Wine and NMR (low field)

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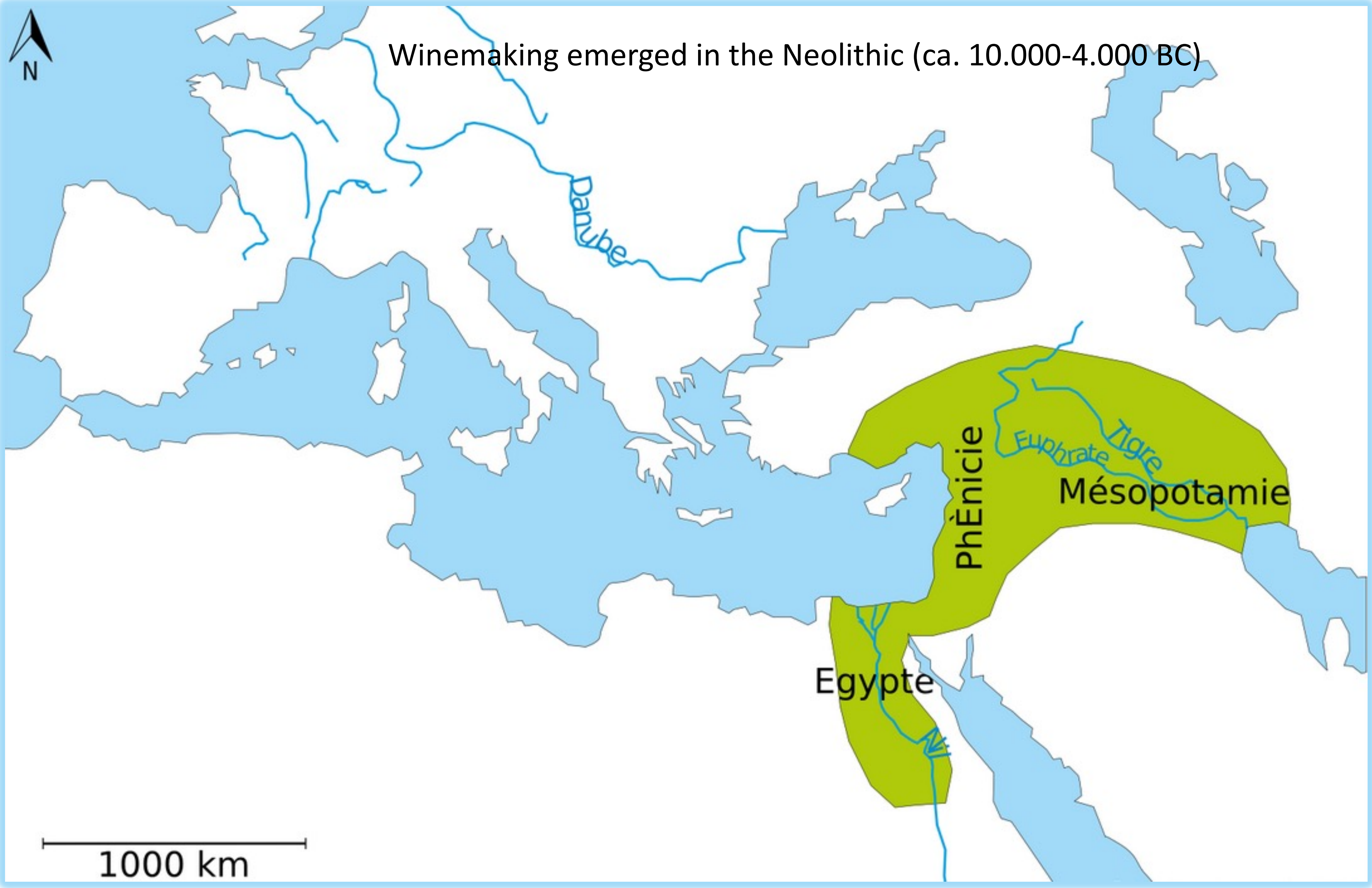
AGRO SUP DIJON

Dyonisos grec god of vine, wine, and its excess
Mosaic dating from the III century AD J.-C
Syria - Shahba Museums
https://www.theoi.com/Gallery/Z12.16.html

Ash, god of the oasis and the vineyards of the western delta of the Nile.
https://fr.wikipedia.org/wiki/Ach_(divinit%C3%A9)

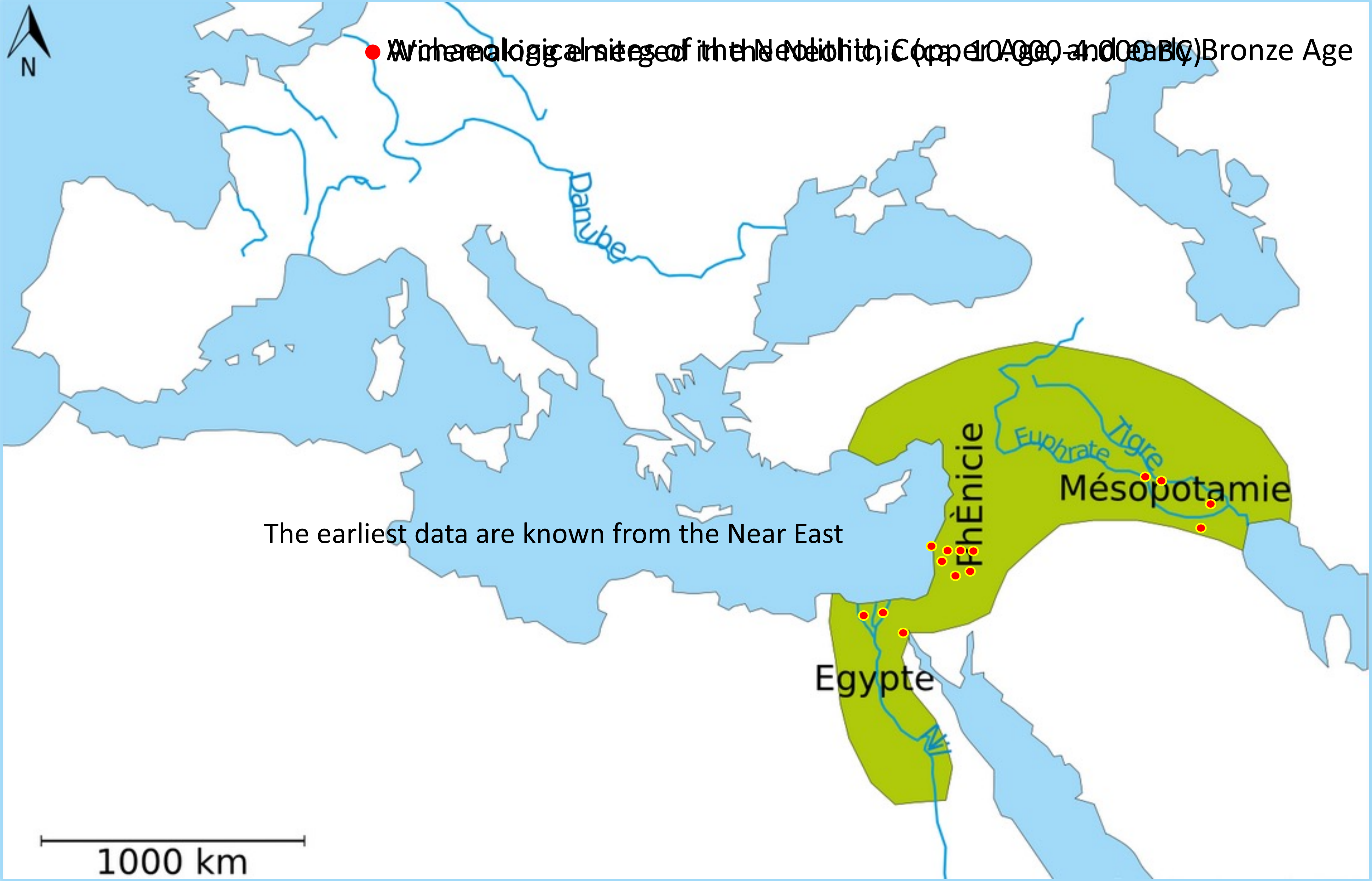
Sucellus, Celtic god of agriculture and wine
-125BC / 500AD
https://fr.wikipedia.org/wiki/Sucellos

Winemaking emerged in the Neolithic (ca. 10.000-4.000 BC)

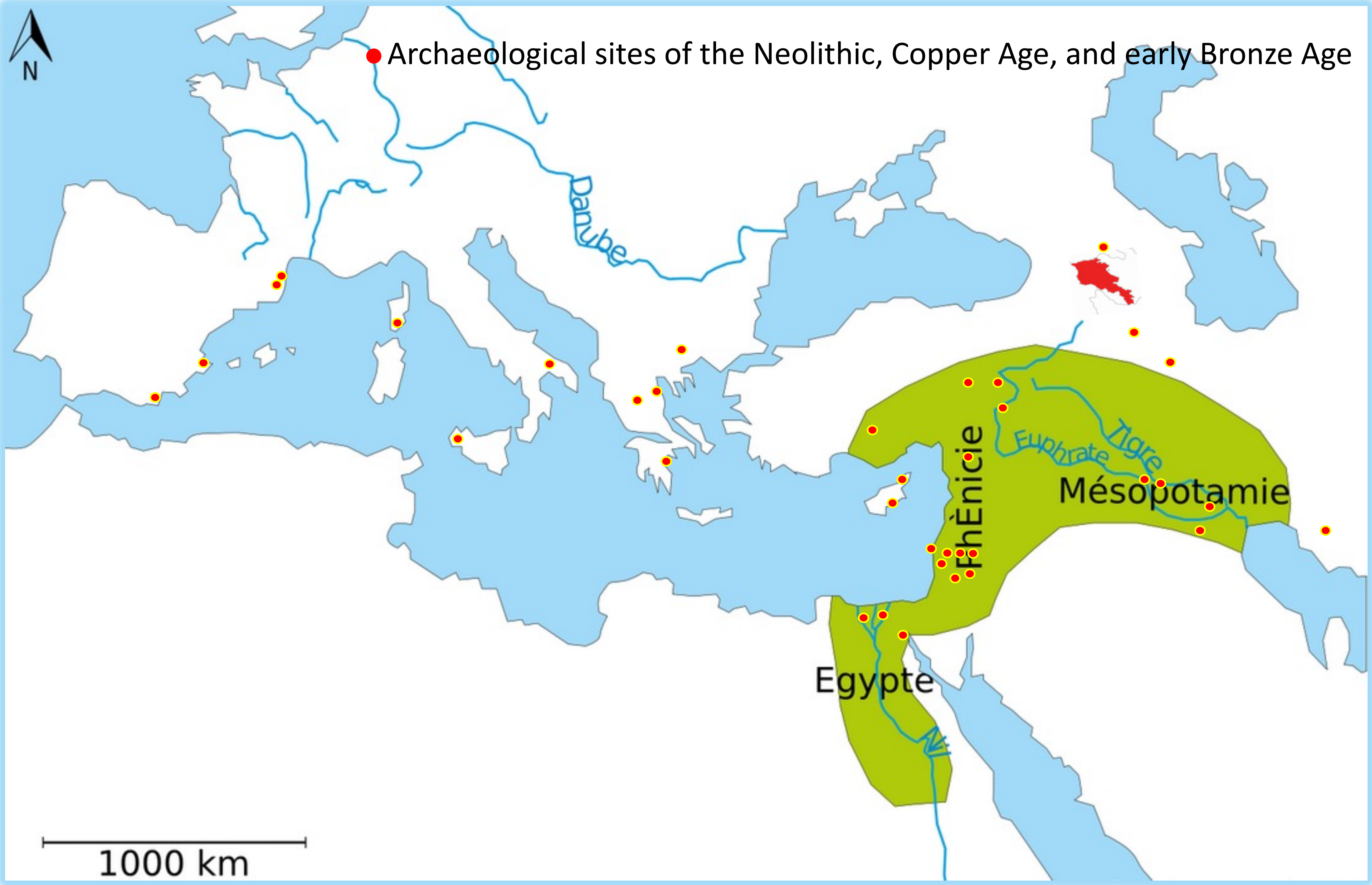


Archaeological sites of the Neolithic (ca. 10.000-4.000 BC)

Winemaking emerged in the Neolithic, Copper Age, and early Bronze Age



The earliest data are known from the Near East



N
Archaeological sites of the Neolithic, Copper Age, and early Bronze Age
Danube
Euphrate
Tigre
PhÈnicie
Mésopotamie
Egypte
Nil
1000 km

A fragment of a fresco portraying harvesting and winemaking. Tomb belonging to Nakht (1500 BC, Theban, Egypt, New Kingdom period, de Garis Davies, 1930)

Oldest vinery (Areni, Armenia - 4100 BC)

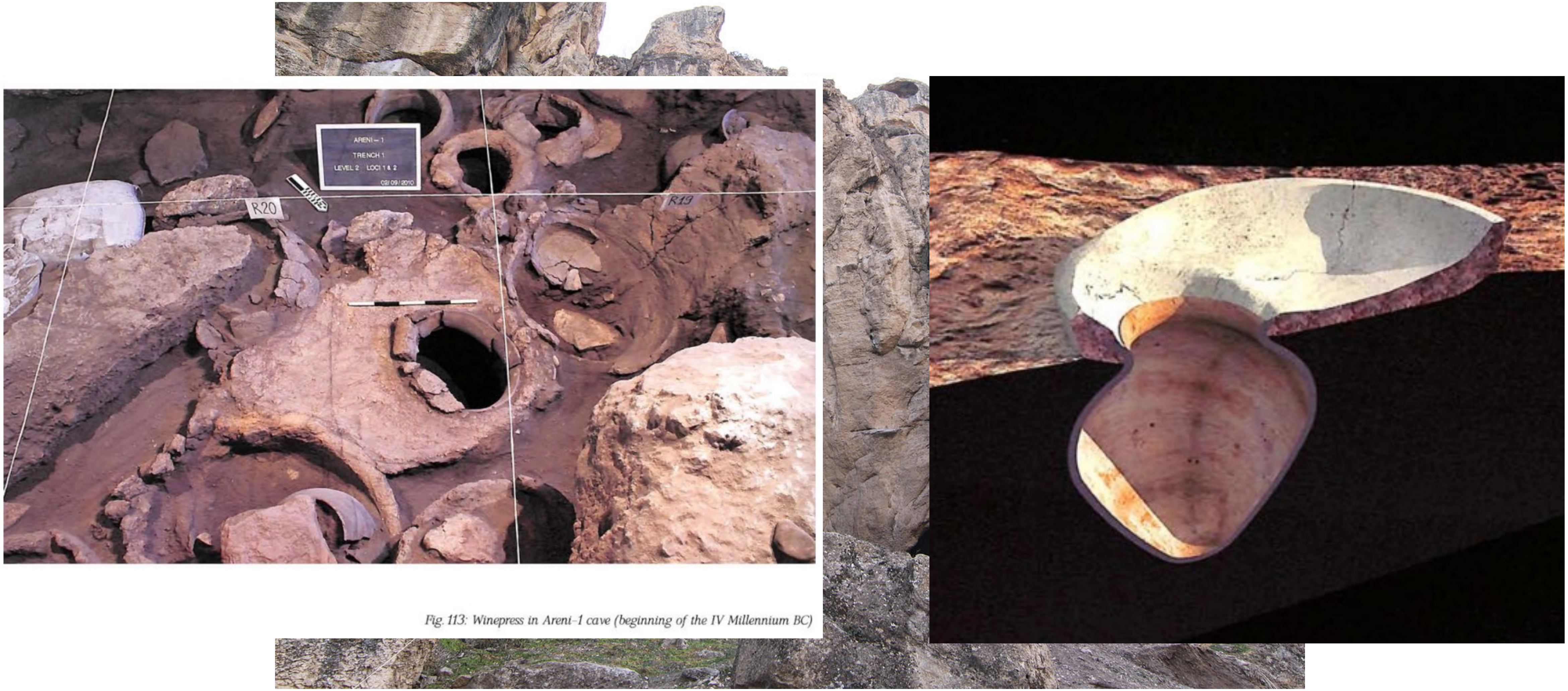
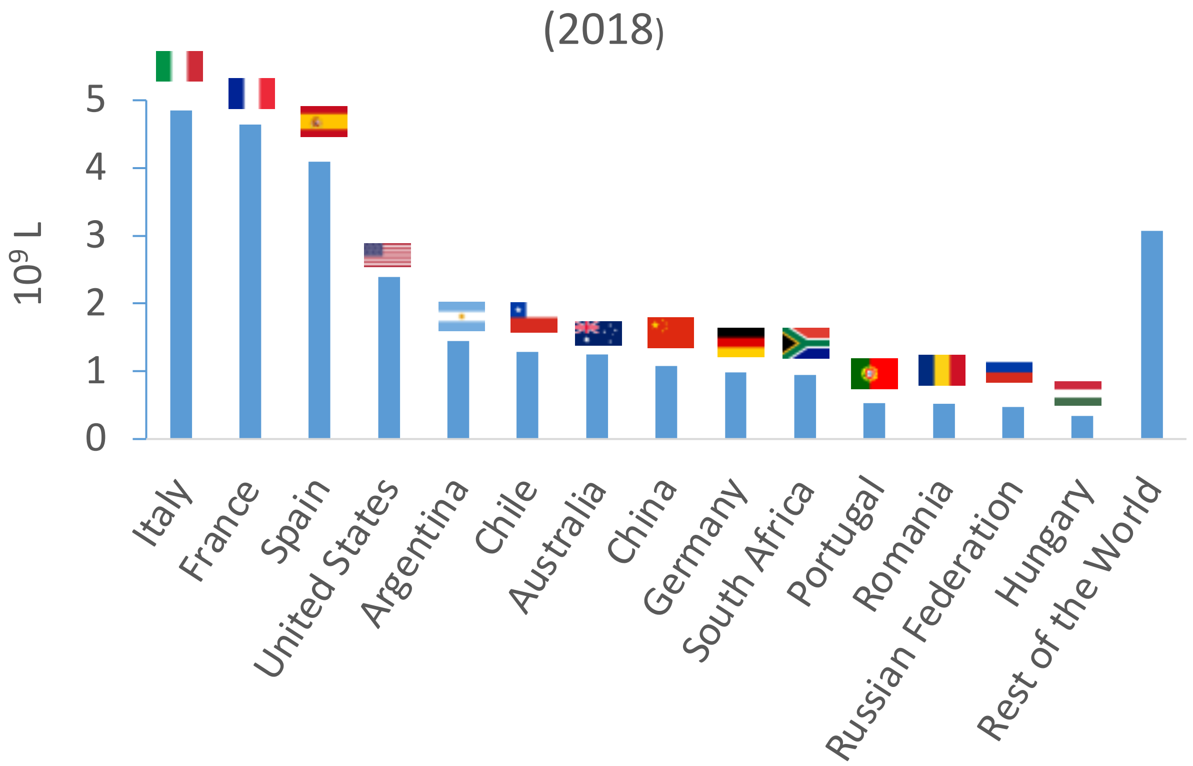


Fig. 113: Winepress in Areni-1 cave (beginning of the IV Millennium BC)

Nelli .A. Hovhannisyan, A.A. Yesayan, A. Bobokhyan, M.V. Dallakyan, S. Hobosyan, B.Z. Gasparyan, A. Danielyan, Z. Muradyan, V. Ter-Ghazaryan, Backbone Branding (Firm), Deutsche Gesellschaft für Internationale Zusammenarbeit, Armenian vine and wine, 2017.

Nowadays wine production

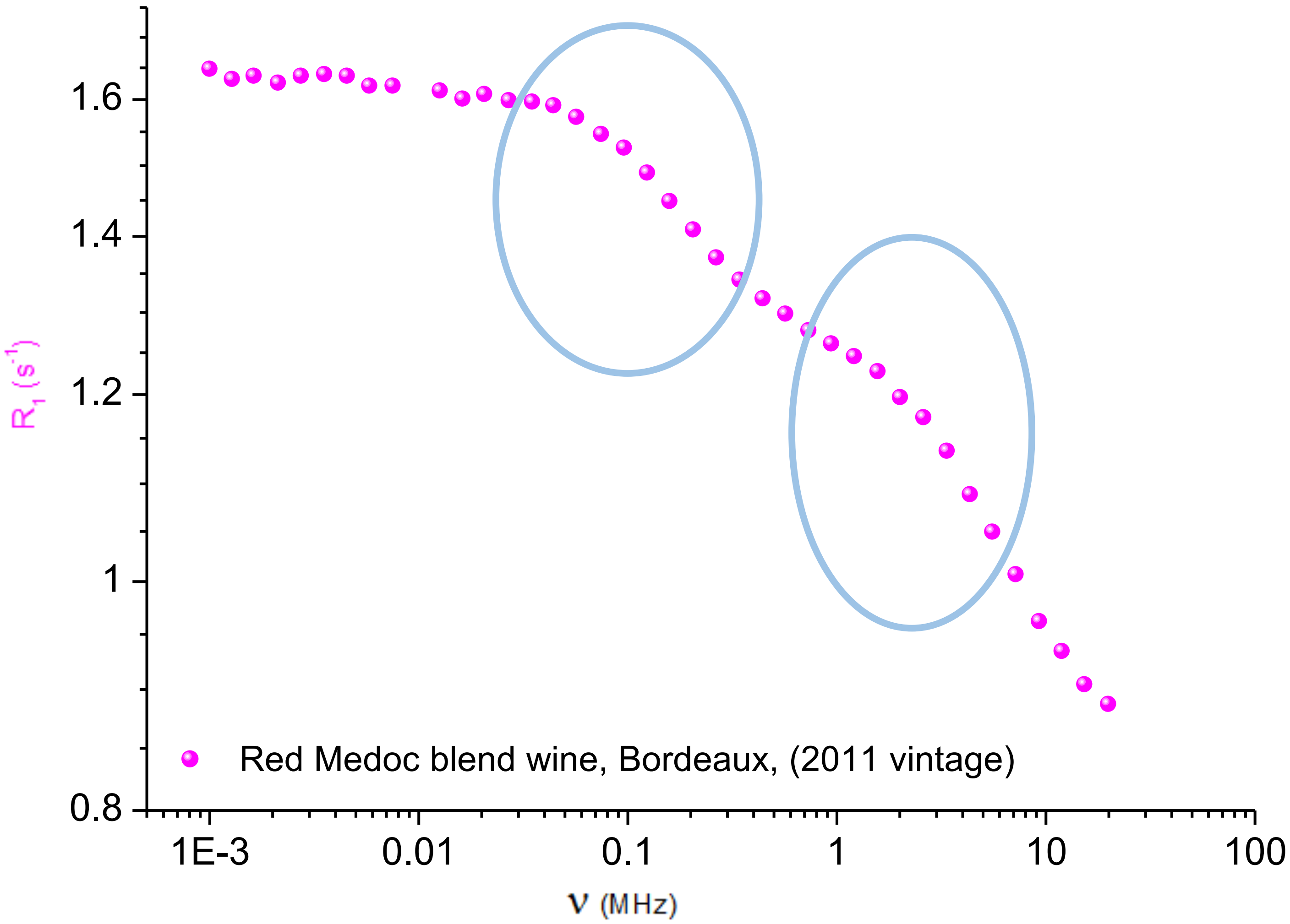


Over the last decade,
World Production ~26 10^9 L/ year.

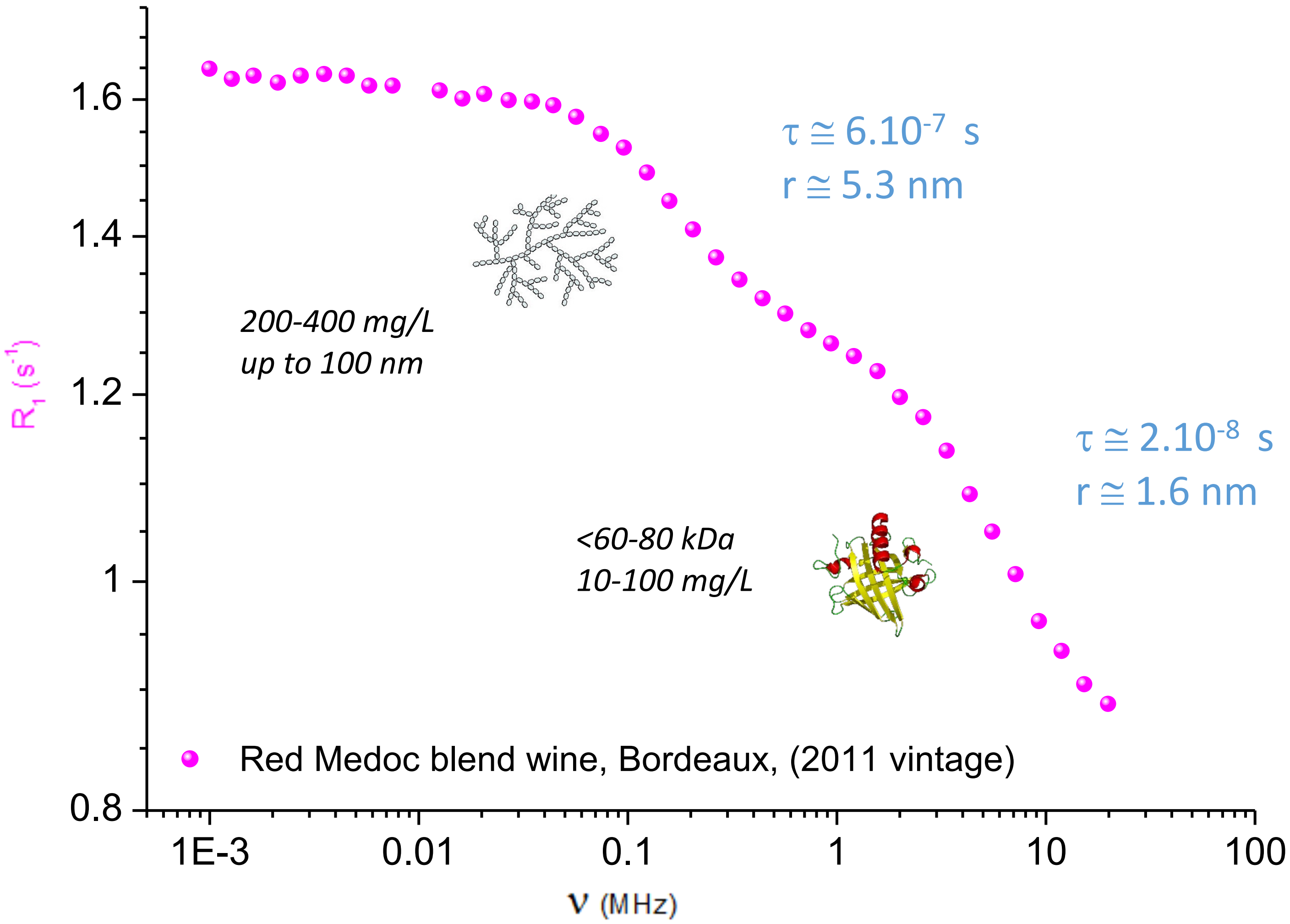
World trade in 2018, 31.3 billion euros.

Adapted from https://en.wikipedia.org/wiki/Winemaking

^{1}H NMRD profile of wine (red Medoc blend)



^{1}H NMRD profile of wine (red Medoc blend)



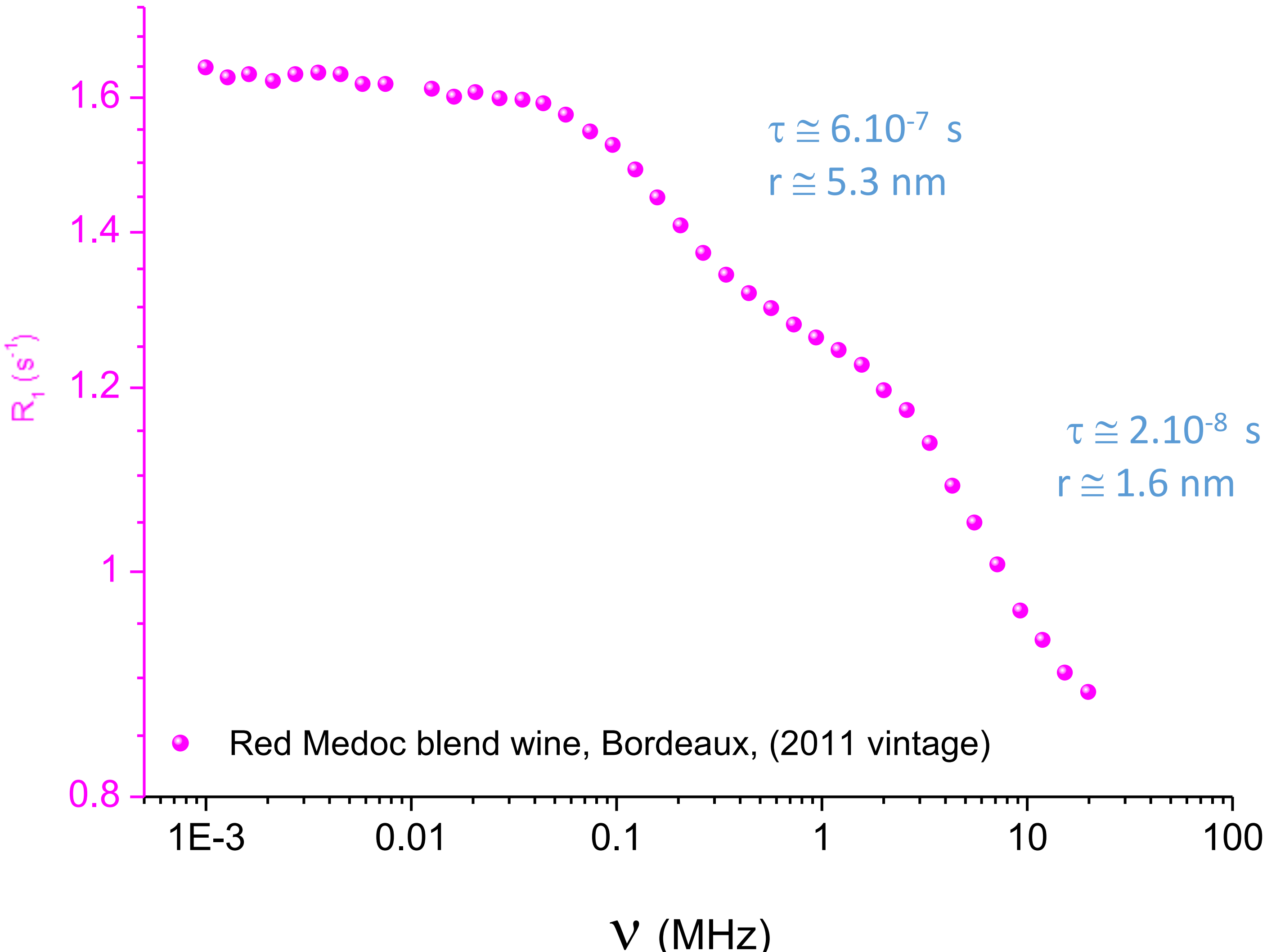
Sometimes some lees, particles in suspension, or crystals may be seen in the wine

Rotational diffusion of big molecules (proteins, polysaccharides) ?

$$\tau_c = \frac{4\pi\eta r^3}{3kT}$$

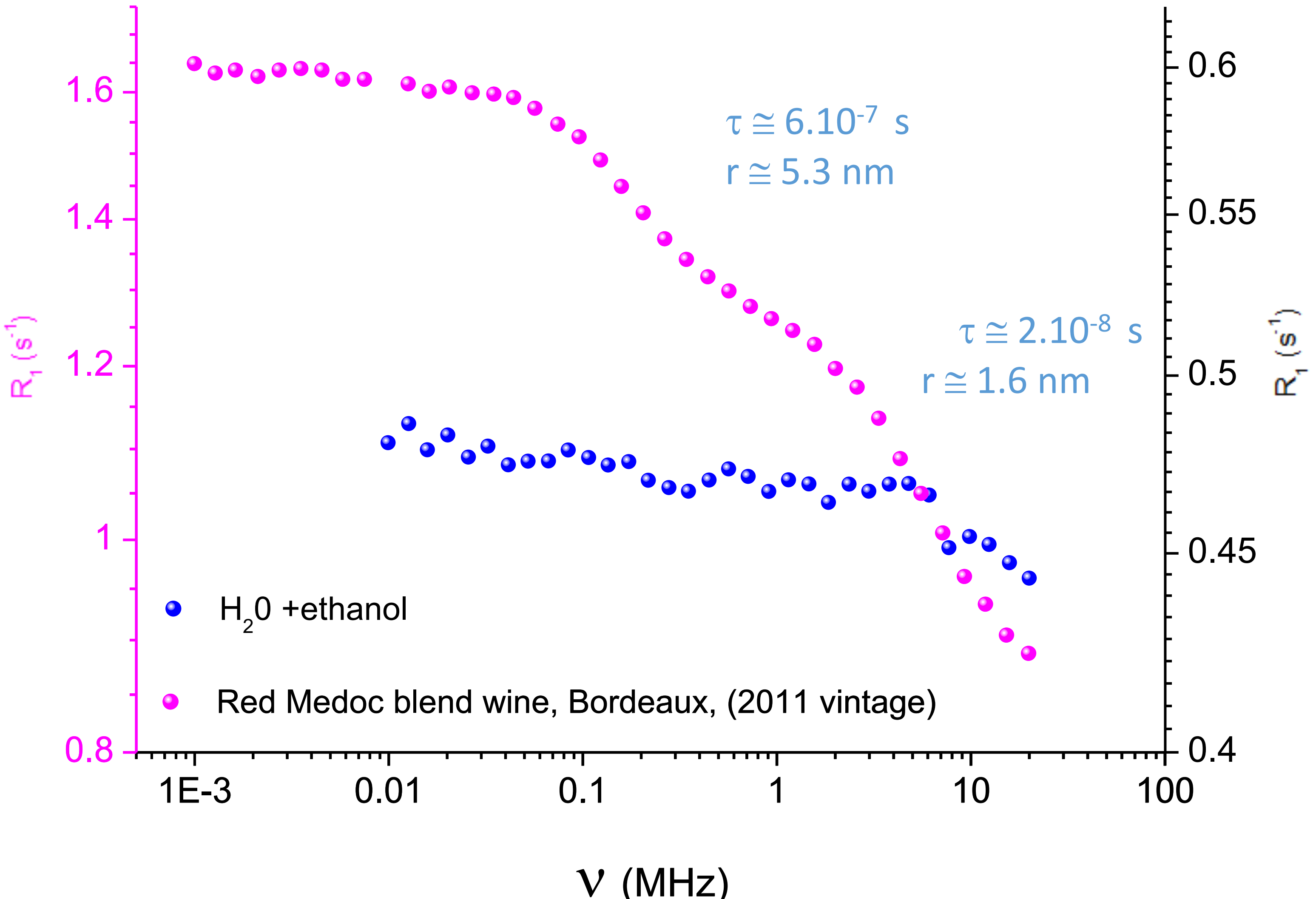
η ~4 mPa.s

NMRD profile of wine (red Medoc blend)



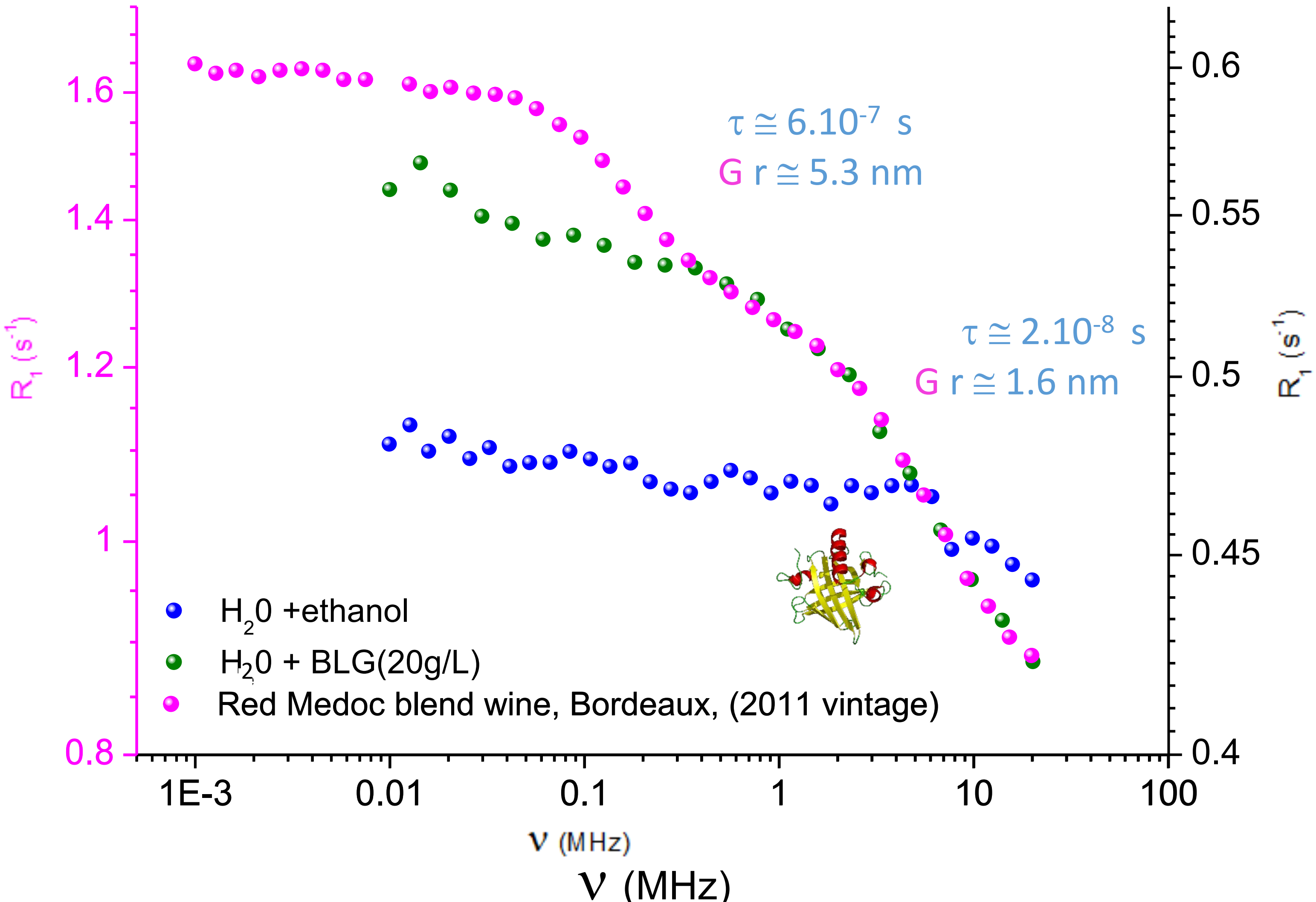
Rotational diffusion of big molecules (proteins, polysaccharides) ?

NMRD profile of wine (red Medoc blend)



Rotational diffusion of big molecules (proteins, polysaccharides) ?

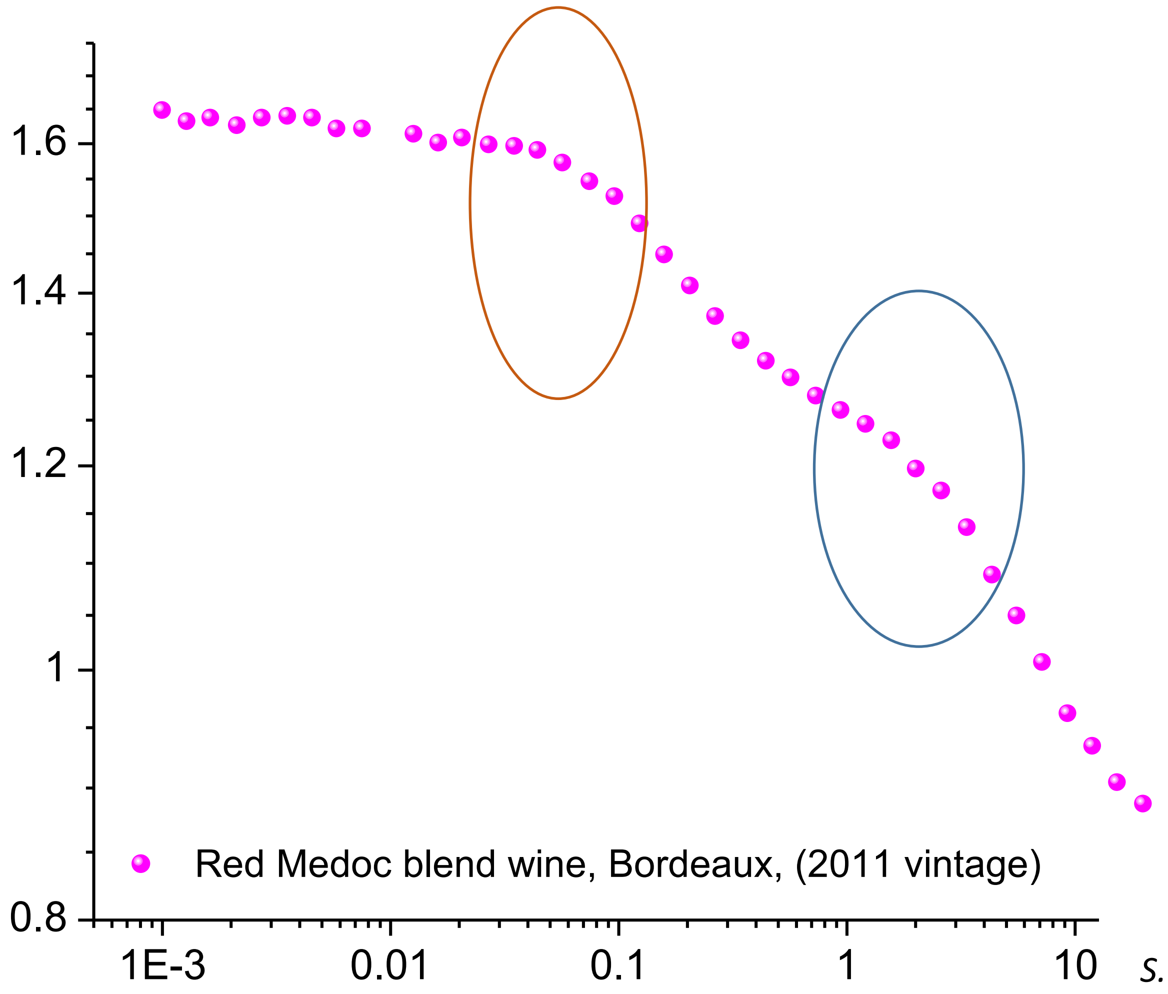
NMRD profile of wine (red Medoc blend)

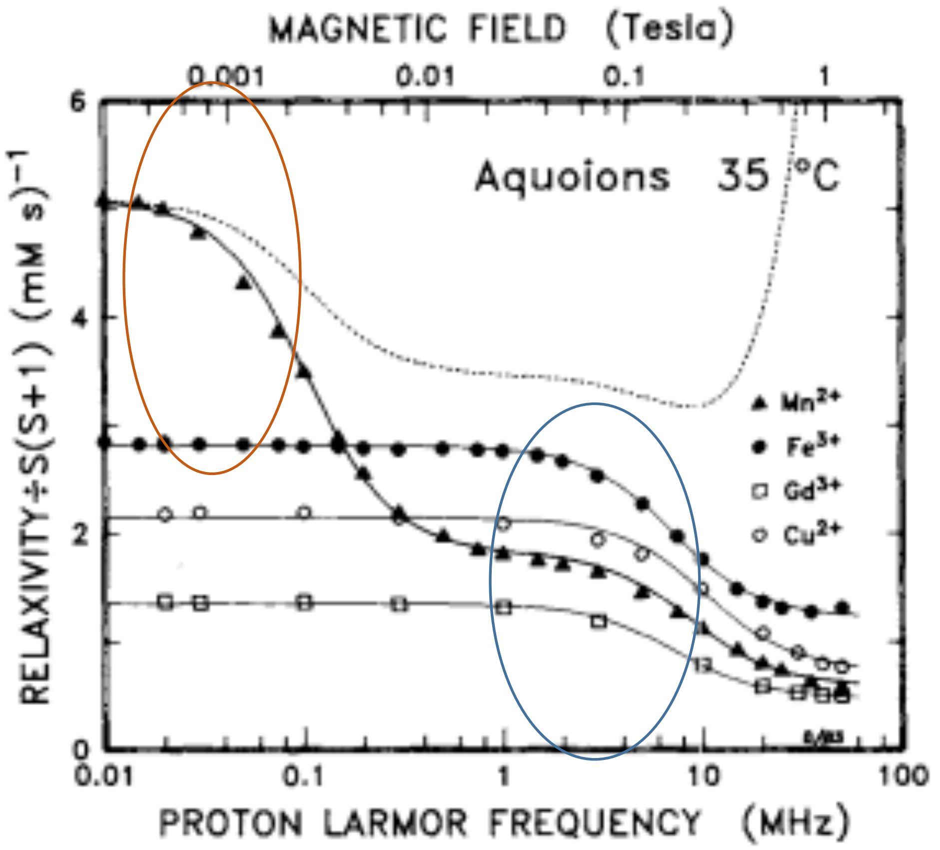


Rotational diffusion of big molecules (proteins, polysaccharides) ?

The concentration and size distribution of such particles in wine would likely be insufficient to explain the NMRD profile features.

NMRD profile of wine (red Medoc blend)





S.H. Koenig, R.D. Brown, Relaxation of solvent protons by paramagnetic ions and its dependence on magnetic field and chemical environment: implications for NMR imaging, Magnetic Resonance in Medicine. 1 (1984) 478–495

Source of metal ions in wines.

Al (insecticide)

Zn (herbicides/ insecticides)

Cu (pesticide)

Cd (phosphate fertilizer)

Fe*

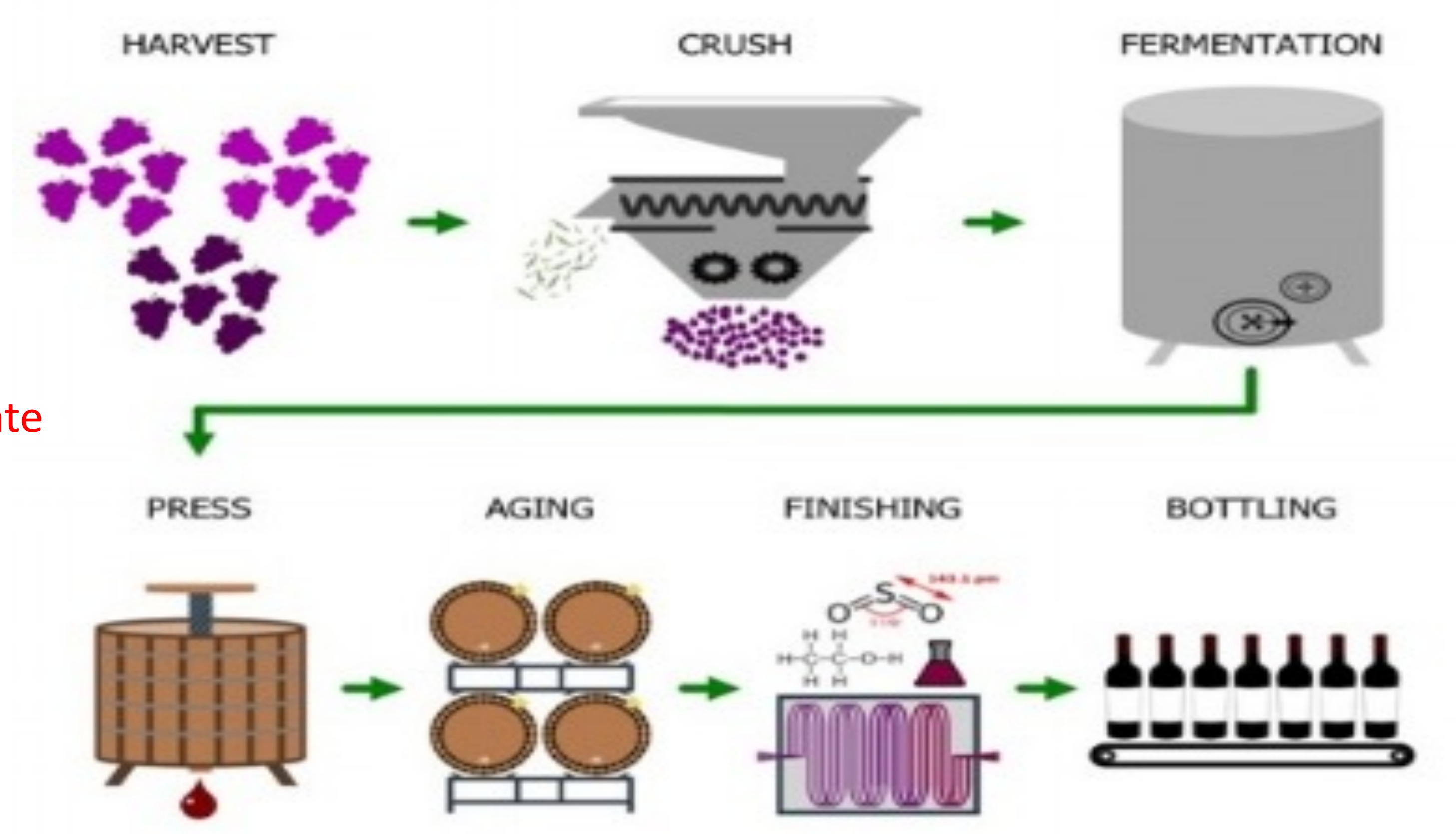
Mn*

Pb

Cr (stainless steel container)

Zn (container)

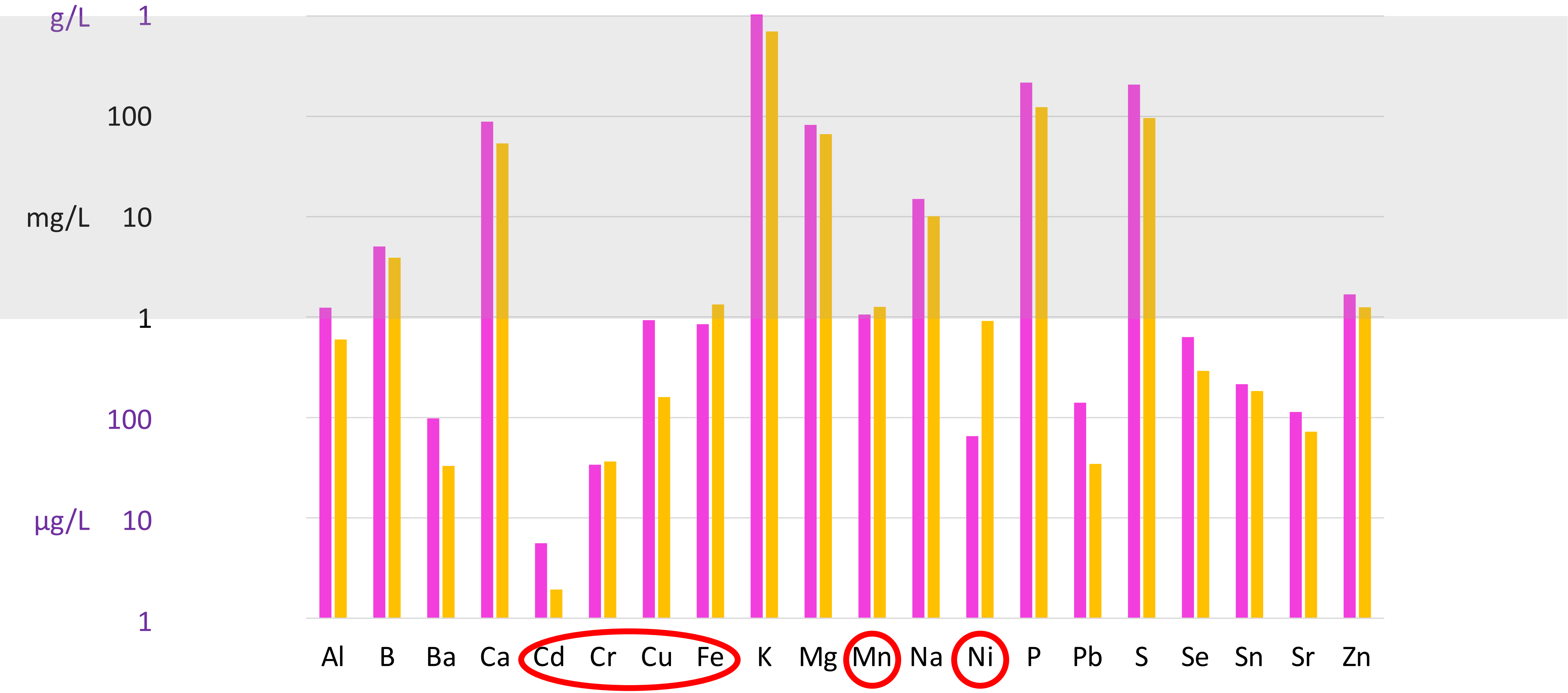
Cu (copper/ bronze materials)



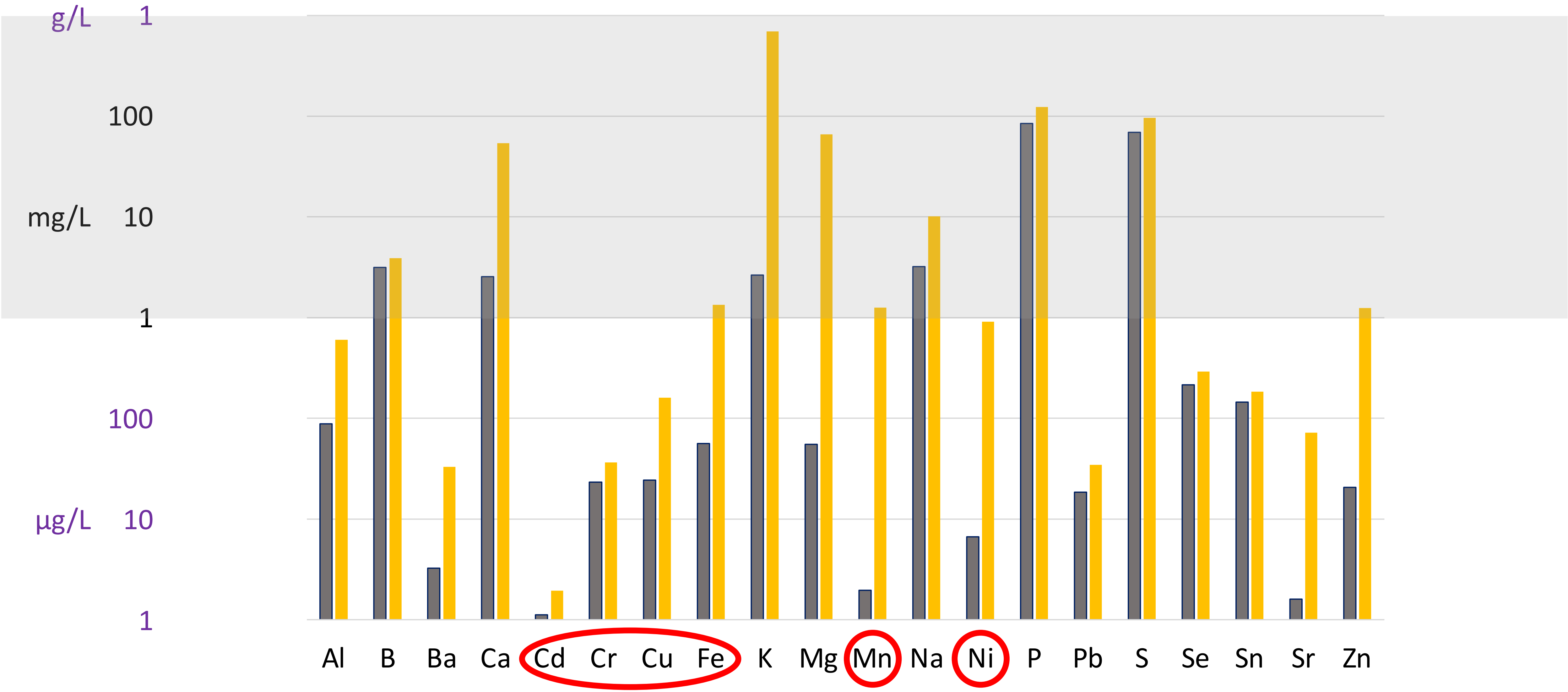
Cu (to eliminate smells from organic sulfur)

Al (use of bentonite for wine fining)

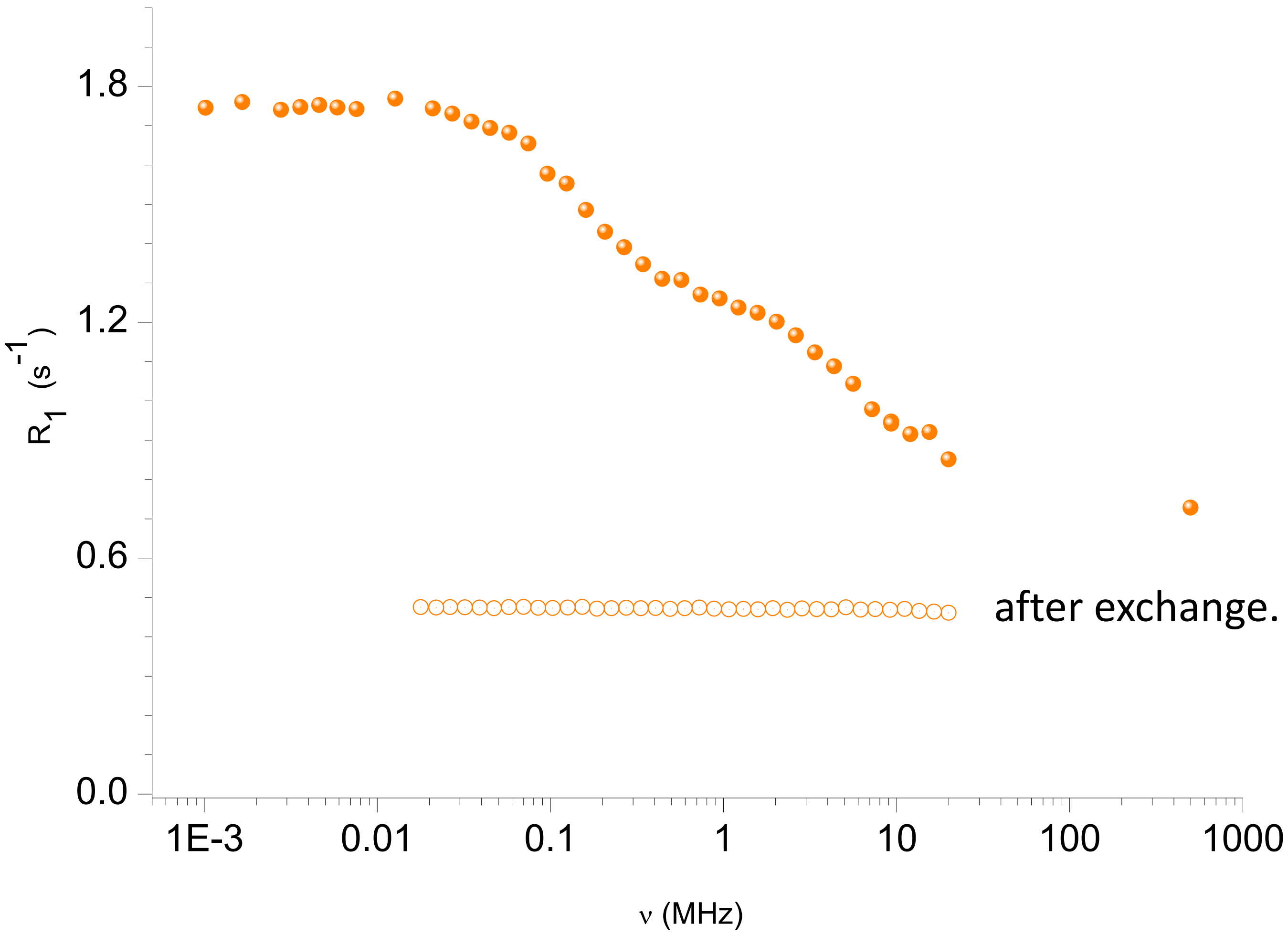
Metal ions in red Medoc blend & white Chardonay (ICP-AES).



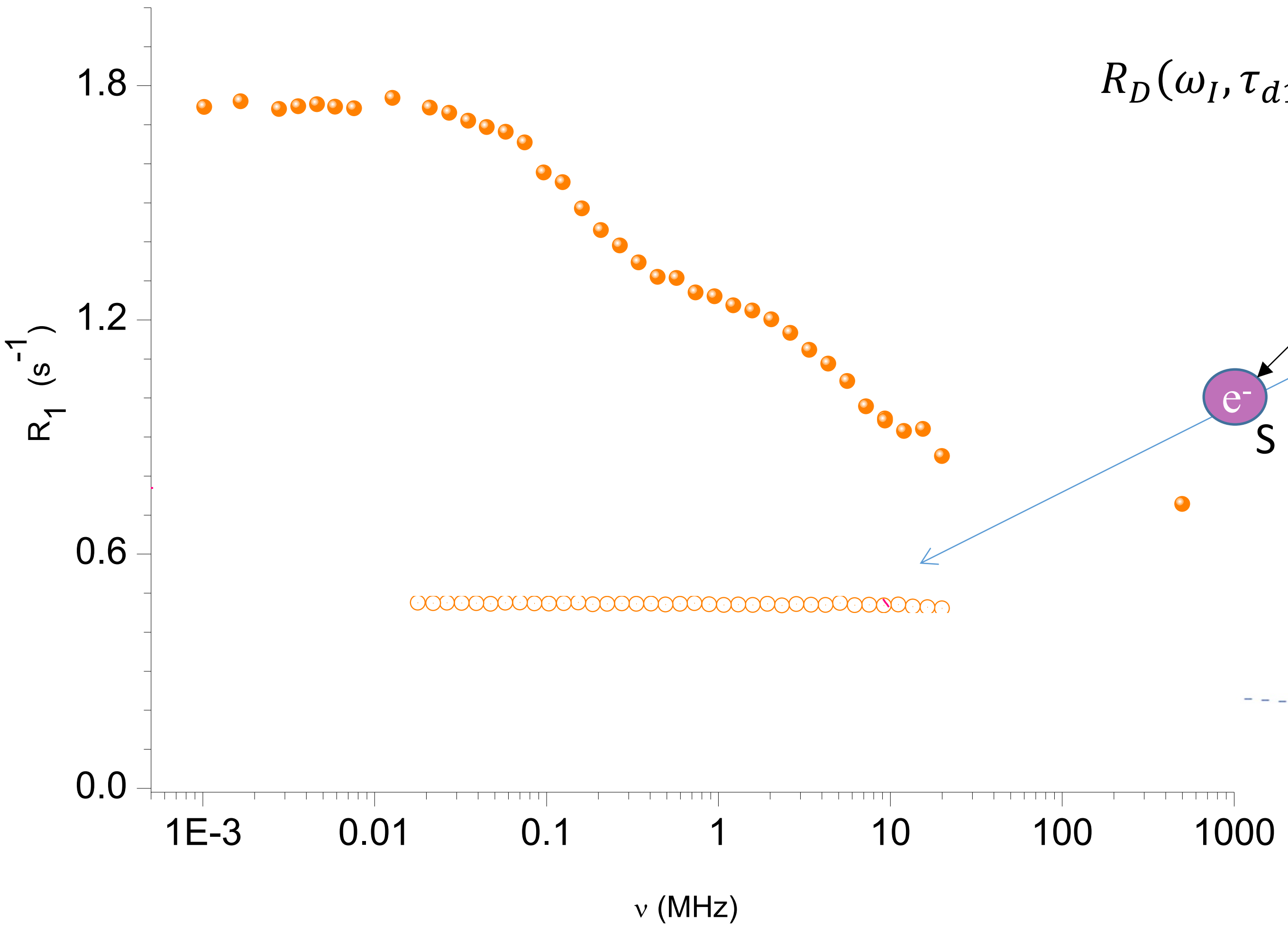
Metal ions in white Chardonay before & after exchange (ICP-AES).



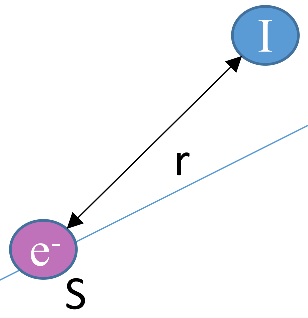
Chardonnay white wine.



Paramagnetic relaxation Solomon mechanism

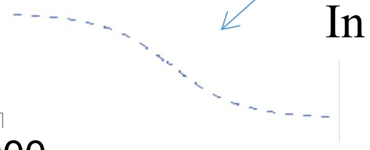


$$R_D(\omega_I, \tau_{d1}, \omega_S, \tau_{d2}) = C_D\left[\frac{7\tau_{d2}}{1+(\omega_S\tau_{d2})^2} + \frac{3\tau_{d1}}{1+(\omega_I\tau_{d1})^2}\right]$$



$$C_D = \frac{2}{15}\left(\frac{\mu_o}{4\pi}\right)^2 \frac{S(S+1)(\gamma_I\,\gamma_S\hbar)^2}{r_{IS}{}^6}$$

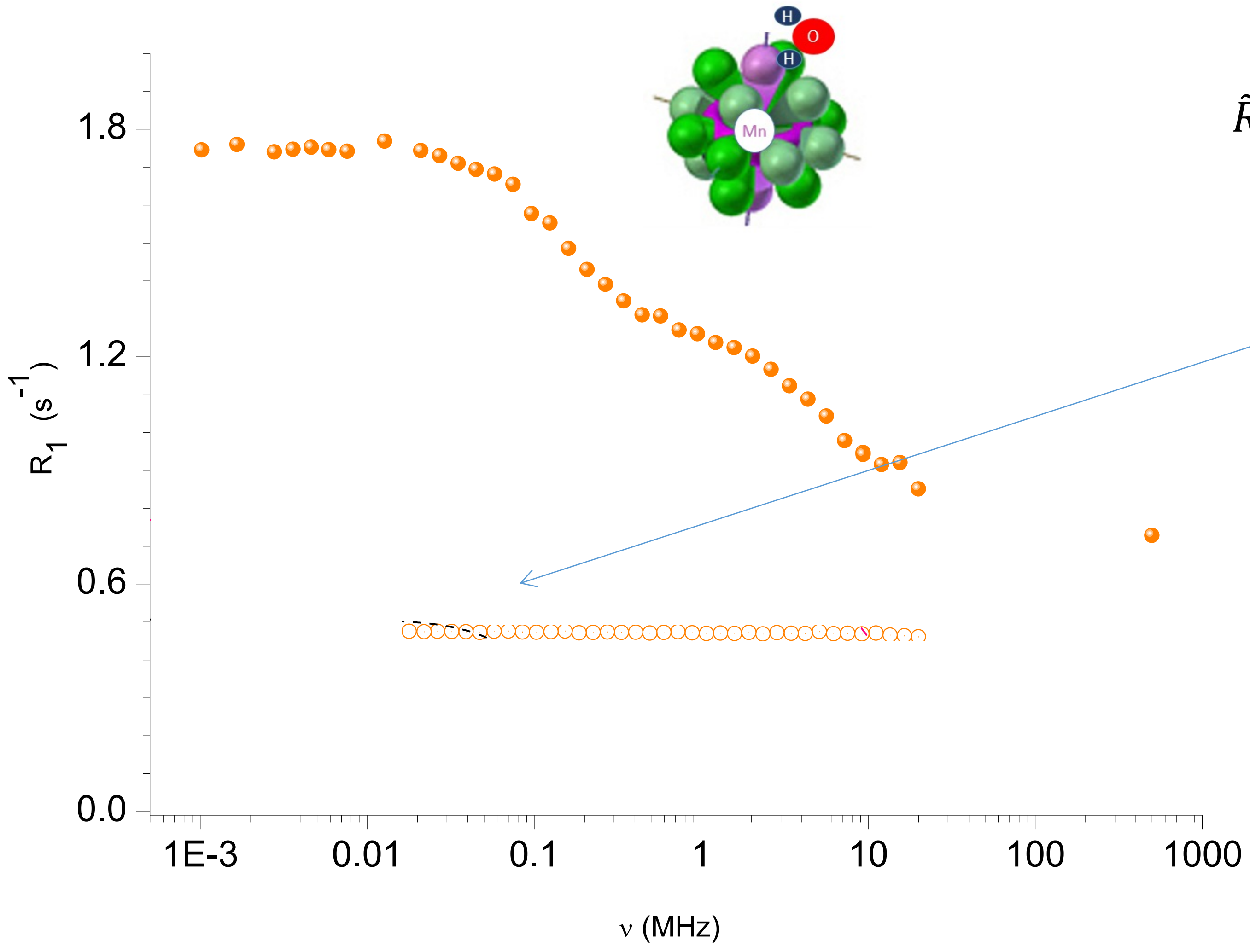
$$\frac{1}{\tau_{di}} = \frac{1}{\tau_R} + \frac{1}{\tau_M} + \frac{1}{\tau_{Si}} \quad (i = 1,2)$$



In practice, at low magnetic field,

$$\tau_{d1} = \tau_{d2} = \tau_d$$

Paramagnetic relaxation, Bloembergen mechanism

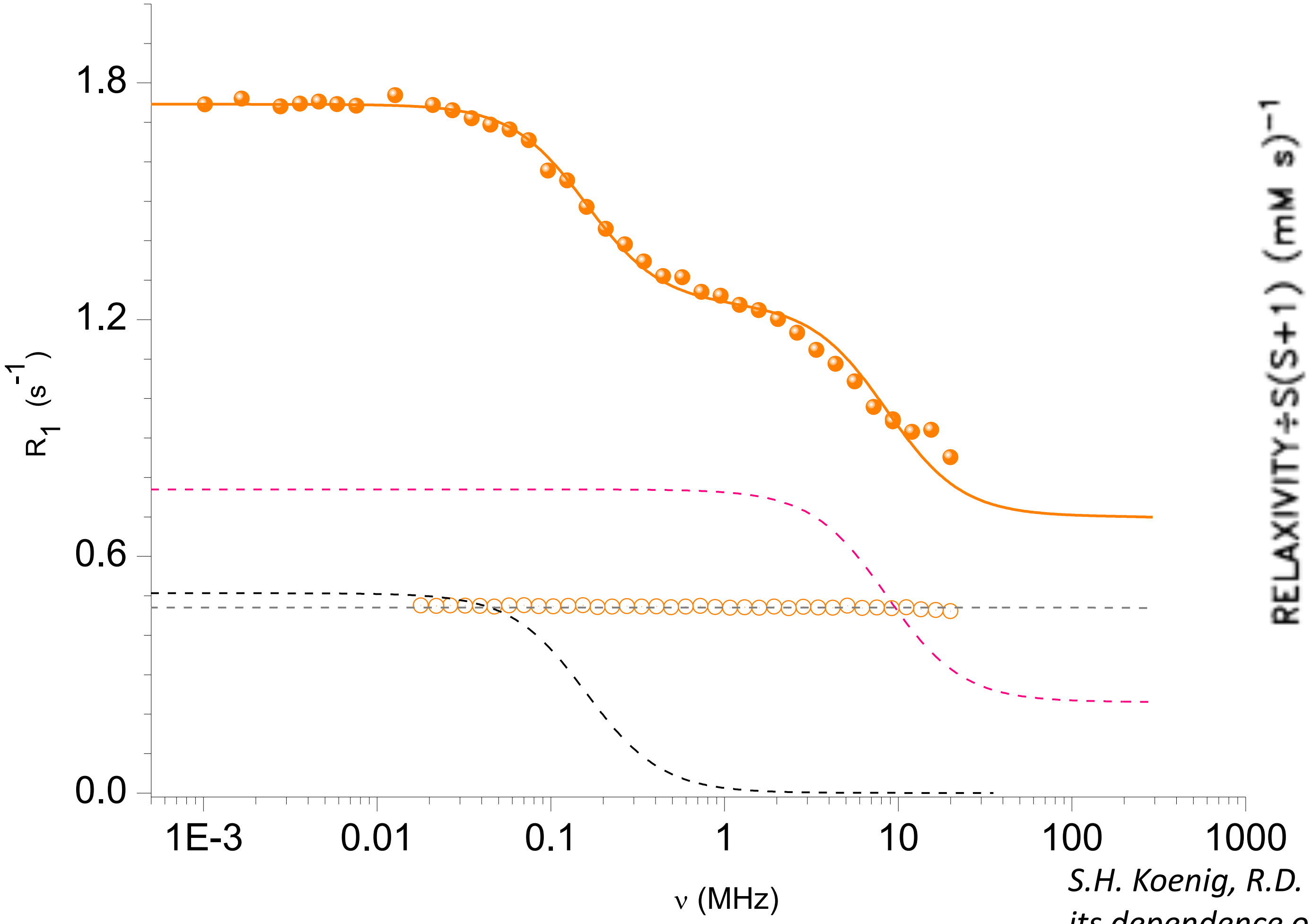


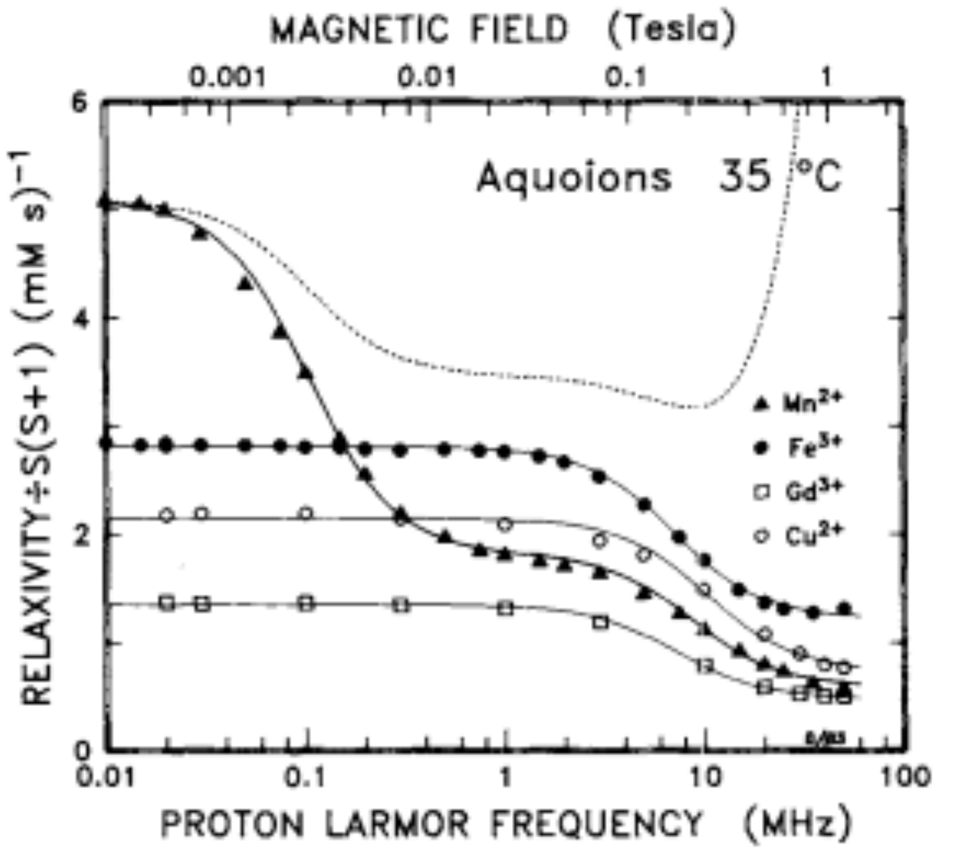
$$\tilde{R}_C(\omega_s, \tau_c) = \tilde{C}_C \left[\frac{\tau_c}{1 + (\omega_s \tau_c)^2}\right]$$

$$\tilde{C}_C = \frac{2A^2 S(S+1)}{3\hbar^2}$$

$$\frac{1}{\tau_c} = \frac{1}{\tau_M} + \frac{1}{\tau_{S2}}$$

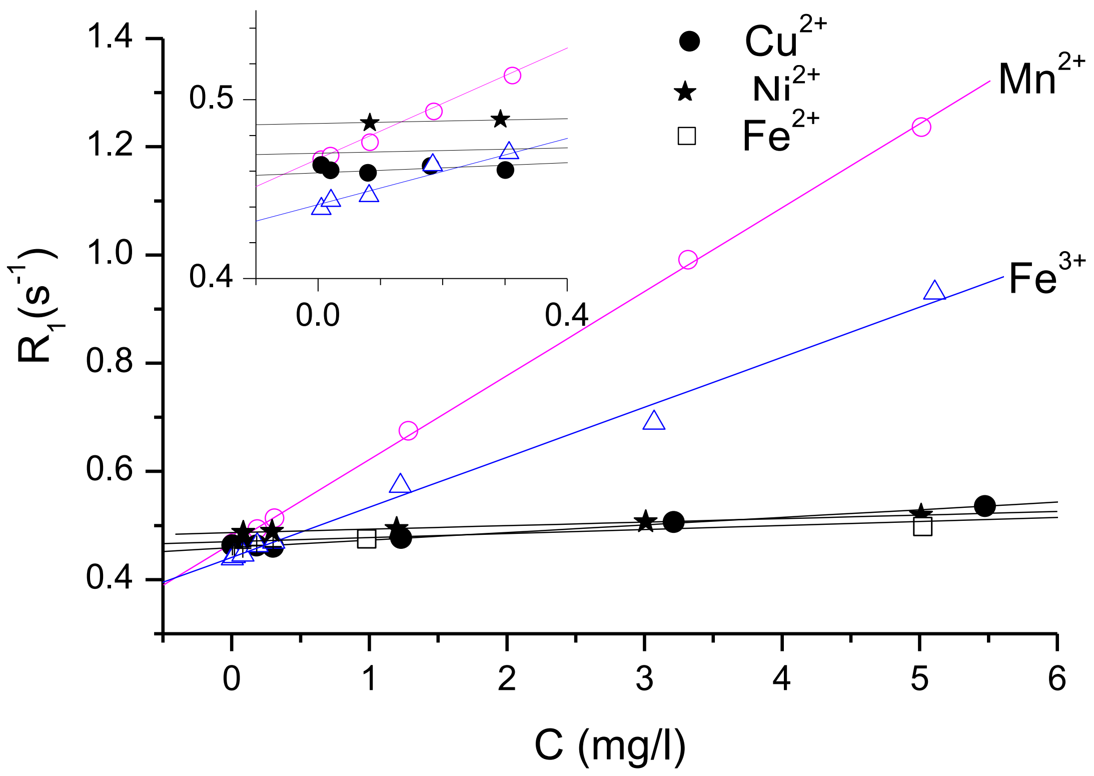
Dia and paramagnetic relaxations.

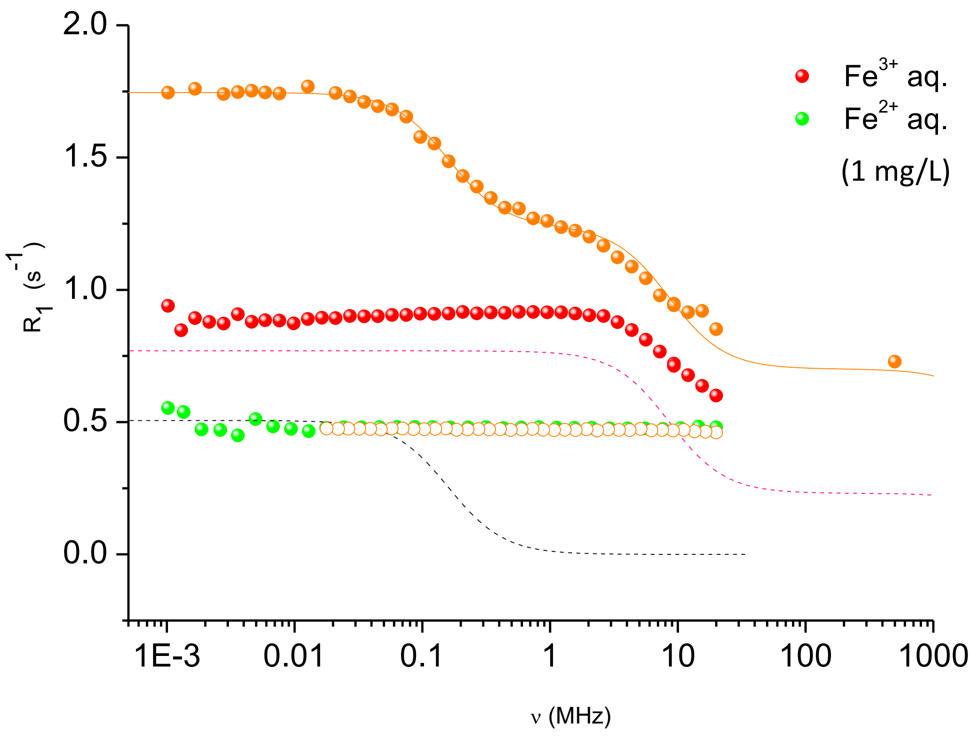


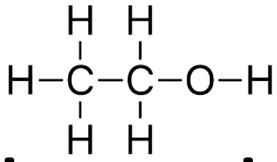


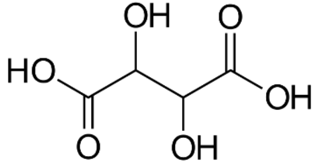
S.H. Koenig, R.D. Brown, Relaxation of solvent protons by paramagnetic ions and its dependence on magnetic field and chemical environment: implications for NMR imaging, Magnetic Resonance in Medicine. 1 (1984) 478–495

Other Contributions.

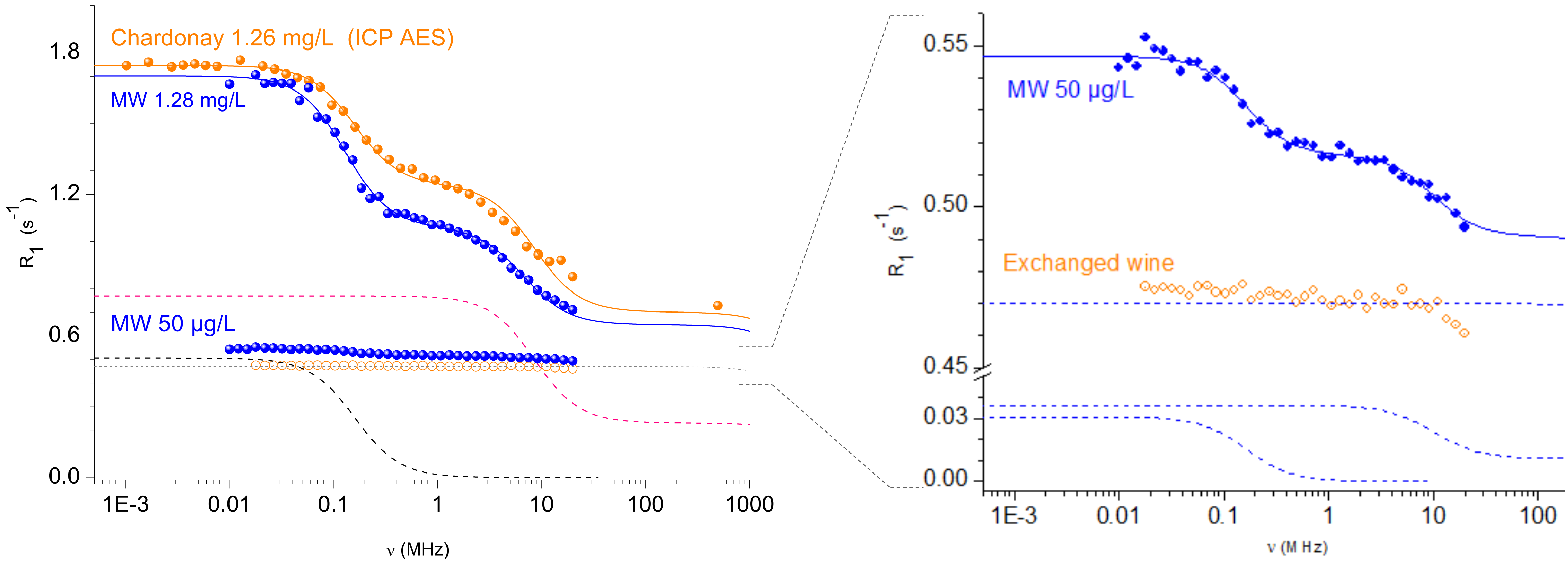








Model wines (H_2O, **ethanol, tart. a. (5g/L))**

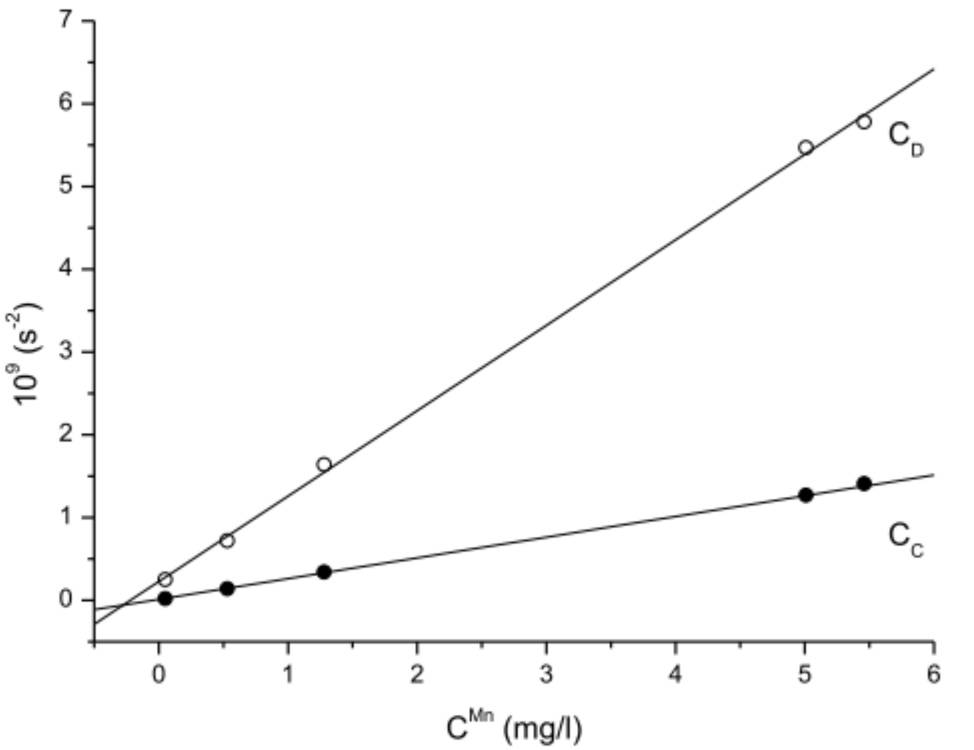


Model wines

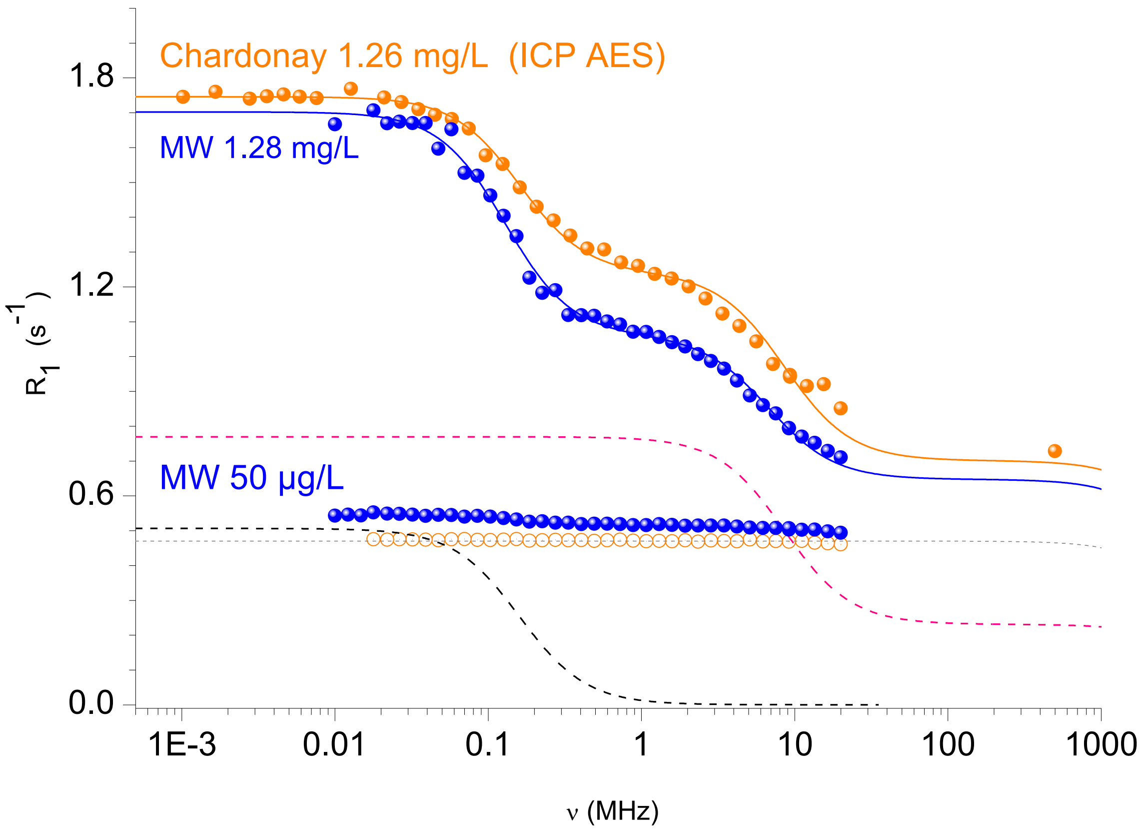
$$R_D(\omega_I, \tau_{d1}, \omega_s, \tau_{d2}) = C_D\left[\frac{7\tau_{d2}}{1+(\omega_s\tau_{d2})^2} + \frac{3\tau_{d1}}{1+(\omega_I\tau_{d1})^2}\right] + \tilde{C}_C\left[\frac{\tau_c}{1+(\omega_s\tau_c)^2}\right]$$

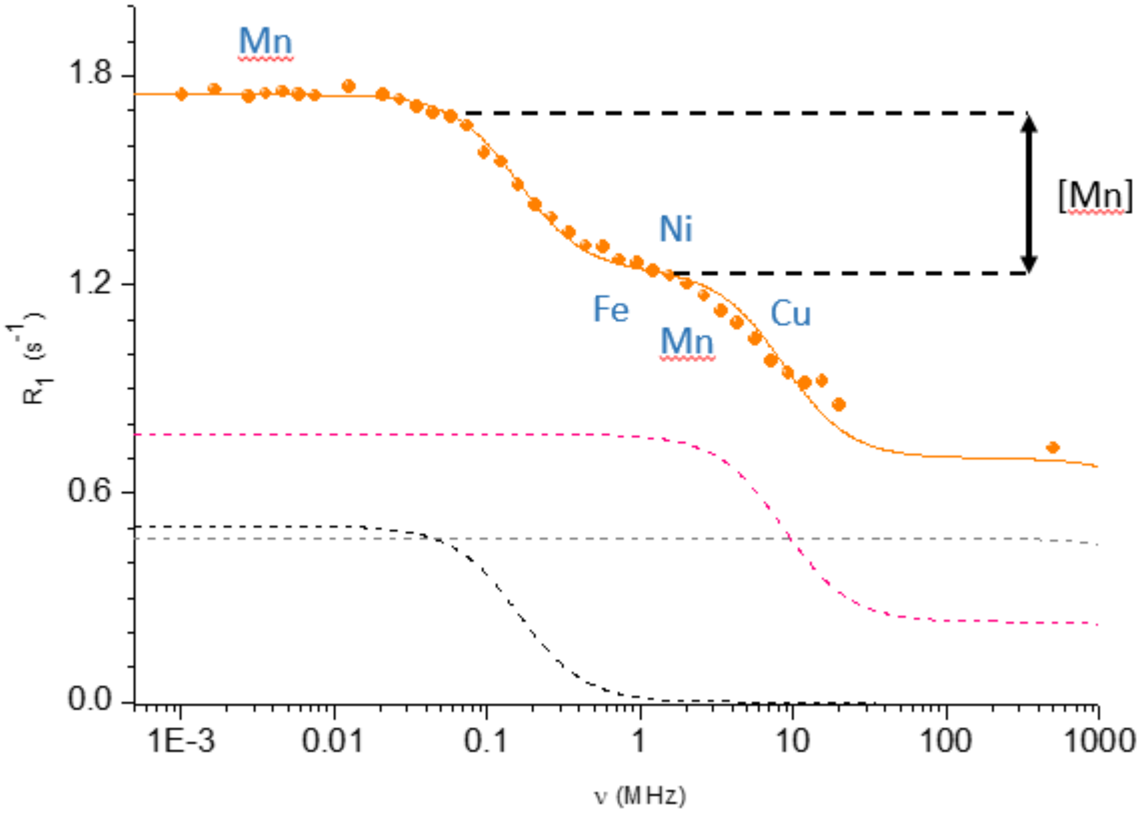
Parameters obtained from refinements of NMRD profiles for the white Chardonnay (W), the red Medoc blend (R) and model wines (MW). MWx refers to model wines containing x/100 mg/L of manganese. $C_{D/C} = pq\tilde{C}_{D/C}$ and numbers in parentheses are last-digit-uncertainties resulting purely from the numerical refinement.

	R_D		R_C	
	C_D (10^9 s^{-2})	τ_d (10^{-11}s)	C_C (10^9 s^{-2})	τ_c(10^{-9} s)
MW546	5.78	3.81 (2)	1.41	1.88 (1)
MW501	5.47	3.78 (2)	1.27	1.86 (2)
MW128	1.64	3.60 (3)	0.34	1.87 (3)
MW053	0.72	3.43 (3)	0.14	1.82 (3)
MW005	0.25	1.80 (2)	0.02	1.50 (4)
Wa	2.73	2.82 (3)	0.33	1.51 (3)
Wb	2.69	2.92 (2)	0.36	1.43 (2)
Ra	2.97	2.56 (2)	0.30	1.28 (3)
Rb	2.07	3.22 (3)	0.30	1.38 (4)

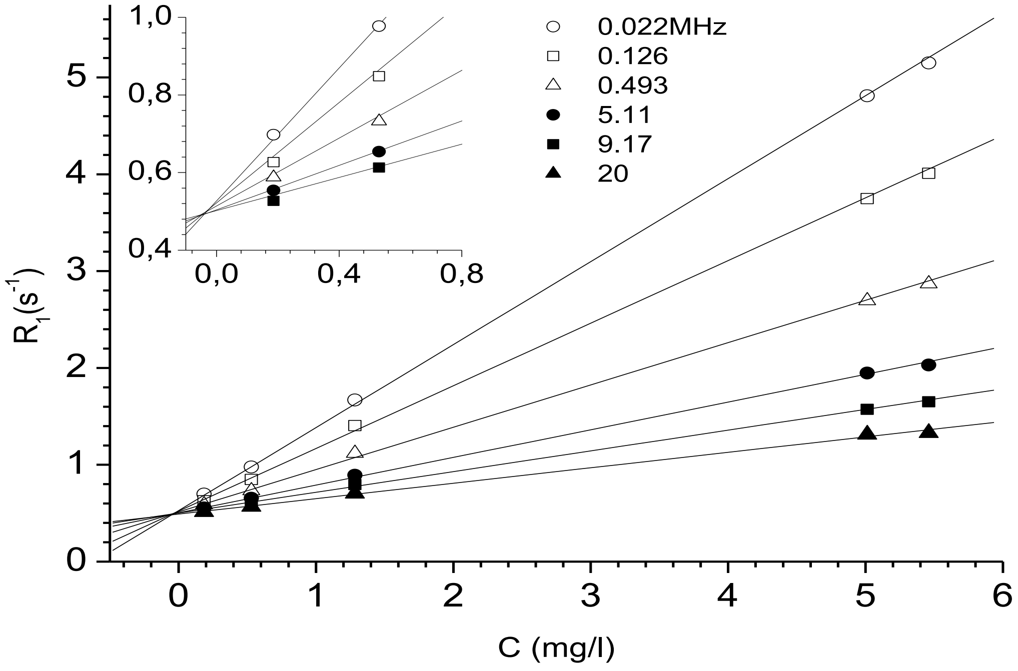


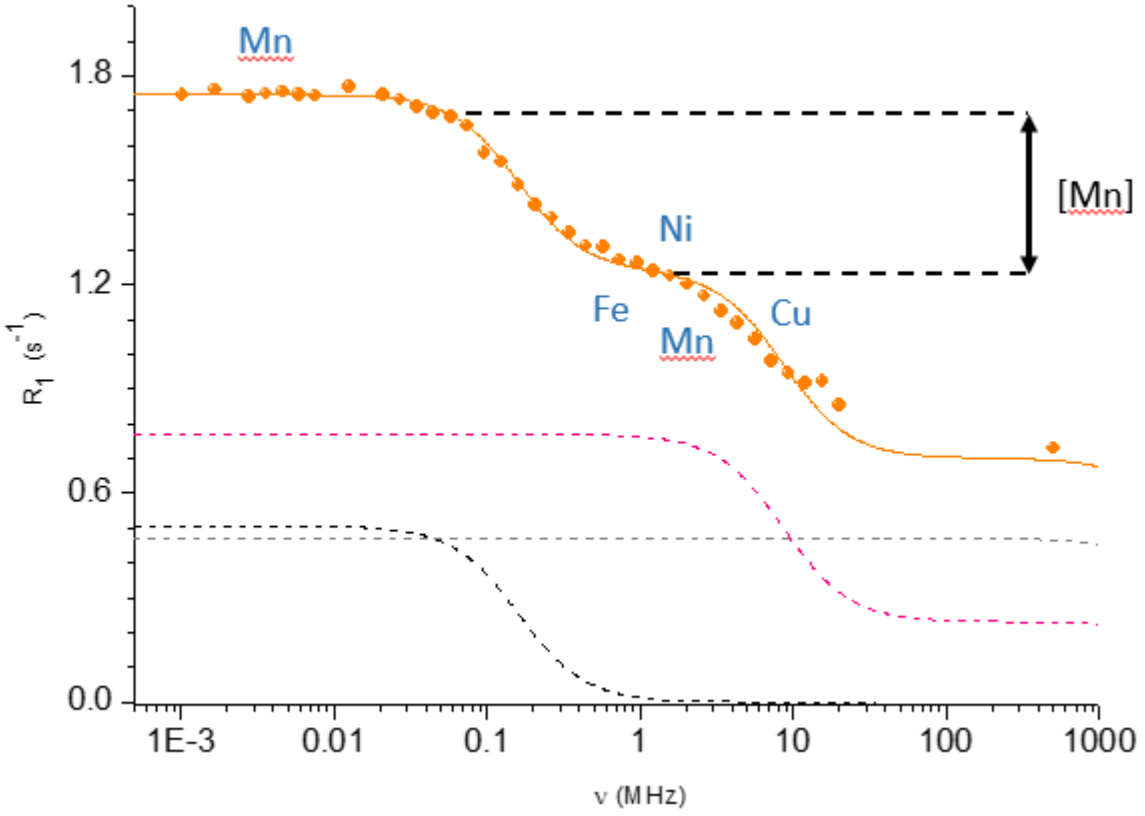
Quantification of Manganese





Quantification of Manganese

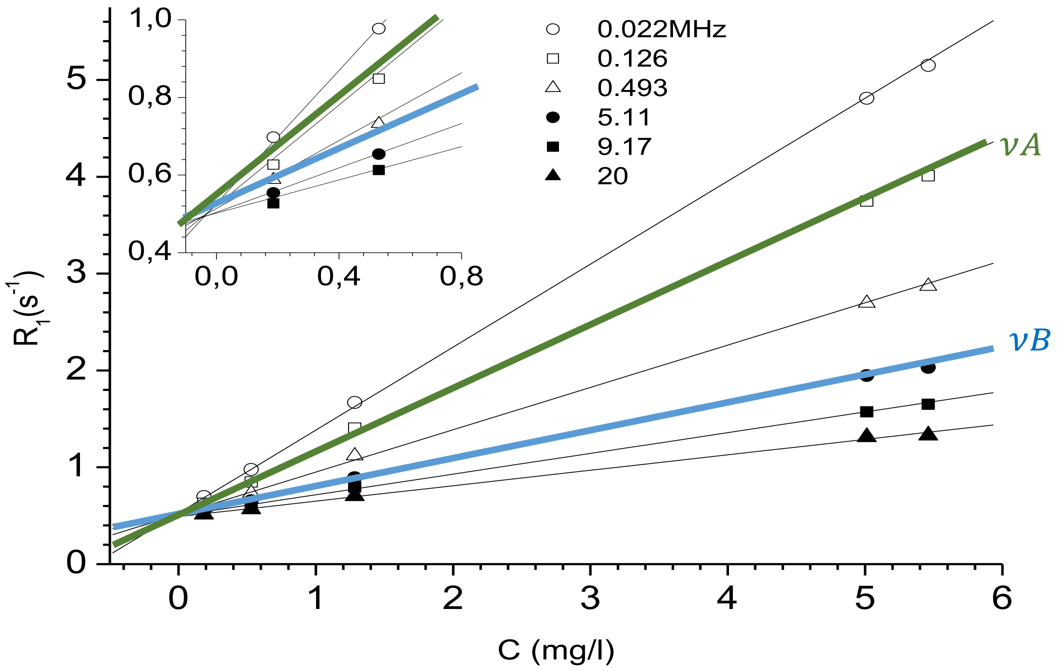


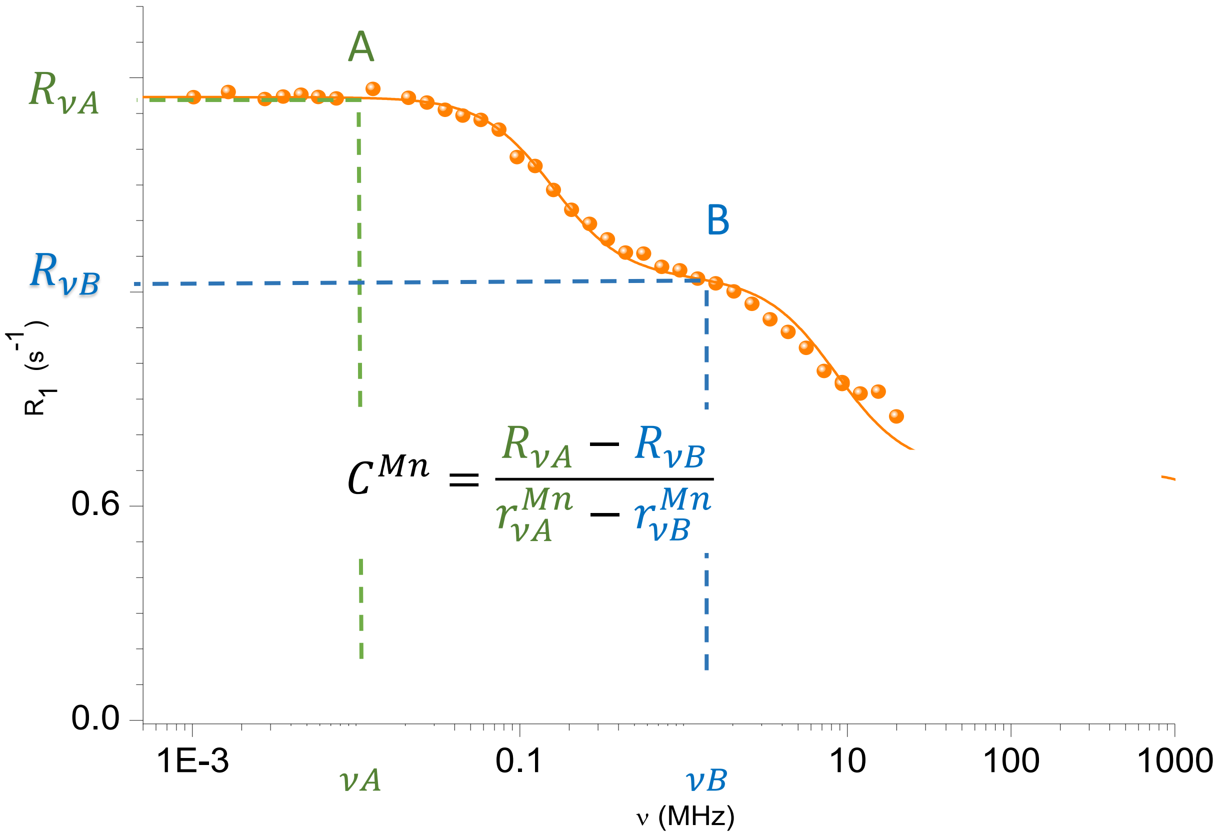


$$R_\nu = R_0 + r_\nu^{Mn} . C^{Mn}$$

Quantification of Manganese

How the relaxation rate evolves with manganese concentration





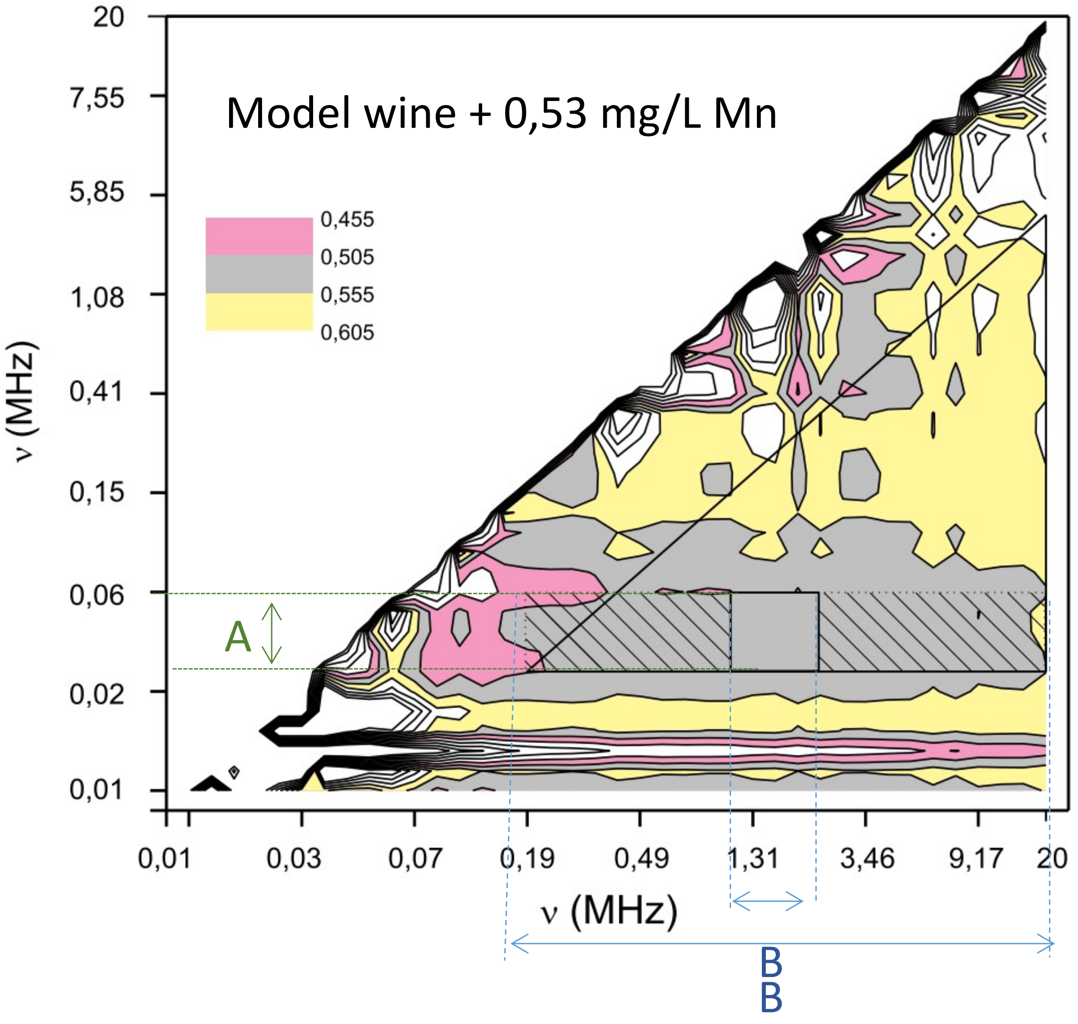
$$C^{Mn} = \frac{R_{\nu A} - R_{\nu B}}{r_{\nu A}^{Mn} - r_{\nu B}^{Mn}}$$

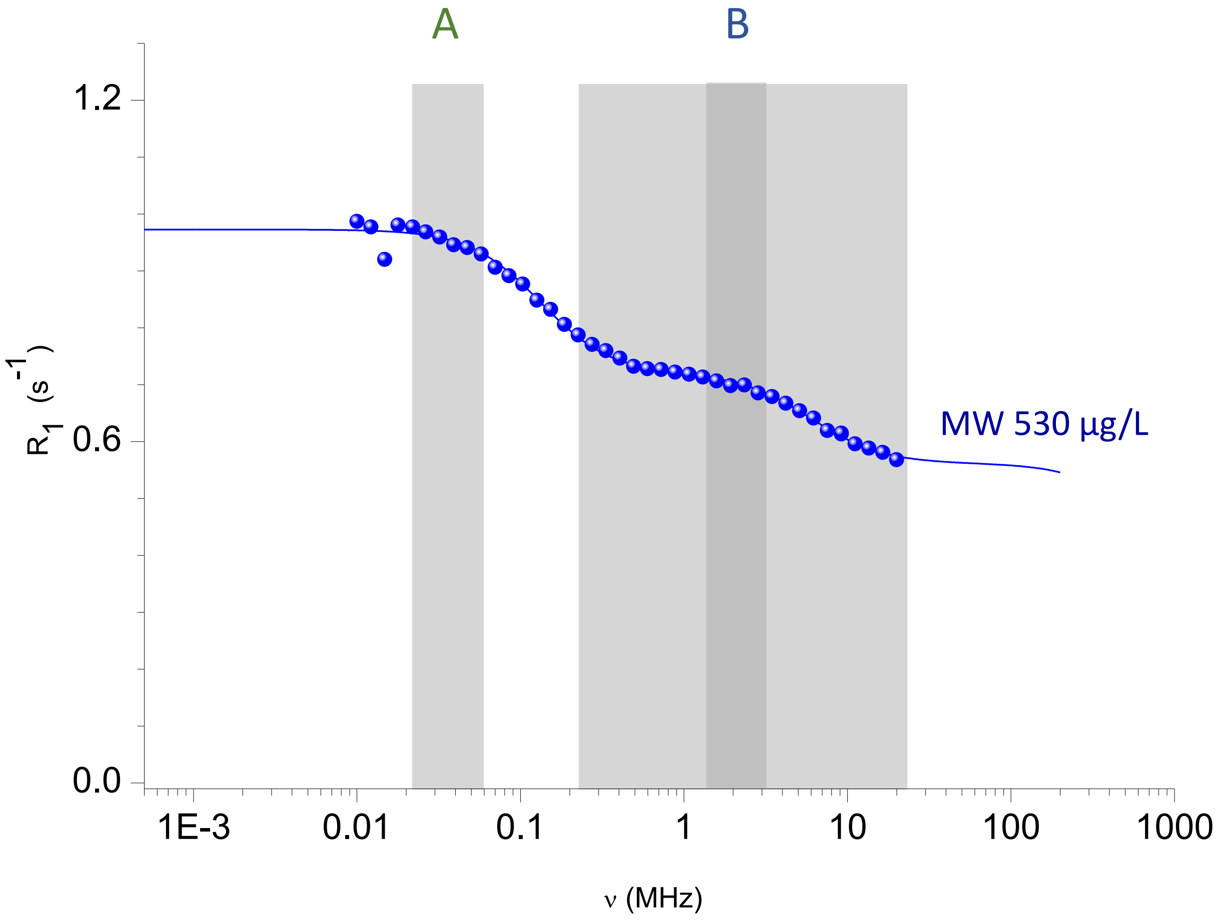
$$R_\nu = R_0 + r_\nu^{Mn} . C^{Mn}$$

Quantification of Manganese

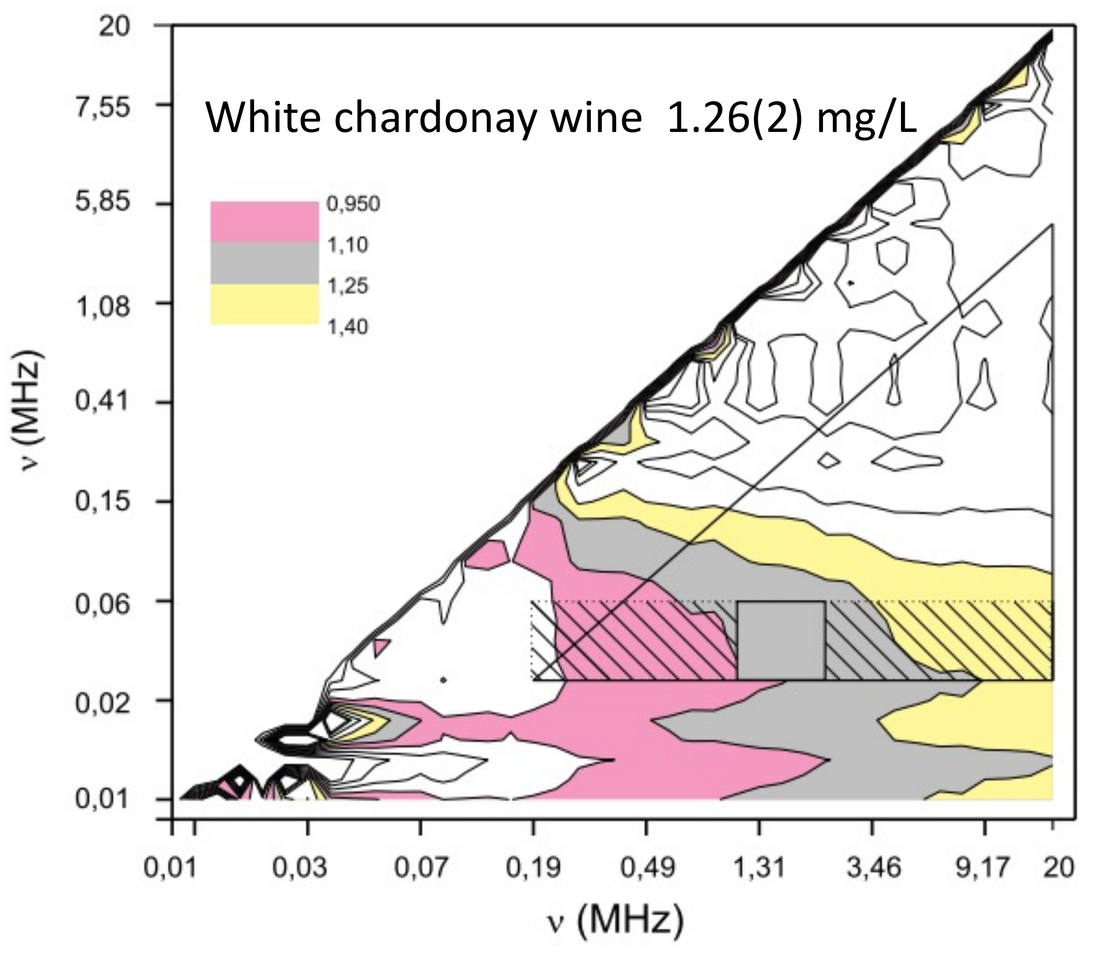
$$C^{Mn} = \frac{R_{\nu A} - R_{\nu B}}{r_{\nu A}^{Mn} - r_{\nu B}^{Mn}}$$

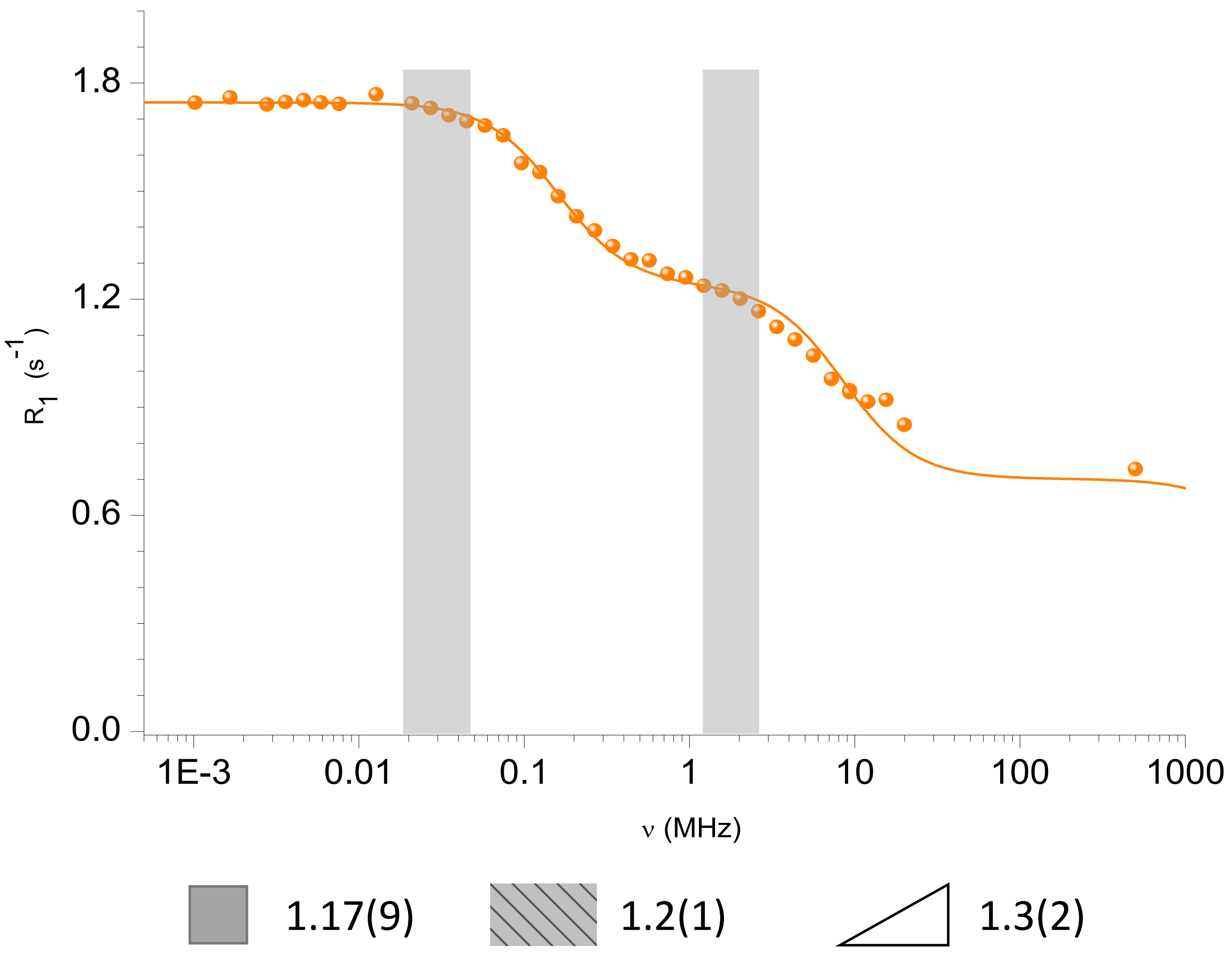
How the relaxation rate evolves with manganese concentration



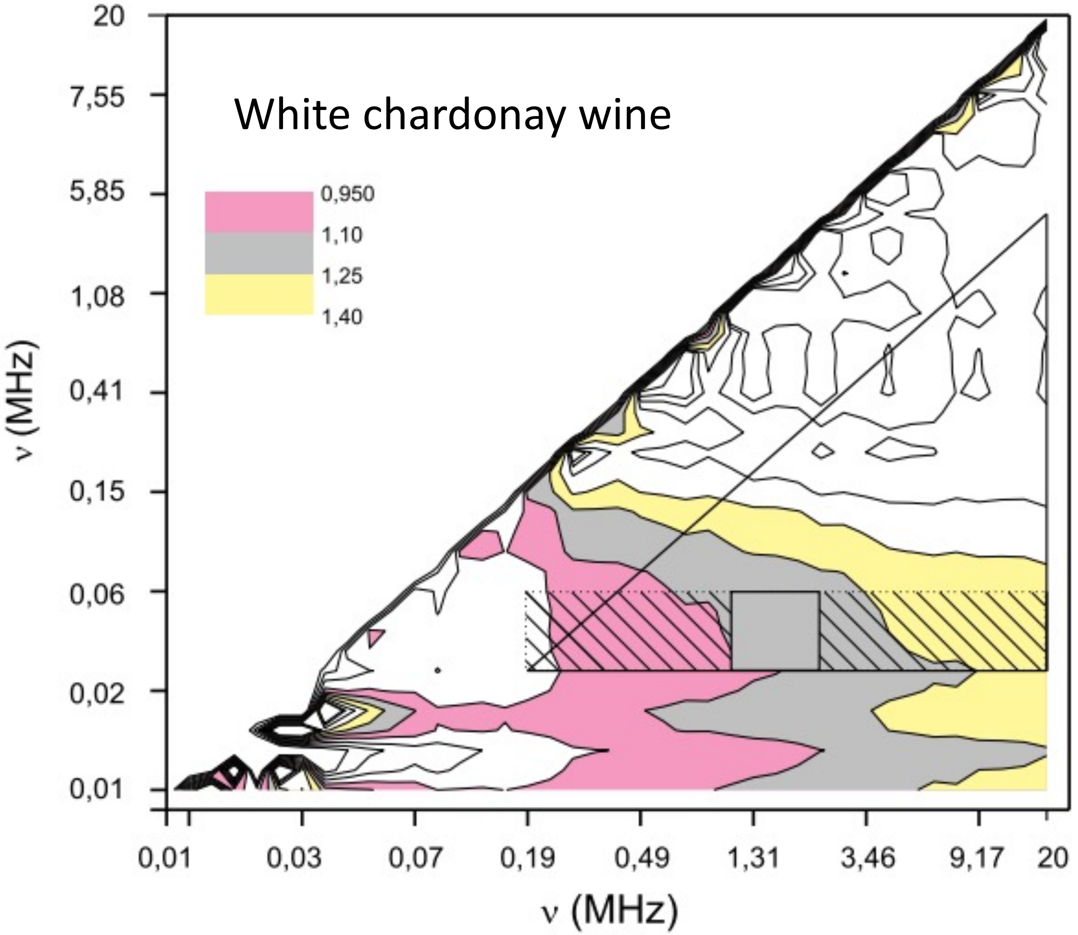


Quantification of Manganese





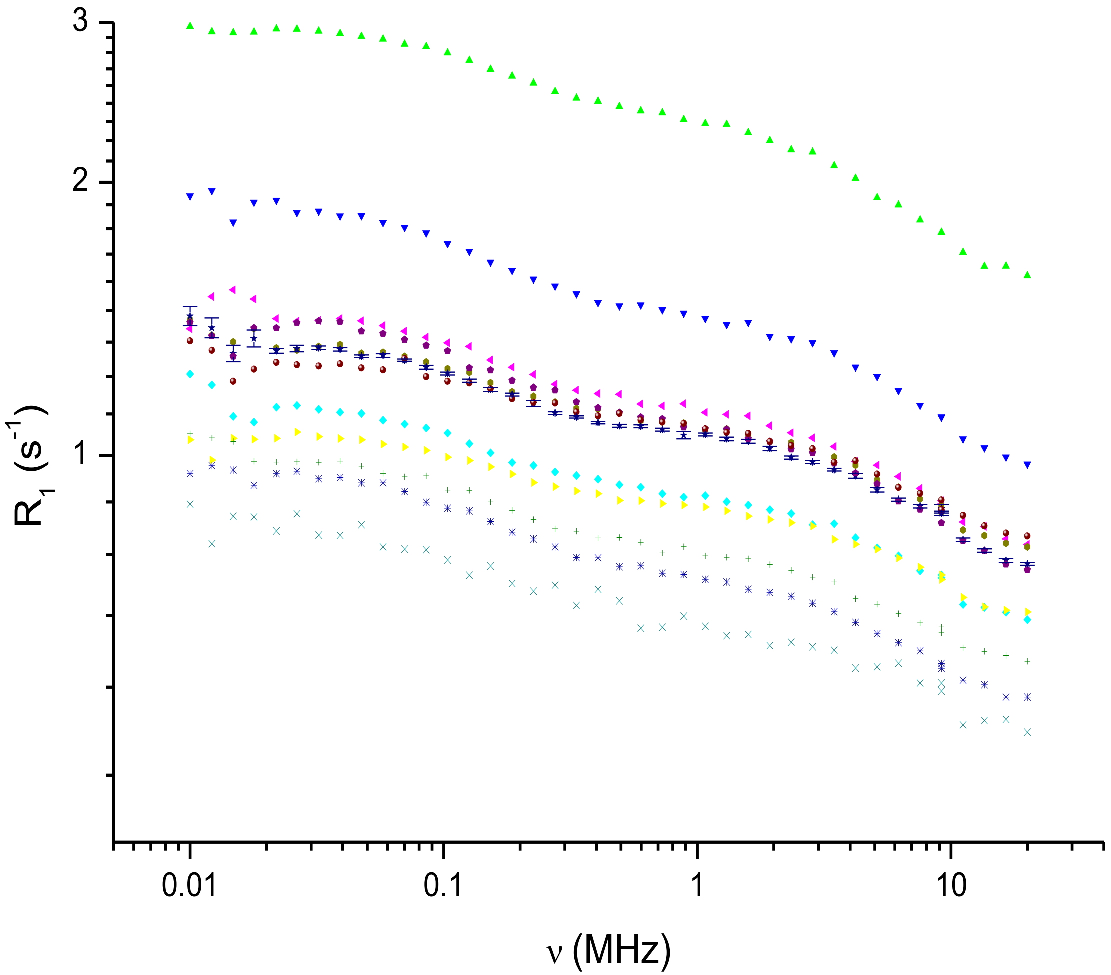
Quantification of Manganese



	Manganese concentration(mg/L)	Square zone	Rectangular zone	Triangular zone
MW546	5.46	5.46 (3)	5.45 (4)	5.5 (1)
MW501	5.01	4.97 (5)	4.97 (6)	5.0 (1)
MW128	1.28	1.34 (8)	1.3 (1)	1.3 (1)
MW053	0.53	0.53 (1)	0.52 (1)	0.53 (5)
MW005	0.05	0.063 (5)	0.063 (6)	0.06 (1)
Wa	1.26 (2)[a]	1.17 (9)	1.2 (1)	1.3 (2)
Wb		1.13 (3)	1.1 (1)	1.4 (2)
Ra	1.06 (2)[a]	0.83 (4)	0.9 (1)	1.2 (3)
Rb		0.91 (5)	0.9 (1)	1.2 (3)
EW	< 0.002[a]	0.009 (6)	0.011 (4)	0.01 (1)

[a] Concentration measured by ICP AES.

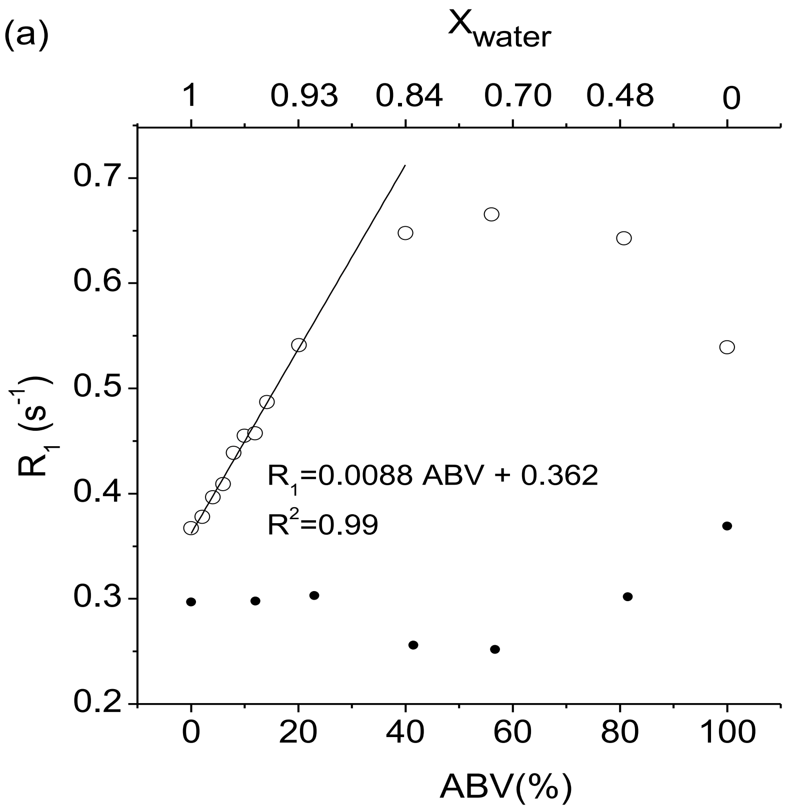
More wines ?



hydroalcoholic solutions (ABV)

(a) Open circles (○) represent the proton spin–lattice relaxation rate at 19.65 MHz and 25 °C of hydroalcoholic solutions versus ABV and Xwater. Filled circles (●) correspond to the ratio of the relaxation rate of the hydroalcoholic solution corrected by the dioxygen contribution over the viscosity

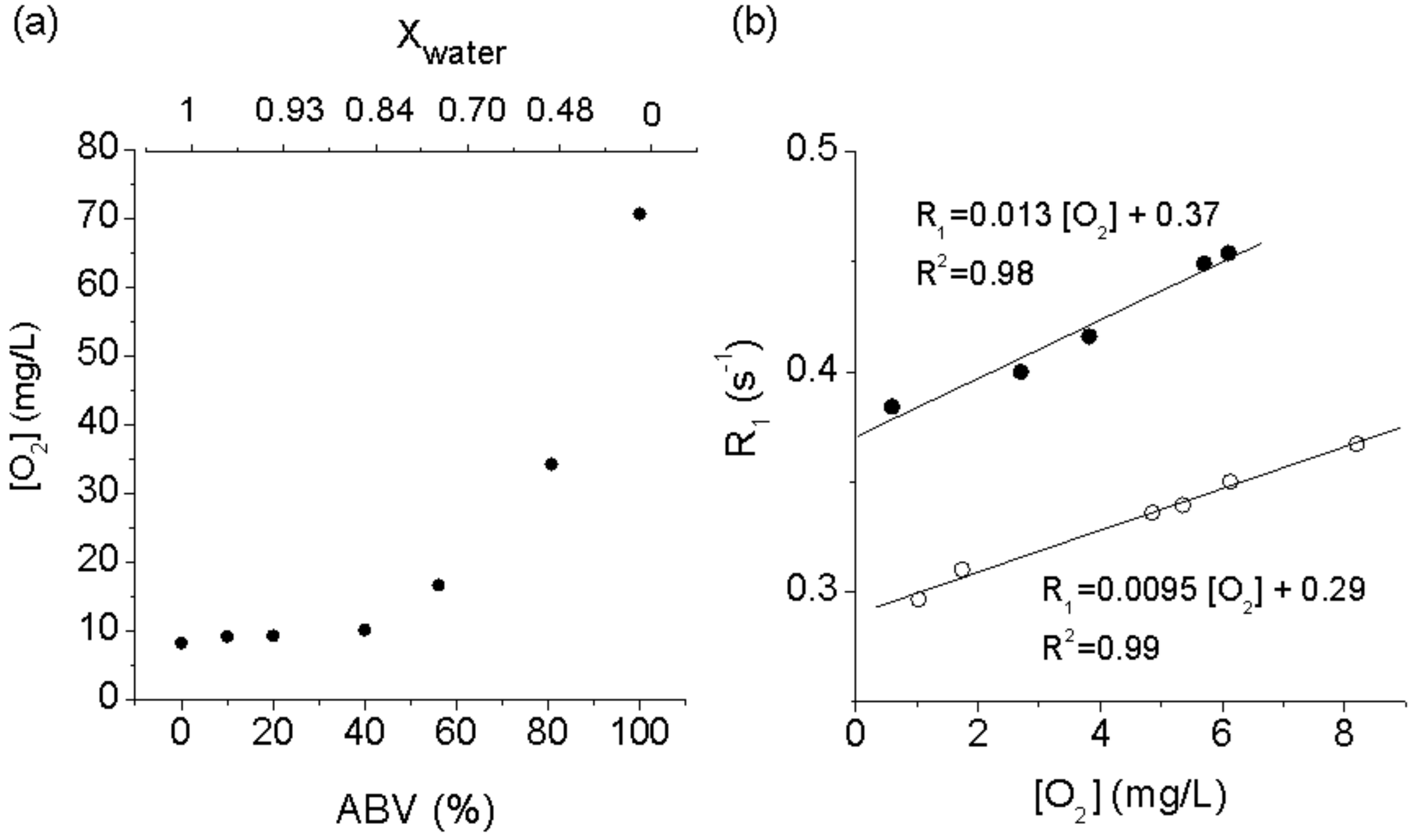
(b) open circles (○) represent the dynamic viscosity of the hydroalcoholic solution, measured at 25 °C, versus ABV and Xwate



hydroalcoholic solutions ($[O_2]$)

(a) Atmospheric equilibrium dissolved dioxygen concentration in hydroalcoholic solutions at 25 °C versus ABV and water molar fraction Xwater.

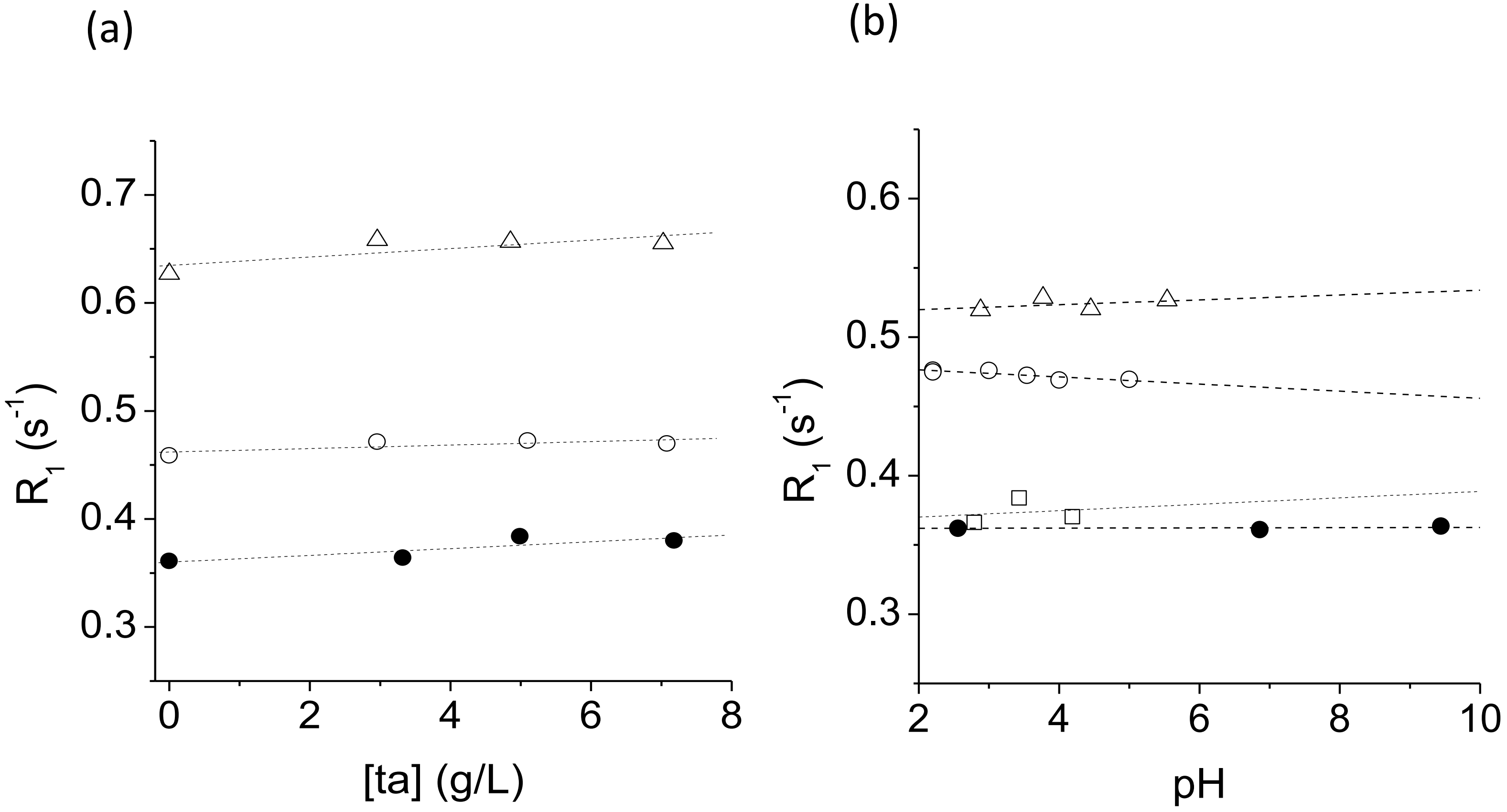
(b) Proton spin–lattice relaxation rate at 19.65 MHz and 25 °C versus the dissolved dioxygen concentration in water (○) and 12% ABV hydroalcoholic solution (●, E12)



Model wine ([Tartaric acid / pH])

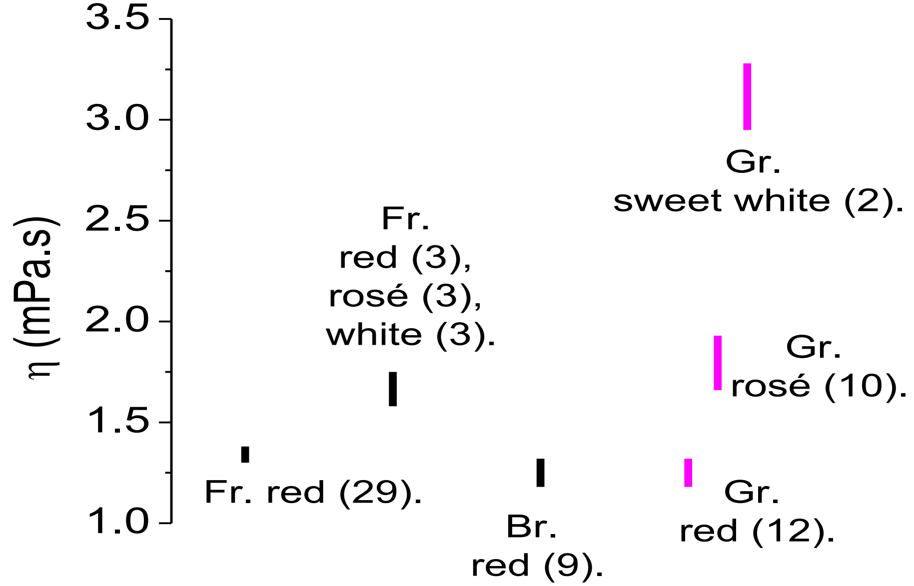
(a) Proton spin–lattice relaxation rate at 19.65 MHz and 25 °C of water (●,Wta), hydroalcoholic solution (○, E12ta), and model wine containing 1.2 mg/L of manganese (Δ, E12taMn1.2) versus tartaric acid concentration. For each solution, the pH was fixed to 2.3, 3.5, and 3.4 for E12taMn1.2, E12ta, and Wta, respectively

(b) Proton spin–lattice relaxation rates at 19.65 MHz and 25 °C of water (●), tartaric acid solutions (□, Wta5), hydroalcoholic solution (○, E12ta5), and manganese solutions (Δ, WMn1.2) versus pH values



Viscosity for various wines

Viscosity domains of various wines. Labels indicate the country, the type, and in brackets, the number of wines measured. (fr. red (29)) corresponds to 29 red wines of the same grape variety (Loire Valley Cabernet Franc) elaborated with a standard protocol but coming from two distinct areas, Anjou and Touraine (Siret et al. 2010); (Fr. red (3), rosé (3), and white (3)) reports 9 wines of 2 vintages from Loire Valley selected according to their typicity and probable differences in terms of viscosity and texture (Siret et al. 2008). (Br. Red (9)) is for 9 types of Brazilian dry red wines from different cultivars and produced by different vineries (Neto et al. 2015). Twentyfour different Greek wines (Yanniotis et al. 2007) of 2 vintages (in fuchsia) are also reported but the measurement was done at 16 °C whilst they were done at 23 and 26 °C for French and Brazilian wines, respectively



Some conclusions

Manganese in wine comes primarily from the soil.
Its concentration is not affected by wineries practices.
It does not seem to form many stable complexes.
Manganese seems to be observable on many type of wine.

Manganese could be a valuable fingerprint for wines.

Relaxometry that could allow easy and precise in situ concentration measurement would then be a technique of choice for wine control.

Some conclusions

An important viscosity variability of the wine can complicate the interpretation of NMRD profiles and relaxation times, (e.g. precluding the determination of the manganese concentration by NMR relaxometry). However, the literature shows that a rather low and narrow range of viscosity (particularly for red and dry white wines) characterises wines and the relaxation times could be interpreted with ease.

As the alcoholic strength increases (e.g. in distilled alcohols), the situation is less straightforward.

(i) The amount of dissolved dioxygen strongly increases and has to be taken into account;
(ii) (ii) the viscosity increases and relaxation mechanisms are further complicated;
(iii) (iii) two main sources of proton may have to be considered simultaneously: ethanol & water

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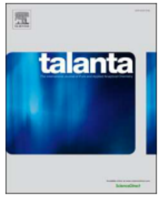

Quantification of manganous ions in wine by NMR relaxometry

Philippe R. Bodart[a,b,*], Adam Rachocki[c], Jadwiga Tritt-Goc[c], Bernhard Michalke[d], Philippe Schmitt-Kopplin[d,e], Thomas Karbowiak[a], Regis D. Gougeon[a]

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Food Analytical Methods (2022) 15:266–275
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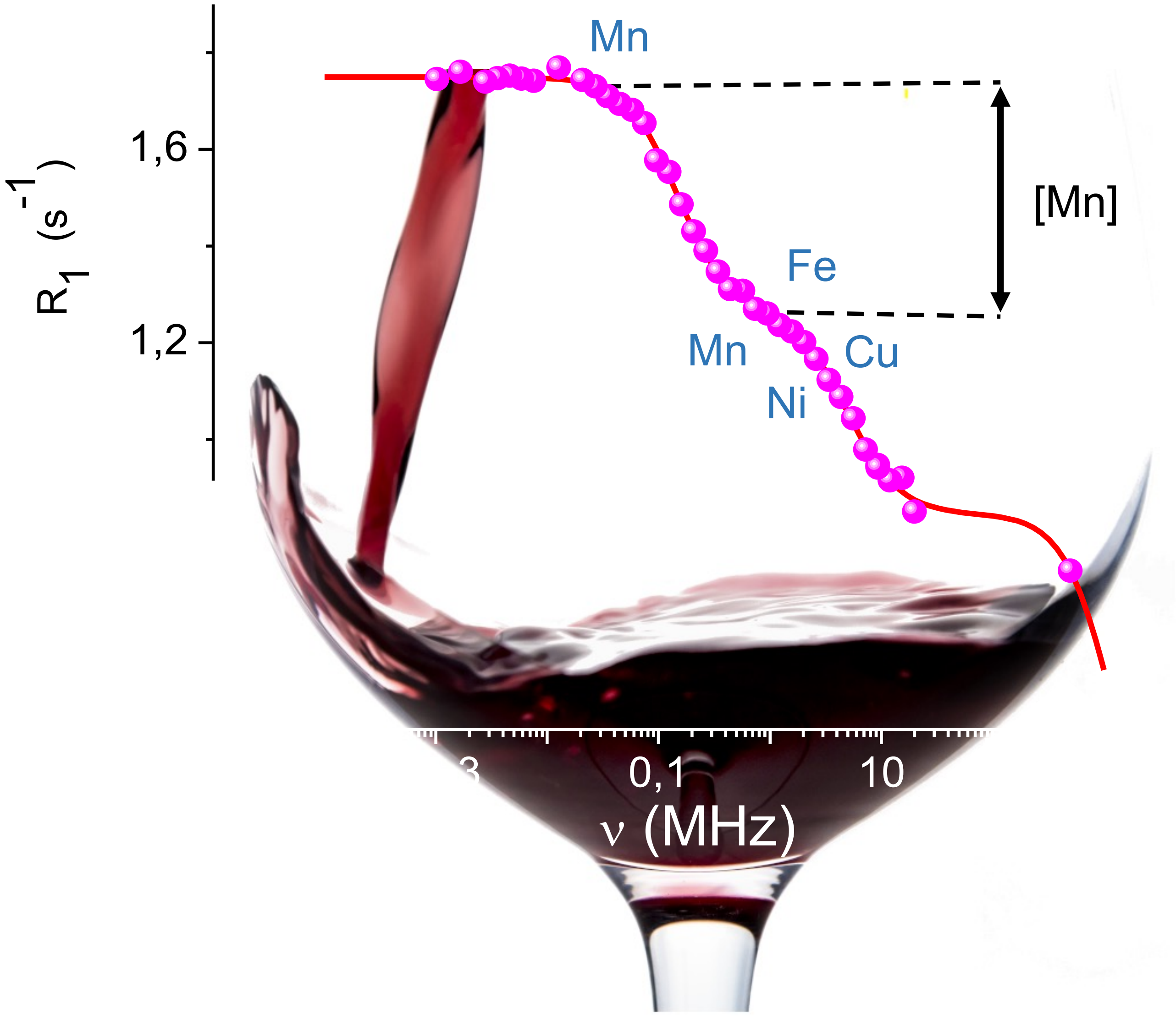
Analysis of the Proton Spin–Lattice Relaxation in Wine and Hydroalcoholic Solutions

Philippe R. Bodart[1] · Aymerick Batlogg[1] · Eric Ferret[1] · Adam Rachocki[2] · Magdalena Knapkiewicz[2] · Syuzanna Esoyan[1,3] · Nelli Hovhannisyan[4] · Thomas Karbowiak[1] · Régis D. Gougeon[5]

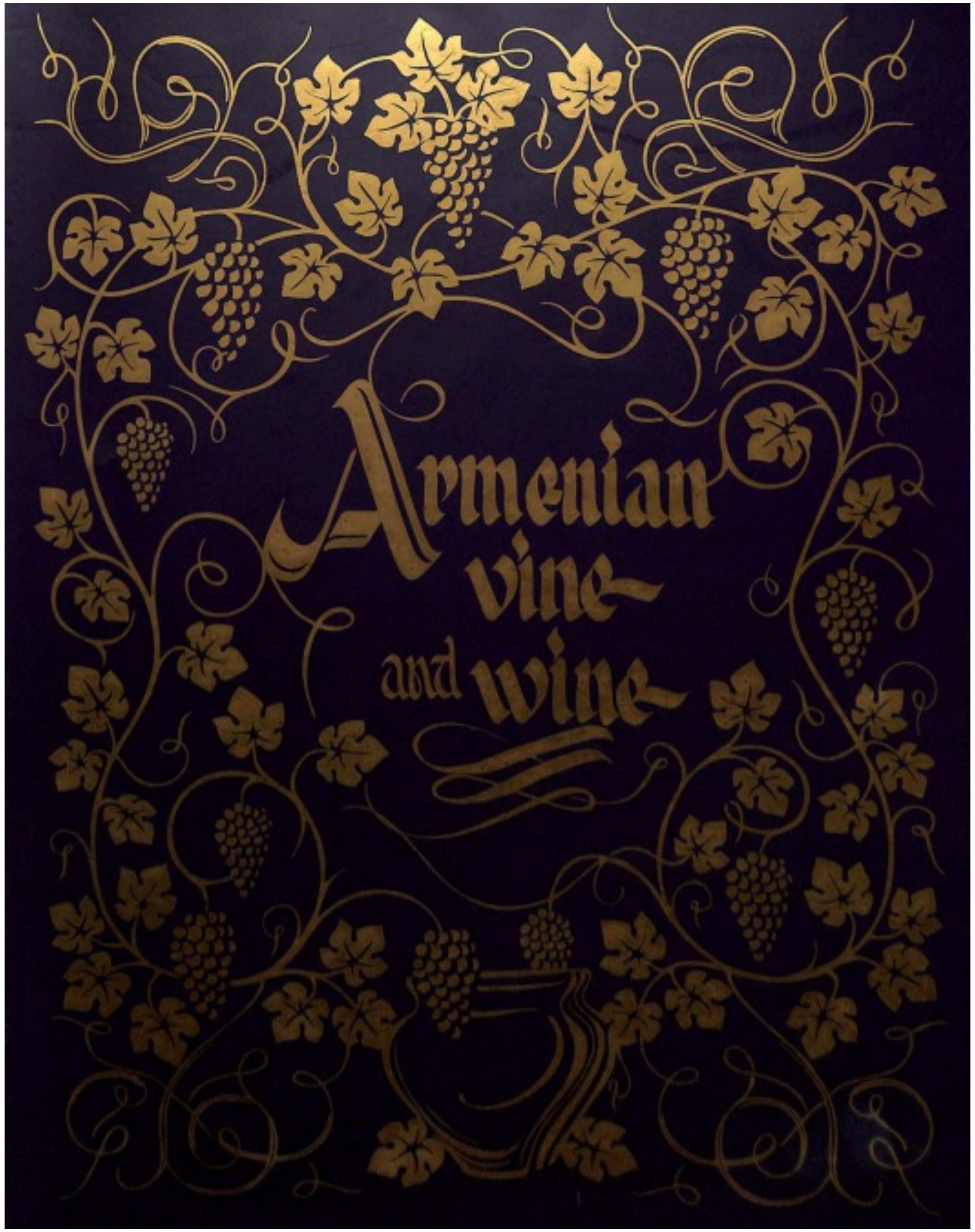
OENO One
VINE AND WINE OPEN ACCESS JOURNAL

Interaction between Armenian clay-based ceramics and model wine during storage

Syuzanna Esoyan[1,2], Camille Loupiac[1], Nelli Hovhannisyan[2], Régis D. Gougeon[3], Thomas Karbowiak[1], Bernhard Michalke[4], Philippe Schmitt-Kopplin[4,5], Claude Fontaine[6], Sabine Valange[6] and Philippe R. Bodart[1*]



Mn
[Mn]
Fe
Mn
Cu
Ni
1,6
1,2
R_1 (s^{-1})
0,1
10
ν (MHz)



Nelli .A. Hovhannisyan, A.A. Yesayan, A. Bobokhyan, M.V. Dallakyan, S. Hobosyan, B.Z. Gasparyan, A. Danielyan, Z. Muradyan, V. Ter-Ghazaryan, Backbone Branding (Firm), Deutsche Gesellschaft für Internationale Zusammenarbeit, Armenian vine and wine, 2017.

In conclusion

- Manganese in wine comes primarily from the soil.
- Its concentration is not affected by wineries practices.
- It does not seem to form many stable complexes.
- Manganese seems to be observable on many type of wine.

Manganese could be a valuable fingerprint for wines.

] Relaxometry that could allow easy and precise in situ concentration measurement would then be a technique of choice for wine control.

- Professor Regis D. Gougeon – Thomas Karbowiac
- Adam Rachocki – Jadviga tritt-Got

Master students

- Aymerick Batlogg
- Manouella Alakik

PhD. Students

- Pierre Fouilloux
- Syuzanna Essoyan

1. Tariba, Blanka. 2011. “Metals in Wine—Impact on Wine Quality and Health Outcomes.” *Biological Trace Element Research* 144 (April): 143–56. https://doi.org/10.1007/s12011-011-9052-7.

Wine can be made from any form of fermented fruit.

In most cases, wine is produced from grapes.

https://pxhere.com/fr/photo/961549

European grape vine or *Vitis vinifera*.

Cabernet, Merlot, Chardonnay, Pinot Grigio, etc.

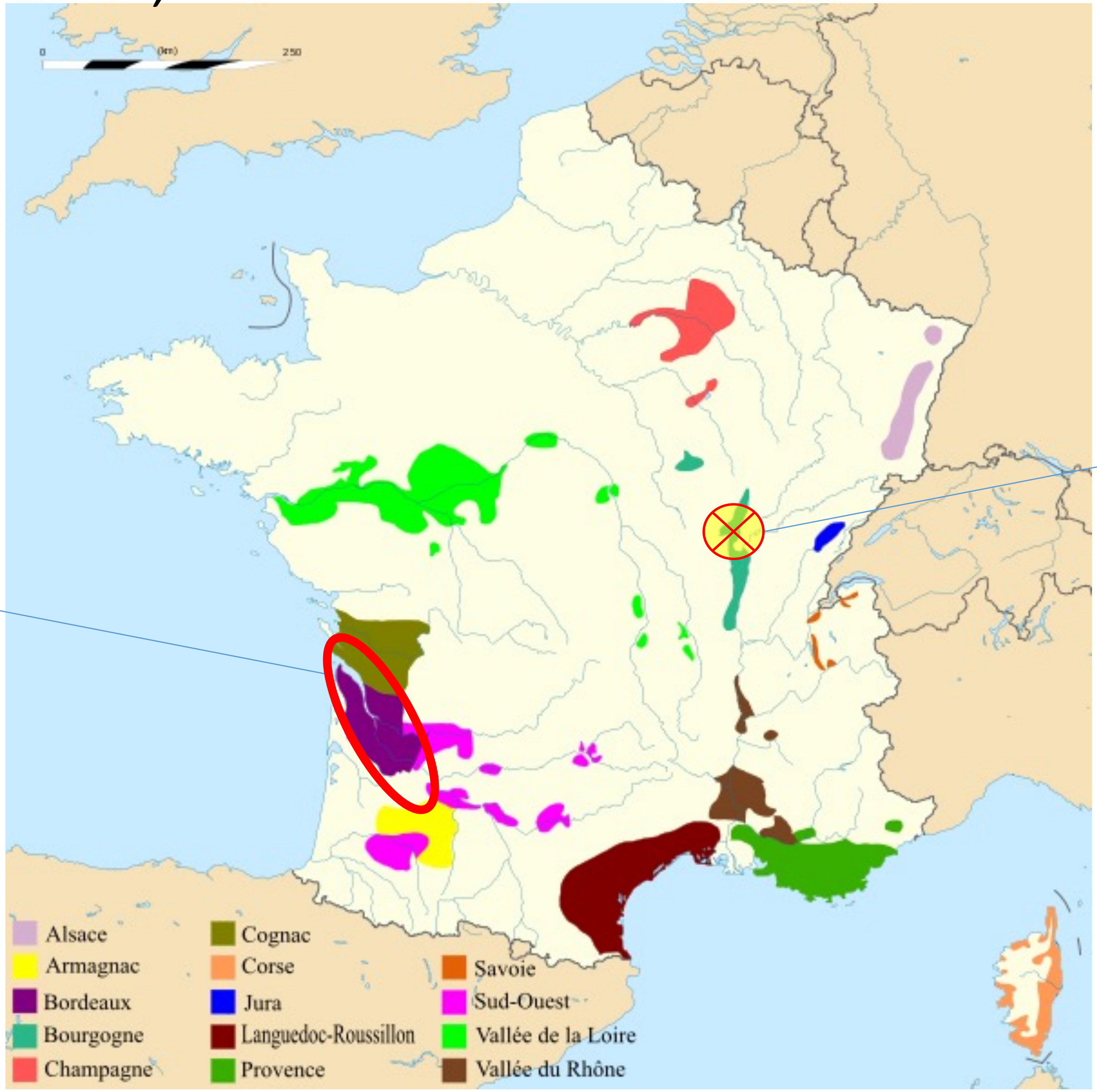
Wine grapes contain seeds, are smaller, sweeter, and have thicker skins than table grapes.

In popular (or advertising) culture, many virtues are associated with a moderate wine consumption.

https://www.austwinetourco.com.au/10-health-benefits-of-drinking-wine/

Two distinct wines, red Medoc blend & white Chardonay

Red Medoc blend wine (2011 vintage), Bordeaux.



Chardonnay white wine (2014 vintage), University of Burgundy.

https://commons.wikimedia.org/wiki/File%3AFrench_vineyards.svg

cost
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IN SCIENCE AND TECHNOLOGY

EURELAX
COST ACTION CA15209

COST is supported by
the EU Framework Programme
Horizon 2020

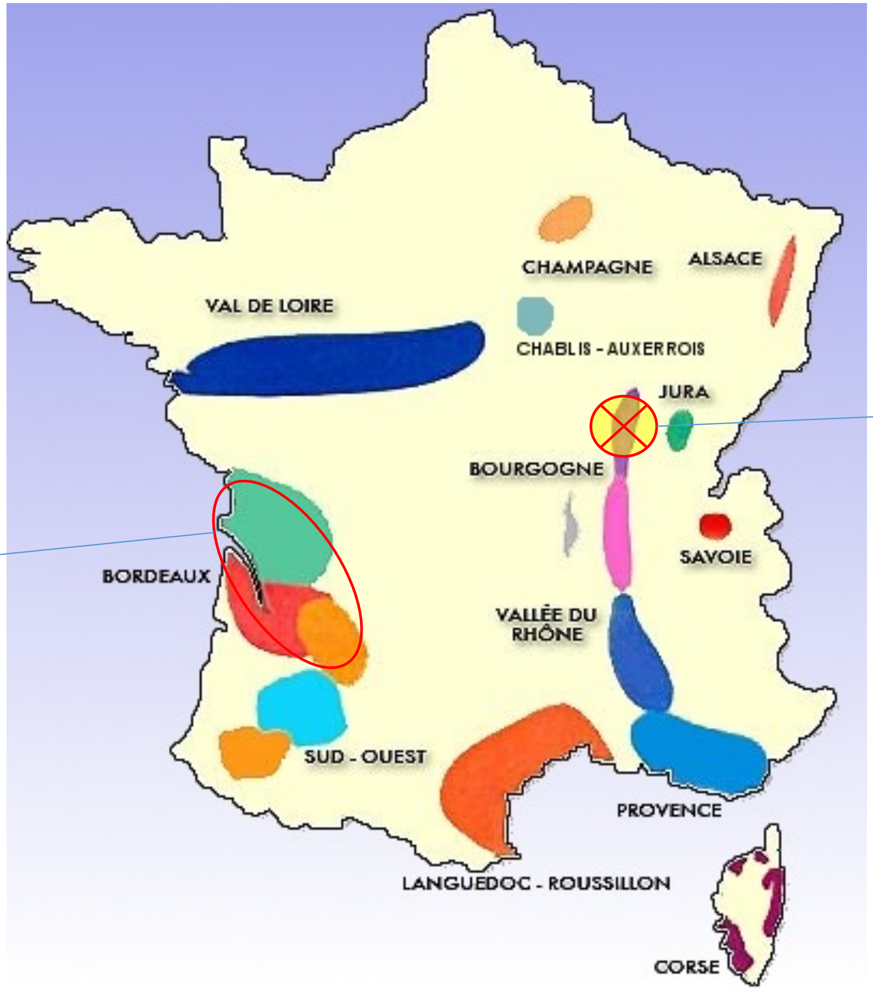
European Network on NMR Relaxometry

http://www.cost.eu/COST_Actions/ca/CA15209

http://eurelax.uwm.edu.pl/

Two distinct wines red Medoc blend & white Chardonay

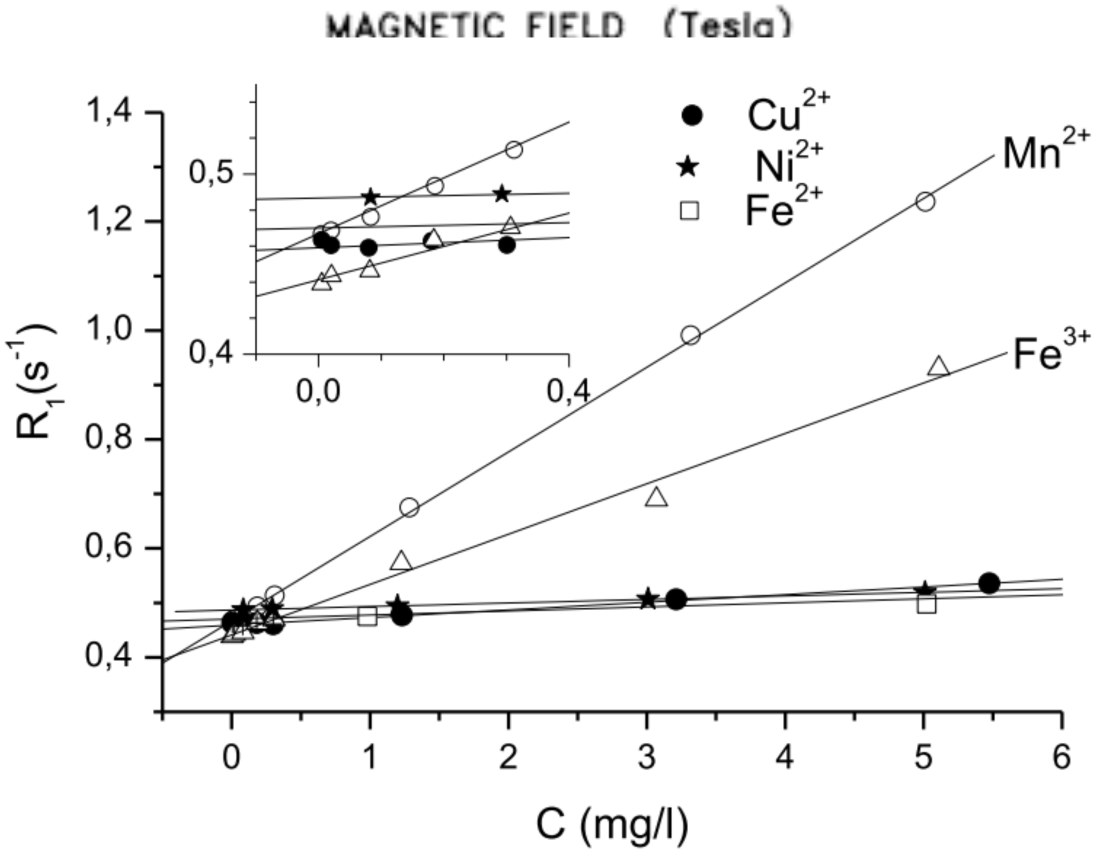
Red Medoc blend wine (2011 vintage), Bordeaux.

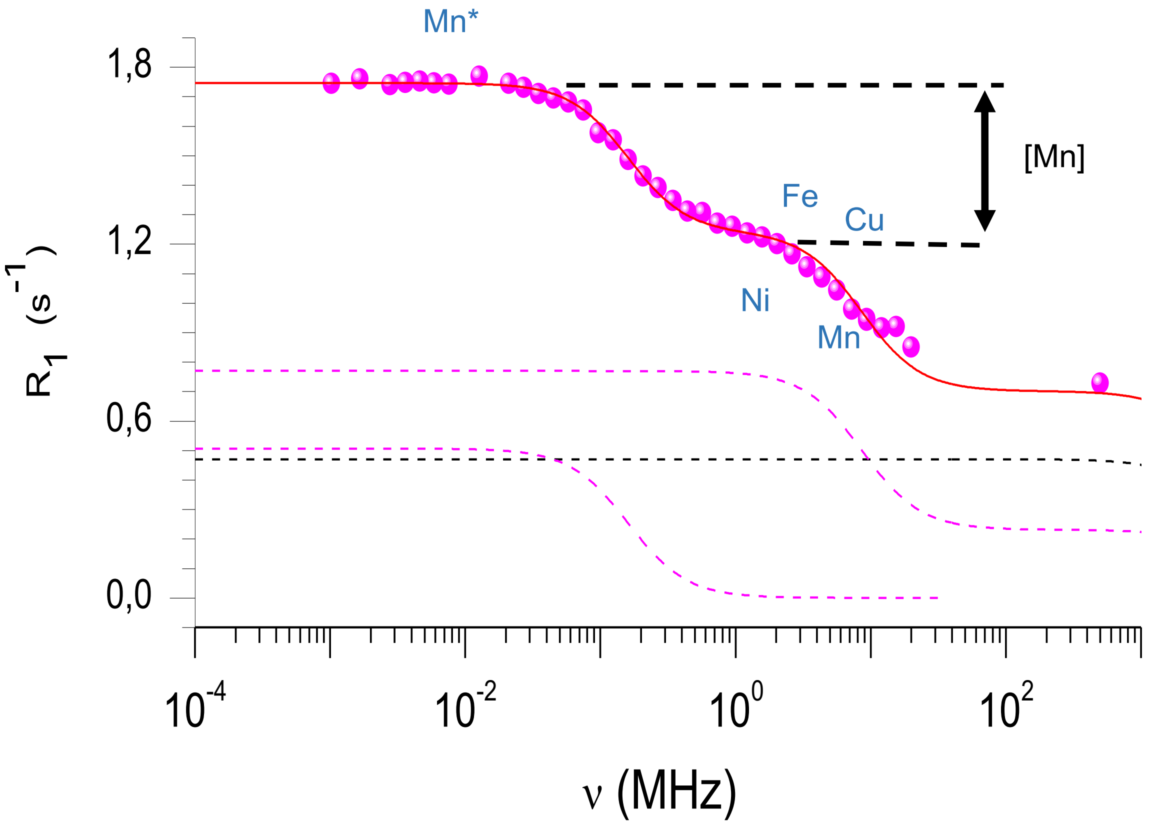


Chardonnay white wine (2014 vintage), University of Burgundy.

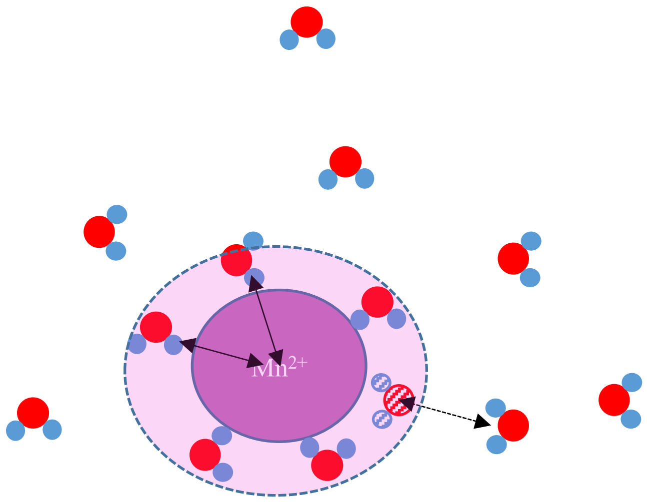
https://commons.wikimedia.org/wiki/File%3AFrench_vineyards.svg

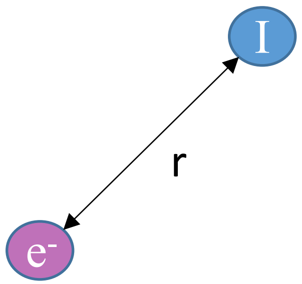
Quantification of Manganese





Paramagnetic relaxation Solomon mechanism





the unpaired electrons are localized at the paramagnetic ion. The relaxation is described by an interaction between an electronic point dipole and a nuclear point dipole

$$\tilde{R}_D(\omega_I, \tau_{d1}, \omega_s, \tau_{d2}) = \tilde{C}_D\left[\frac{7\tau_{d2}}{1+(\omega_s\tau_{d2})^2} + \frac{3\tau_{d1}}{1+(\omega_I\tau_{d1})^2}\right]$$

$$\tilde{C}_D = \frac{2}{15}\left(\frac{\mu_o}{4\pi}\right)^2 \frac{S(S+1)(\gamma_I\,\gamma_S\hbar)^2}{{r_{IS}}^6}$$

$$\frac{1}{\tau_{di}} = \frac{1}{\tau_R} + \frac{1}{\tau_M} + \frac{1}{\tau_{Si}}$$

In practice, at low magnetic field,

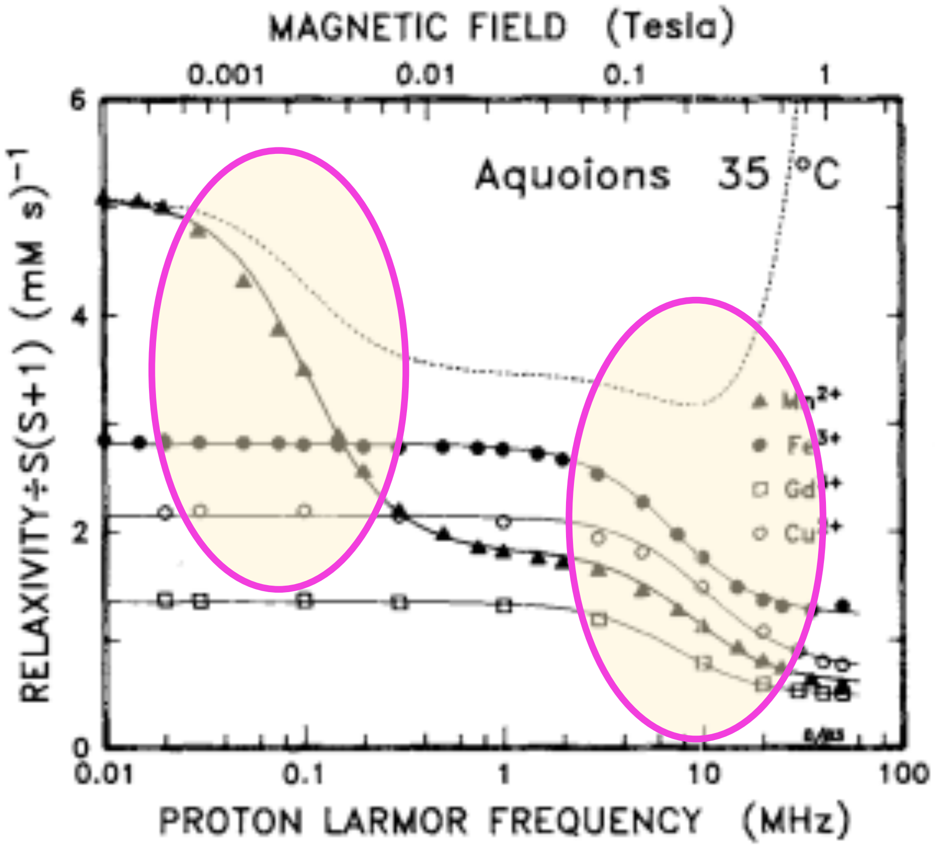
$$\tau_{d1} = \tau_{d2} = \tau_d$$

What is the spin of the electron ?, what is a dipole

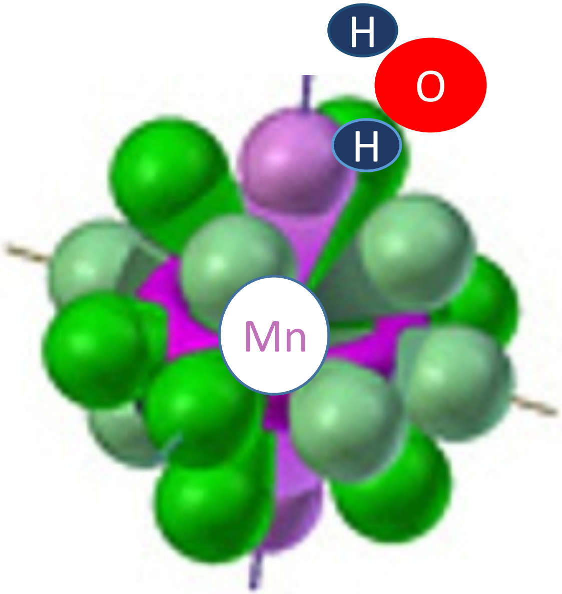
Paramagnetic relaxation Solomon mechanism

Bloembergen mechanism

Delocalization of the electronic wave function of the paramagnetic nuclei to the physical location of I-nuclei
(fermi contact interaction)



Bloembergen mechanism
Solomon mechanism



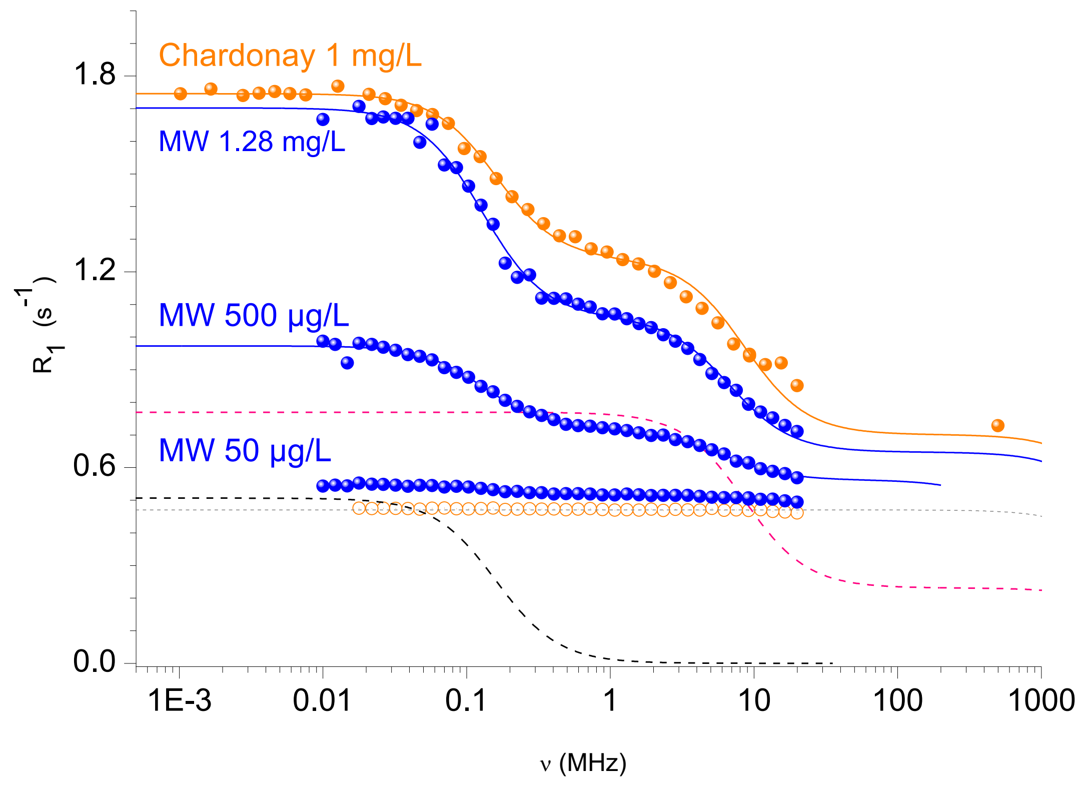
$$\tilde{R}_C(\omega_s, \tau_c) = \tilde{C}_C \left[\frac{\tau_c}{1 + (\omega_s \tau_c)^2} \right]$$

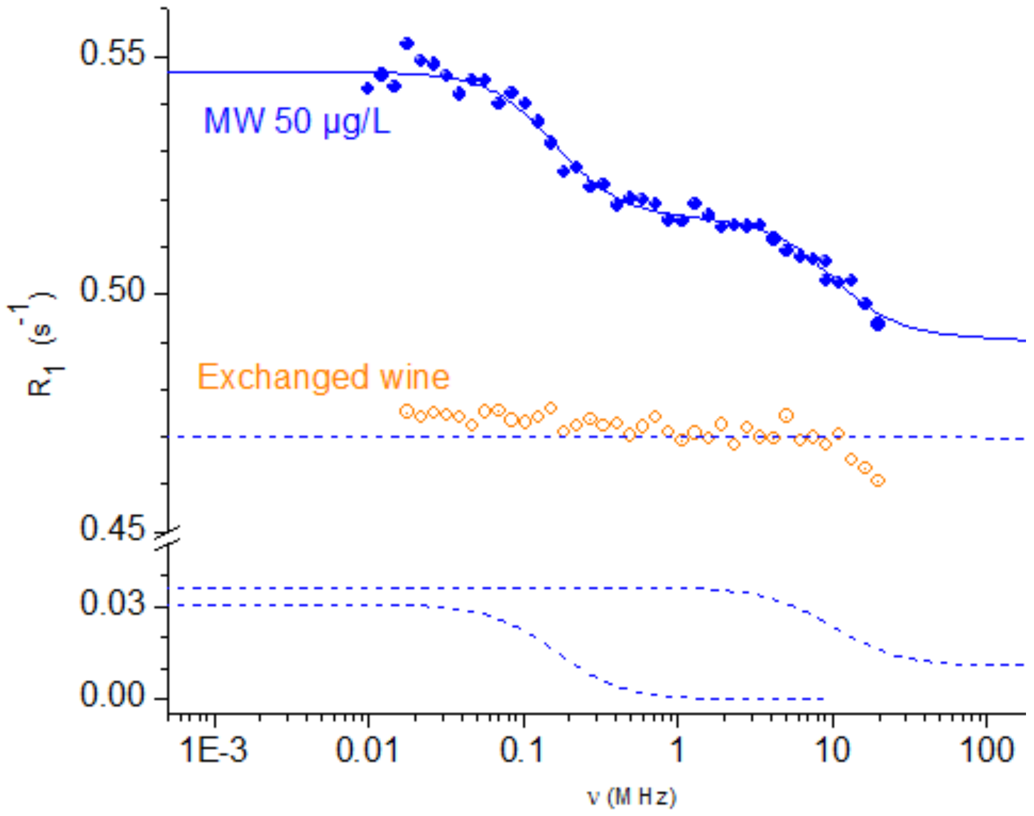
$$\tilde{C}_C = \frac{2A^2 S(S+1)}{3\hbar^2}$$

$$\frac{1}{\tau_c} = \frac{1}{\tau_M} + \frac{1}{\tau_{S2}}$$

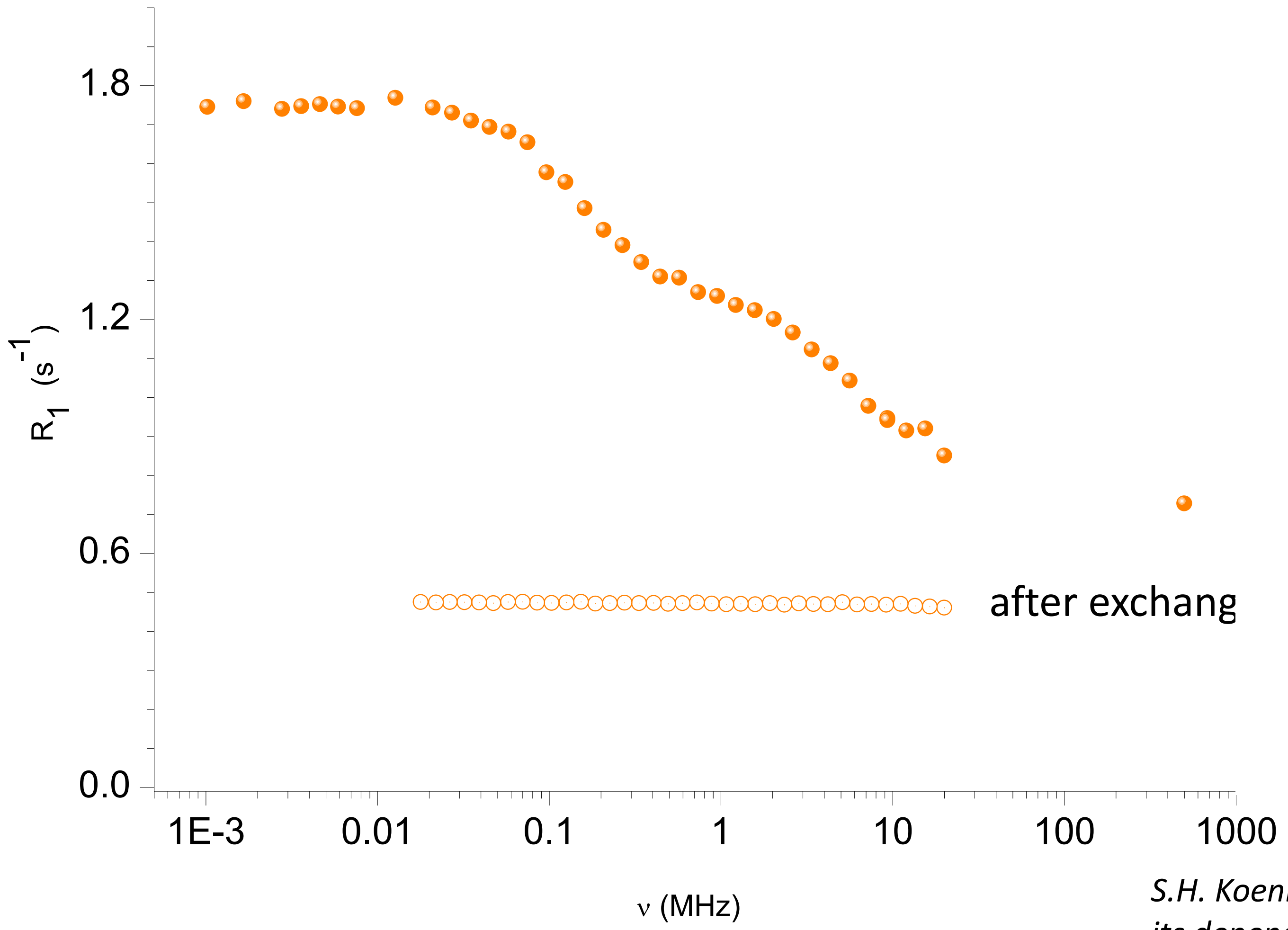
What is tau s2

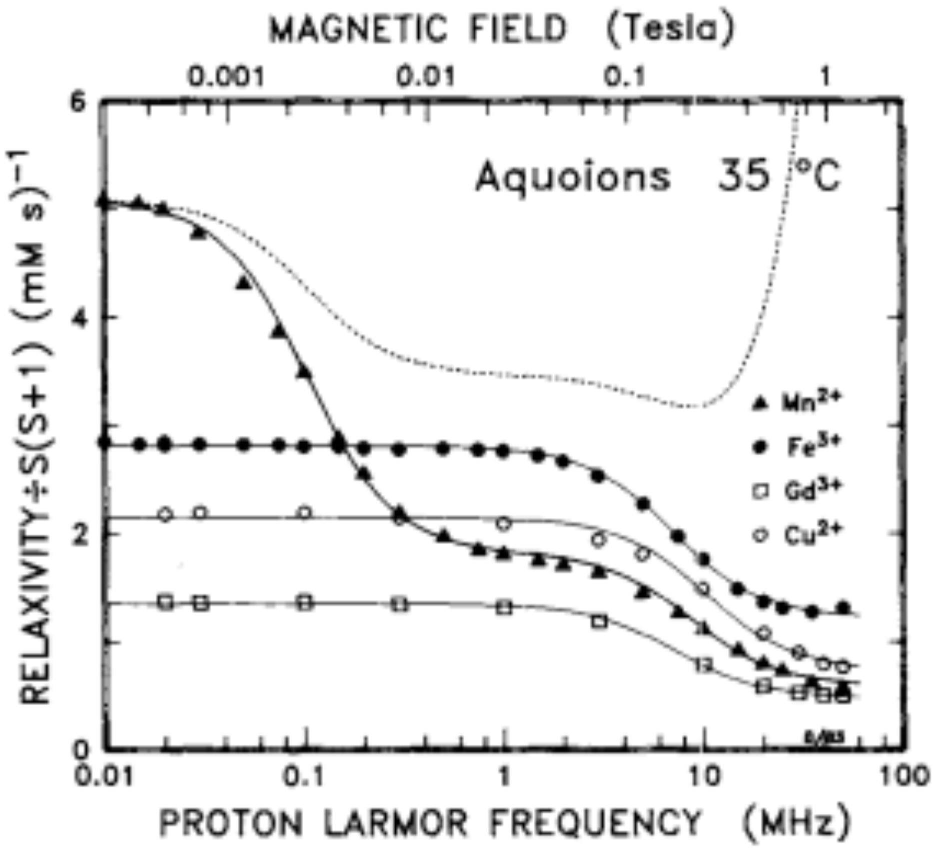
Model wines


Chardonay 1 mg/L
MW 1.28 mg/L
MW 500 µg/L
MW 50 µg/L
1.8
1.2
0.6
0.0
R1 (s-1)
1E-3
0.01
0.1
1
10
100
1000
ν (MHz)

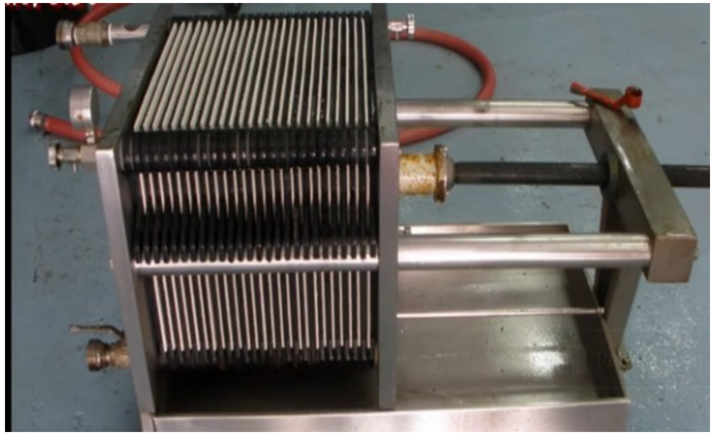

MW 50 µg/L
Exchanged wine
0.55
0.50
0.45
0.03
0.00
R1 (s-1)
1E-3
0.01
0.1
1
10
100
ν (MHz)

Chardonnay white wine.

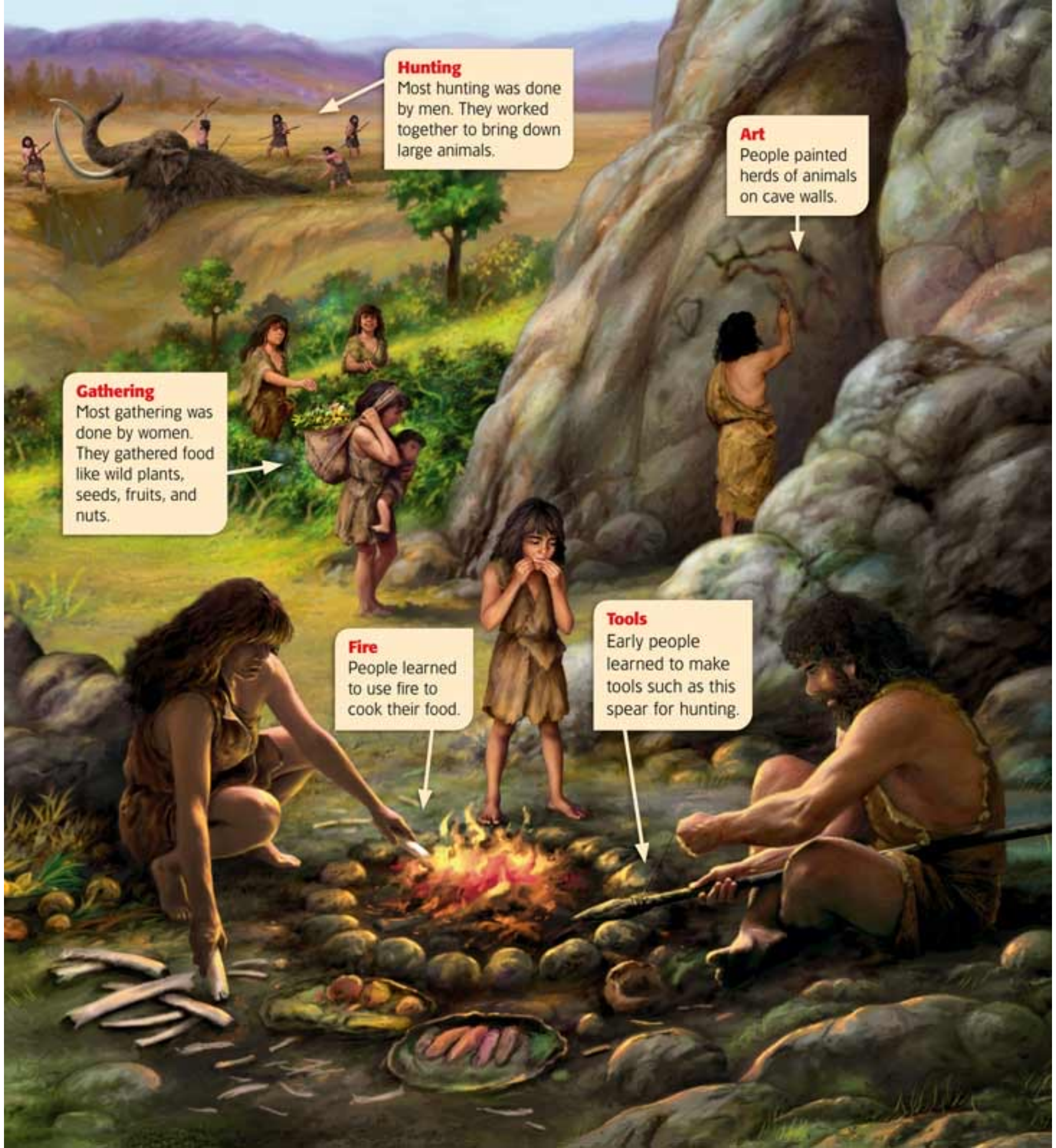




S.H. Koenig, R.D. Brown, Relaxation of solvent protons by paramagnetic ions and its dependence on magnetic field and chemical environment: implications for NMR imaging, Magnetic Resonance in Medicine. 1 (1984) 478–495




3014


Hunting
Most hunting was done by men. They worked together to bring down large animals.
Art
People painted herds of animals on cave walls.
Gathering
Most gathering was done by women. They gathered food like wild plants, seeds, fruits, and nuts.
Fire
People learned to use fire to cook their food.
Tools
Early people learned to make tools such as this spear for hunting.

Harvesting and wine production scene, Etruscan plate, 600 BC, (Cabinet des médailles de la bibliothèque nationale de France Paris)

image-20141222-31573-ndz6l1.webp

Caravaggio's 1595 masterpiece Bacchus

Illumination from a copy of *Li livres dou santé* by Aldobrandino of Siena (XIII century).

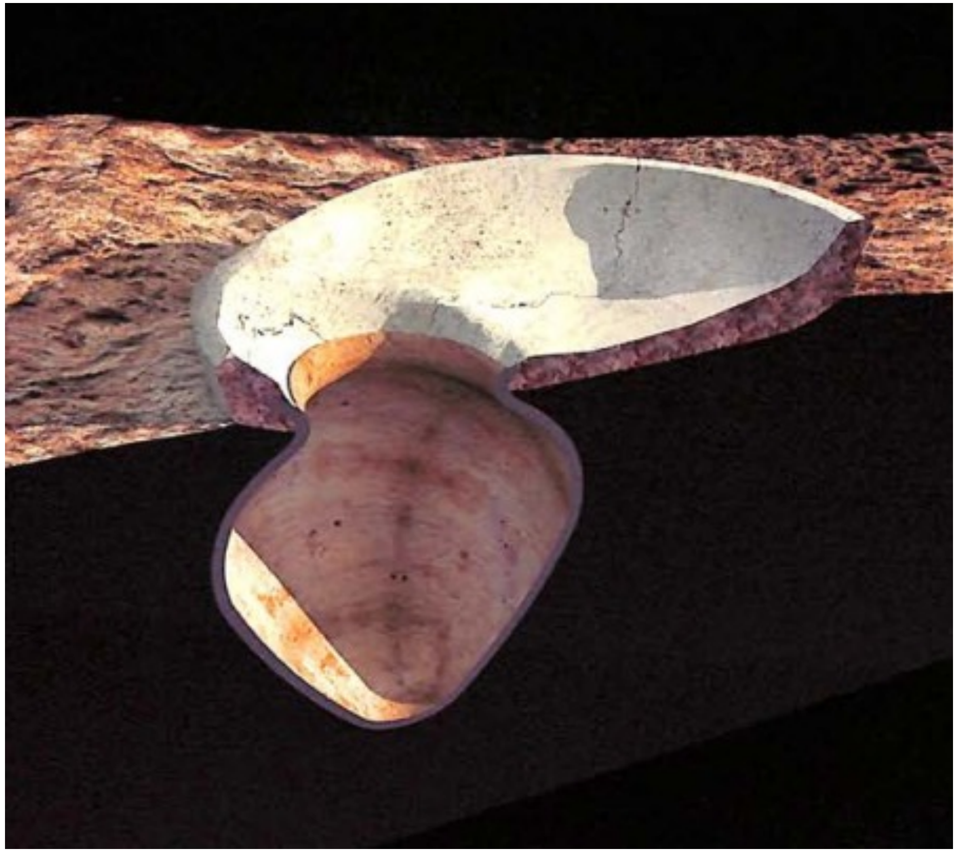
In popular (or advertising) culture many virtues are associated with moderate wine consumption.

https://www.austwinetourco.com.au/10-health-benefits-of-drinking-wine/

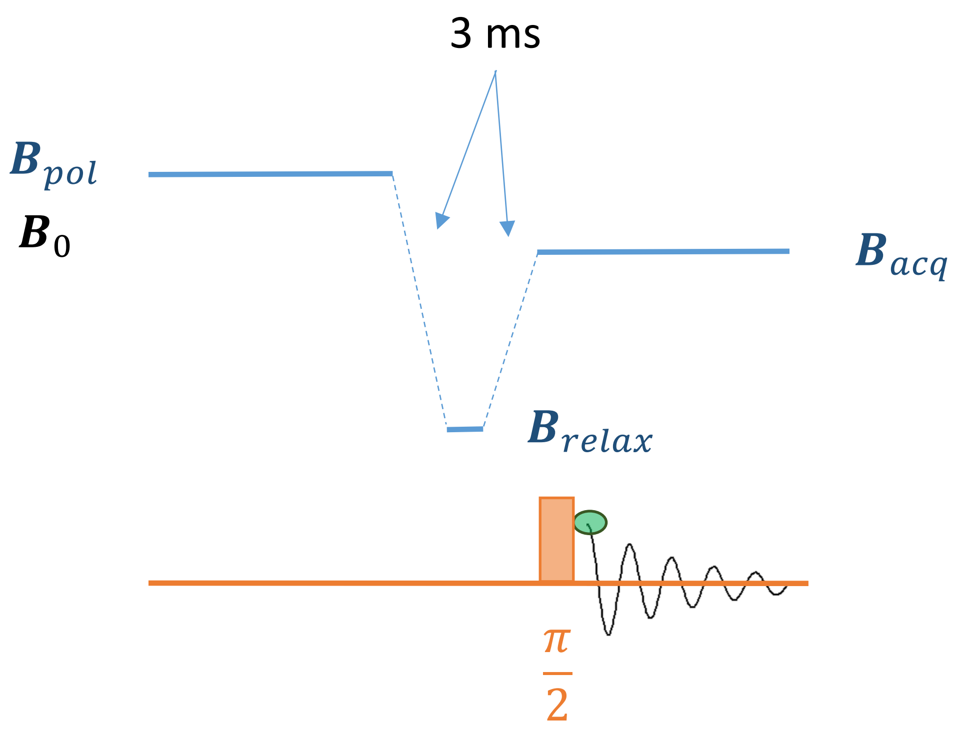
Does wine helps to relax?
Is wine a good relaxing agent?

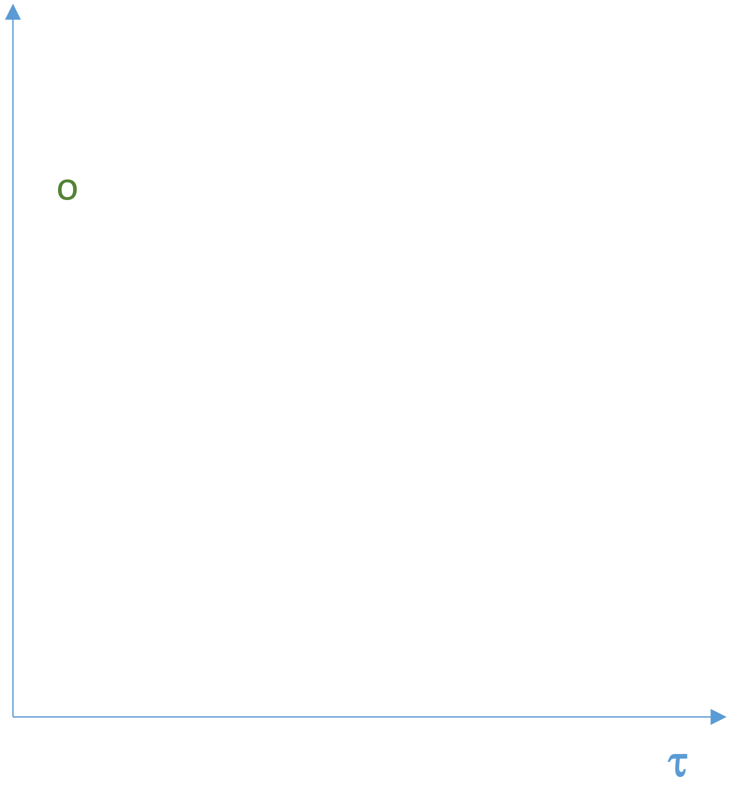
Relaxomety experiments …

Oldest vinery (4100 BC – Areni, Armenia)

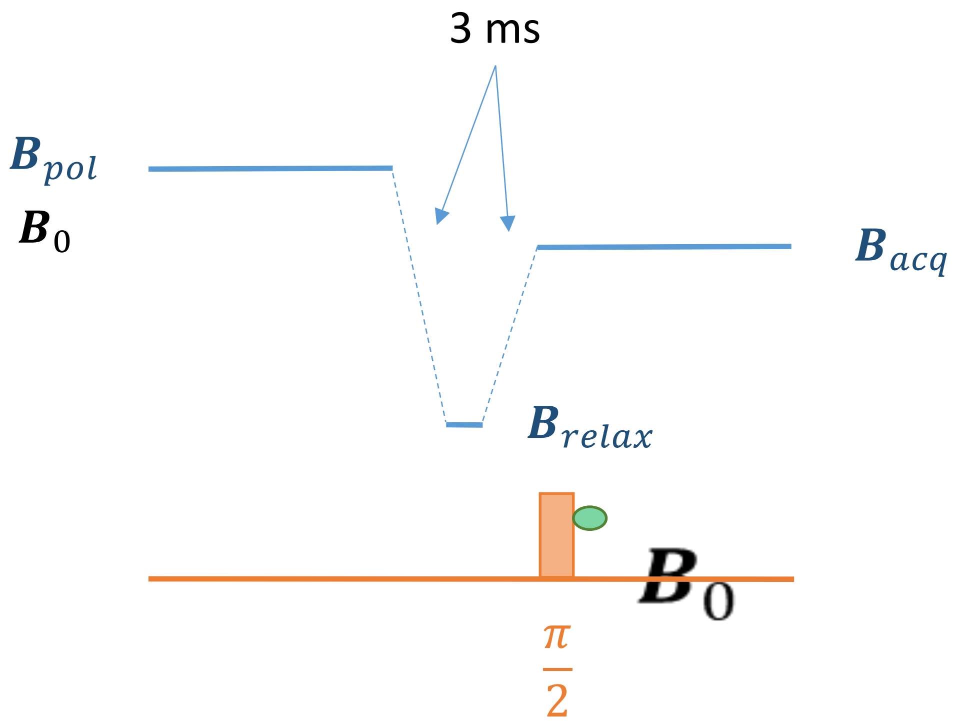


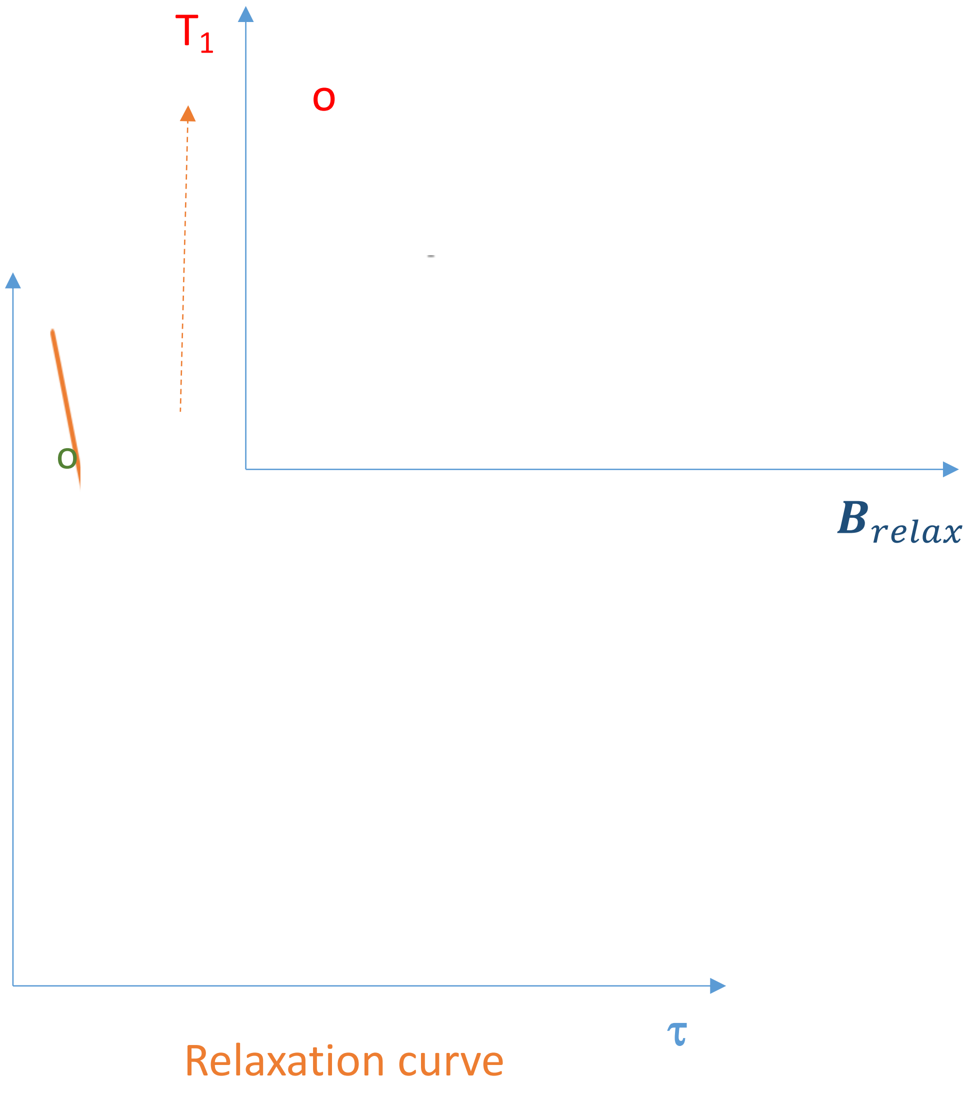
What relaxomtry experiment did we perform?



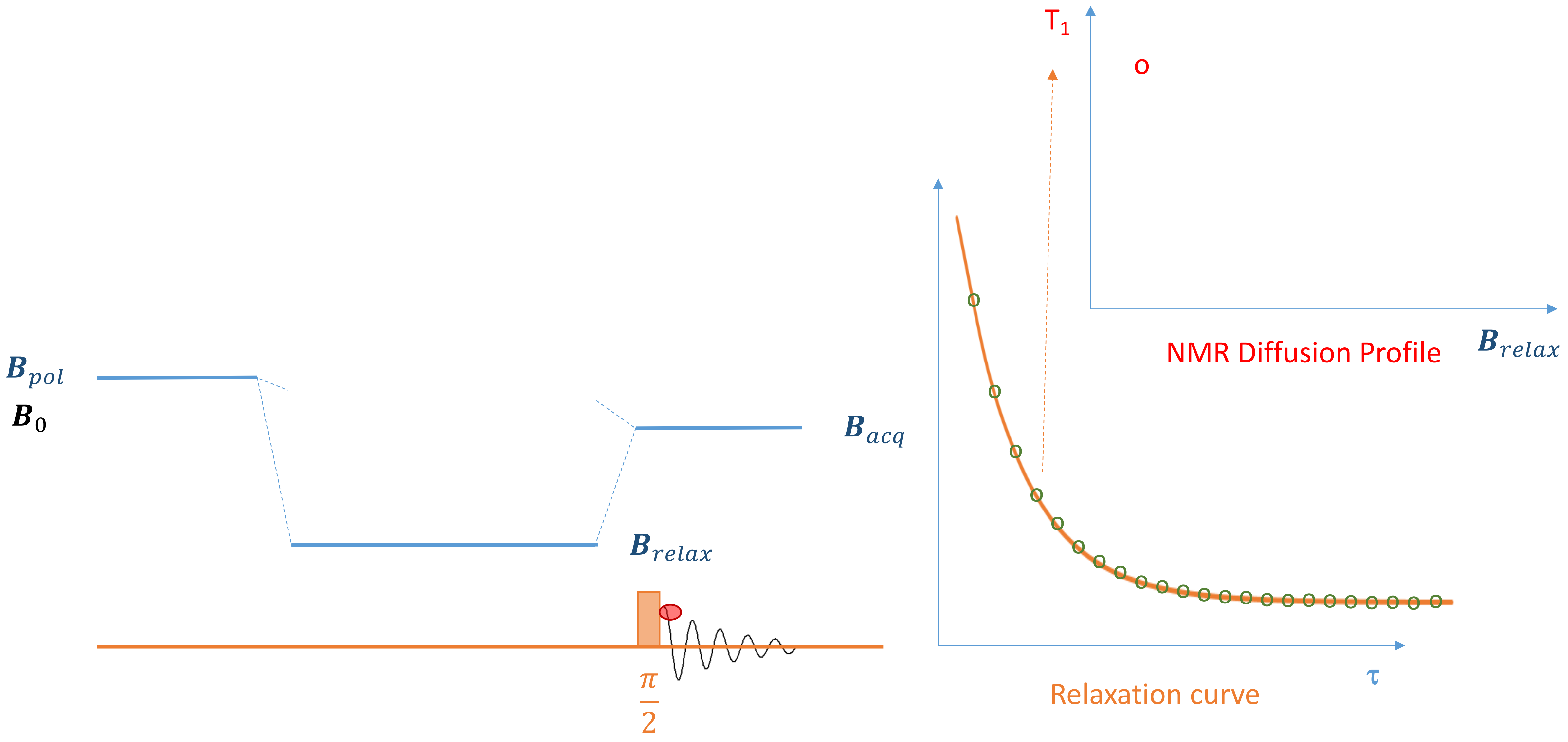


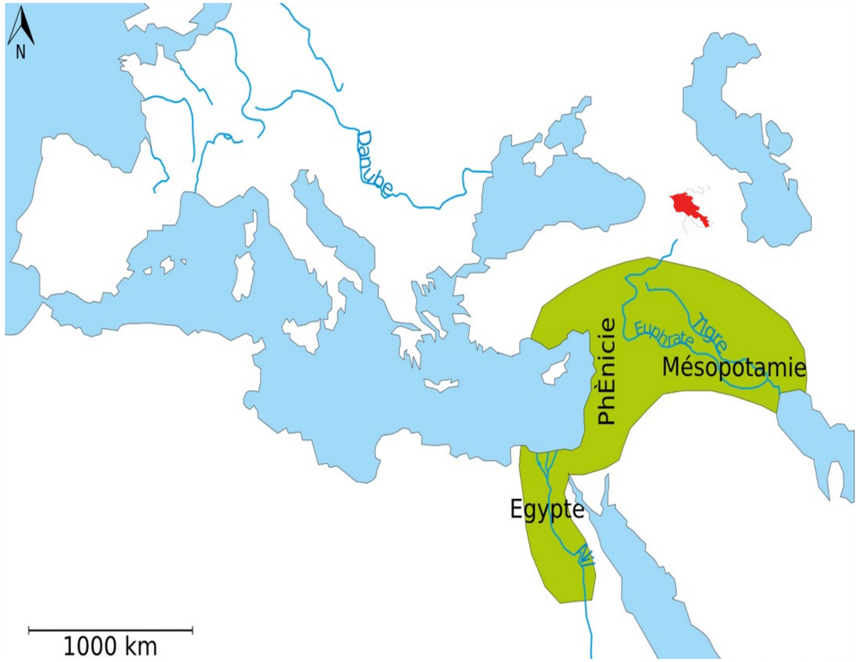
principle of relaxomtry experiment





principle of relaxomtry experiment

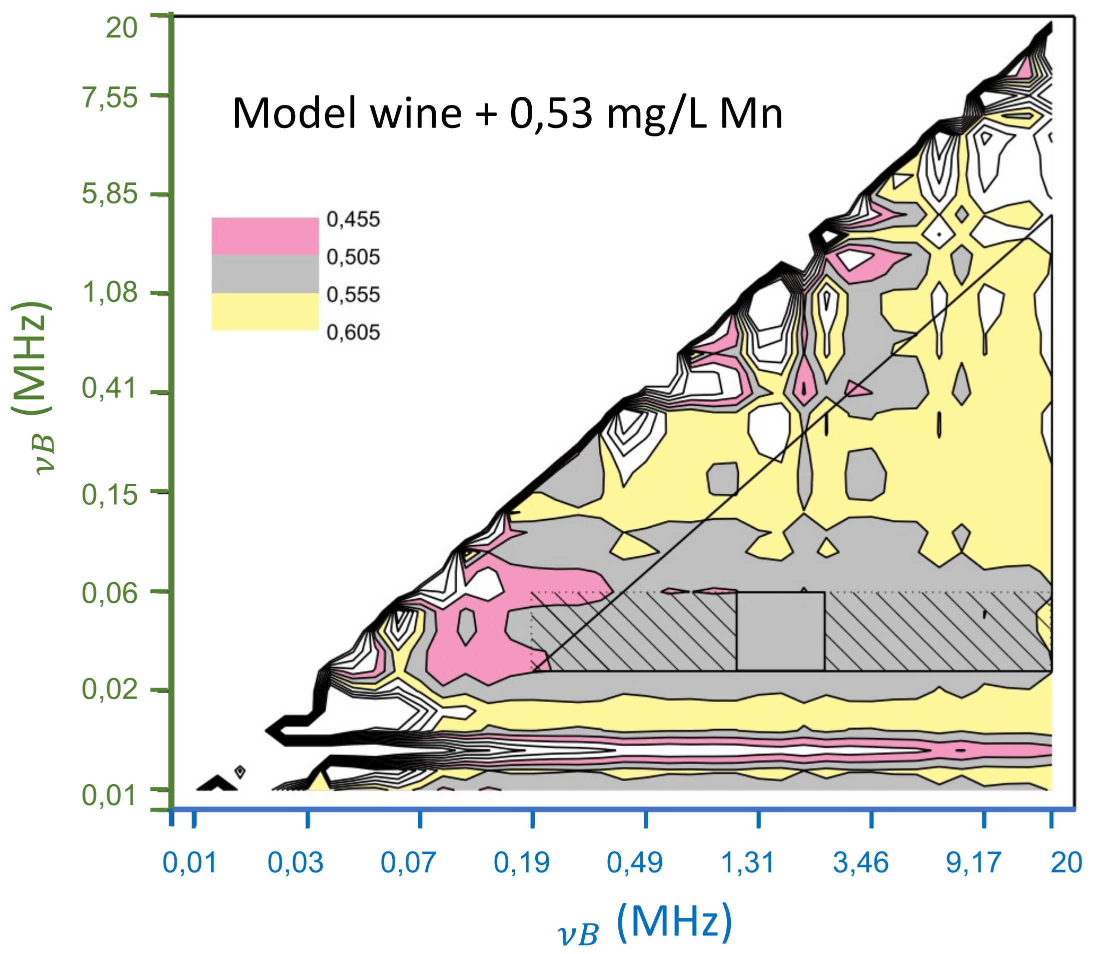


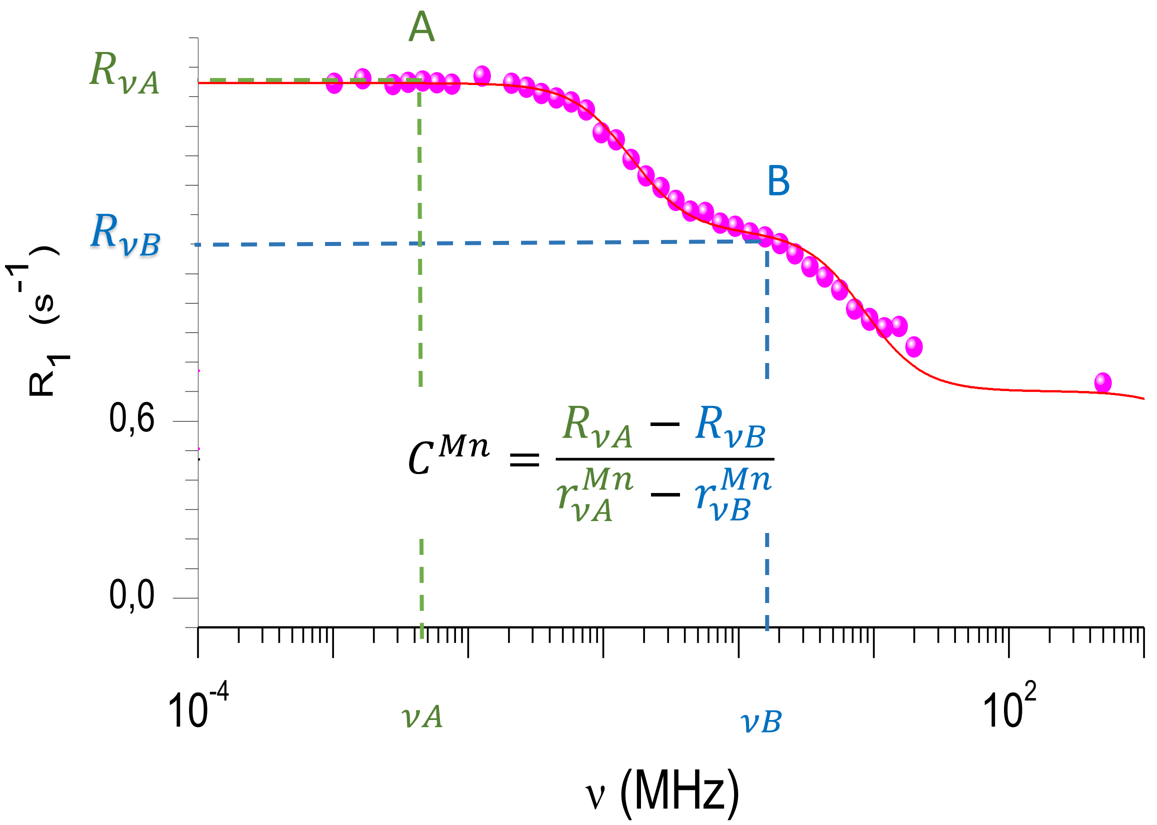


N
Danube
PhÈnicie
Euphrate
Tigre
Mésopotamie
Egypte
Nil
1000 km


Sea
Tigris River
Euphrates River
Fertile
Crescent
Mediterranean
Sea
N
W
E
S
Persian Gul

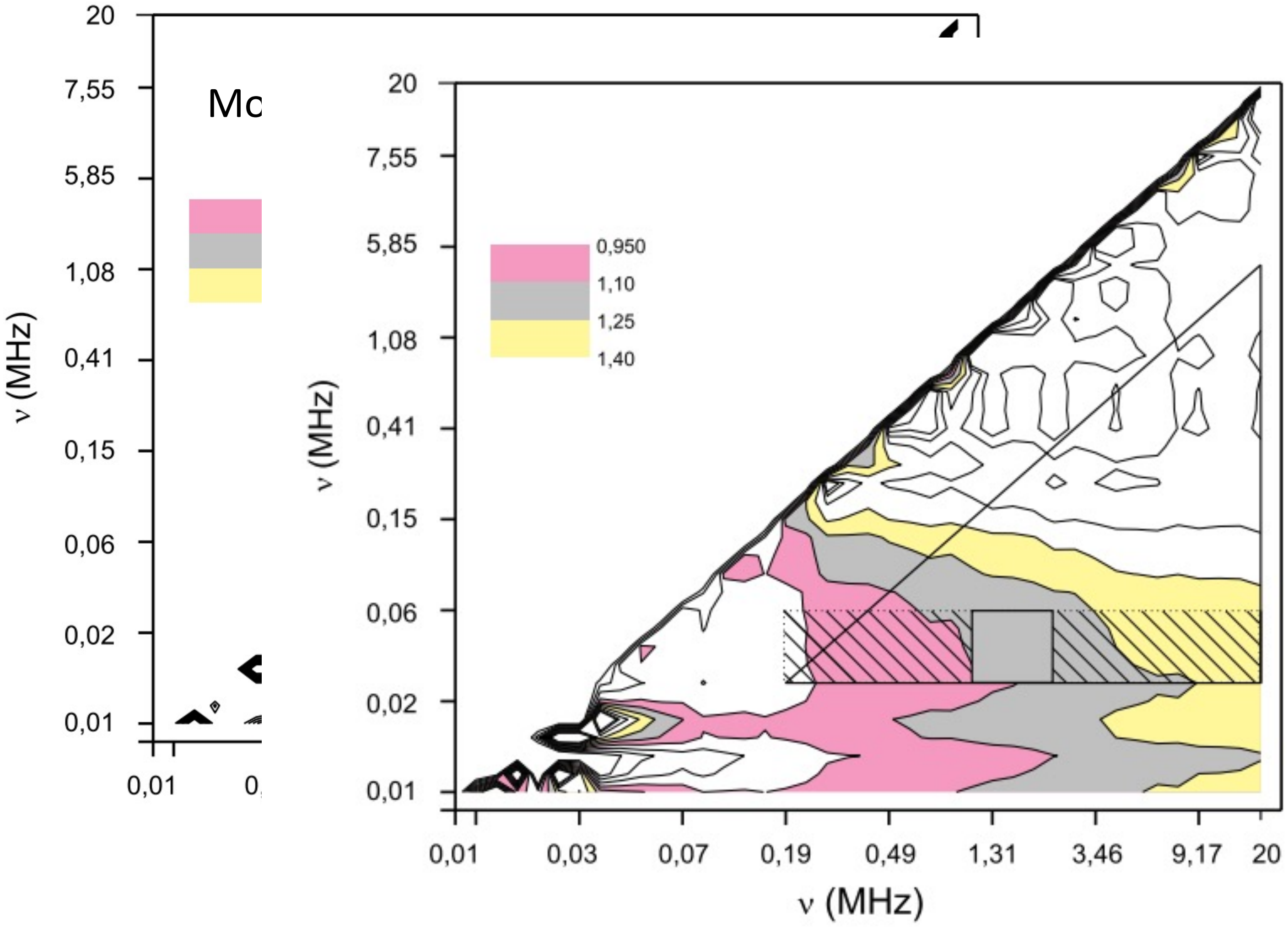
Quantification of Manganese





$$C^{Mn} = \frac{R_{\nu A} - R_{\nu B}}{r_{\nu A}^{Mn} - r_{\nu B}^{Mn}}$$

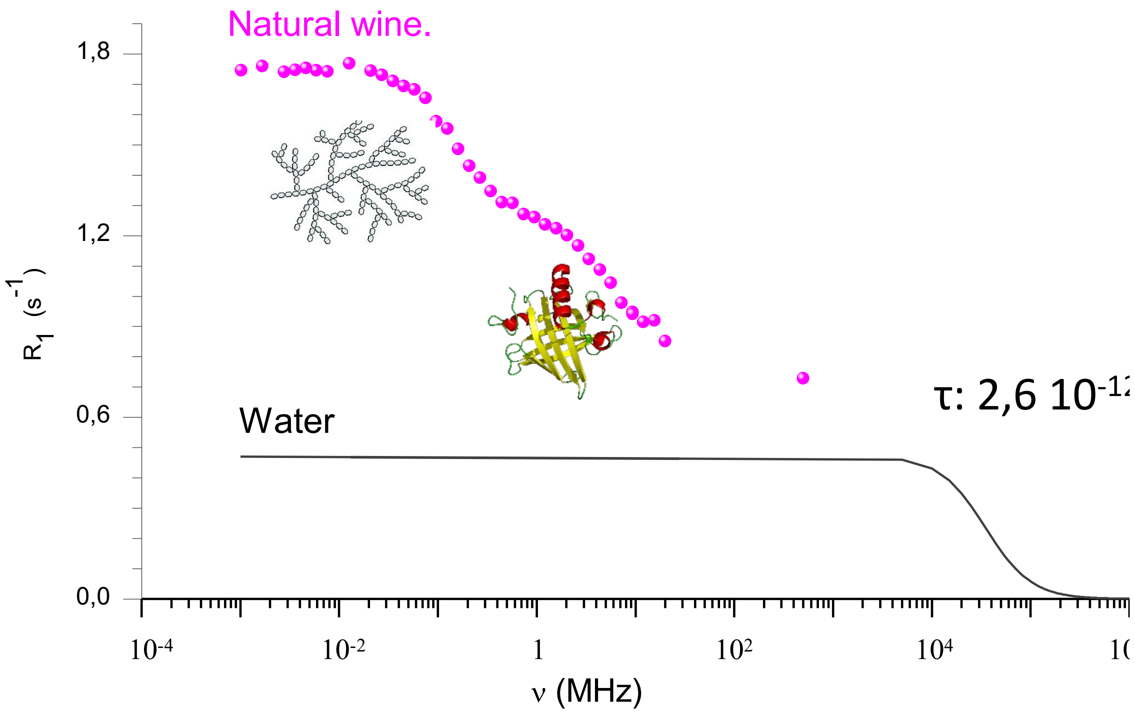
Quantification of Manganese



langanese oncentration	Square zone	Rectangular zone	Triangular zone
.46	5.46 (3)	5.45 (4)	5.5 (1)
.01	4.97 (5)	4.97 (6)	5.0 (1)
.28	1.34 (8)	1.3 (1)	1.3 (1)
.53	0.53 (1)	0.52 (1)	0.53 (5)
.05	0.063 (5)	0.063 (6)	0.06 (1)
.26 (2)[a]	1.17 (9)	1.2 (1)	1.3 (2)
	1.13 (3)	1.1 (1)	1.4 (2)
.06 (2)[a]	0.83 (4)	0.9 (1)	1.2 (3)
	0.91 (5)	0.9 (1)	1.2 (3)
< 0.002[a]	0.009 (6)	0.011 (4)	0.01 (1)

ration measured by ICP AES.

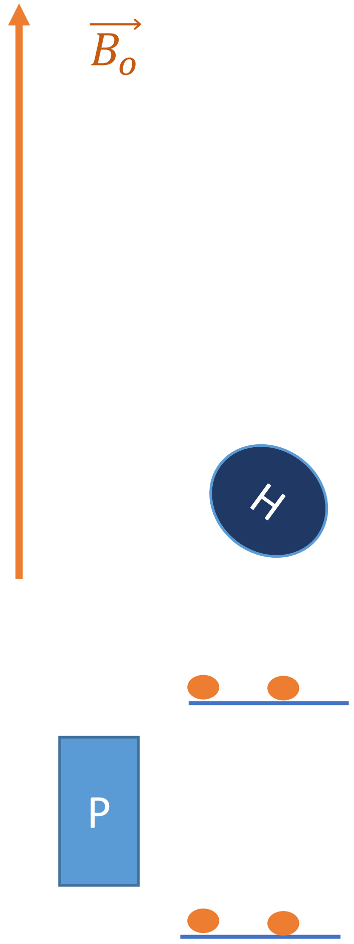
NMRD profile of wine (white Chardonay)

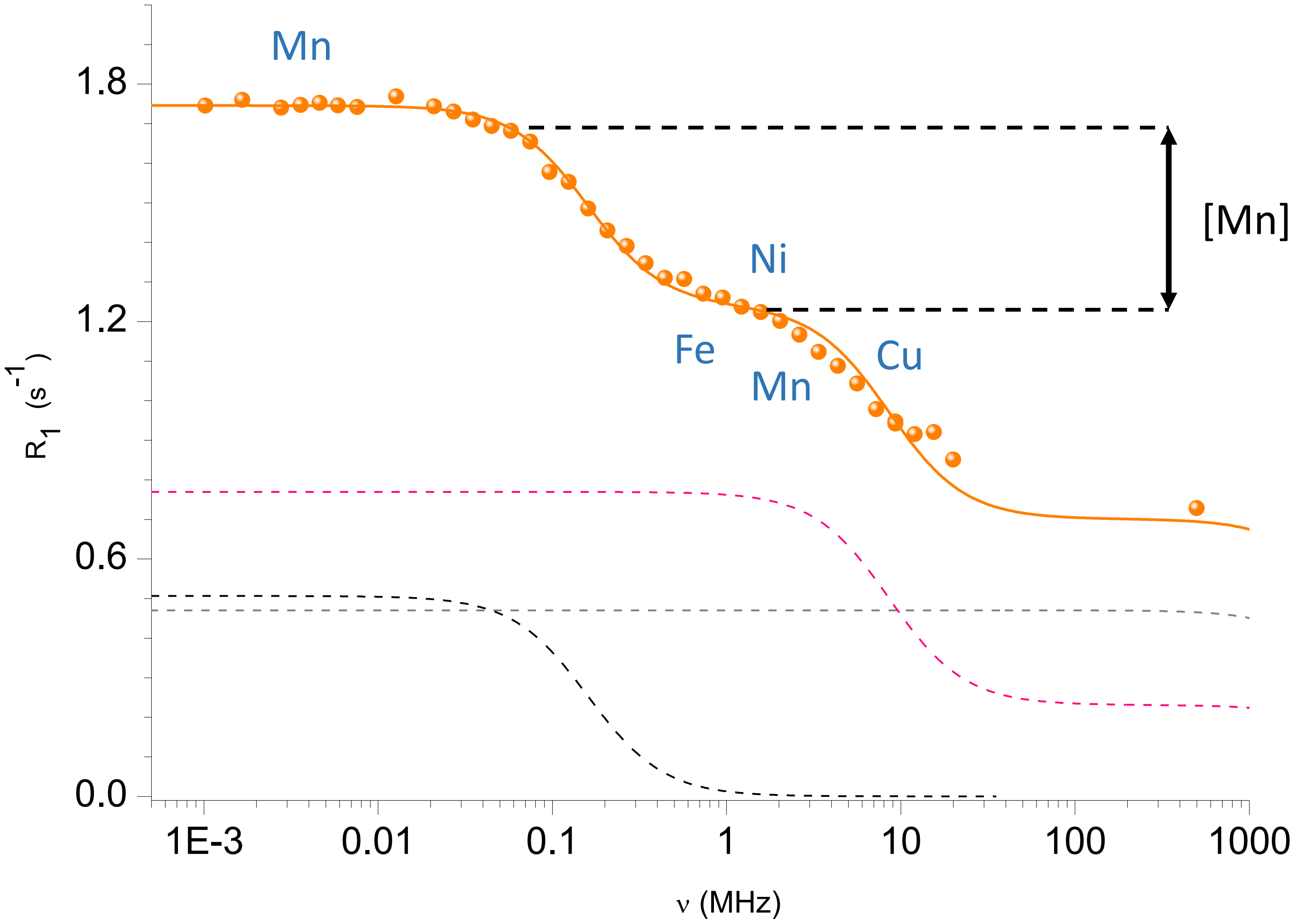


Concentrations (mg/L) of paramagnetic elements measured in the white Chardonnay (W), the red Medoc (R) and the exchanged wine (EW) by ICP-AES.

	Mn	Fe	Cu	Ni	Cd
W	1.26 (2)	1.34 (2)	0.160 (2)	0.91 (1)	0.0019 (1)
EW	< 0,002	0.056 (3)	0.024 (1)	< 0,007	< 0,001
R	1.06 (2)	0.85 (1)	0.93 (1)	0.065 (1)	0.0056 (3)

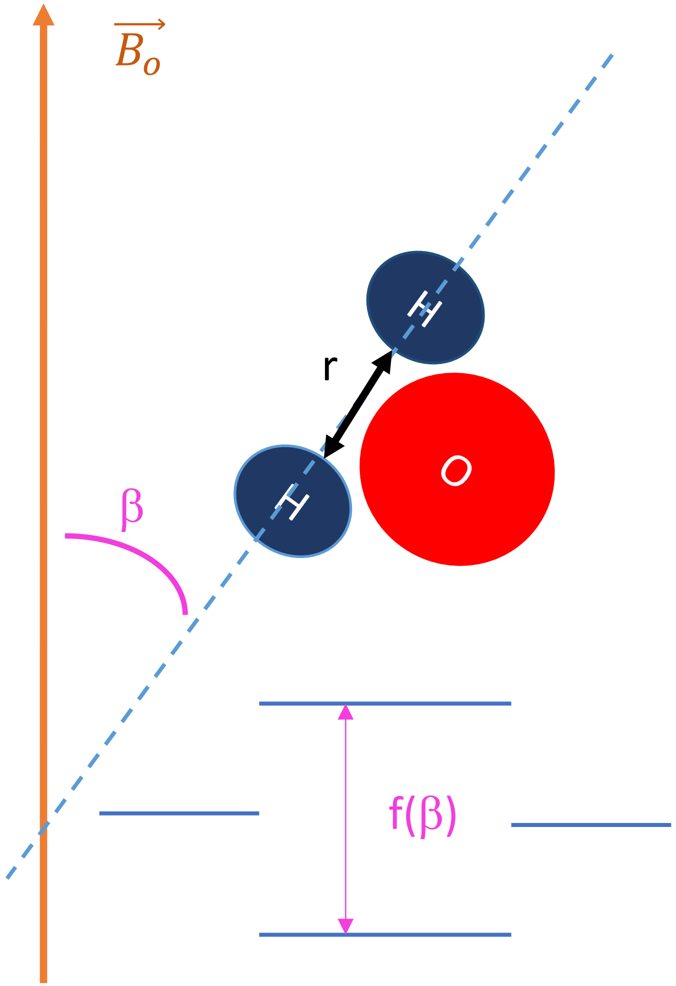
Basic dipolar relaxation mechanism





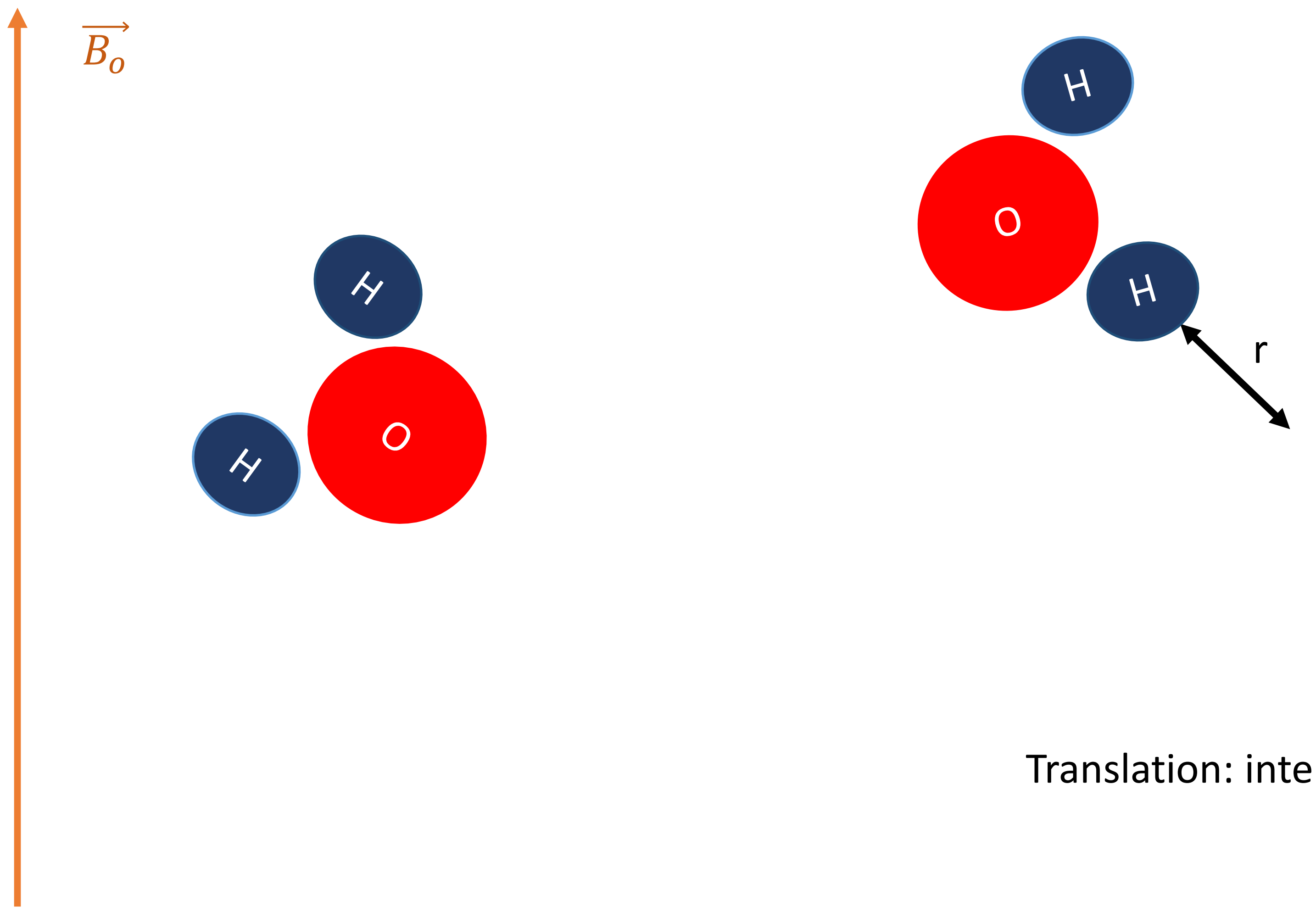
Mn
Ni
Fe
Mn
Cu
[Mn]
1.8
1.2
0.6
0.0
R_1 (s^{-1})
1E-3
0.01
0.1
1
10
100
1000
ν (MHz)

Basic dipolar relaxation mechanism



Rotation: intra molecular relaxation
Rotational isotropic diffusion

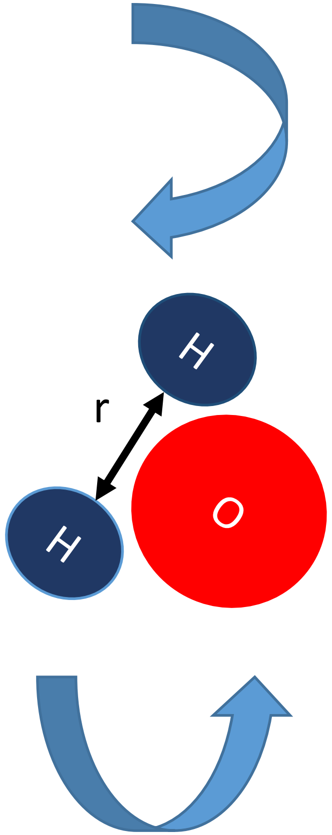
Basic dipolar relaxation mechanism



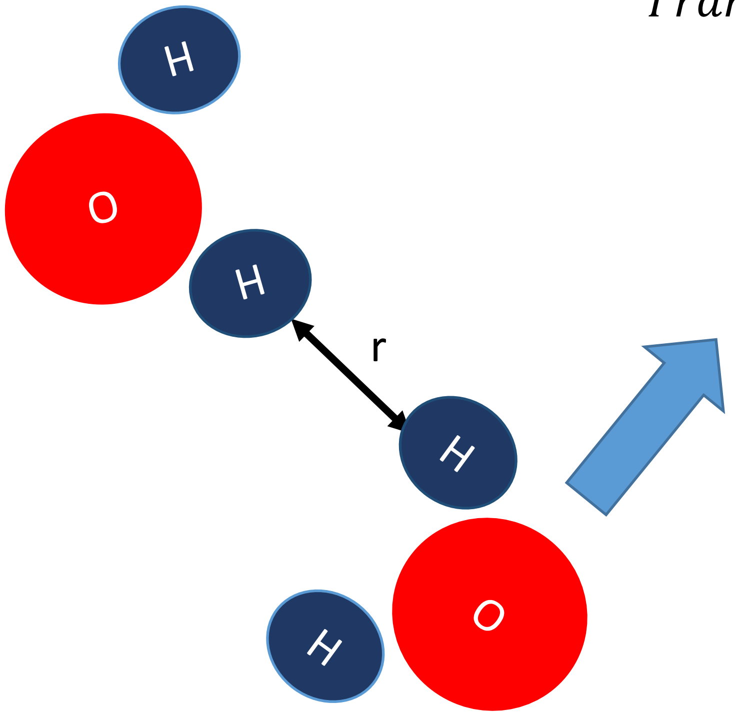
Translation: inter molecular relaxation

Basic dipolar relaxation mechanism

Rotation



Translation



$R_1 = \frac{1}{T_1}$

$$R_1 = R_1^{intra} + R_1^{inter}$$

BPP relaxation model

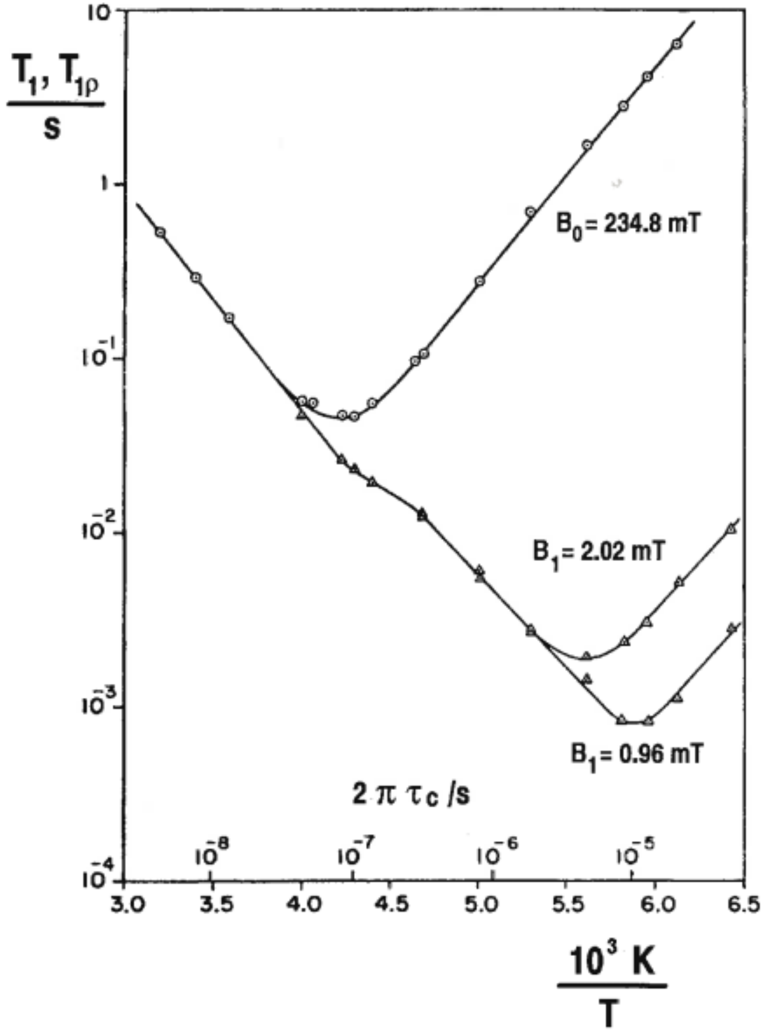
Dipolar interaction ($H_2 0$),
intramolecular contribution
Isotropic rotational diffusion

$$\frac{1}{T_1}(\omega_I,\tau_c) = R_1(\omega_I,\tau_c) = \tilde{C}_o\left[\frac{\tau_c}{1+(\omega_I\tau_c)^2} + \frac{4\tau_c}{1+4(\omega_I\tau_c)^2}\right]$$

$$\tilde{C}_o = \frac{3}{10}\left(\frac{\mu_o}{4\pi}\right)^2 \frac{{\gamma_I}^4\hbar^2}{{r_{II}}^6}$$

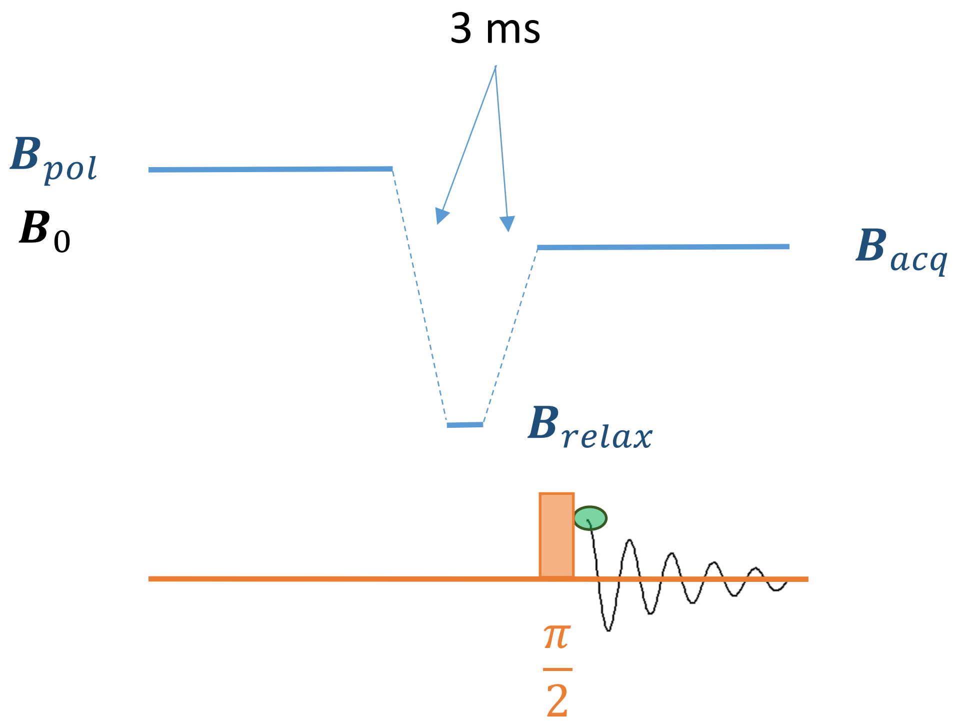
τ_c: correlation time

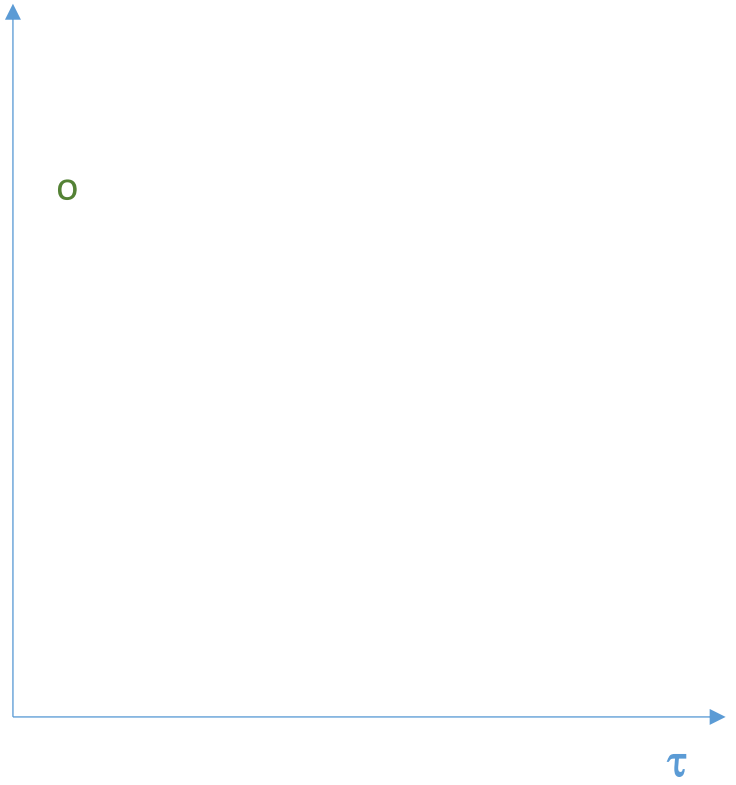
N. Bloembergen, E.M. Purcell, R.V. Pound, Relaxation effects in nuclear magnetic resonance absorption, Phys. Rev. 73 (1948) 679–712



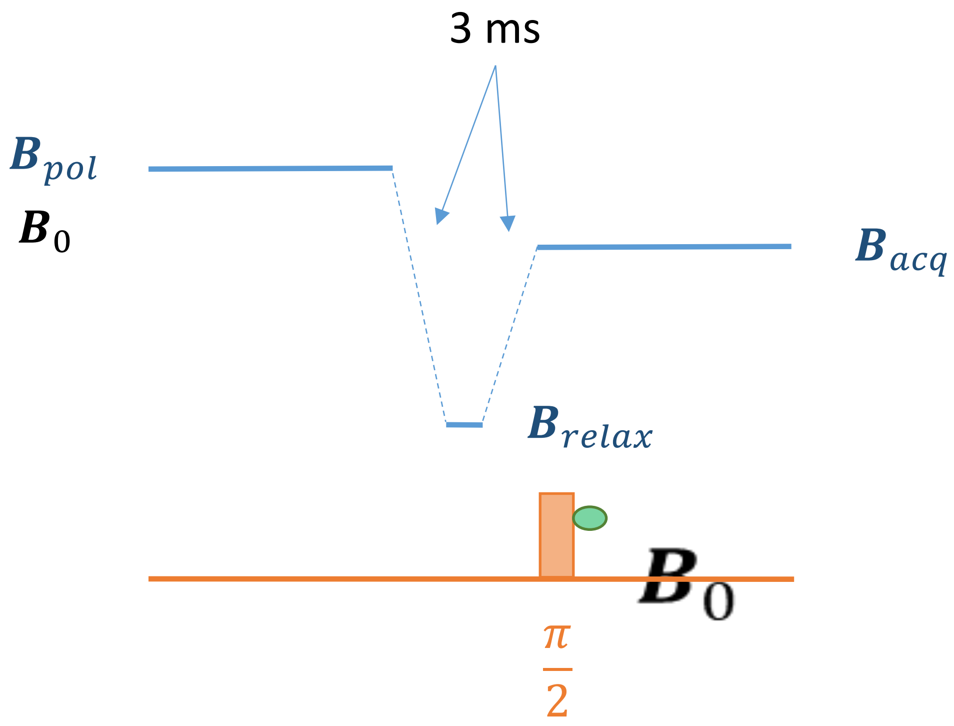
D.C. Look I.J. Lowe J. C hem. Phys. 44 (1966) 2995

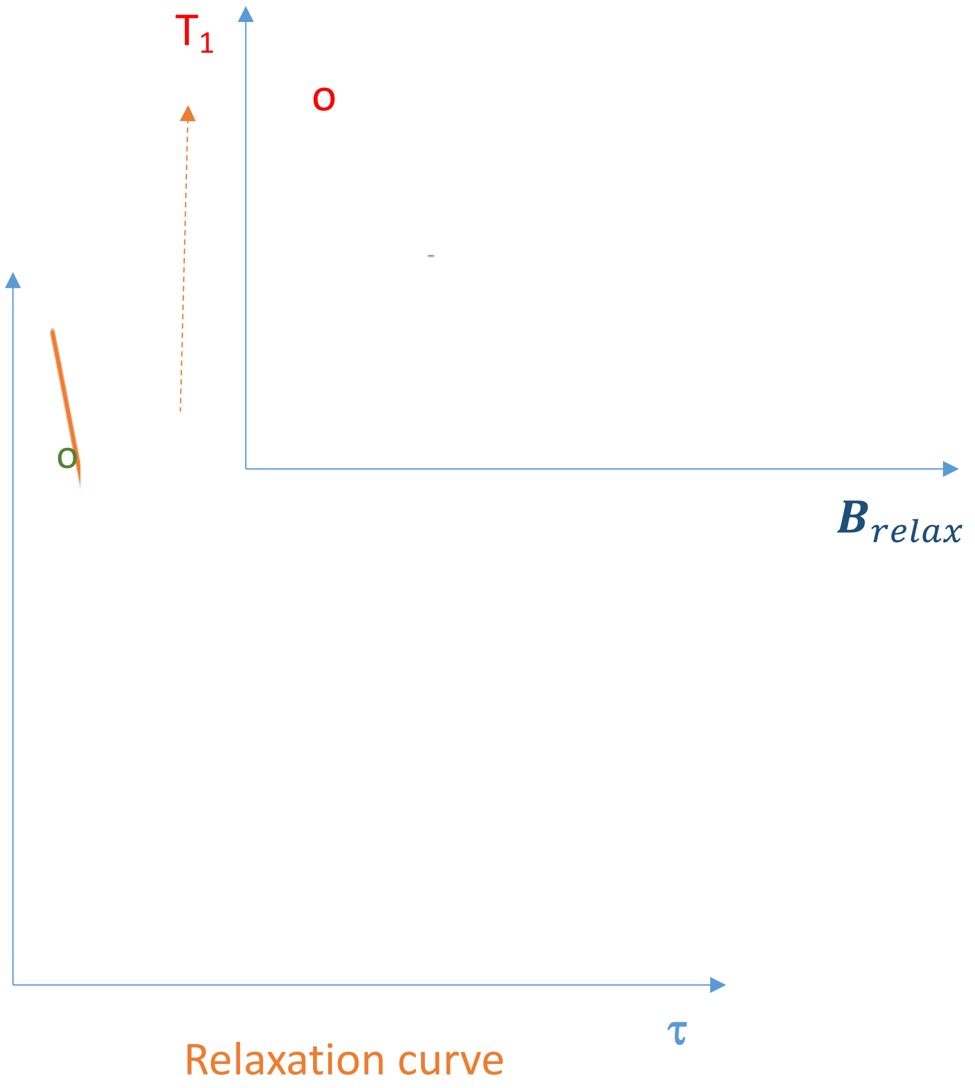
principle of relaxomtry experiment



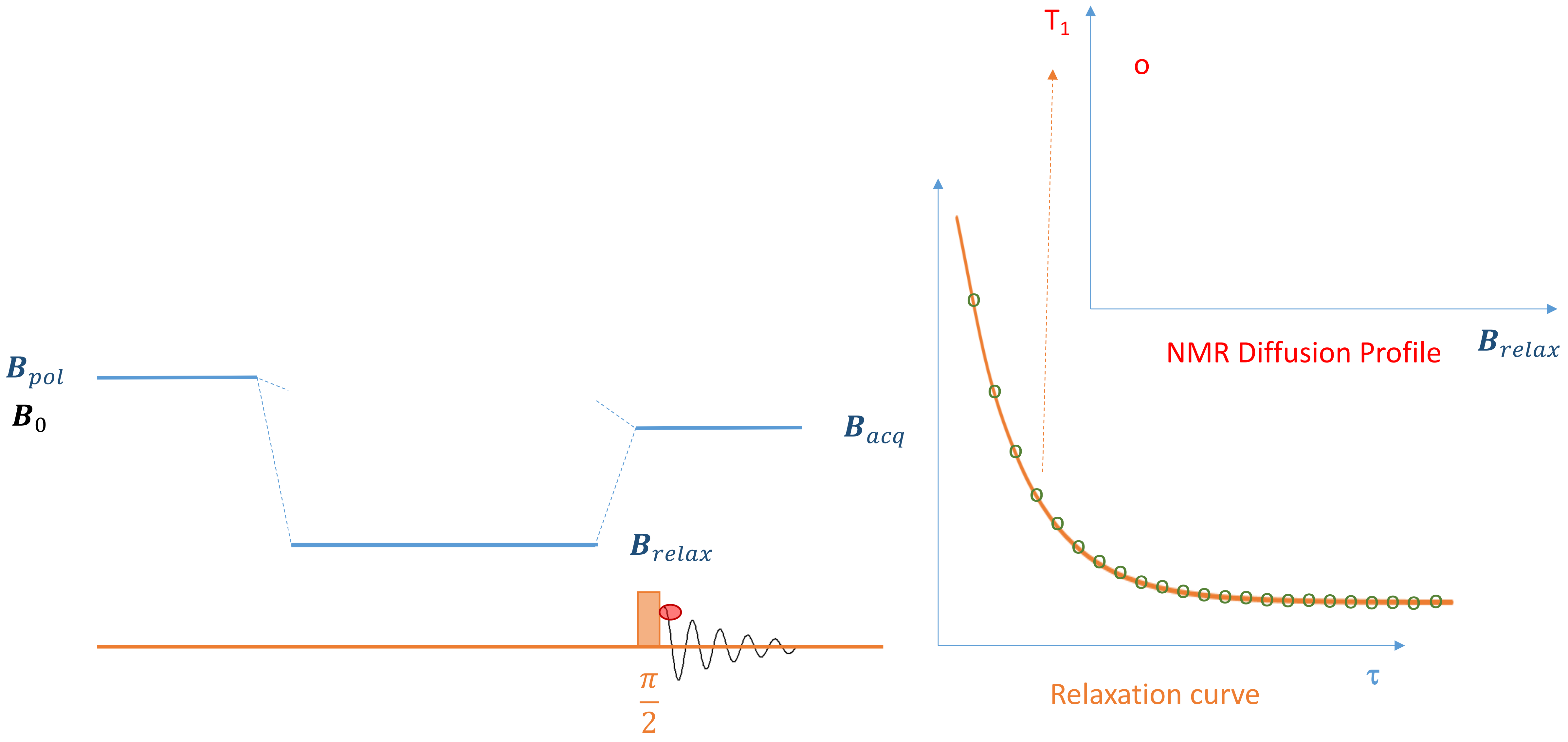


principle of relaxomtry experiment



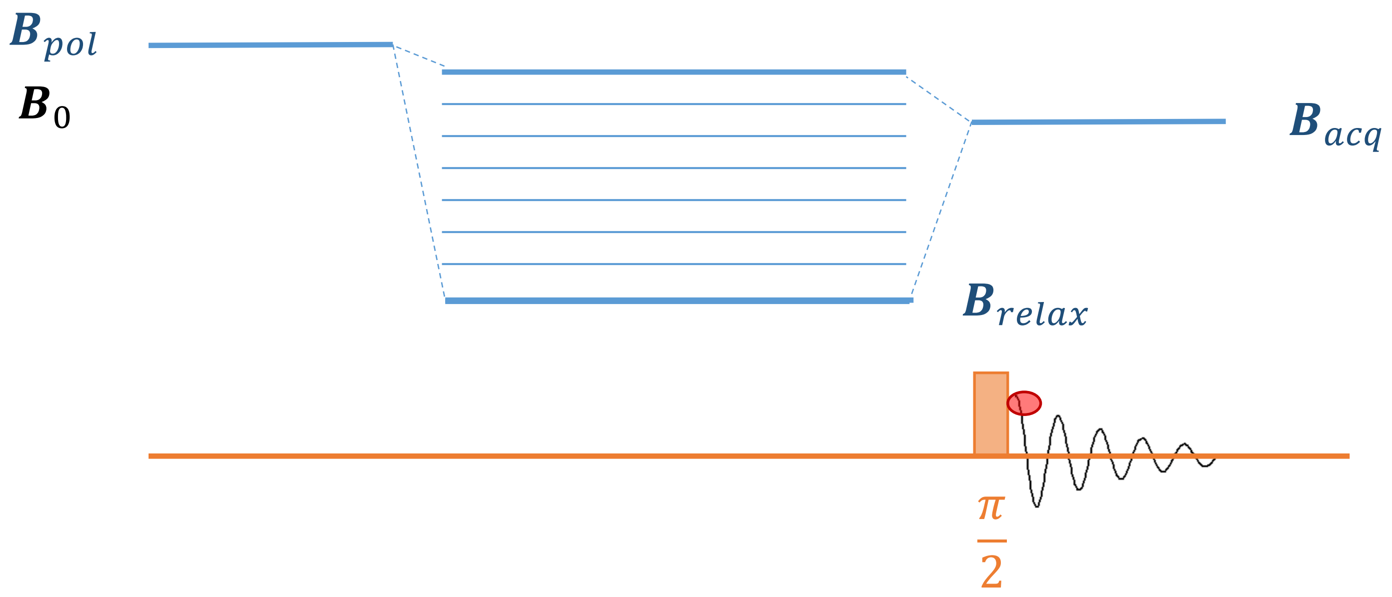


principle of relaxomtry experiment



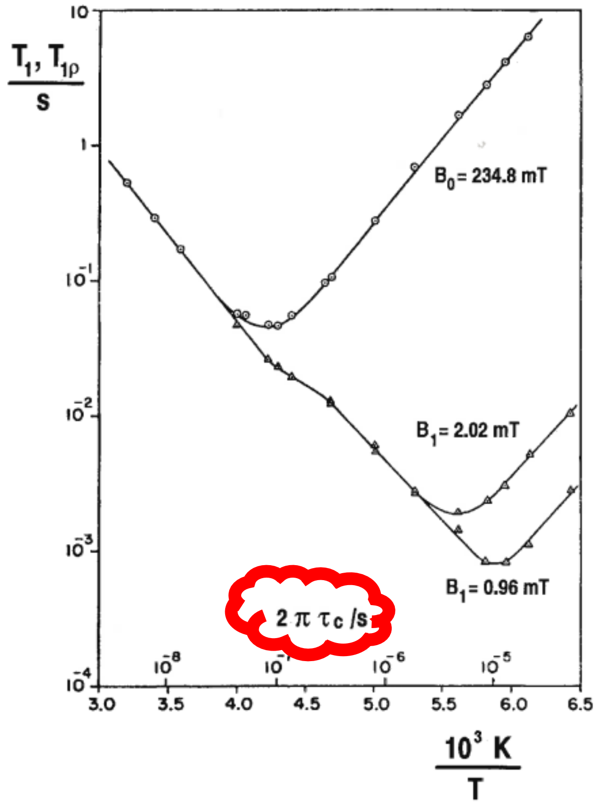
technical aspects

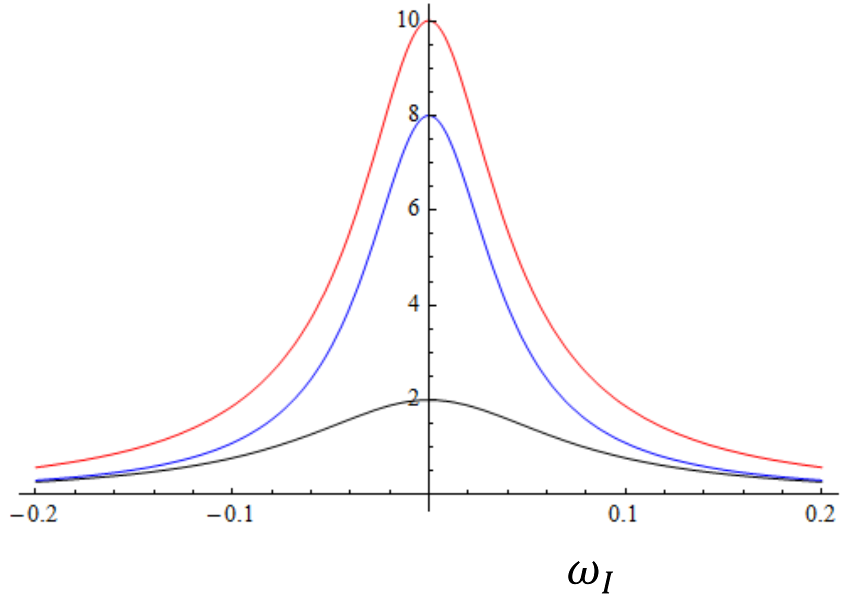
- $\boldsymbol{B}_{acq}$ allows a single tunning for all larmor frequencies
- $\boldsymbol{B}_{relax}$ can varie from 40 MHz to 10 kHz
- Low Relaxation field (~ kHz)
- Switching time (2-3 ms)

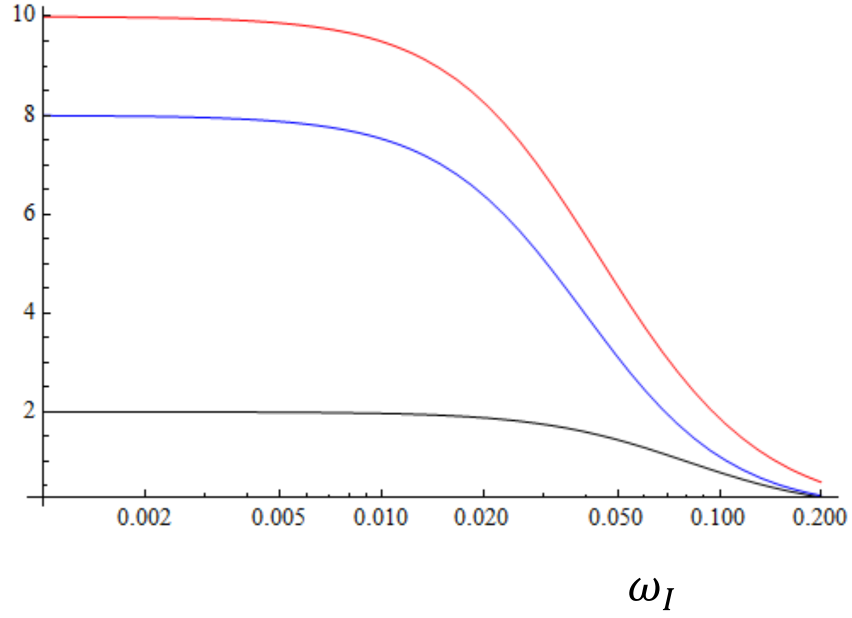


BPP relaxation model

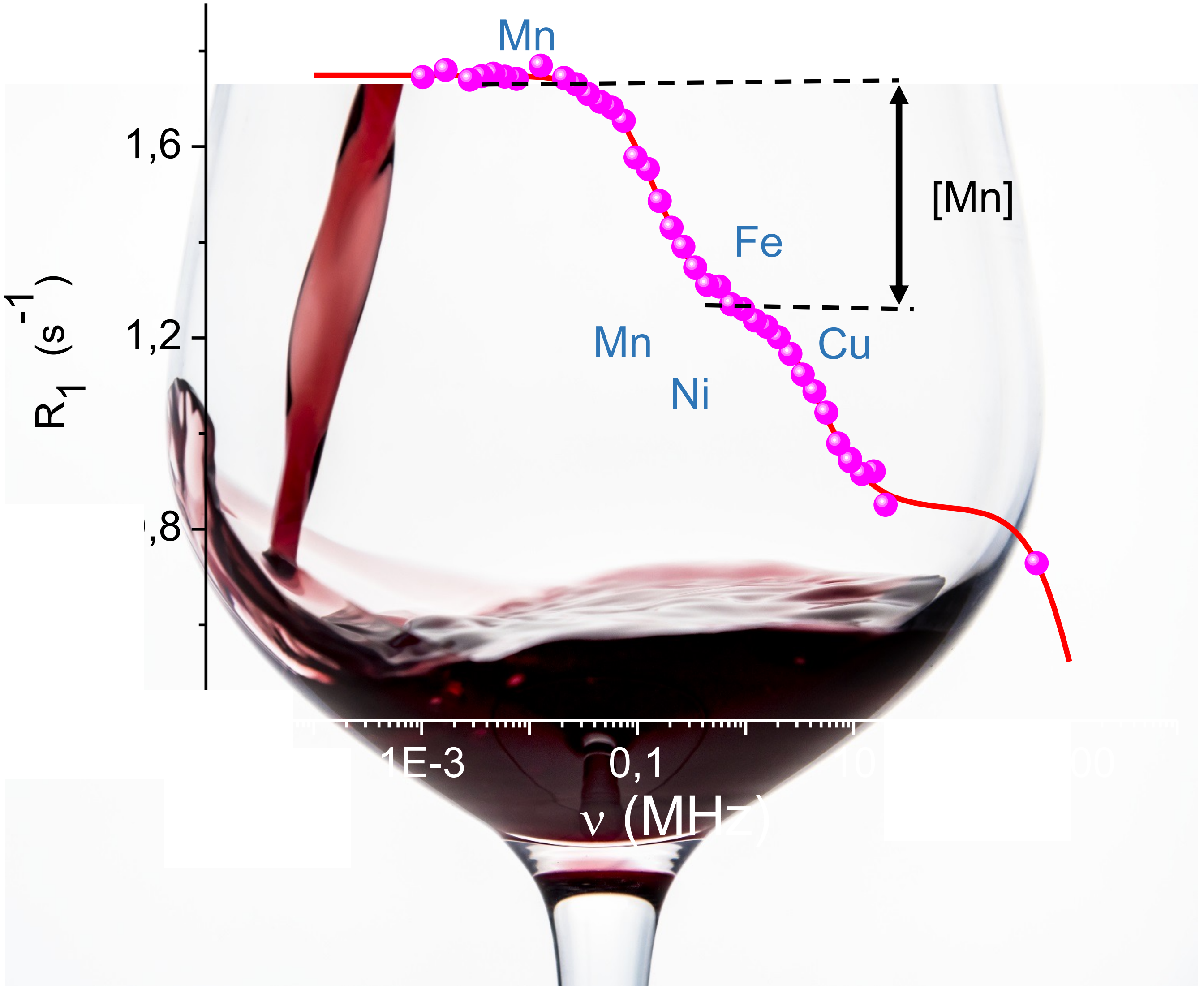
$$\frac{1}{T_1}(\omega_I, \tau_c) = R_1(\omega_I, \tau_c) = \tilde{C}_o \left[\frac{\tau_c}{1 + (\omega_I \tau_c)^2} + \frac{4\tau_c}{1 + 4(\omega_I \tau_c)^2}\right]$$



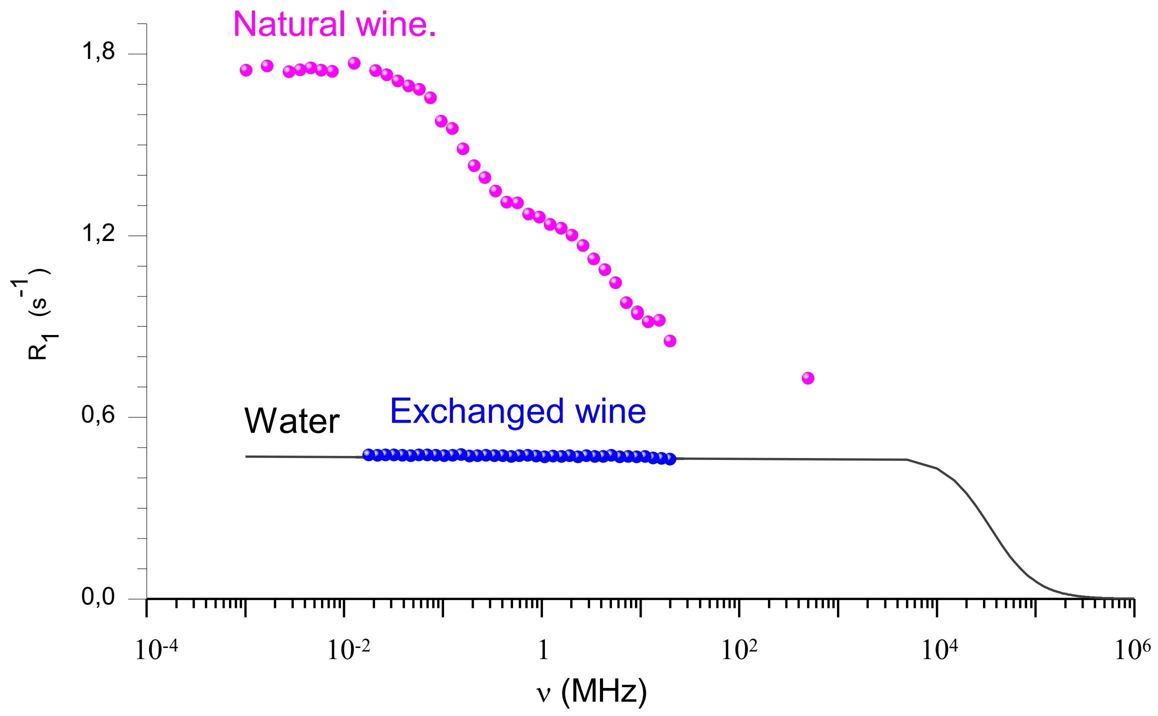


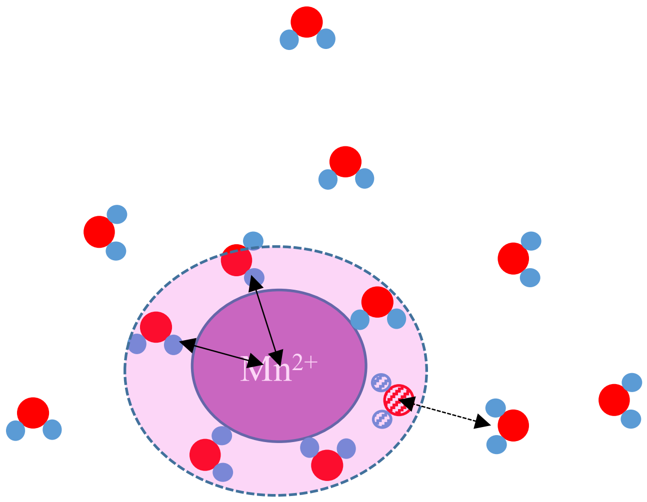


NMR Diffusion Profile


Mn
[Mn]
Fe
Mn
Cu
Ni
1,6
1,2
,8
R_1 (s^{-1})
1E-3
0,1
ν (MHz)

NMRD profile of wine (white Chardonay)



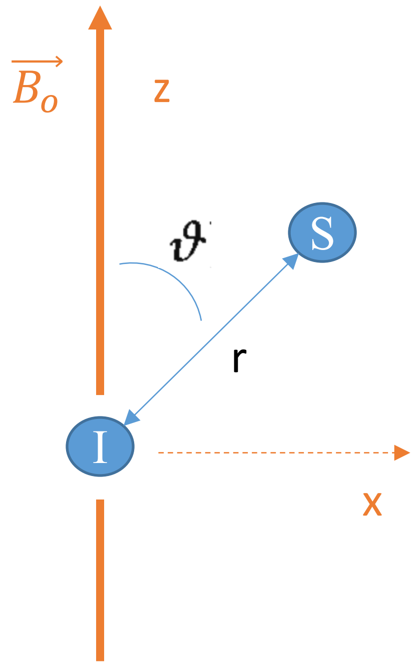

Mn^{2+}

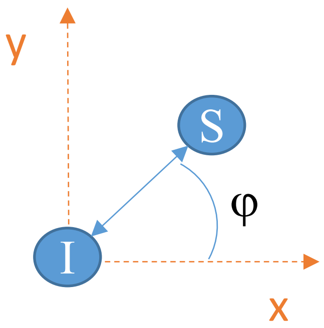
Dipolar relaxation

$$\mathcal{H}_0 = -\hbar\omega_I I_z - \hbar\omega_S S_z$$

$$\mathcal{H}_d = f_d \sum_{k=-2}^{2} F^{(k)} \mathcal{O}^{(k)}$$

$$f_d = \frac{\mu_0}{4\pi}\gamma_I \gamma_S \hbar^2$$





$$\begin{aligned}
F^{(0)} &= F^{(0)*} = r^{-3}\,(1 - 3\cos^2\vartheta) \\
F^{(1)} &= F^{(-1)*} = r^{-3}\,(\sin\vartheta\cos\vartheta\; e^{-i\varphi}) \\
F^{(2)} &= F^{(-2)*} = r^{-3}\,(\sin^2\vartheta\; e^{-2i\varphi}) \\
\mathcal{O}^{(0)} &= \mathcal{O}^{(0)\dagger} = I_z S_z - \tfrac{1}{4}(I^+S^- + I^-S^+) \\
\mathcal{O}^{(1)} &= \mathcal{O}^{(-1)\dagger} = -\tfrac{3}{2}(I^+S_z + I_z S^+) \\
\mathcal{O}^{(2)} &= \mathcal{O}^{(-2)\dagger} = -\tfrac{3}{4} I^+ S^+
\end{aligned}$$