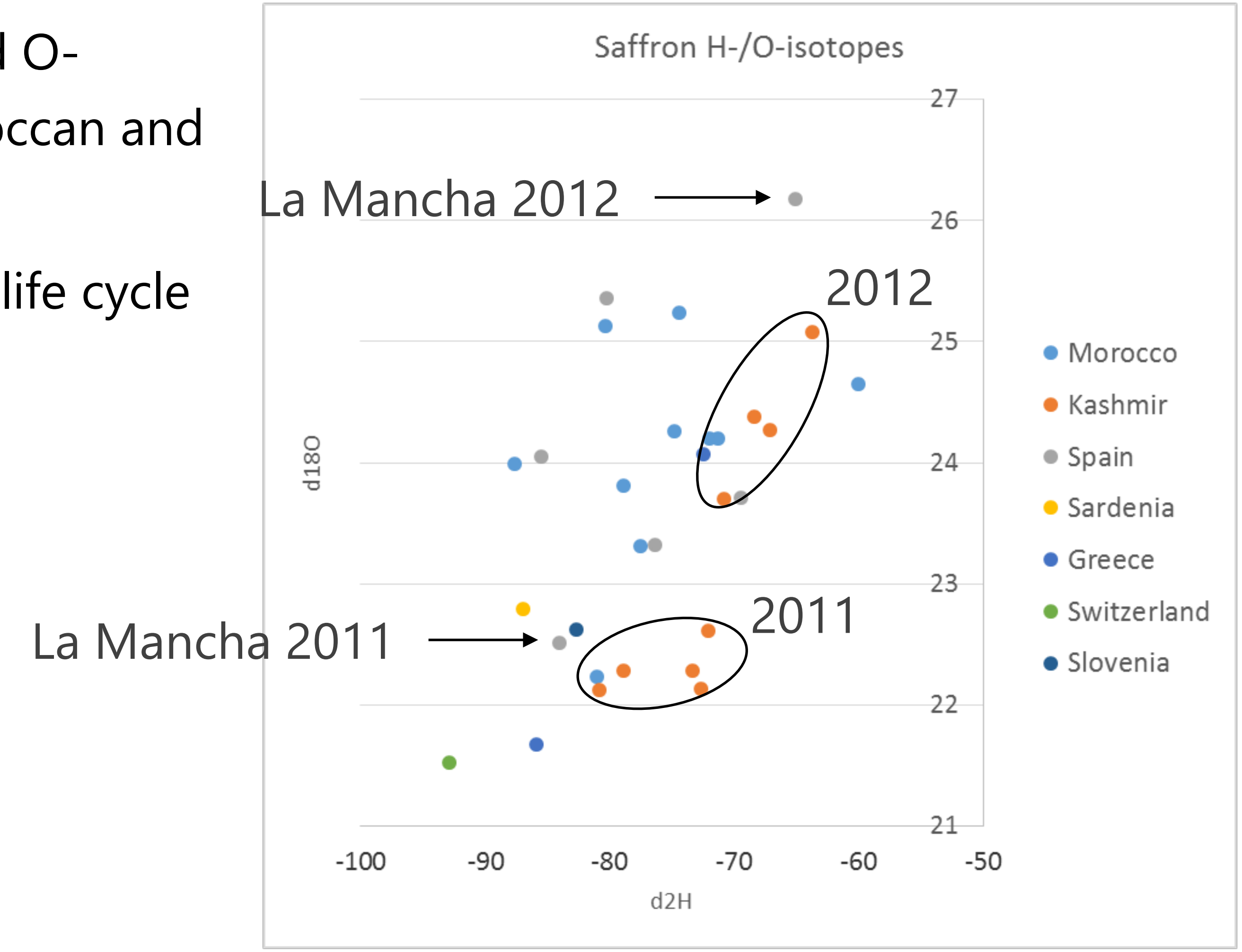
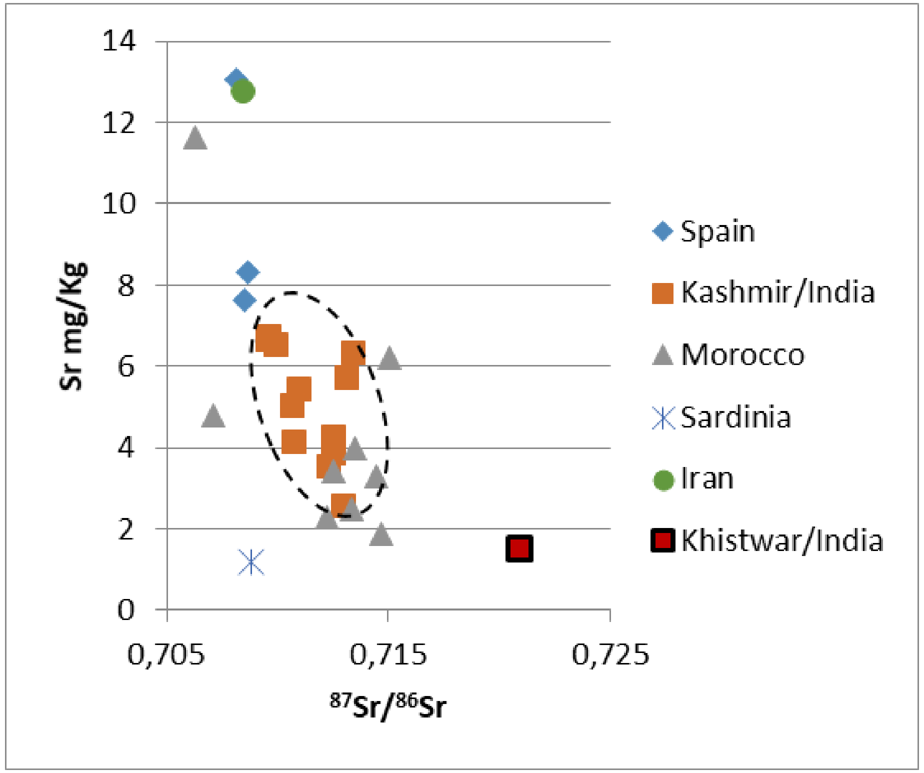
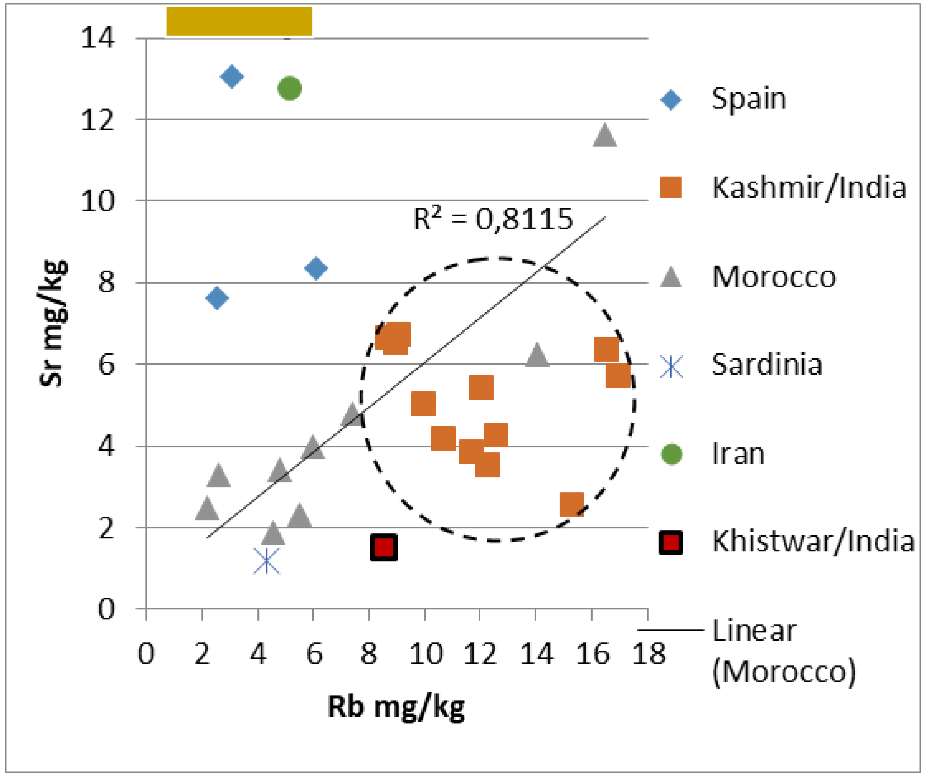


$^{87}Sr/^{86}Sr$ and element concentrations





Conclusions

- Saffron is a difficult commodity with respect to control its geographic origin. Still, control is urgently needed.

- In our study, $d^{15}N$ showed best differentiation potential for geographic origin. However, this easily can be anthropogenically influenced and altered, and might be an anthropogen result.

- Annual reference samples are best option, but expensive and requires much efforts.

- Combination of different analytical/(molecular) methods will improve power of differentiation.

Colleagues and collaborators

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- Bruria Heuer

Thank you for your attention!