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Stable oxygen isotope content of water of EU data-bank wines from Italy, France and Germany

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Abstract The application of oxygen isotope analysis to wine water (according to EU regulation no. 822/97) to determine a wine's origin, and check that it has not been adulterated is gaining increasing importance in both laboratories and industry. Using samples of Italian, French and German wines from the EU wine data bank (EU-DB), good agreement between the results from participating laboratories was demonstrated. Close correlations between the oxygen isotope contents of must and related wine water were found for samples from all countries. Based on the results of the $\delta^{18}\text{O}$ values for EU-DB wines from 1991 to 1996 from Italy, France and Germany, we describe and discuss the main factors which are responsible for the variation of the oxygen isotope ratios of wine water. The examination of spiked samples demonstrated the usefulness of $\delta^{18}\text{O}$ analysis for the detection of the watering down of wine. The possibility of origin assignment, preferably if the determination of the $\delta^{18}\text{O}$ value by isotope ratio mass spectrometry (IRMS) is employed together with the determination of the site-specific hydrogen isotope content of wine ethanol by ^2H -NMR and the measurement of $\delta^{13}\text{C}$ values of ethanol by IRMS, is outlined.

Key words Wine · Oxygen isotopes · Adulteration control · Origin assignment · European Union data bank

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Introduction

Among the innovative methods for authenticity control and origin assignment of foods and beverages, stable isotope ratio analysis has gained remarkable importance within the last years for the quality assessment of wine, spirits, fruit juices, flavours, oils, honey and maple syrup [1–18]. For the analysis of wine, the first officially adopted stable isotope method in the EU was the determination of the site-specific D/H ratio by NMR for wine ethanol, mainly to provide evidence of the addition of beet sugar [3]. A more recent stable isotope method is the determination of ^{18}O in wine water by isotope ratio mass spectrometry [19], and the determination of ^{13}C in wine ethanol will soon be used. The EU has already installed a system of data banks for all wine-producing countries within the EU (EU regulation 2676/90, 3 October 1990), primarily for the D/H data provided by ^2H -NMR, which has been gathered since that date, but which already includes data describing carbon and oxygen isotopes, too. These results have shown the importance of using not only the hydrogen isotope ratio for ethanol, but also carbon and oxygen isotope data of ethanol and water, respectively for reliable proof of a wine's authenticity and origin [15, 20–25, 27–28]. Such multielement isotope analyses have generally been found to give a better indication of the nature of a natural product than the analysis of only one element's stable isotope ratio, for example in the case of fruit juices and flavours [5–7, 10, 11, 17]. For the widespread application of these isotopic methods it is necessary to know and to understand the natural range of variation of the stable isotope ratios of different elements.

In the case of oxygen isotopes in plant water, the main factor which affects the $\delta^{18}\text{O}$ value is the source of plant-available water, usually groundwater (resulting from precipitation). Further, the climatic conditions of a location, which already influence the isotopic characteristics of the precipitation, additionally modify the transpiration of leaves and fruit, which always causes

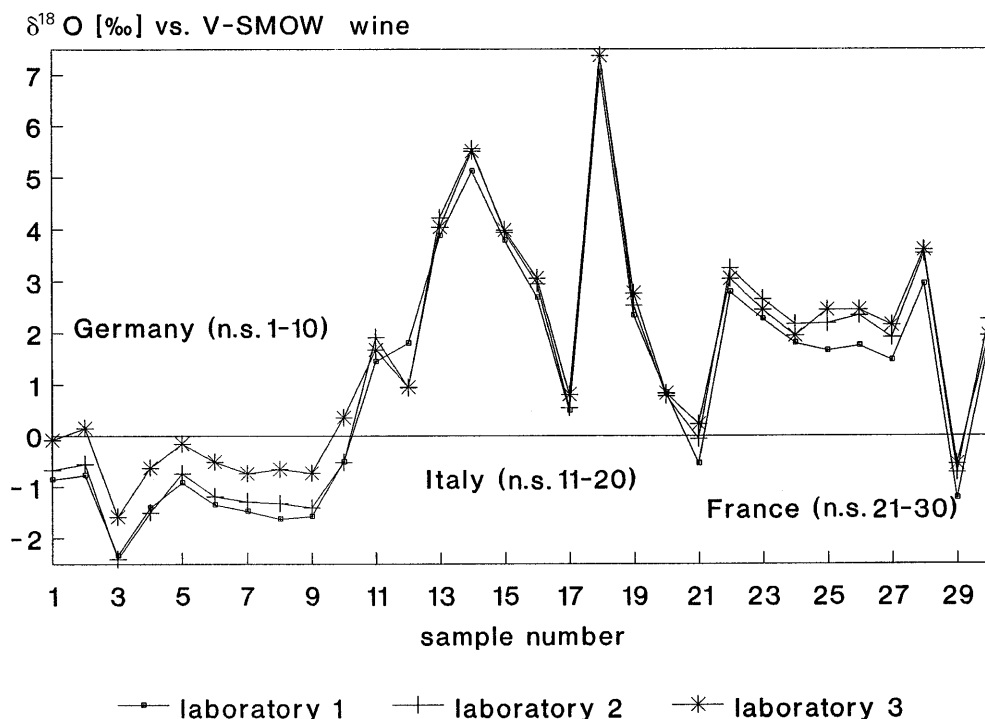
an enrichment of the heavy oxygen and hydrogen isotopic contents of plant water as compared with ground-water [26–28]. The extent of this enrichment differs not only according to climatic conditions but possibly other factors, too, which are discussed below. As the $\delta^{18}\text{O}$ values of EU data-bank (EU-DB) wines should primarily be a basis for detecting the watering down of wine, e.g. addition of tap water or groundwater, knowledge of the natural range of $\delta^{18}\text{O}$ values of wine water is very important. Therefore, by using the $\delta^{18}\text{O}$ values of EU-DB wine samples from Italy, France and Germany measured during a 6-year period, which included more than 4500 single results, we have attempted to describe the main factors which affect their ^{18}O content and its variation in unadulterated wine. In addition, we report the results of some interlaboratory comparison measurements of musts, wines, and distillation residues, and correlations of the ^{18}O content of water from grape must and its related wine.

Materials and methods

The must and wine samples were used directly for the determination of the ^{18}O content of the water according to the method of Epstein and Mayeda [20], which has been modified for wine [27–29] and the subject of an interlaboratory comparison organised for the OIV recently [30].

The measurements were performed versus laboratory standard water, calibrated using the V-SMOW (Vienna Standard Mean Ocean Water) scale using SMOW (Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation) water, as described for fruit juices [31]. The reproducibility of the measurements was 0.2‰ or better (in one laboratory); the comparability of the results between the laboratories is discussed below.

Fig. 1 Interlaboratory comparison of the $\delta^{18}\text{O}$ values of wine water of 30 samples of authentic wine from Germany, Italy and France. V-SMOW Vienna Standard Mean Ocean Water



Results and discussion

Interlaboratory comparison

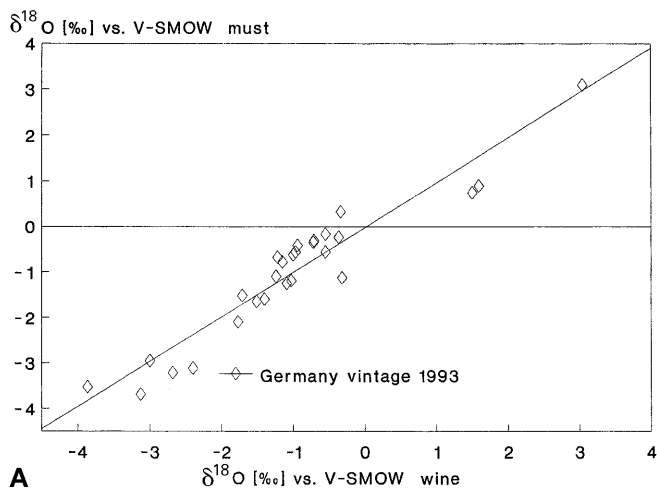
A prerequisite for comparing the results from different laboratories is to know what differences exist between them with respect to the calibration of the standard gas employed and, possibly, the different preparation systems used. To determine these differences, 30 samples of authentic EU-DB wine, ten from each country, with typical ^{18}O contents, were distributed to each laboratory at the very beginning of this interlaboratory project and the ^{18}O contents of the samples were measured by each. The results (Fig. 1) showed that there was generally good agreement between the data of the laboratories, with a mean inter-laboratory difference of 0.02–0.83%. The results were comparable with respect to reproducibility and repeatability (r and R) to those from earlier interlaboratory comparison (CEN TC 174 WG 1) on fruit juices [31] ($r=0.32\%$, $R=0.43$) and from a recent inter-laboratory study undertaken by the OIV (Office international de la Vigne et du Vin) on wine samples [30] ($r=0.244$, $R=0.497$).

The agreement between the laboratories (R value) could probably be improved, if EU standard wines with different $\delta^{18}\text{O}$ values were available and distributed by the EU, e.g. as is the case for BCR (Bureau Communautaire Reference) ethanols used as standards for ^2H -NMR measurements. In addition, since 1994, EU member-state laboratories involved in the measurement of EU-DB wines regularly participate in a project for the measurement of the $\delta^{18}\text{O}$ values of wine (proficiency tests) on a long-term basis.

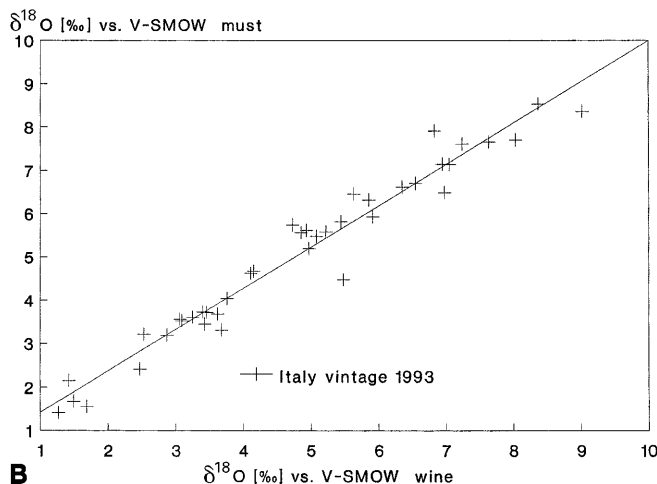
Comparison of the $\delta^{18}\text{O}$ value in must, wine and residue following distillation

In this study we determined the oxygen isotope content of water from must, related wines, and, in the case of 22 samples of French wines, the residue following distillation [which was performed for the separation of ethanol for D/H and ^{13}C analysis using an automated distillation control system (ADCS)].

The aim was to check if, as earlier work had indicated [27, 28], the difference in the $\delta^{18}\text{O}$ values between must and related wine really was negligible (about 0.2%), as this would mean that there is no influence of fermentation on the $\delta^{18}\text{O}$ value of wine (during which a remarkable amount of oxygen is removed from the wine as carbon dioxide). The second question was, how does distillation introduce a remarkable shift in the ^{18}O content of wine water? From the results (Fig. 2A, B must and wine from Italy and Germany, vintage 1993; Fig. 3 wine and distillation residue from France, vintage 1993) it was evident that the enrichment of ^{18}O during the fermentation process was rela-



A



B

Fig. 2A, B Correlation between the $\delta^{18}\text{O}$ values of water from must and the related wines from Germany (A) and Italy (B)

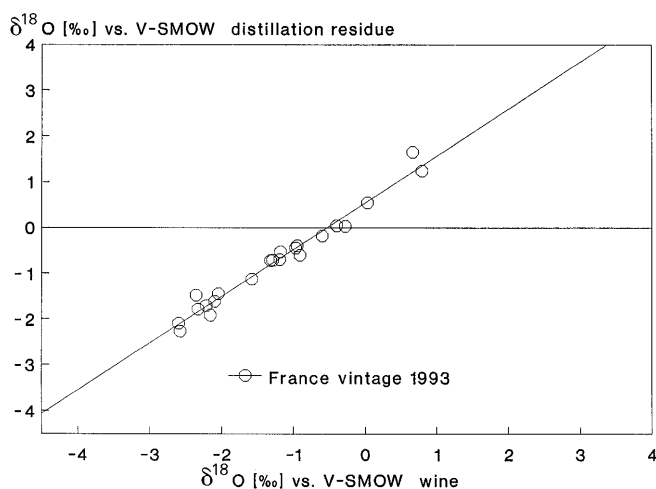


Fig. 3 Correlation between the $\delta^{18}\text{O}$ values of wine water and the related distillation residue of French wine

tively insignificant (about 0.2%) but the influence of distillation on the ^{18}O content was significant, although not large, even if this was only true for a specific distillation system (Cadiot ADCS). As different distillation systems are in use within the EU (Cadiot, Bullio, Normag), and have already been found to produce slightly different isotopic values for distillates, if not applied in an appropriate way [32], the same can be suspected for the ^{18}O contents of the distillation residues. Thus, in order to avoid an additional source of error or disagreement between different EU laboratories, the direct measurement of ^{18}O in wine has been accepted as an officially recognised method recently [19].

Range and annual variation of ^{18}O content of wines

It should be noted that, unlike the stable isotope parameters, $(\text{D}/\text{H})_{\text{I}}$ (deuterium/hydrogen ratio of the methyl group), $(\text{D}/\text{H})_{\text{II}}$ (deuterium/hydrogen ratio of methylene group of ethanol) and $\delta^{13}\text{C}$ of ethanol, the $\delta^{18}\text{O}$ value of must or wine water is more rapidly influenced and altered by changing climatic conditions (within a few days remarkable changes may occur, e.g. see Fig. 4A, B showing the trend of $\delta^{18}\text{O}$ values in wine from Germany and France during the harvesting period).

In Figs. 5A–D the mean ^{18}O values for wine from different regions in France and Germany for 1993 and 1994 are given; this information has already been published in detail for Italy [15, 33, 34]. Some examples of the ranges of these values for the same region in different years from 1991 to 1996 are given in Table 1. It was clear (Figs. 5A–D, Table 1) that, generally, wine from southern France or Italy was remarkably high in ^{18}O ($\delta^{18}\text{O} > 5\%$) as compared to most wine from Germany, northern Italy or certain parts of France (north, north-east, alpine regions, where the $\delta^{18}\text{O}$ value was from +1 to -2% usually, and sometimes, due to specific climatic

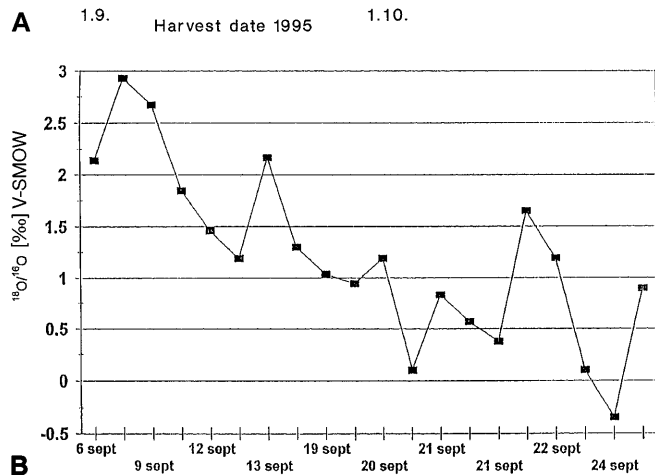
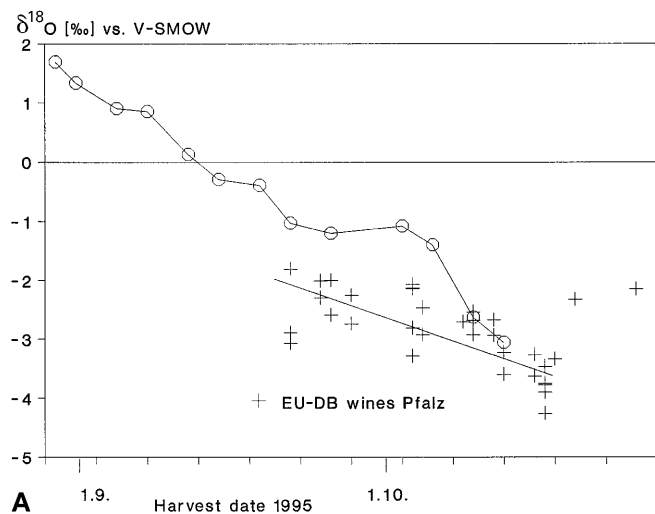
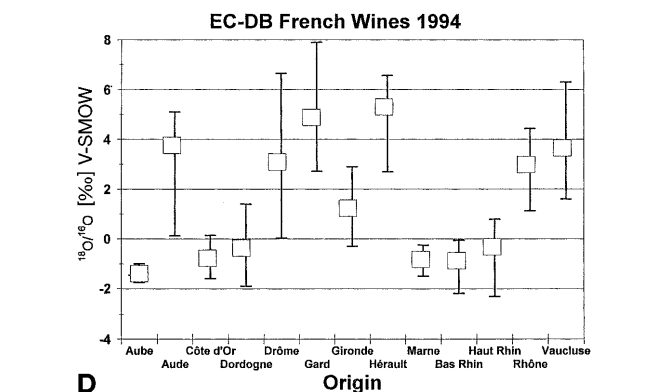
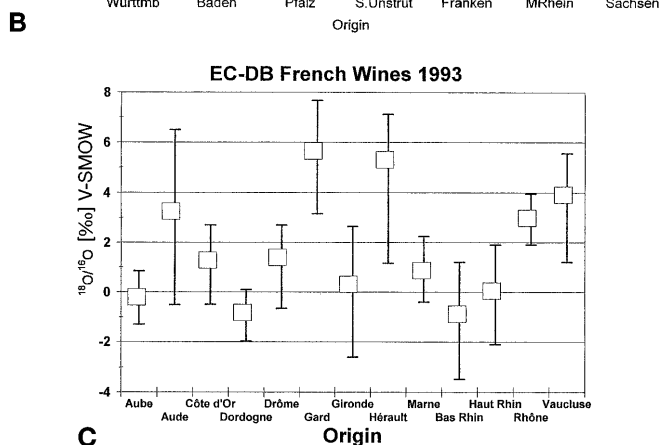
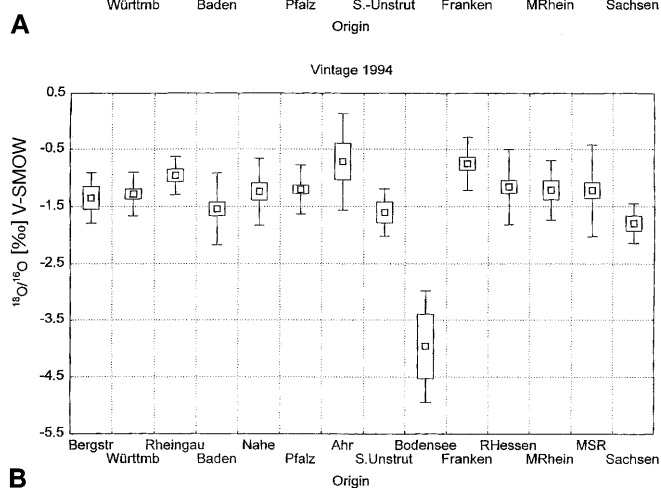
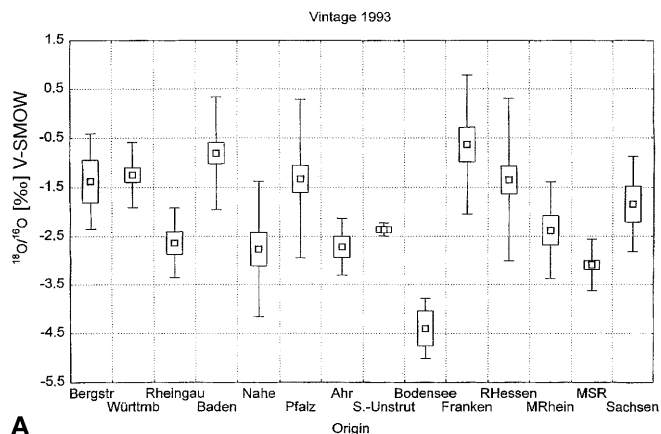


Fig. 4A, B Trend of the $\delta^{18}\text{O}$ values of wine water during the harvesting period for a certain region and vintage in Germany (**A**; Pfalz, 1995) and France (**B**; Bordeaux 1994). \circ Samples from the same vineyard, *EU-DB* EU data bank samples

conditions, even lower), as has already been described [15, 22–25, 28, 33, 34]. The reason for this is that precipitation and soil water in southern Europe is enriched with ^{18}O and ^2H , as compared to that in northern European, especially alpine regions (due to the effects of temperature, altitude, distance from the sea, and amount of precipitation [28]). Differences in the isotopic content of water supplied to the vines are additionally increased as a consequence of higher evaporation of water from vines growing in dry and hot environments as compared to those from cooler and more humid locations. As a result, the differences between the ^{18}O contents of the vines and, subsequently, must and wine

Fig. 5A–D Box-whisker diagrams for mean $\delta^{18}\text{O}$ values of water in EU-DB wines from German (**A**, **B**) and French (**C**, **D**) wine-producing regions for two different years with remarkably different absolute $^{18}\text{O}/^{16}\text{O}$ ratios. (*centrepoint* = mean, *box* = mean \pm SE, *whisker* = mean \pm SD. *Bergstr* Bergstraße, *Würtmb* Württemberg, *S-Unstrut* Saale-Unstrut, *Bodensee* Lake Constance, *RHessen* Rheinhessen, *MRhein* Mittelrhein, *MSR* Mosel-Saar-Ruwer)



D

Table 1 Mean $\delta^{18}\text{O}$ values in [‰] (\pm SD, n given in parentheses) and variation between vintages of EU data-bank wines from wine-producing regions in Italy, France and Germany as examples showing the variability of the $\delta^{18}\text{O}$ values in different years

Country (regions)	Vintage		Variation
Germany	1993	1994	
Ahr	-2.72 ± 0.58 (7)	-0.72 ± 0.85 (7)	2.00
Mittelrhein	-2.38 ± 0.99 (11)	-1.23 ± 0.53 (10)	1.15
Mosel	-3.12 ± 0.52 (32)	-1.25 ± 0.79 (34)	1.87
Nahe	-2.69 ± 1.40 (15)	-1.32 ± 0.58 (13)	1.37
Rheingau	-2.64 ± 0.72 (9)	-0.96 ± 0.33 (9)	1.68
Italy	1993	1996	
Abruzzo	$+5.16 \pm 0.85$ (16)	$+0.71 \pm 1.01$ (16)	4.45
Calabria	$+7.06 \pm 0.71$ (8)	$+2.83 \pm 1.29$ (15)	4.23
Campania	$+4.40 \pm 0.88$ (17)	$+1.11 \pm 1.31$ (30)	3.29
Emilia Romagna	$+3.31 \pm 1.21$ (18)	-0.84 ± 0.98 (36)	4.15
Lazio	$+5.05 \pm 1.17$ (11)	$+1.64 \pm 1.50$ (29)	3.41
Marche	$+3.90 \pm 0.91$ (51)	-0.57 ± 1.19 (30)	4.47
Molise	$+5.66 \pm 1.31$ (6)	$+1.19 \pm 0.72$ (15)	4.47
Puglia	$+7.05 \pm 1.28$ (37)	$+2.38 \pm 1.65$ (41)	4.67
Umbria	$+4.15 \pm 1.12$ (33)	$+1.03 \pm 1.05$ (37)	3.12
Veneto	$+2.53 \pm 1.89$ (47)	$+0.02 \pm 1.25$ (46)	2.51
France	1993	1994	
Aube	-0.17 ± 0.60 (10)	-1.46 ± 0.35 (10)	1.29
Cote d'Or	$+1.20 \pm 1.30$ (8)	-0.80 ± 0.60 (8)	2.00
Drome	$+1.40 \pm 1.27$ (7)	$+3.13 \pm 2.01$ (7)	1.73
Marne	$+0.97 \pm 0.68$ (14)	-0.70 ± 0.60 (14)	1.67

water from such different regions are usually even higher than those found for the water supplied to the plants from the soil.

The variation between years was particularly evident for certain years for wine from some regions in Germany, Italy (even southern Italy) and France (Table 1, Fig. 5A–D).

Regional and temporal variations of ^{18}O contents

The mean values and range of variation for the different regions of each country (Fig. 5A–D; Table 1) could be roughly interpreted as indicating a trend of decreasing ^{18}O contents from the south to the north of Italy and France (and thus from warm to colder areas) [15, 33, 34]. In Germany, no such clear regional pattern was evident; the German wine-producing regions are too similar with respect to climate, and in most cases the mean $\delta^{18}\text{O}$ values were within a range of from 0 to -1.5‰ (Fig. 5A, B), and 1993 wine from the Nahe, Ahr, Mittelrhein and Mosel-Saar-Ruwer regions had exceptionally low $\delta^{18}\text{O}$ values (from -2.5 to -3.0‰), and wine from the Lake Constance area often exhibited peculiarities with $\delta^{18}\text{O}$ values even lower than -5‰ . The vintages of 1995 and 1996 showed unusually low ^{18}O contents of wine water for all German regions. To our present knowledge, the variation in, and, especially very low $\delta^{18}\text{O}$ values, which could easily be interpreted as indicating the addition of water when this type of specific information is not available, were a result of cold and humid climatic conditions during the harvesting of the grapes in certain regions and the low ^{18}O content of the precipitation, e.g. for the Lake Constance region or for Piemonte, Trentino and Alto Adige. This showed that the time of harvest is a very

critical factor in the case of wines from regions which experience climatic instability and rapid changes of climatic parameters, such as temperature or humidity, during the harvest. Our results, as well as data from the literature [33, 34], gave clear evidence of remarkable shifts in the $\delta^{18}\text{O}$ values towards more negative values within a relatively short period of time (Fig. 4A, B). In some years this effect was very pronounced, as the grapes which ripened first were harvested under favourable climatic conditions, while those harvested later (due to the variety) were affected by worse climatic conditions. For Germany, in 1993, favourable conditions were present at the beginning of the harvest (which was early that year) but they deteriorated as the harvest continued and a significant reduction in the $\delta^{18}\text{O}$ values occurred (Fig. 6A, 1993). In contrast, in 1994, unfavourable climatic conditions were present even before the harvest began, and we observed low ^{18}O contents from the beginning of the harvest, but no remarkable decrease towards the end of the harvest (Fig. 6B, 1994).

The same could often be observed for wines from northern Italian regions, such as the Alto Adige, Trentino, and Piemonte [15], and even more southern regions often exhibited a remarkable decline in the $\delta^{18}\text{O}$ values of wine, but, with the exception of years with extreme climatic conditions, the $\delta^{18}\text{O}$ values remained higher for wine from southern regions (Fig. 6A, B; Puglia 1993, 1994).

Variations of ^{18}O content caused by the variety

From the strong impact of climate during the ripening and harvesting of grapes it was clear that varieties which mature early (in Germany, e.g. Ortega, Spätbur-

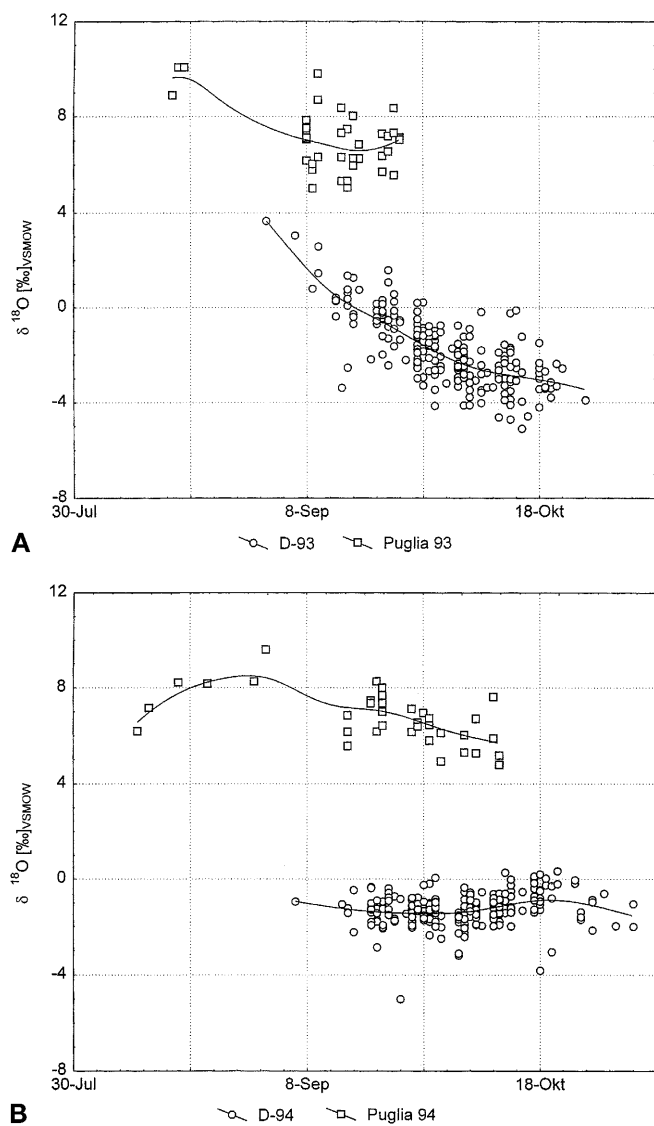


Fig. 6A, B General trend of the $\delta^{18}\text{O}$ values in wine water for EU-DB wines from Germany (D) and from the Italian region of Puglia in 1993 (A) and 1994 (B) in relation to the harvesting date

gunder, Müller-Thurgau; in Italy often white varieties such as chardonnay and pinot grigio) usually lead to higher $\delta^{18}\text{O}$ values of the wine water, as compared to late-ripening varieties (in Germany, e.g. Silvaner, Riesling; in Italy most of the red varieties), if “normal” climatic conditions prevail. As the most important parameters are the harvesting date together with the specific climatic conditions experienced by the grapes of a vintage, a late-ripening variety, which is, for certain reasons, harvested early, may produce wine with a high $\delta^{18}\text{O}$ value, while an early-ripening variety, harvested late, will behave like a late-ripening one (i.e. produce wine with low $\delta^{18}\text{O}$ values). Thus, the influence of the variety on the $\delta^{18}\text{O}$ values is an indirect one, and for the reliable evaluation of the $\delta^{18}\text{O}$ value of a given wine, assuming that the country and region of origin is

known, the year of harvest, the climate during the ripening time and the harvesting date must be taken into account.

Influence of location

Unpublished results for wines from the German region of Franken produced over a 6-year period indicated that there was an effect due to location, as certain places always gave higher $\delta^{18}\text{O}$ values than the mean values, while others regularly showed low ^{18}O contents of wine water. But, as mentioned above, the harvesting date must be taken into account too, and as the same varieties are always harvested from the same area (i.e. either early-ripening or late-ripening varieties), the influence of the harvesting date could even be interpreted as an indirect effect of location. However, there was indeed an effect of the location per se, as shown by an experiment, employing repeated sampling of wine prepared from two locations close to each other (a few kilometres distance), using the same grape variety (Riesling) from the same region (Pfalz) harvested at the same time (13–29 September 1993). Both wines showed a very constant difference in their $\delta^{18}\text{O}$ contents (Fig. 7) of about 1.5‰, which was not affected by the reduction in their $\delta^{18}\text{O}$ values due to changing climatic conditions. The main difference between the locations is the type of the soil; one has a high amount of sand, while the other has an appreciably high content of clay, which causes differences in water movement and the velocity of water supplied to the plants. This leads to different $\delta^{18}\text{O}$ values of the water in must and wine, too. The influence of location on the $\delta^{18}\text{O}$ values of wine should be studied further, in order to enable the prediction of peculiarities in the $\delta^{18}\text{O}$ values of wine from certain vineyards.

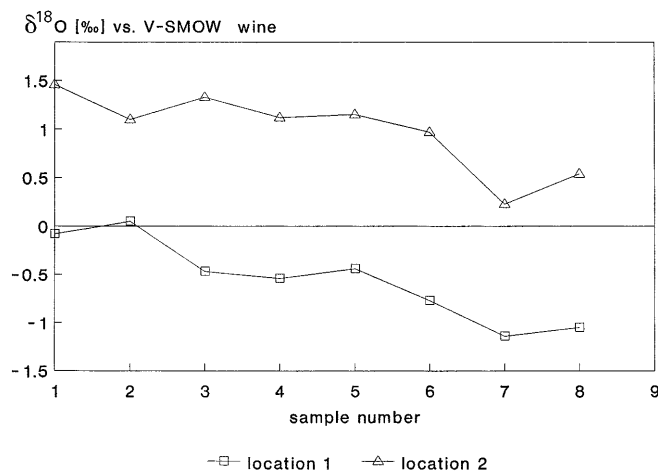


Fig. 7 $\delta^{18}\text{O}$ values of wine water during the harvesting period for wine from the same region (Pfalz, Germany), vintage (1993) and variety (Riesling), harvested on the same dates and at vineyards located about 5 kilometers from each other, but with different soil conditions. Location 1 clay soil, location 2 sandy soil

Results for spiked samples

One aim of this project was to check the usefulness and the comparability of the results for spiked samples. To achieve this three samples of watered-down wine were produced after mixing specific quantities of tap water to unadulterated musts from France, and northern and southern Italy. The results showed (Table 2) that, in spite of slightly different absolute ^{18}O contents found for the same samples by the different laboratories, the degree of adulteration as calculated from the $\delta^{18}\text{O}$ values was in good agreement with the real value, and the results from the three laboratories concerning the amount of added water compared well. Even though this experiment using spiked samples has no great applicability, as the water used to dilute a wine and the original, unadulterated wine are not usually available in the case of suspicious wines, the results prove the workability of the method. In practice, the genuine wine is represented by selected EU-DB samples, which have to be chosen carefully, and for the water a reasonable $\delta^{18}\text{O}$ value must be employed, too (i.e. the known $\delta^{18}\text{O}$ value for groundwater of the region where the wine originates).

Conclusions and perspectives for further work

The $\delta^{18}\text{O}$ values of wine water can be a useful parameter for the detection of water addition to wines. According to the results of our investigation, the $\delta^{18}\text{O}$ results for a given sample of EU-DB wine must be interpreted after having carefully taken into account the vintage, the region of origin, and the harvesting date (if available), together with detailed knowledge of climatic parameters for the region of production during the harvest. Further, the additional determination of the $\delta^2\text{H}$ values of wine water and the correlation of $\delta^{18}\text{O}$ and

Table 2 Spiked (watered-down) wine samples from Italy (sample A northern Italy, sample B southern Italy) and from France (C) produced by addition of known amounts of water. Water added (%) calculated from the $\delta^{18}\text{O}$ values for the wine water determined by laboratories I–III. n.d. Not detected

Must plus water	$\delta^{18}\text{O}$ (‰) in wine water			Water addition (%)		
	I	II	III	I	II	III
A	+2.51	+3.06	+2.75	–	–	–
Water	–10.13	–10.00	–10.00	–	–	–
A +10% Water	+1.28	+1.66	+1.45	9.7	10.7	10.2
A +30% Water	–1.24	–0.97	–1.10	29.7	30.9	30.2
B	+5.31	+5.48	+5.40	–	–	–
B +10% Water	+3.59	+3.95	+3.80	11.1	9.9	10.4
B +30% Water	+0.46	+0.78	n.d.	31.3	30.5	–
C	+5.03	+5.49	+5.25	–	–	–
Water	–6.12	–6.04	–5.80	–	–	–
C +10% Water	+3.78	+4.38	+4.15	11.2	9.6	10.0
C +15% Water	+3.24	+3.68	+3.50	16.1	15.7	15.8
C +20% Water	+2.75	+3.11	+3.05	20.4	20.6	19.9

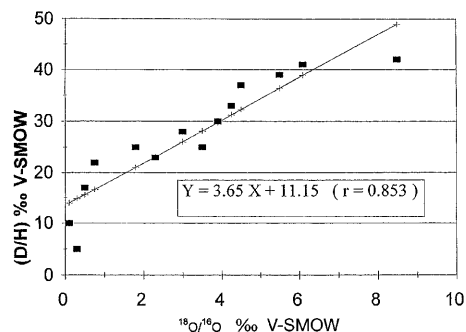


Fig. 8 Correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water of authentic French wine, 1994 vintage

$\delta^2\text{H}$ values (Fig. 8) has been found to be useful for the confirmation of the watering-down of wine, but it must be taken into account that the $\delta^2\text{H}$ value of wine water changes radically during fermentation; this shift in the D/H ratio is related to the amount of sugars converted into ethanol. Additionally, the direct measurement of $\delta^2\text{H}$ values in wine water is not possible, as all available methods for this require the use of wine which does not contain ethanol, which means the residue remaining after distillation has to be employed. Recently, a method based on the platinum-catalysed equilibration of the distillation residue of wine with hydrogen gas was described as a fully automated, commercially available method for the measurement of D/H in wine water [35].

The $(\text{D}/\text{H})_{\text{II}}$ values, that is the hydrogen isotope ratio of the methylene group of ethanol as measured by ^2H -NMR, also correlated with the $\delta^{18}\text{O}$ values (Fig. 9; [33, 34]). However, the correlation was also affected by the amount of sugar converted into ethanol.

To prove the authenticity of a certain wine, the combination of the $(\text{D}/\text{H})_{\text{I}}$, $(\text{D}/\text{H})_{\text{II}}$ and $\delta^{13}\text{C}$ values of the ethanol and the $\delta^{18}\text{O}$ value of the wine water was found

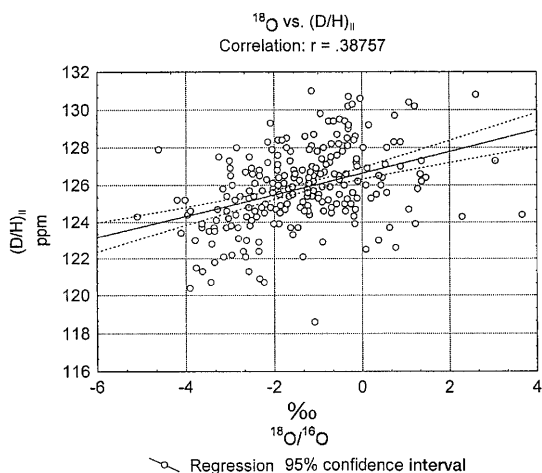


Fig. 9 Correlation between the $\delta^{18}\text{O}$ values of wine water and the $(\text{D}/\text{H})_{\text{II}}$ values of wine ethanol for German EU-DB wines, vintage 1993

to give the most reliable indication of origin [15, 33, 34], when the results were compared to those for the EU-DB wines of the same vintage from the same region. The additional measurement of the strontium isotope ratio could possibly be used to confirm the regional provenance assignment [36]. New experiments should also be carried out in order to correlate the oxygen isotope content of the organic ingredients of wine (ethanol, methanol, glycerol) with that of the water, in order to possibly enable the internal standardization of the $\delta^{18}\text{O}$ measurement of the wine water by comparing the $\delta^{18}\text{O}$ value of water and organic substances. As this requires the use of techniques for the oxygen isotope analysis of organic substances which have only been developed very recently [37, 38], this type of research has only just been initiated, and the technique will probably only be available for use in routine analyses in some years' time.

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