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Uses of profiling trace metals in wine with ICP-MS and Mass Profiler Professional (MPP) for the wine industry

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Why are metals in wine of interest?

Chemistry Central Journal
ChemistryCentral

Research article

Open Access

Heavy metal ions in wines: meta-analysis of target hazard quotients reveal health risks

Declan P Naught

Wine Spectator

Study of Wine's Heavy Metal Hazard Raises Doubts Among Other Experts

Researchers say a large glass per day may contain unsafe levels of certain metals, but other scientists question the extent of the problem

SCIENTIFIC AMERICAN™

Jeers! Hazardous levels of metals found in wines

Are we swallowing toxic elements with every sip of vino?

Decanter.com

Heavy metals in wine could pose health risk

Why are metals in wine of interest?

- Heavy metals* health concerns (Marais & Blackhurst, 2009)
  - displacement of essential elements
  - catalysts
- Winegrowing (Pereira, 1988; Aceto, 2003)
  - metals present in soil, fertilizers and pesticides
  - essential elements in plant cells
- Winemaking (Pereira, 1988; Aceto, 2003)
  - elemental impact on yield, sugar levels, amino acids, …
  - yeast activity and fermentation
  - wine stability and oxidation
- Provenance
  - geographical origin based on (rare earth) elements (REE)

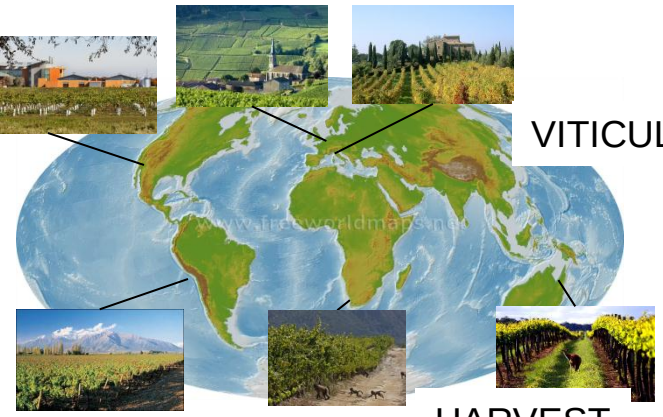
* *As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Mo, Ni, V and Zn*

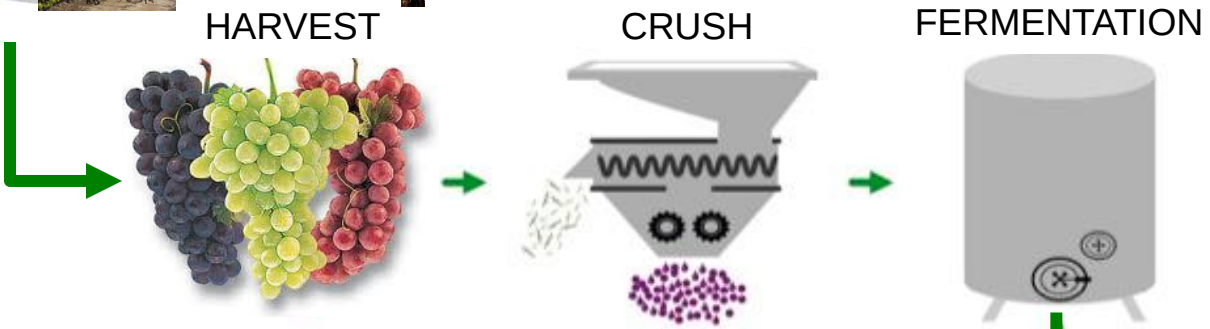
Maximum acceptable limits contained in wine

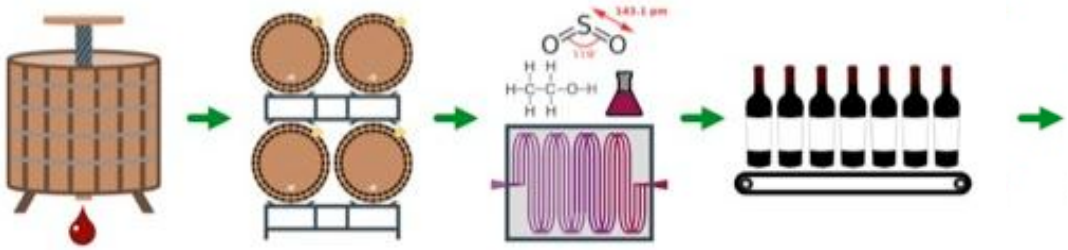
International Organization of Vine and Wine (OIV) limits some elements in wines in the ppm and ppb range (OIV-MA-C1-01)

Element	**[mg/L]**
Boron (B)	80
Zinc (Zn)	5
Bromine (Br)	1
Copper (Cu)	1
Arsenic (As)	0.2
Lead (Pb) (after 2007)	0.15
Silver (Ag)	0.1
Cadmium (Cd)	0.01

Elemental analysis from grapes to wine







STORAGE

http://silversmithvineyards.com/wp-content/uploads/2011/09/winemaking_500.jpeg

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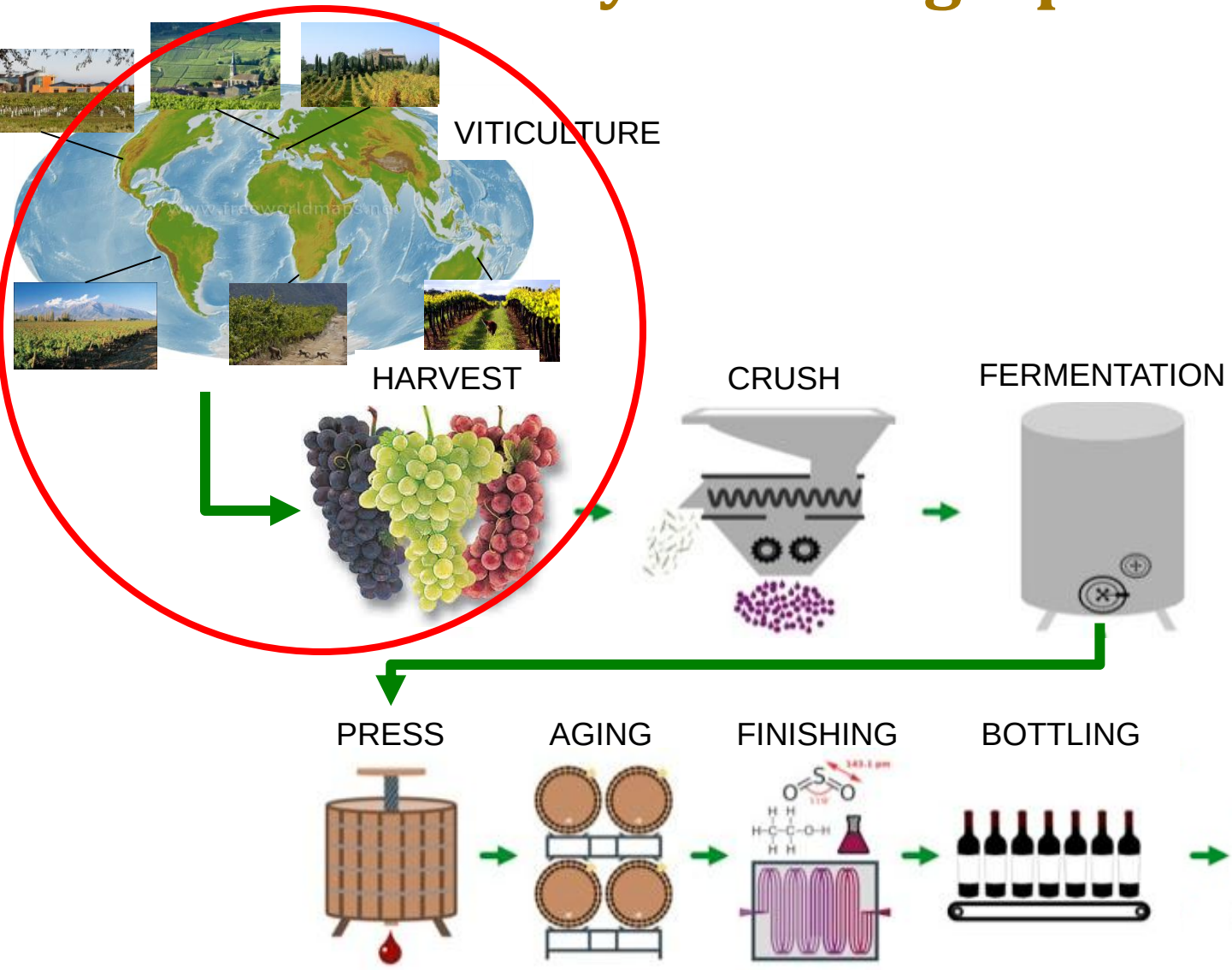

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Effects of soil on the metal content of wine grapes

The metal composition of grapes is a reflection of

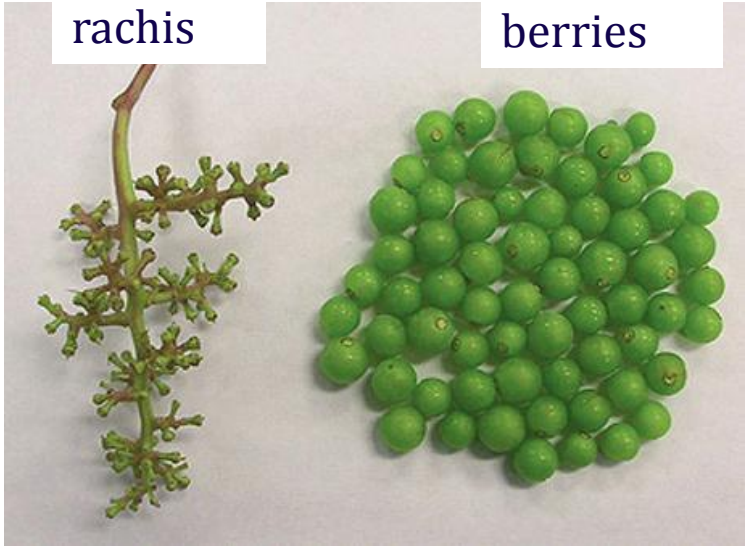
- mineral uptake of the grapevine from the soil
- natural and viticultural surface accumulation (e.g. Cu, Pb, …)
- hydrologic flows affecting the soil composition

Effects of soil on the metal content of wine grapes

This ongoing study profiles the elemental composition of samples from one vineyard, including

- soil
- plant tissue (rachis, leaves, …)
- wine grapes

over the ripening period



Picture from: Erincik et al. 2002. Plant Health Progress doi:10.1094/PHP-2002-0702-01-RS.

Sampling

- one block in a research vineyard in Northern California
- block was planted in 1999 on coombs gravelly loam soil
- 10.6 acres (4.28 hectares) of Cabernet Sauvignon vines
- 4’ x 4’ VSP trellis system; cordon trained and spur pruned
- vineyard is part of other research projects with regards to soil chemistry

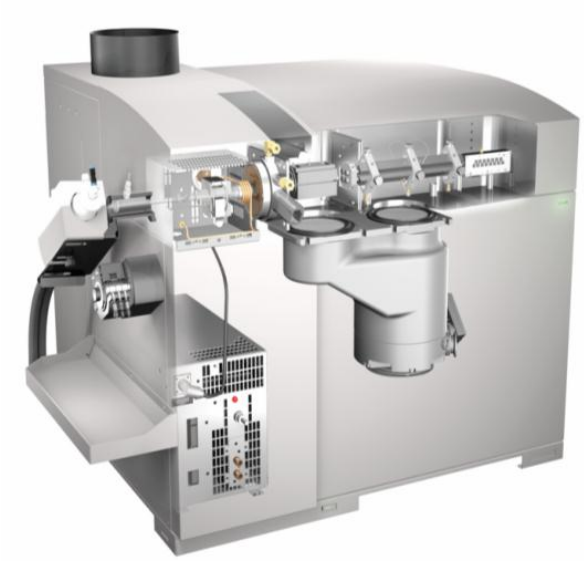
Sample Preparation

microwave digestion of samples (Milestone UltraWAVE)

- berries, plant tissue, soil (dried) in triplicate
  + 4 mL conc. ultrapure HNO_3
  + 1 mL ultrapure water
- digested samples are diluted with ultrapure water for analysis

Instrumentation for Elemental Profiling

- Agilent 7700x ICP-MS
  - RF power 1.5 kW
  - Carrier gas flow 1 L/min
  - OSR^3 collision cell gas flow (He) 4.3 mL/min
  - MicroMist nebulizer, Scott double-pass spray chamber cooled to 2° C
- calibration from 0.1 to 500 ppb
  - 52 calibrated elements
  - internal standard mix (IS) covering the m/z range from 6 – 238
  - matrix-matched (6% HNO_3)
- analysis of diluted digested samples in triplicate



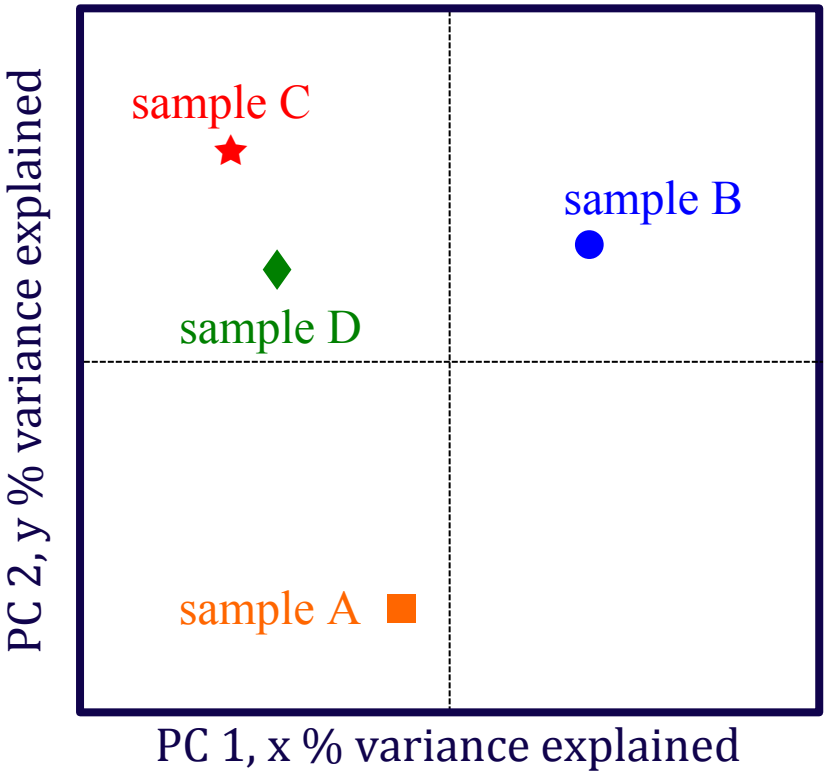
Data Analysis

- Mass Profiler Professional (MPP)
- exploratory analysis with Principal Component Analysis (PCA)
- statistical evaluation of differences with Analysis of Variance (ANOVA)

Data Analysis – How to read PCA plots

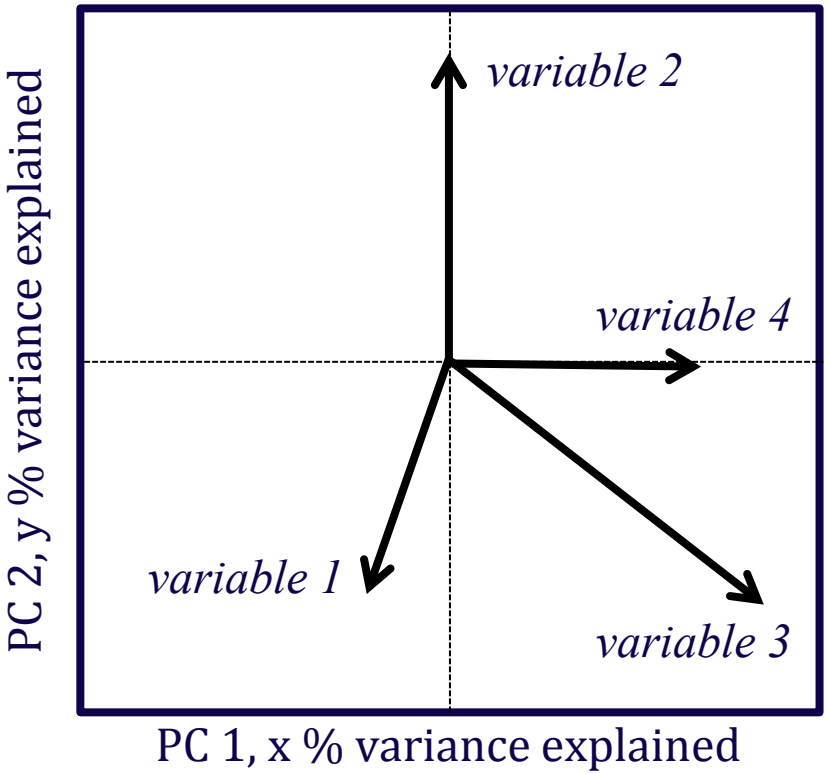
Score Plot

- samples positioned according to their similarities



Loadings Plot

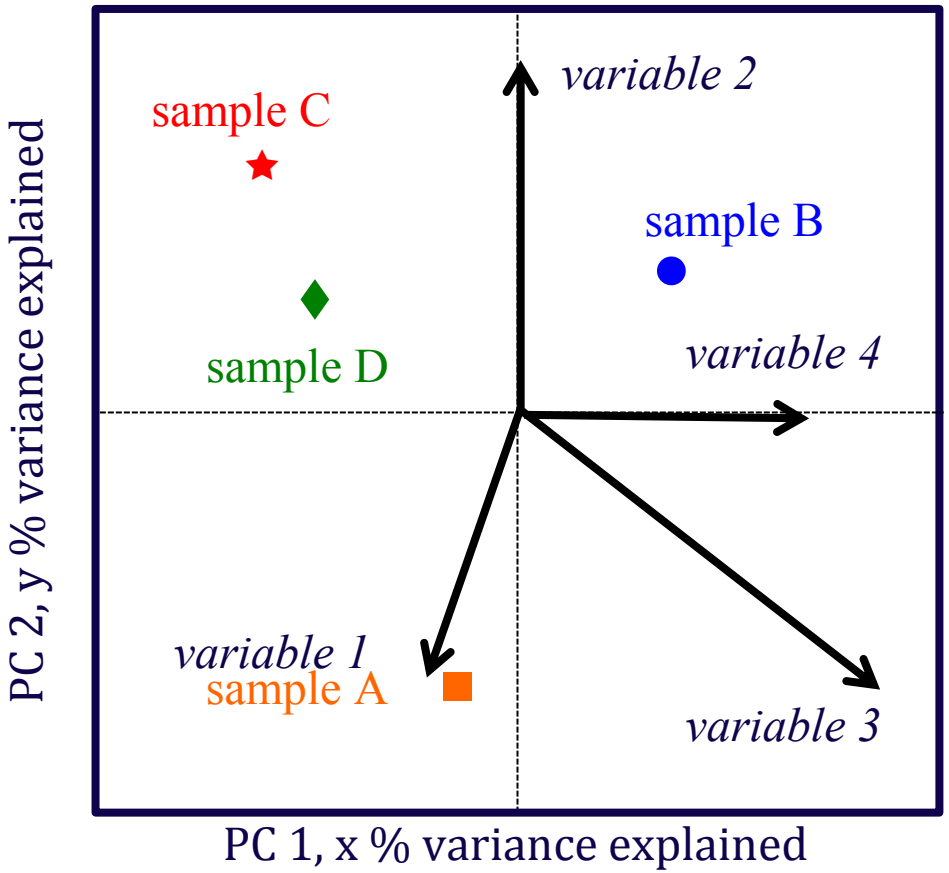
- elements responsible for the sample differences



Data Analysis – How to read PCA plots

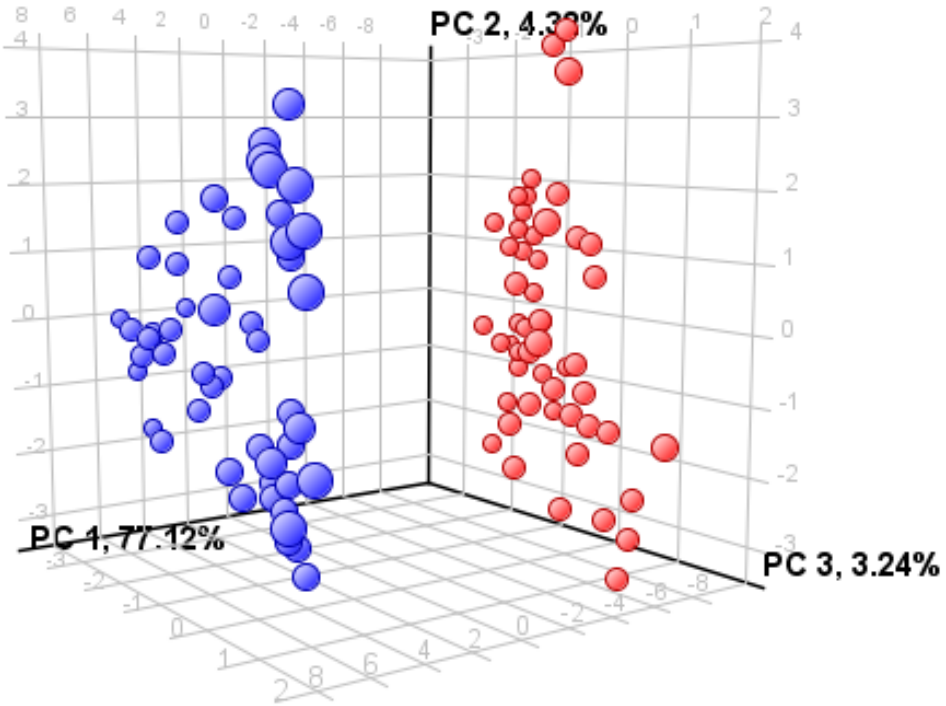
Bi-Plot

- merging of score and loadings plot into one bi-plot



Preliminary results – grapes & plant tissue

- Plant tissue and berries were picked at different locations within the vineyard block (green triangles)
- grapes and plant tissue are well separated



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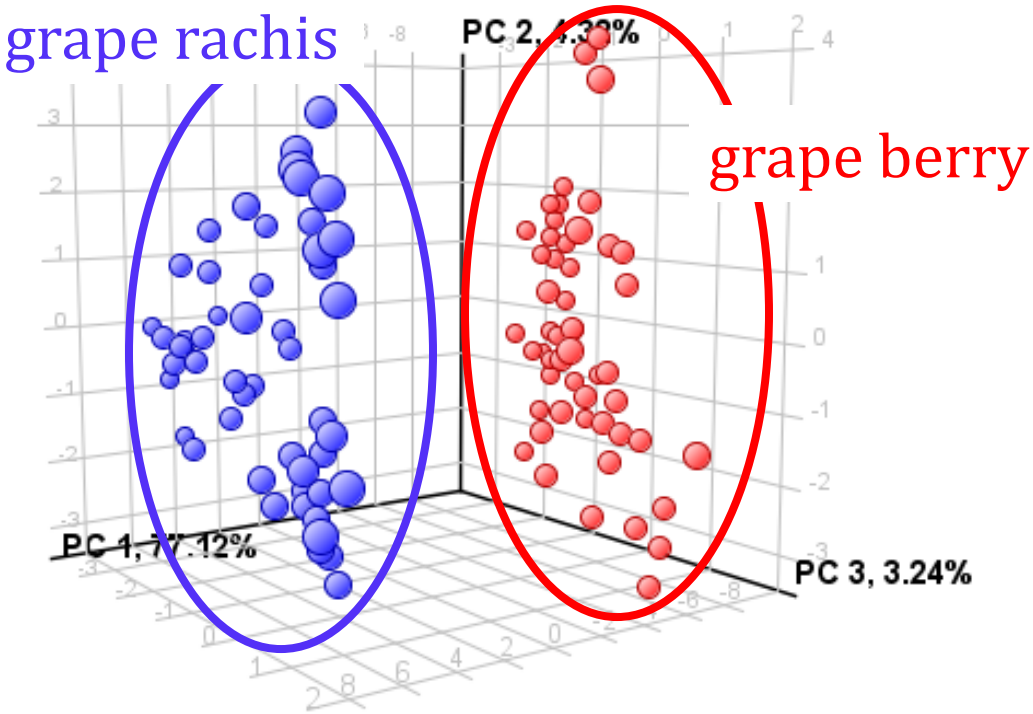
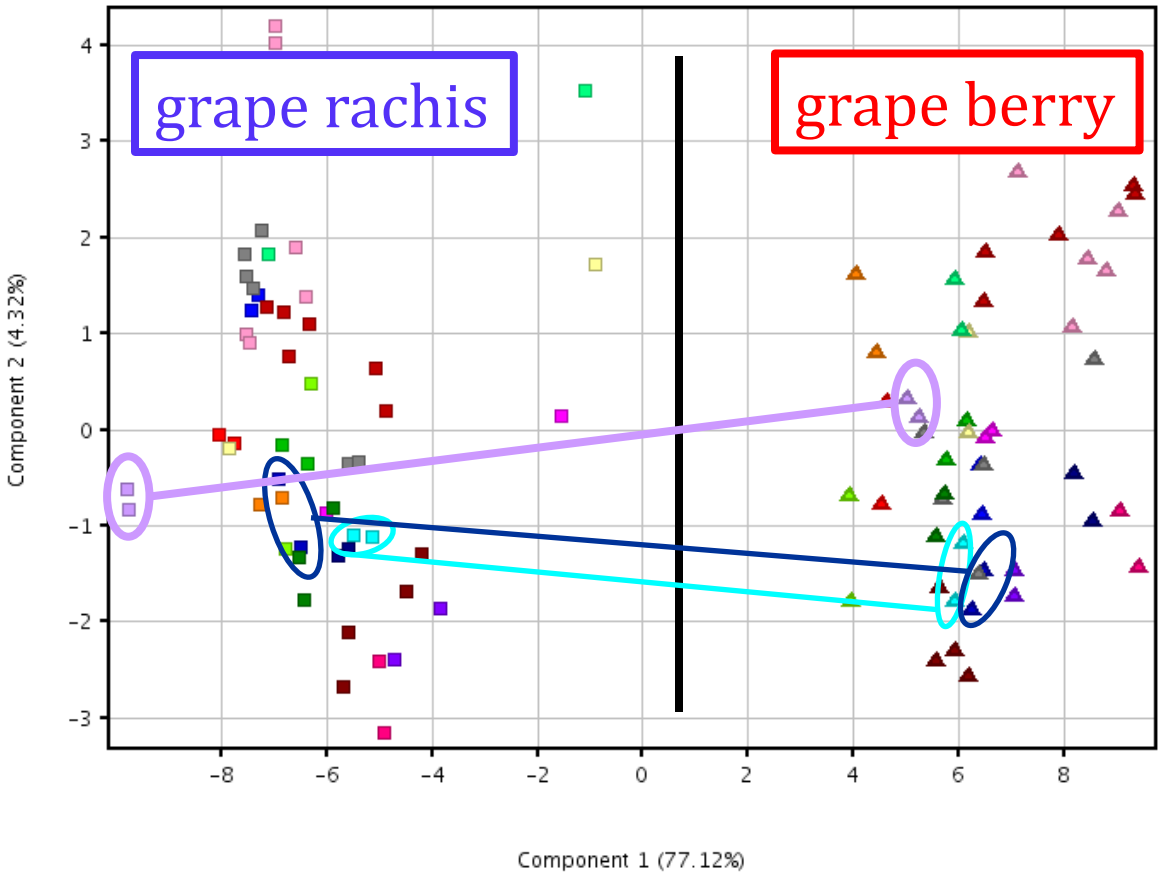


Which elements are responsible for this separation?

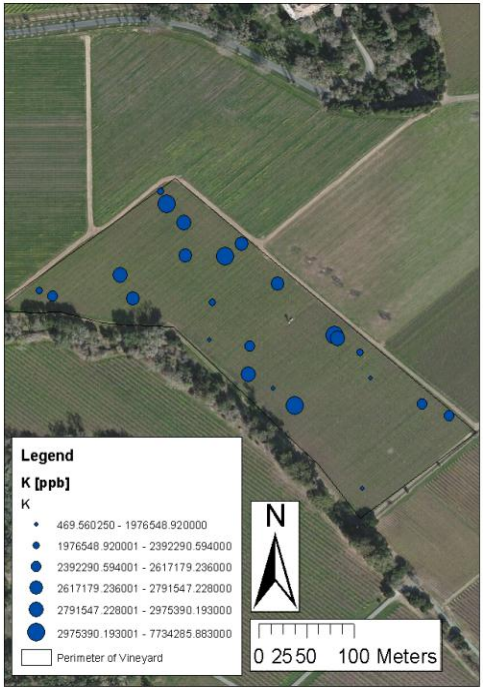
- Berries and rachis from the same row show similar elemental composition



Local differences in selected elements in grape berries

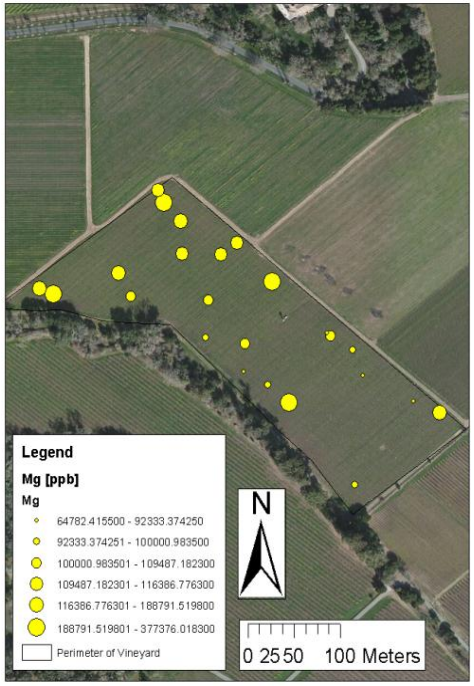
Potassium

- major element needed for vine health (besides N and P)
- precipitates after fermentation as hydrogen tartrate



Magnesium

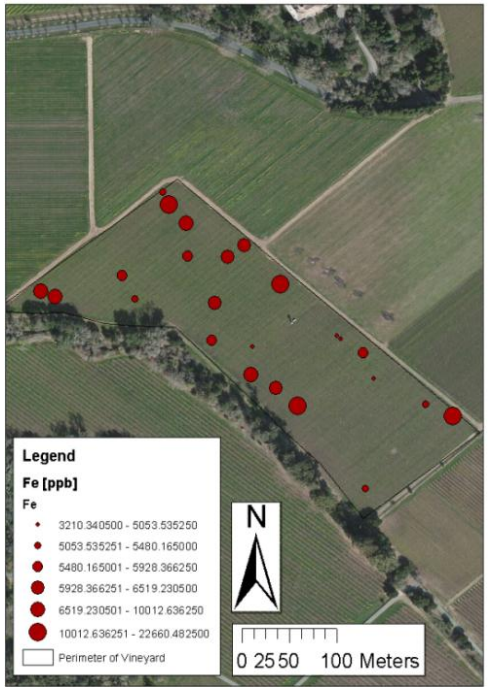
- essential for chlorophyll formation
- important for tartrate stability and wine acidity



Local differences in selected elements in grape berries

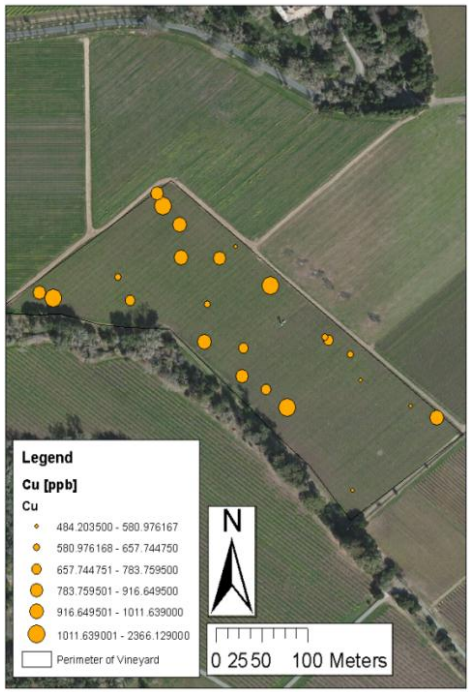
Iron

- trace nutrient for vines
- present in wine as Fe^{2+} and Fe^{3+}
- wine stability (turbidity, oxidation)



Copper

- used in fungicides in vineyard
- present as Cu^{+} and Cu^{2+}
- wine stability (turbidity, oxidation, taste)



How can these elemental differences be explained?

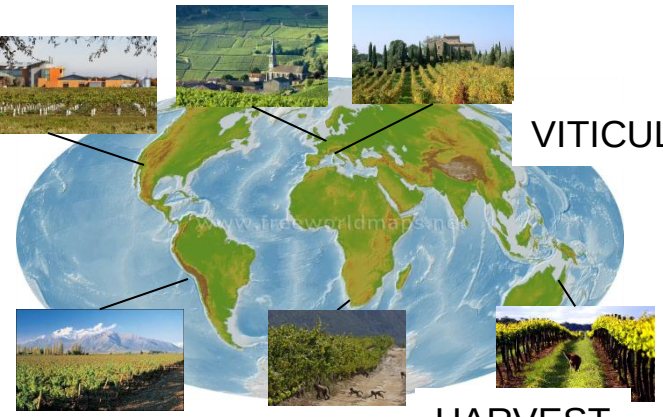
- large differences in the sub-surface water flows found by hydrological studies
- changes in of sub-surface water flows may increase leaching of elements

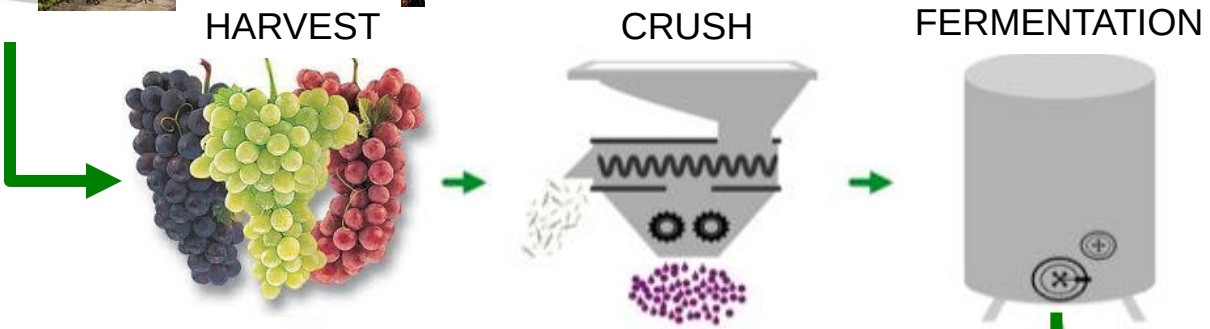
Conclusions and Future Work

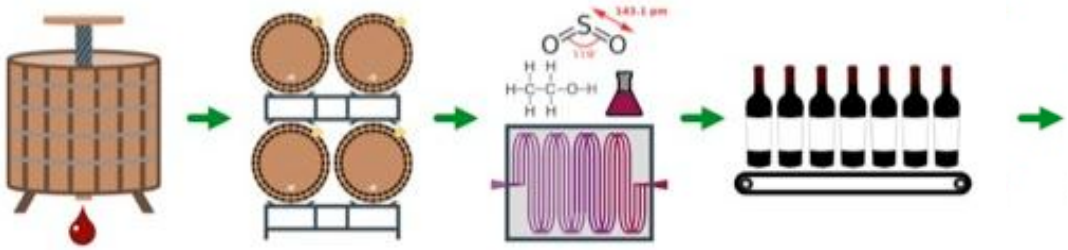
- elemental variation in the same vineyard block from row to row
- elemental variation within different parts of the vine (rachis vs. grape berries)
- elemental differences observed could be the result of differences in sub-surface water flows

- ➢ soil analysis will elucidate how much of the elemental variation observed in the plant tissue is due to the soil
- ➢ analysis of other plant tissue (e.g. leaves, roots, etc.) will elucidate elemental transport within the plant

Elemental analysis from grapes to wine







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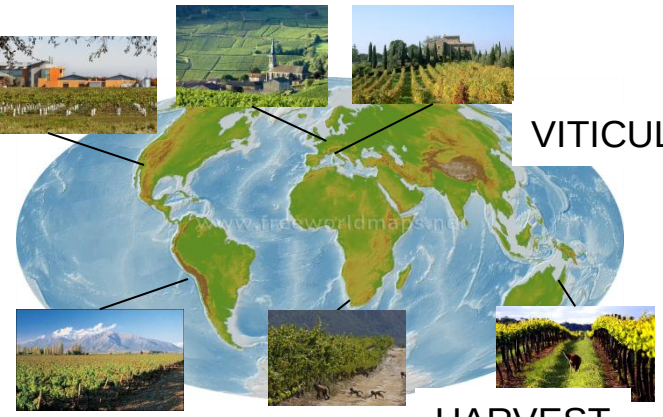
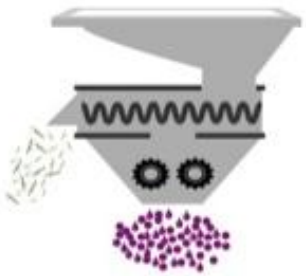


HARVEST

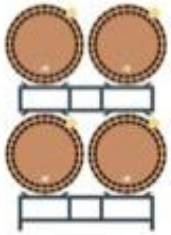
CRUSH



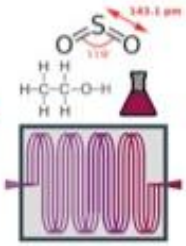
FERMENTATION

PRESS

AGING



FINISHING



BOTTLING

STORAGE

http://silversmithvineyards.com/wp-content/uploads/2011/09/winemaking_500.jpeg

Impact of storage conditions on the elemental composition of Cabernet Sauvignon red wine

- 1 Cabernet Sauvignon(2009, Central Coast, CA)
- finished wine, but not fined with bentonite
- 4 packaging configurations
  - 3 L bag-in-box
  - natural cork closure
  - screw cap with tin-PVDC liner
    - normal fill height
    - high fill height
- 3 storage temperatures (6 months)
  - 10° C
  - 20° C
  - 40° C

Hopfer et al. (2013) J. Anal. Atom. Spectrom. **28**:1288–1291
Hopfer et al. (2013) J. Agric. Food Chem. **61**:3320-3334

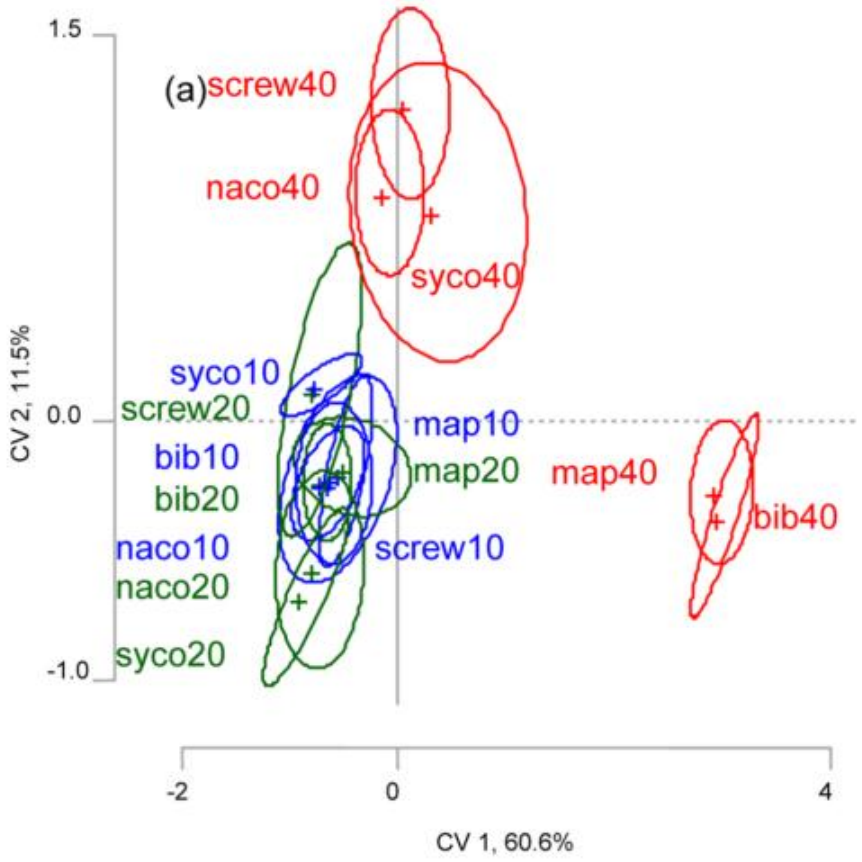
Effect of storage temperature & wine packaging

significant differences

- sensory attributes
- volatiles
- polyphenols

⇒ storage temperature

⇒ wine packaging



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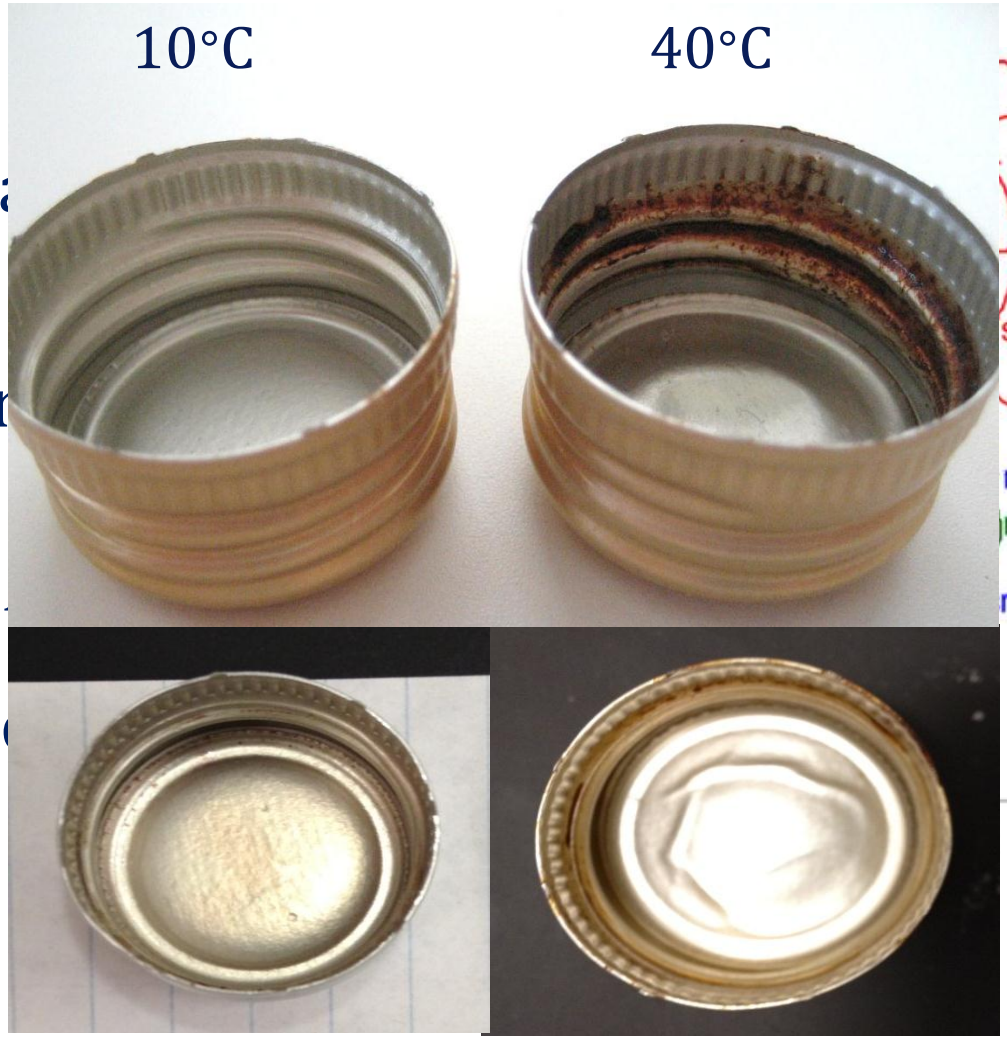

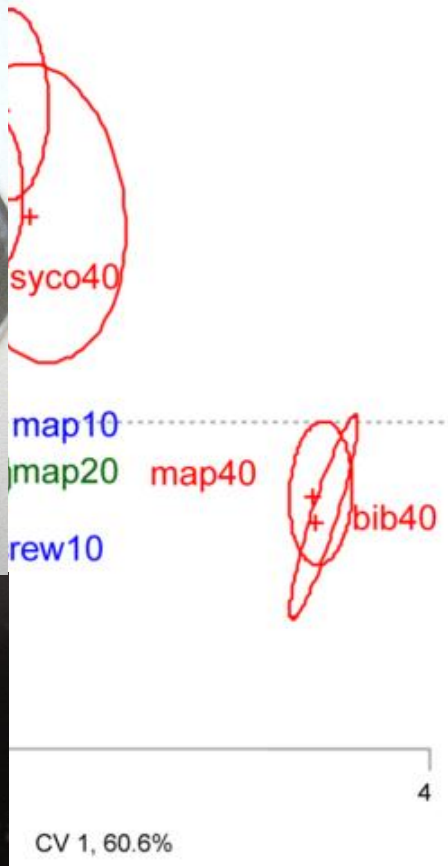

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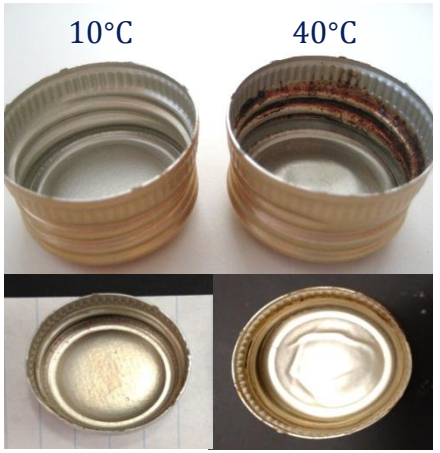
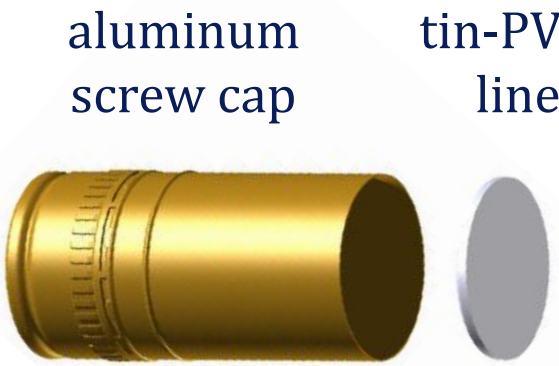
Elemental profiling of wine

- visual damages to the inside of the screw cap closures
- panelists perceived a “metallic” flavor in some samples
- screw caps with tin-PVDC liner





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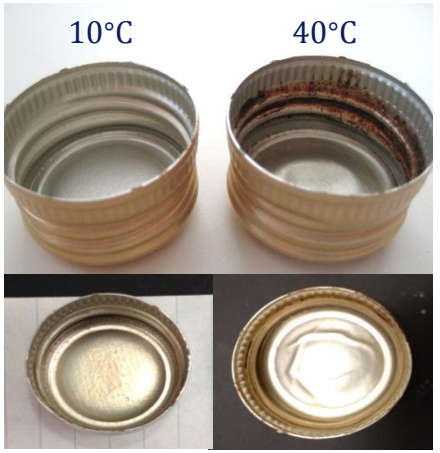
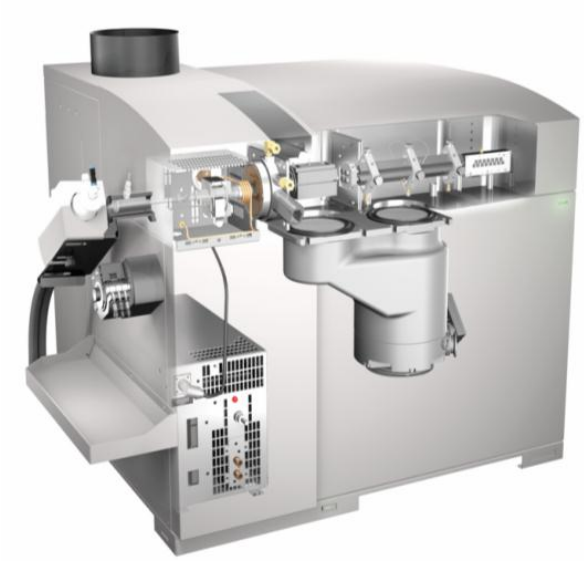


? *leaching of elements into the wines from the packaging* ?

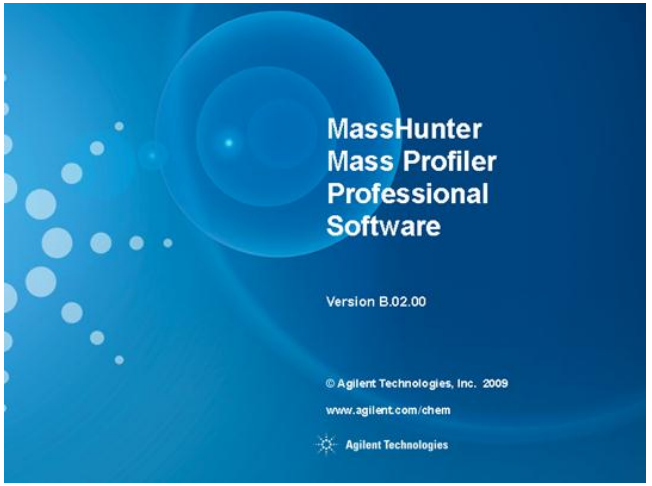
Elemental Analysis - Instrumentation

- Agilent 7700x ICP-MS
  - RF power 1.5 kW
  - Carrier gas flow 1.03 L/min
  - OSR^3 collision cell gas flow (He) 4.3 mL/min and 10 mL/min for As and Se
  - MicroMist nebulizer (1.1 L/min nebulizer flow)
- quantification from 0.1 to 500 ppb
  - 20 monitored and quantified isotopes
  - LODs between 0.001 and 0.04 ppb
  - internal standard mix (IS) covering the m/z range from 6 – 238
  - matrix-matched (4% EtOH, 1% HNO_3)
- direct analysis (1:3 dilution in 1% HNO_3) in triplicate

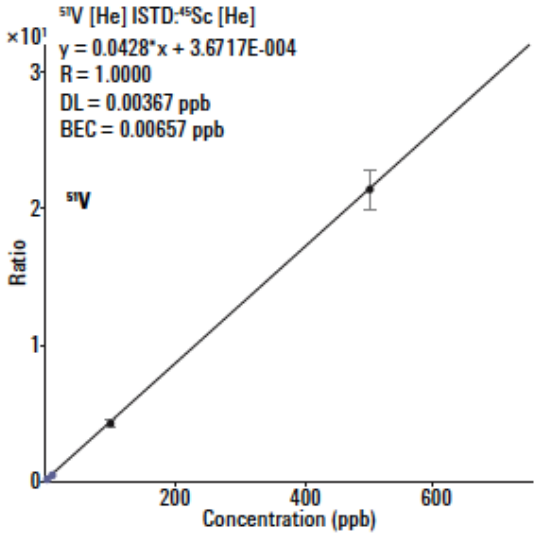


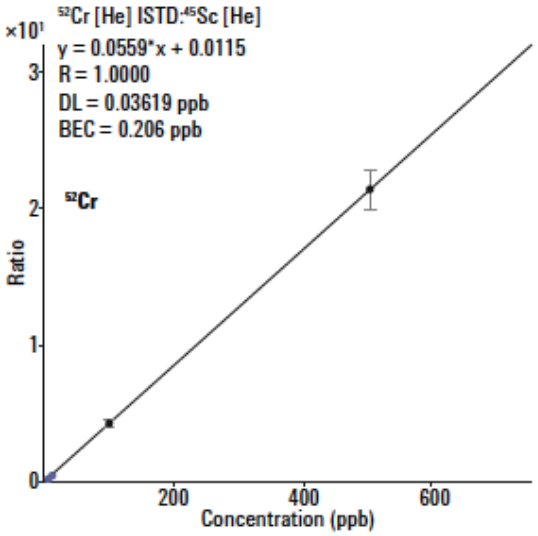
Elemental Analysis – Data Analysis

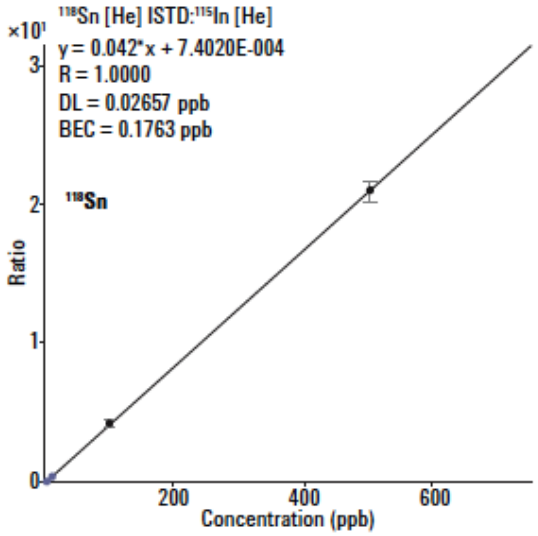
- MassHunter Mass Profiler Professional software (Agilent, v. B.02.00)
- selection of isotopes for each element based on LOD (n = 7 sample blanks) and literature
- Analysis of variance (ANOVA, $P \leq 0.05$)
- Principal Component Analysis (PCA, correlation matrix) on significantly different elements

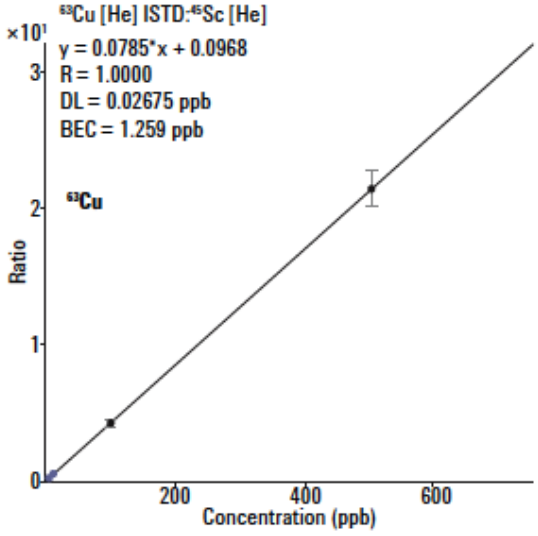


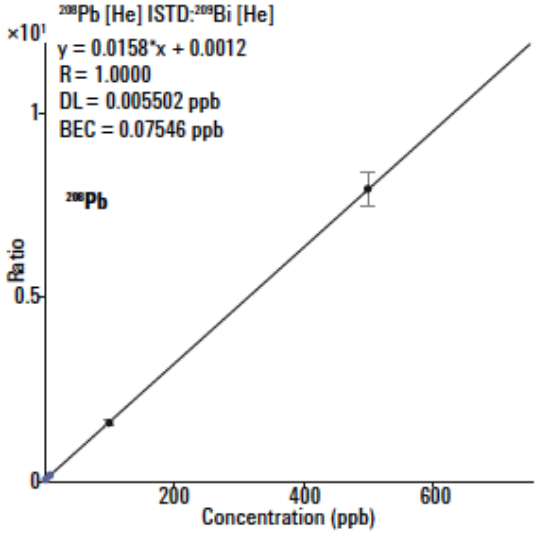
Calibration curves for the 5 significantly different elements





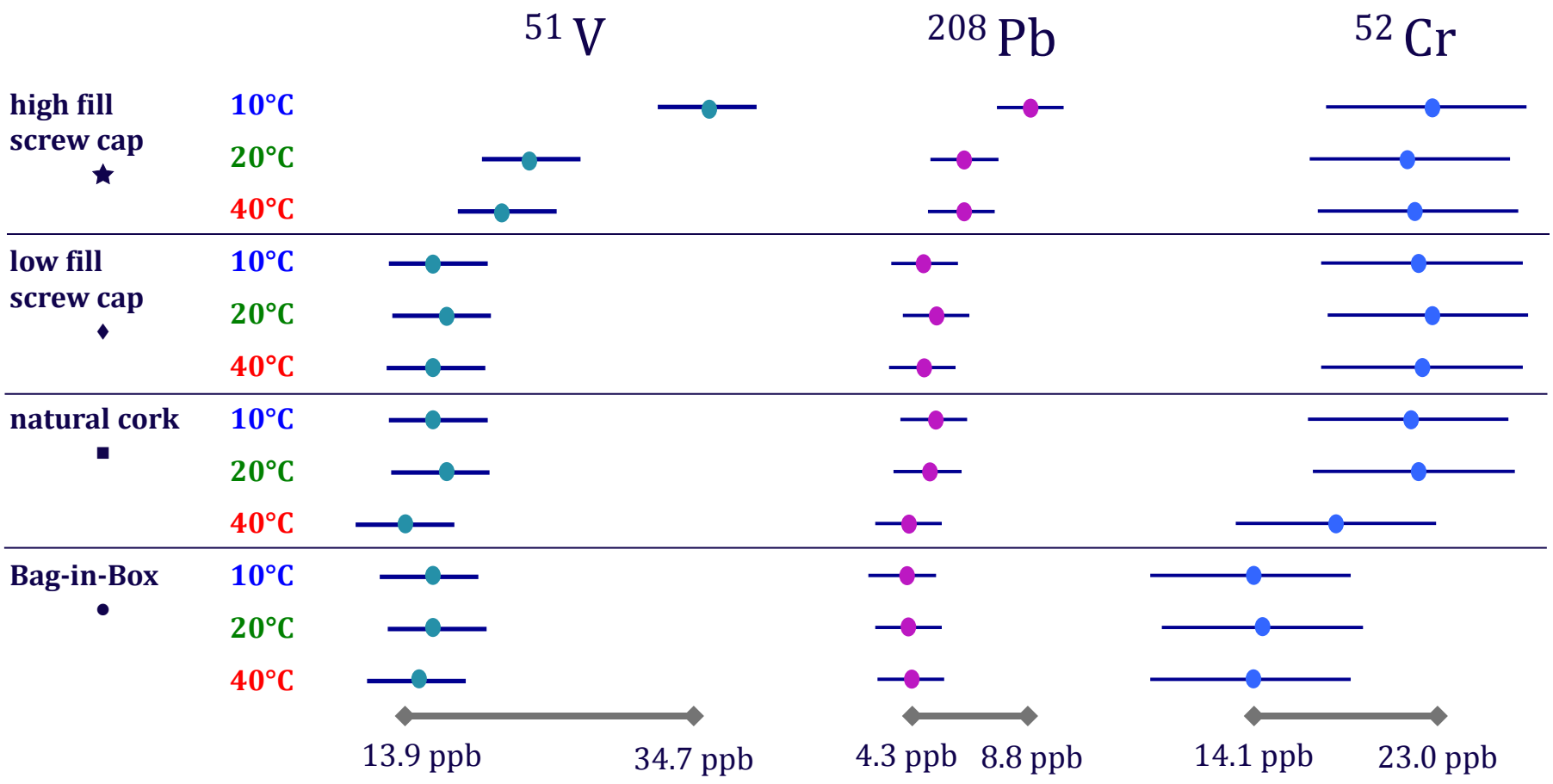






http://www.chem.agilent.com/Library/applications/5991-2570EN.pdf

Significant elemental differences ($P \leq 0.05$)



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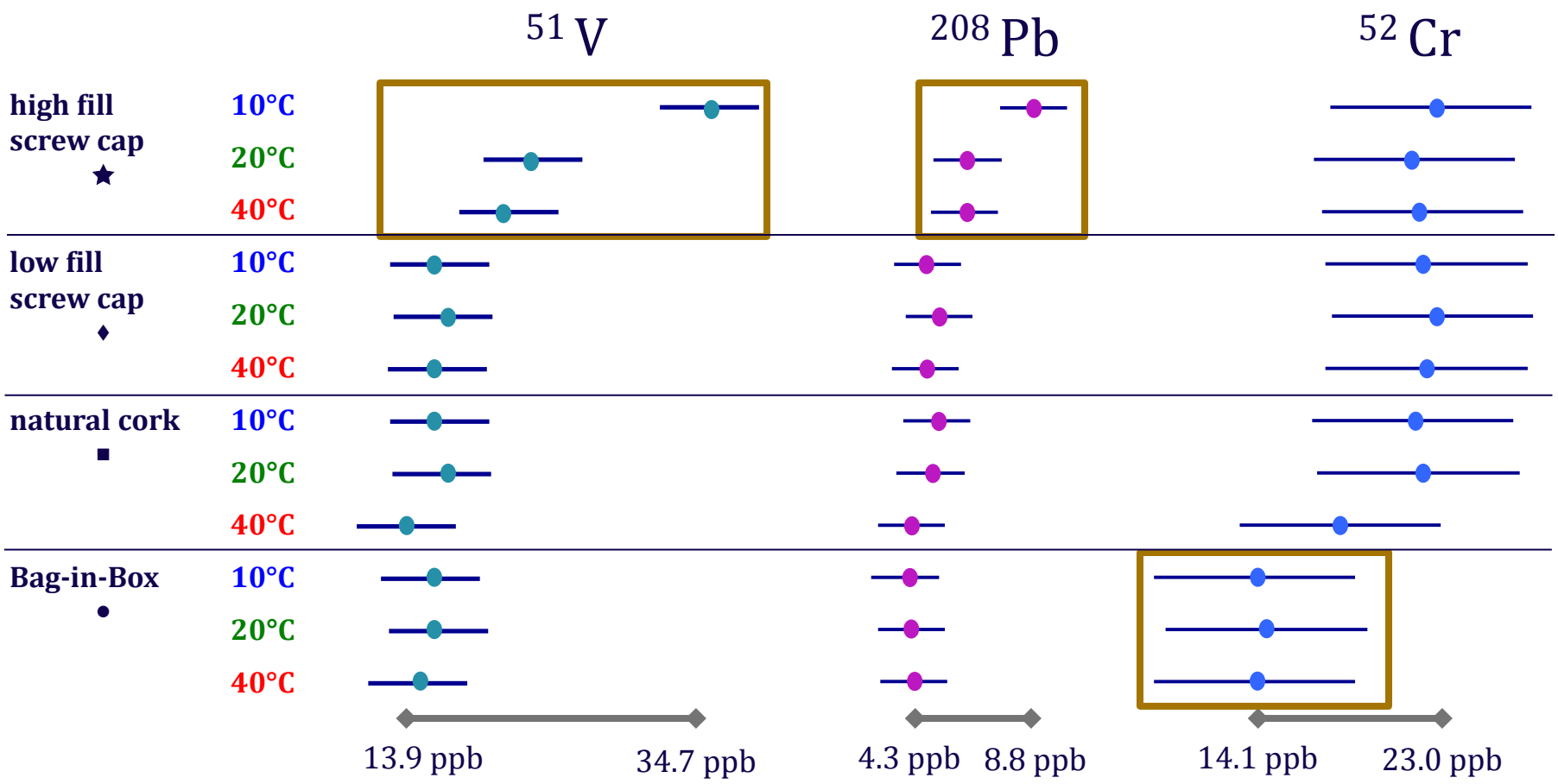
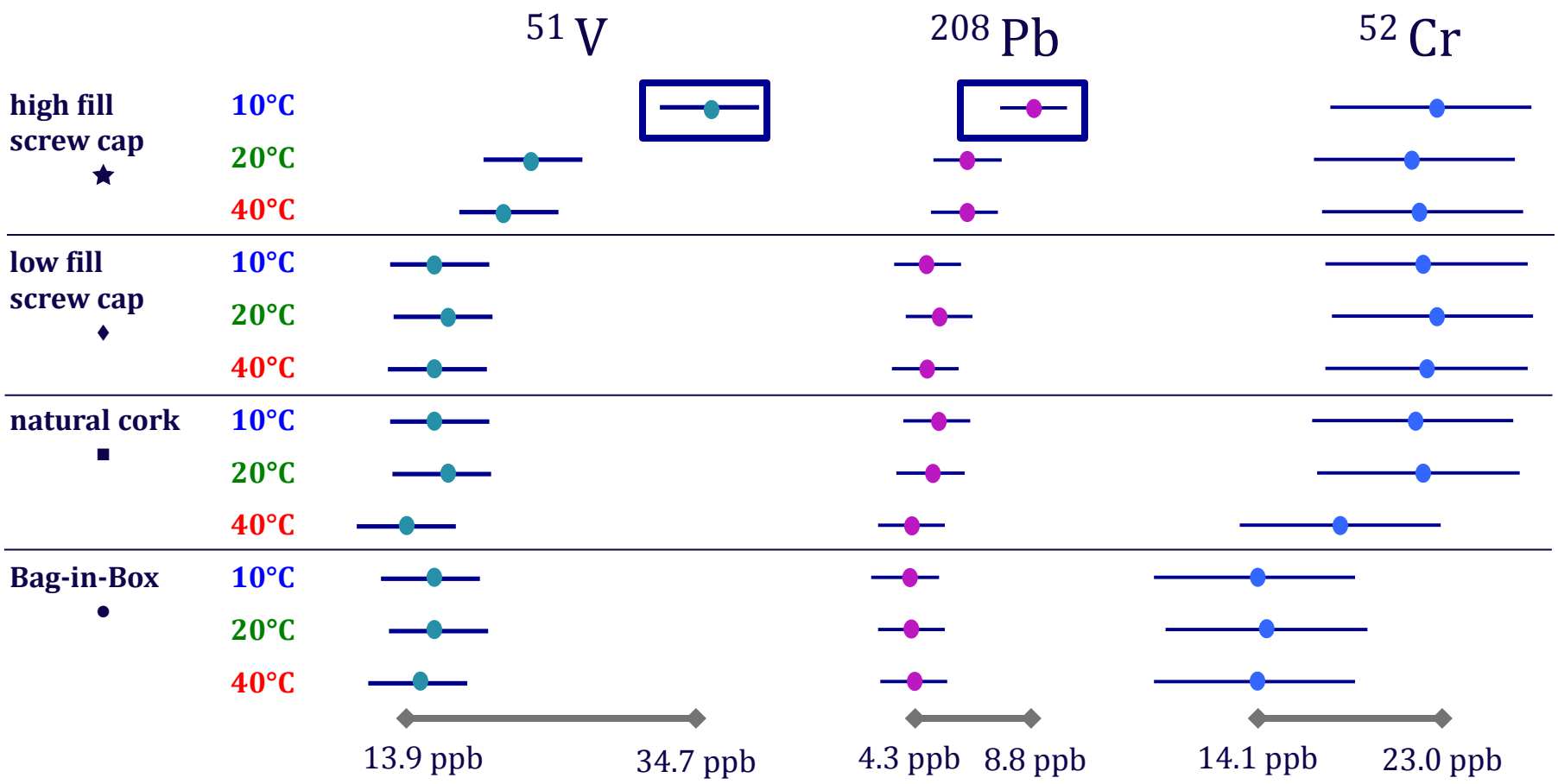


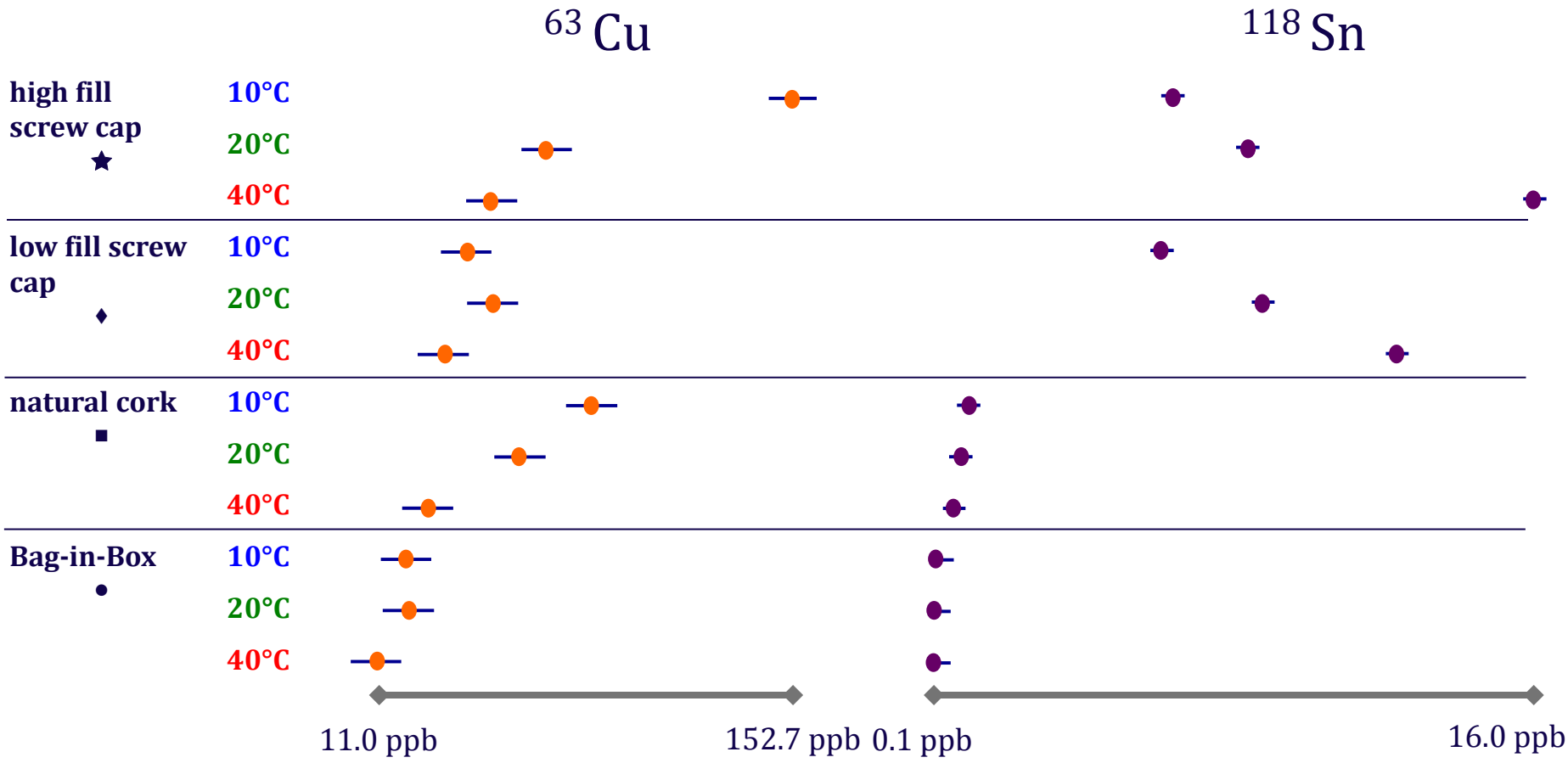
packaging effect

Significant elemental differences ($P \leq 0.05$)



temperature effect

Significant elemental differences ($P \leq 0.05$)



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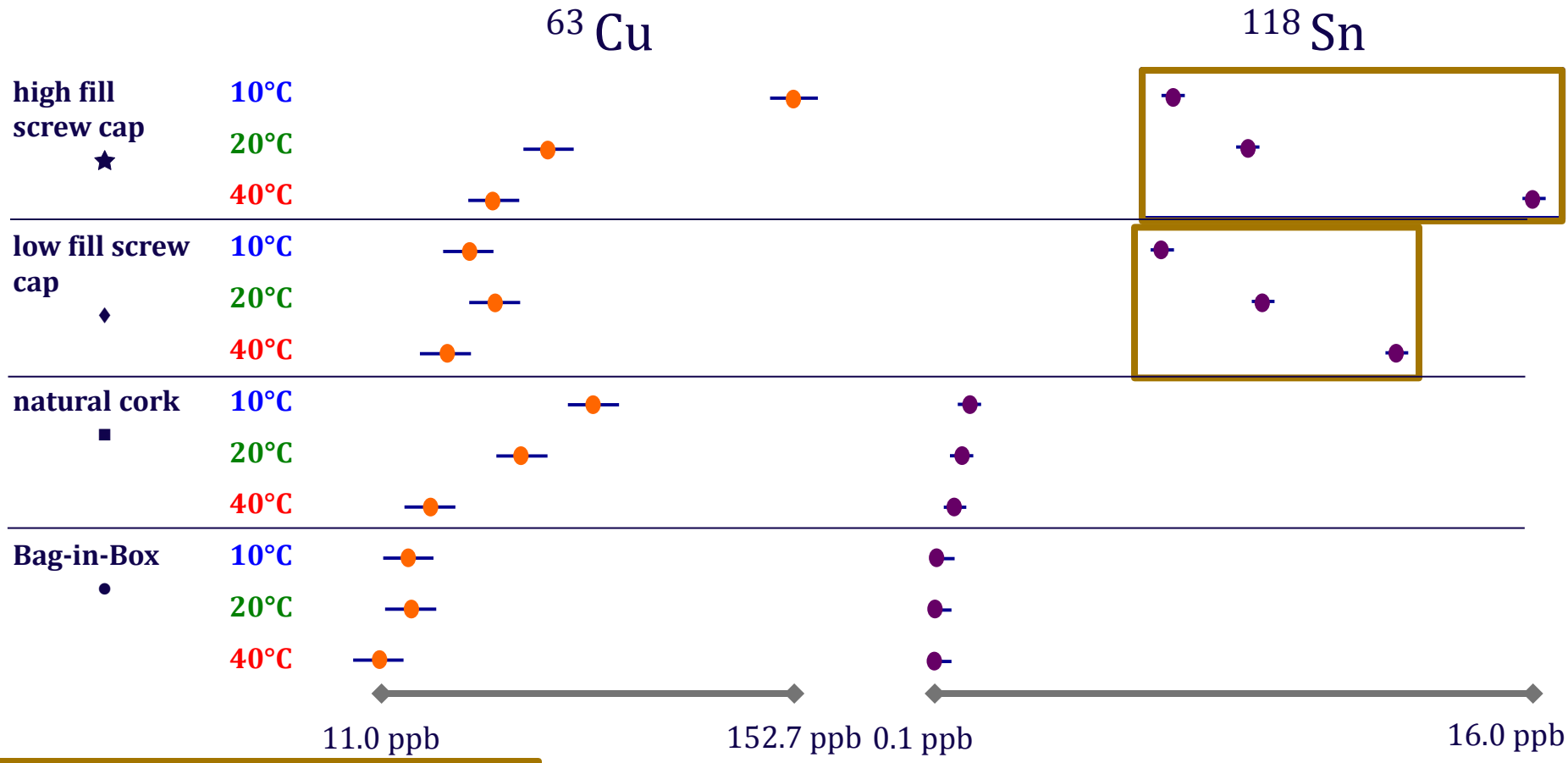

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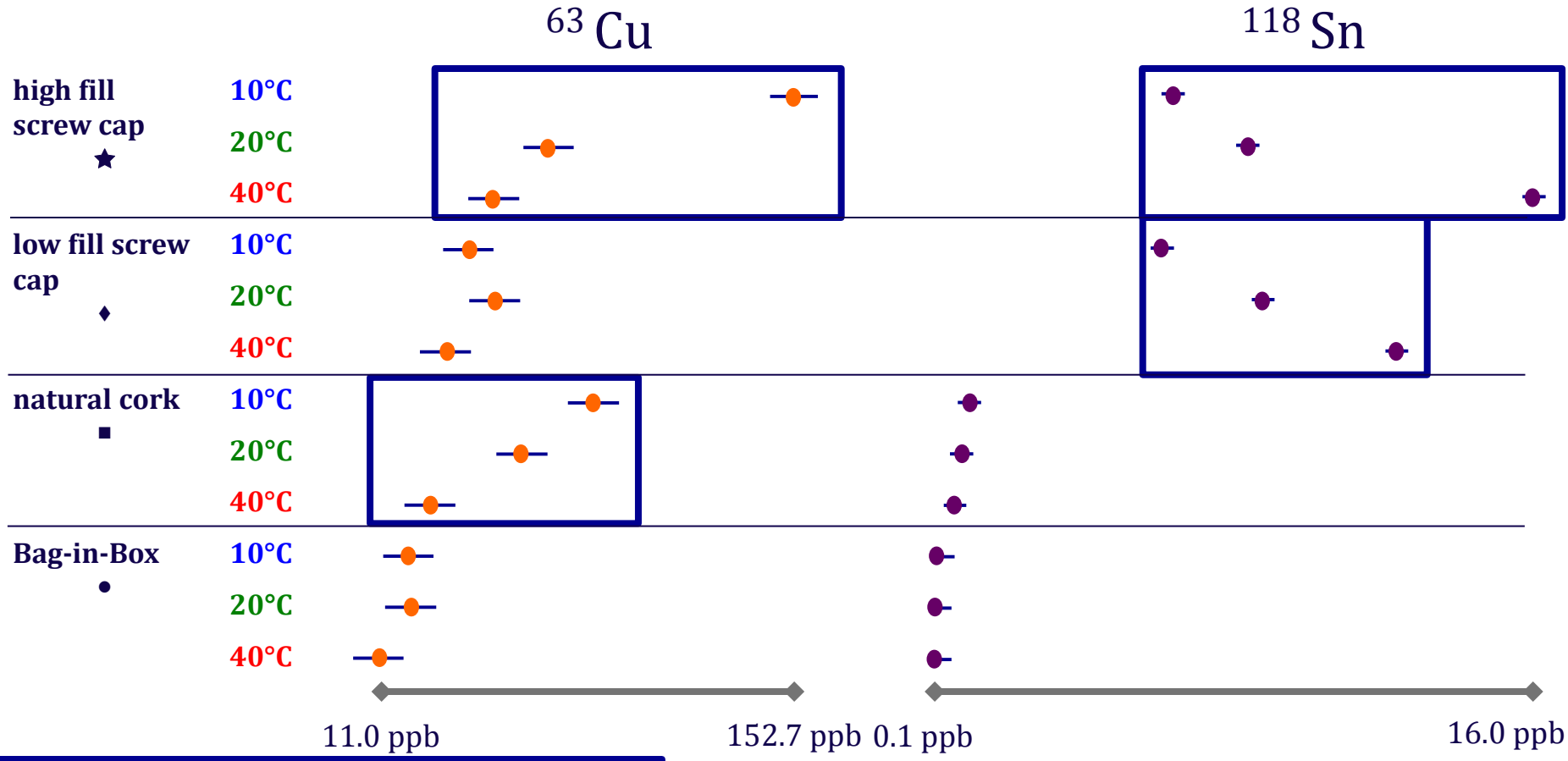
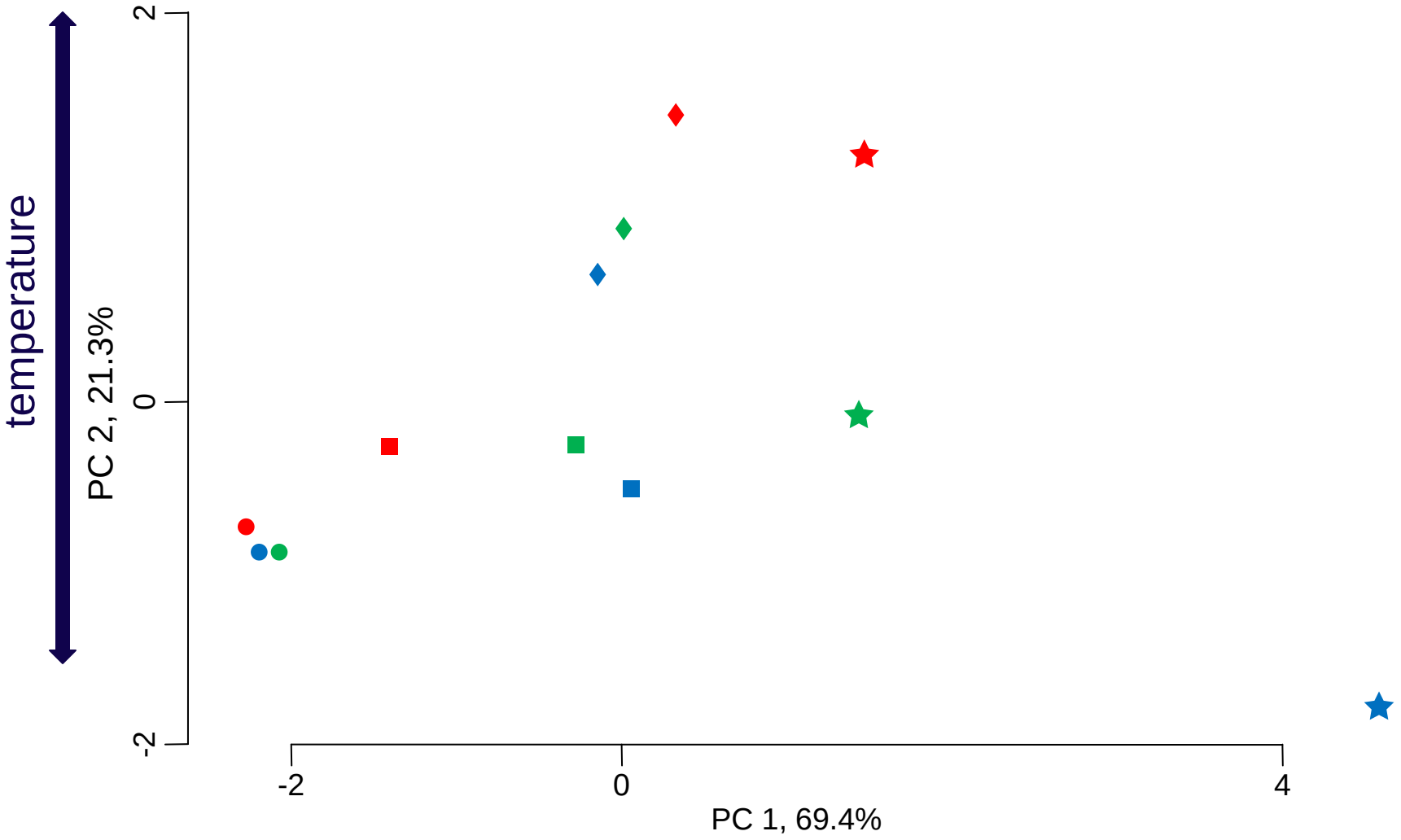
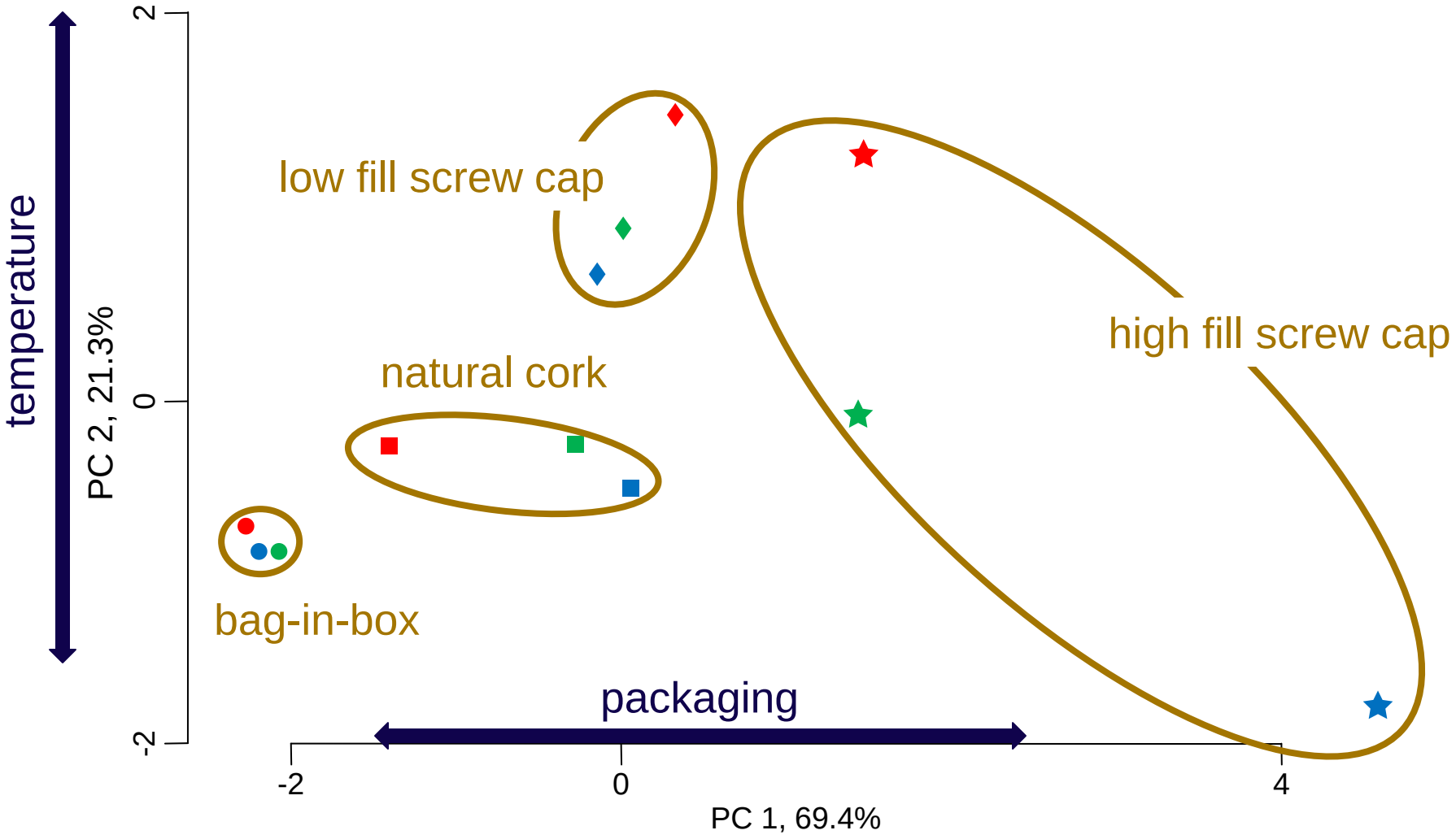


temperature effect

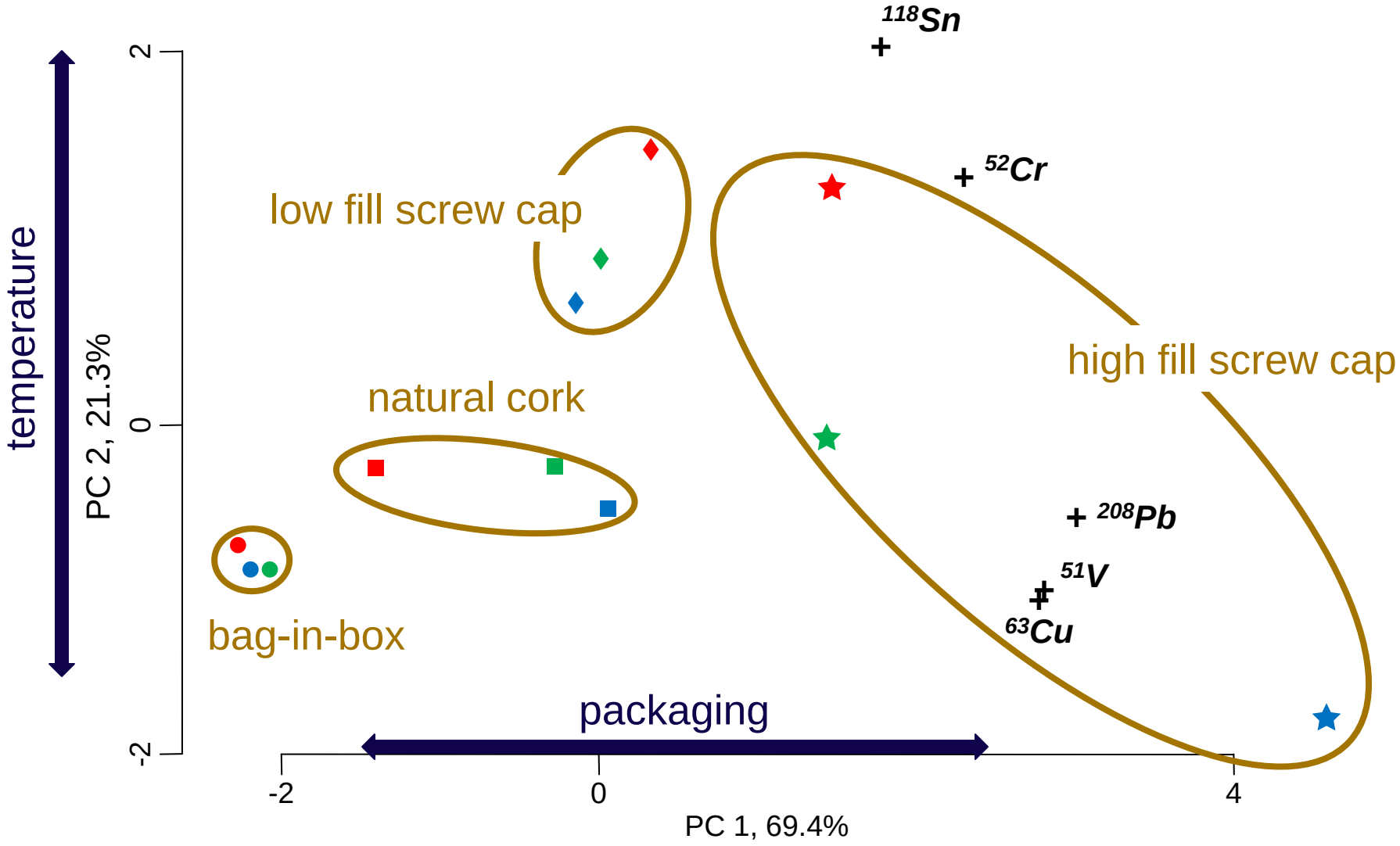
Separation of Samples by PCA



Separation of Samples by PCA



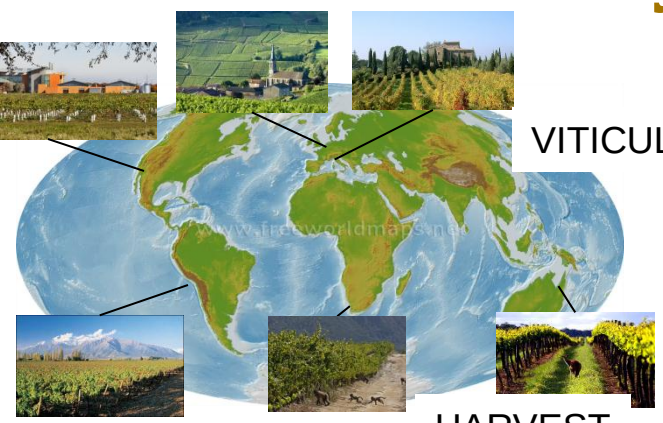
Separation of Samples by PCA

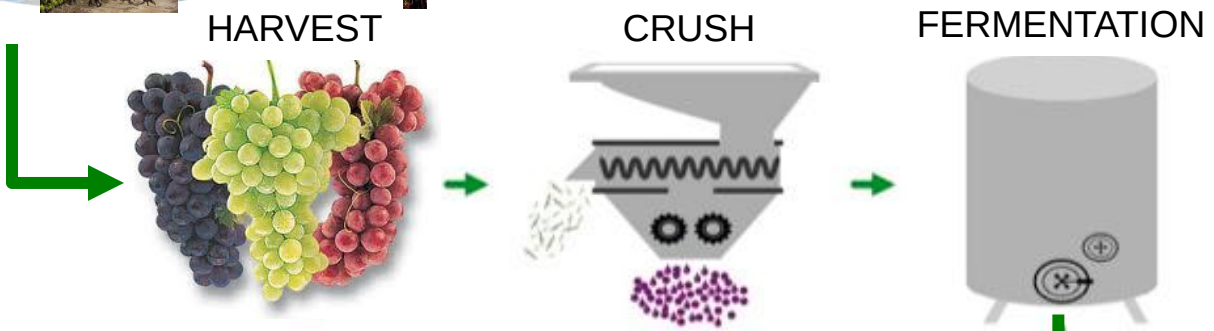


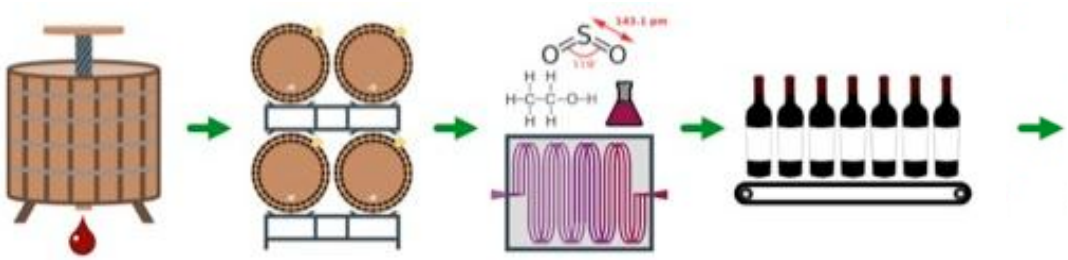
Conclusion

- significant differences in 5 elements due to storage conditions of a Cabernet Sauvignon red wine
- elemental profile of wine is altered by packaging configuration
- storage temperature has some smaller effect
- some indication for processing impact on the elemental composition of wine
- elements measured are below maximum OIV levels in the low to mid ppb range

Elemental analysis from grapes to wine



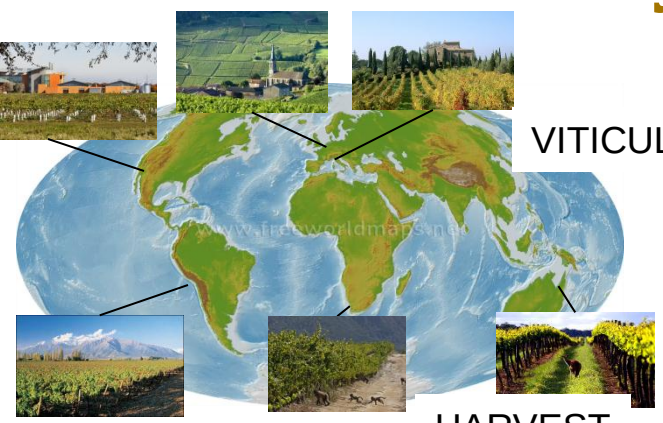




STORAGE

http://silversmithvineyards.com/wp-content/uploads/2011/09/winemaking_500.jpeg

Elemental analysis from grapes to wine

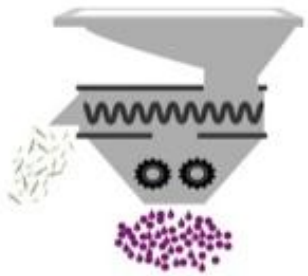


VITICULTURE

which elements to choose?

HARVEST

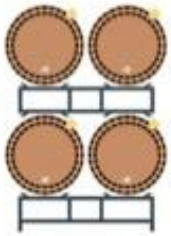
CRUSH



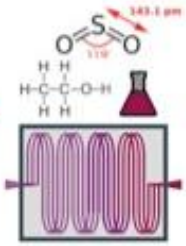
FERMENTATION

PRESS

AGING



FINISHING



BOTTLING

STORAGE

http://silversmithvineyards.com/wp-content/uploads/2011/09/winemaking_500.jpeg

Acknowledgments

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