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Determination of CO_2 origin (natural or industrial) in sparkling bottled waters by $^{13}C/^{12}C$ isotope ratio analysis

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Abstract

This paper describes an isotope control method designed to identify the origin of CO_2 in sparkling bottled waters. The method is based on the analysis of the $^{13}C/^{12}C$ ratio in the dissolved inorganic carbon (DIC) of carbonated bottled water. Natural carbonated natural water has $\delta^{13}C_{PDB}$ (DIC) values between $-8‰$ and $+7‰$. Generally, the industrial carbon dioxide injected into mineral bottled water is produced from hydrocarbons by burning or chemical processing. Hydrocarbons, and their derived CO_2, are characterised by a low $^{13}C/^{12}C$ ratio. Thus, a single analysis distinguishes the carbon dioxide in the bottled water (i.e. either from a natural source or added exogenous CO_2 of industrial origin). Rarely, CO_2 can be obtained from other industrial sources, mainly as a by-product of fermentation plants. Nevertheless, the carbon isotope fingerprint allows detection of the industrial gas injected in most of these cases.

Keywords: Natural carbonated water; Sparkling water; Carbon-13; CO_2

1. Introduction

From the 1970s several isotope techniques that allow checking the authenticity of natural food products by isotope techniques have been discovered and developed. In this way, the differentiation between cane and beet sugars, the identification of honeys, the discrimination between natural and synthetic vanillas or the differentiation of animal protein and fat are a few of the possibilities cited by Hillaire-Marcel (1986). Some of these methods are based on techniques of dating by radioactive isotopes. Thus the ethanol of a recent wine has a natural level of ^{14}C decay but wines adulterated with synthetic alcohol show a notable reduction of such radioactivity. Other methods make good use of the small variations that isotope ratios of light elements show in materials. Many physical, chemical and biological processes cause a significant isotope fractionation of light elements. This paper develops one of these methods, based on the analysis of stable isotopes. The result of only one analysis of the ratio $^{13}C/^{12}C$ allows detection of the origin of the CO_2 in bottles of sparkling water. The method is able to detect whether the carbon dioxide is naturally merged with the water or whether it is of industrial origin and was added to the water in the bottling plant.

The bottled water market worldwide is over 70×10^9 l annually. Still water rather than sparkling water is the leading segment in volume sales, having approximately 2/3 of the market, except in Eastern Europe where the sparkling form is more popular (Rowlands, 2001). Germany, Italy and France remain the most important

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manufacturers and consumers of sparkling water with more than 100 l/capita annually. Germany produces more than 6×10^9 l from 285 manufacturers, while, in Italy, the production is 800 million litres (Fortuna, 1993).

The European Union normative distinguishes three kinds of sparkling bottled water according to the Council Directive 80/777/EEC (Anonymous, 1980):

(a) *naturally carbonated natural mineral water* means water whose content of carbon dioxide from the spring after decanting, if any, and bottling is the same as at source, taking into account, where appropriate, the reintroduction of a quantity of carbon dioxide from the same water table or deposit equivalent to that released in the course of those operations and subject to the usual technical tolerances.
(b) *natural mineral water fortified with gas from the spring*, i.e. water whose content of carbon dioxide from the water table or deposit after decanting, if any, and bottling is greater than that established at source.
(c) *carbonated natural mineral water*, i.e. means water to which has been added carbon dioxide of an origin other than the water table or deposit from which the water comes.

The use of a natural or an industrial gas in the bottling of effervescent water is not relevant from a health point of view. But, in some sites, the deep CO_2-rich waters emerge with traces of toxic substances. In those circumstances, the purification of fluids is essential in order to maintain the legal limits. In 1989, North Carolina regulators issued a report stating that the famous Perrier's bottled water was contaminated with benzene. Apparently, the filters of active carbon used for the purification of gas in the bottling plant were saturated and not renewed in time. Water with a relatively high content of benzene was bottled and sold in the USA and Europe. In 1990, the US Food and Drug Administration made Perrier drop the words *Naturally Sparkling* from its label since investigators had discovered that Perrier artificially carbonated its water after taking it out of the aquifer. Certainly the famous Perrier shock promoted the use of industrial CO_2 in order to avoid sanitary and legal troubles.

2. Materials and methods

2.1. Methodological basis

Carbon has two stable isotopes (^{12}C, ^{13}C) and six radioactive isotopes of which ^{14}C is perhaps the best known by its use as a dating method of organic material. Abundance of the two stable isotopes is about 98.9% and 1.1%, respectively, and the proportion of ^{14}C is less than 10^{-12}% (IUPAC, 1991).

The carbon isotope composition, $^{13}C/^{12}C$, is usually indicated in delta notation, $^{13}\delta$ (‰) or $\delta^{13}C_{PDB}$ (‰), defined by the formula

$$\delta^{13}C = [R_{(sample)}/R_{(standard)} - 1] \times 1000,$$

where R is the molar ratio of the heavy to light isotope, $^{13}C/^{12}C$. International agreement recognised a fossil in calcium carbonate, the Pee Dee Belemnite (PDB), $R = 0.0112372$ as standard $\delta^{13}C = 0$‰. Positive $^{13}\delta$ means a relative enrichment of the material in the heavy isotope with respect to the PDB and negative $^{13}\delta$ values mean a lighter composition than PDB.

Inorganic carbon in natural water consists of the following species and concentrations:

(a) Gaseous CO_2, (CO_{2g}),
(b) Dissolved CO_2, (CO_{2aq}),
(c) Dissolved carbonic acid H_2CO_3, $(H_2CO_3) + (CO_{2aq})$,
(d) Dissolved bicarbonate, (HCO_3^-),
(e) Dissolved carbonate, (CO_3^{2-}),
(f) Solid calcium carbonate $CaCO_{3(s)}$ or generically $MCO_{3(s)}$.

The total dissolved inorganic carbon (DIC) generally is the sum of (H_2CO_3), (CO_{2aq}), (HCO_3^-) and (CO_3^{2-}). The concentration of carbonic acid, (H_2CO_3), is negligible. All these species constitute the so-called carbonate system at a dynamic equilibrium. A complex temperature-dependent chain of chemical equilibria is involved between the carbonic species of the water.

2.2. ^{13}C analysis

There are two experimental procedures to obtain the CO_2 required to carry out the analysis of $\delta^{13}C$ in carbonic waters.

(a) *Gaseous CO_2, $\delta^{13}C$.* Sampling, purification and analysis of the CO_{2g} spontaneously exsolved from the water. This method is usually chosen by vulcanologists, who are accustomed to work with gaseous samples.
(b) *Dissolved inorganic carbon, $\delta^{13}C$.* Trapping dissolved inorganic carbon species in the form of $BaCO_3$ or $SrCO_3$ precipitate and carrying out the subsequent quantitative extraction of the CO_2 in the laboratory. Also, this is the ordinary way to sample carbon in order to date groundwater by means of ^{14}C.

In this work method used in Section b was used. DIC was precipitated as $BaCO_3$ by adding saturated solutions of NaOH (to pH > 11) and $BaCl_2$. The solid was separated by centrifugation, rinsed with distilled water and dried at 60 °C. Solid samples were powdered and converted to CO_2 by reacting (at 90 °C) with anhydrous H_3PO_4 (103%) in a vacuum line. Isotope ratio $^{13}C/^{12}C$ of CO_2 was then measured in an isotope ratio mass spectrometer (VG Prism II) using the standards NBS-18 and IAEA-CO-1. The analytical precision in δ was better than 0.2‰.

2.3. $^{13}C/^{12}C$ values in natural carbon geochemical pathways

The isotope composition of DIC in the carbonate systems varies, depending on the contribution of multiple sources and sinks of carbon. Each of these sources contributes to the DIC of groundwater in diverse $^{13}\delta$ compositions and proportions. The $^{13}\delta$ of any groundwater represents a balance struck between all of these processes. The dissolution of CO_{2g} in water produces an enrichment of 3–10 $^{13}\delta$ units, depending on temperature. Furthermore, the precipitation of calcite in the medium will result in an isotopically lighter CO_2 in solution.

Initially, rainwater infiltrates the soil after dissolving a small amount of atmospheric CO_2, which has a $^{13}\delta$ value around −8‰ (Fig. 1). Then rainwater also takes up biogenic CO_2 in the soil zone. It comes from the microbial decomposition of soil organic matter and from root respiration of plants. Soil CO_2 in temperate climates, where Calvin plants live (Calvin photosynthetic pathway, C-3 plants, $^{13}\delta \approx -27‰$) usually has a value of about −22‰ while, in hot and semi-arid areas, the $^{13}\delta$ is −8‰ (Hatch–Slack photosynthetic pathway, C-4 plants, $^{13}\delta \approx -13‰$).

After infiltration, there are two main possibilities of circulation of the water through the aquifer, depending on the lithology:

(a) Aquifers formed by minerals without carbon; the chemical reactions during the flow of water (silicate hydrolysis, redox process, ionic exchange) produce non-significant shift in DIC isotope composition.

(b) Aquifers consisting of marine limestone. Dissolution of calcite by means of the classic reaction

$$CO_2 + H_2O + CaCO_3 \Rightarrow Ca^{2+} + 2HCO_3^-$$

could change the $^{13}C/^{12}C$ ratio. Most marine carbonate rocks have $^{13}\delta$ = −2‰ to 1‰, which produce $^{13}\delta$ (DIC) ≈ −11‰ in temperate climates.

Natural carbonated water is a type of groundwater which receives a high CO_2-gas supply from a different source besides the atmosphere or soil. This gaseous contribution is named deep CO_2. This supply is able to arise from diverse sources and contributes definitely to the genesis of natural carbonated waters. Geochemical processes which can produce large amounts of deep CO_2 are the following:

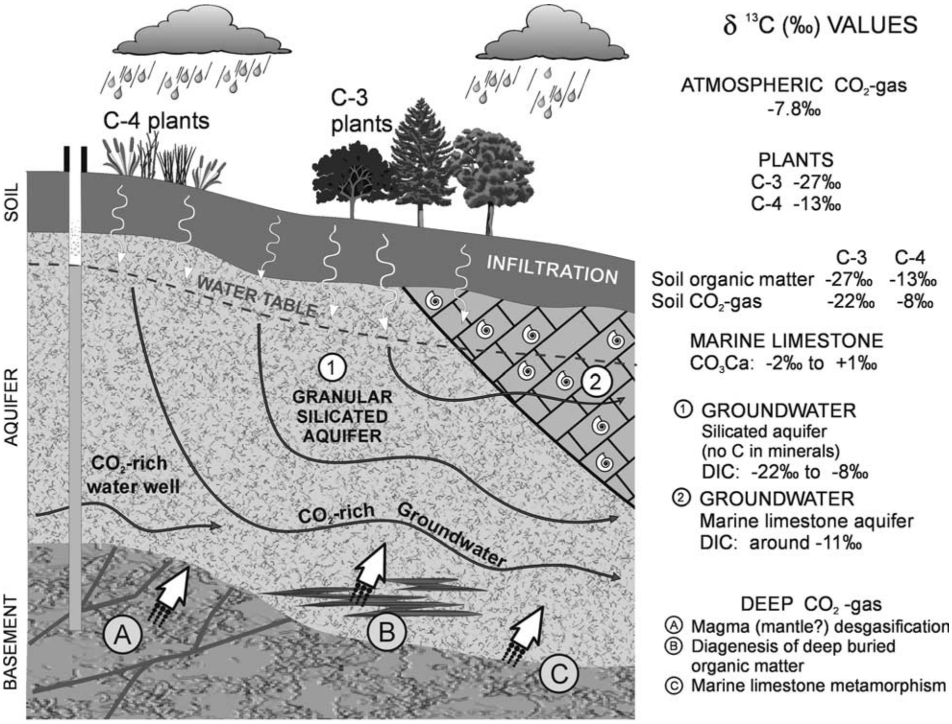

Fig. 1. Values of $\delta^{13}C$ in some geochemical pathways. Not to scale.

(a) Metamorphism of marine carbonate rocks, which produces $^{13}\delta$ (CO$_2$) with similar values to the original marine limestone, between 1‰ and −2‰.
(b) Diagenesis of buried organic matter in deep sedimentary basins.
(c) Mantle-derived magmatic fluids, in which the dominant gas is CO$_2$ with $^{13}\delta$ (CO$_2$) values from −4.7‰ to −8‰ (Barnes, Irwin, & White, 1978).

Theoretically, metamorphism of rocks with high contents of organic matter (oil shale), could free carbon dioxide gas enough to give rise to CO$_2$-rich waters.

3. Results

3.1. C-13 values in natural carbonated waters

Hillaire-Marcel (1986), in a general review centred on the application of isotopes in food control, pointed out a potential use of the $^{13}C/^{12}C$ ratio in order to discover whether the CO$_2$ of a sparkling bottled water was natural or derived from industrial injection. The original article includes only three values of $\delta^{13}C$ (CO$_2$) of natural carbonated waters and estimates the average value of the industrial CO$_2$ as −47‰. The three cited waters are Saratoga (USA), Perrier (France) and Peter Val (France) which show similar values: −5.2‰, −4.4‰ and −4.1‰, respectively. After this previous work, we have not found any more published references to the method. Recent data of $^{13}\delta$ in natural CO$_2$-rich waters give a wider range of values than the three indicated. Also the industrial CO$_2$ can be produced from several sources. Perhaps, in some particular cases, the $^{13}\delta$ fingerprint does not discriminate between an artificial and a natural origin of the gas of the bottles.

As a first step, an inventory was made of carbonic waters in the Iberian Peninsula. The exploitation of CO$_2$-rich waters is traditional as medicinal waters in Spain and Portugal. For this reason, most carbonic springs and wells are well-known. As a second step, sampling of waters was carried out, followed by the analytical work. The isotopic results are compiled in Table 1. This shows $^{13}\delta$ (DIC) values between −6.0‰ and +2.6‰ with an average value of −2.8‰.

The Iberian carbonic water samples come from three different geological sites:

(a) Galicia and North of Portugal. CO$_2$-rich waters are located on plutonic and metamorphic rock. There is no volcanic rock in this region.
(b) Catalonia. Likewise the springs are sited on plutonic rock but in this area there are outcrops of recent volcanic rock (Late Tertiary-Quaternary). It seems that the origin of natural carbon dioxide is related to the volcanic episodes.
(c) Campos de Calatrava. This is an area with relatively modern volcanic activity (Late Tertiary); nevertheless the points where CO$_2$-rich water emerges are on the border of sedimentary basins.

In principle, natural carbonic waters can originate in other different geological contexts from the three referred to from the Iberian Peninsula, for instance by diagenesis of organic matter in deep sedimentary basins. For this reason, an exhaustive search of bibliographical data about isotopic composition of CO$_2$-rich waters all over the world was carried out. The data capture is in Table 2 and the graphic representation is shown in Fig. 2. Most of the $^{13}\delta$ (DIC) values are in the range of the Iberian water samples. However, in Saratoga Springs (USA), one sample shows a $^{13}\delta$ (DIC) value of −7.9‰ and the Turkish region of Kuzuluk/Adapazari has a $^{13}\delta$ (DIC) value as positive as +6.7‰.

Many of the $^{13}\delta$ values in Table 2 correspond to the analysis of gaseous CO$_2$ directly sampled in the springs or wells. This is because CO$_2$-gas data are frequently collected in volcanic zones, in areas with geothermal anomalies or in specific works on the geochemical origin

Table 1
Carbon isotopic analysis of natural carbonated waters. Springs and wells in the Iberian Peninsula

Name	Location	$\delta^{13}C_{VPDB}$ (DIC)
	Galicia, NW Spain	
Gándara spring	Mondariz	−2.0
Val spring	Mondariz	−4.0
Villaza spring	Villaza	−0.2
Cabreiroá well	Verín	−4.0
Fontenova spring	Verín	−0.9
	North Portugal	
Main spring	Melgaco	−1.2
Borehole	Pedras Salgadas	+2.6
Caldas de Chaves	Chaves	−1.8
Fte. Salus well	Vidago	−3.2
Spring	Bem Saude	−0.5
AC-18 well	Vidago	−1.0[a]
ACP1 well	Vilarelho da Raia	−6.0[a]
	Gerona, Catalonia, NE Spain	
San Narciso	Caldas de Malavella	−4.0
La Mina fountain	Caldas de Malavella	−4.0
Bell-Lloc spring	Santa Cristina de Aro	−3.7
Panedes spring	Santa Cristina de Aro	−4.5
La Pólvora well	Gerona City	−0.6
San Gregorio spring	San Gregorio	−3.3
Corominas spring	San Gregorio	−2.9
Font Picant	Amer	−5.0
Font Picant	San Hilario Sacalm	−4.8
	Campos de Calatrava, Central Spain	
Granátula spring	Granátula de Calatrava	−4.9
Las Tiñosas spring	Solana del Pino	−3.6
Agria spring	Puertollano	−5.6
El Chorrillo spring	Pozuelo de Calatrava	−2.2

[a] Data from Marques et al. (2001).

of terrestrial fluids. The $^{13}\delta$ (CO_2) values are lighter than the same results for $^{13}\delta$ on DIC, according to theoretical fractionation factors.

3.2. C-13 values of industrial CO_2

Carbon dioxide has many industrial applications. In addition to its use in carbonating soft drinks and other effervescent beverages, CO_2 is used as a lightweight refrigerant in the transportation of perishable foods, atmosphere additive in greenhouses, to fill fire extinguishers, as shielding gas in the arc welding process, or as a gas propellant. Consumption of liquid carbon dioxide in the main industrial countries (United States, Western Europe and Japan) in 2002 amounted to 10.6 million metric tons (Suresh & Ishikawa, 2003).

Carbon dioxide can be manufactured by different industrial processes and from diverse sources. The simplest way for soft drinks companies to get the gas is to have their own CO_2 generator. These autonomous plants produce a flue gas rich in CO_2 from the combustion of liquid petroleum or desulphurised natural gas. Besides the specific production plants dedicated exclusively to manufacturing of CO_2, any energy power plant, by combustion of hydrocarbons, supplies a by-product gas consisting mostly of carbon dioxide and nitrogen. Combustion of coal also generates a large amount of gas but with carbon dioxide in low concentration, but these emissions are not commonly recovered for CO_2 production. The main CO_2 source on an industrial scale is as by-product of the synthetic ammonia process (Greenwood & Earnshaw, 1997) in which the H_2 is obtained from oxidation of hydrocarbons: natural gas, light petroleum gases or naphtha. The controlled oxidation of ethylene is another industrial source of carbon dioxide. Again the carbon comes from hydrocarbons.

In all these processes, in which the gas comes from fossil fuels, the carbon isotope composition of the carbon dioxide is identical to the original hydrocarbon because of the negligible isotope fractionation factors involved. The range of negative $^{13}\delta$ values of fossil fuels is wide. The reason is the complicated biogeochemical processes that are involved in the degradation of terrestrial and marine plant material, ultimately into natural gas, liquid petroleum and coal. Degens (1969) made a compilation of 8000 analyses of reduced organic carbon from the literature; the carbon isotope data in crude oils of various geologic ages varies from −18‰ in most recent petroleums (Teriary) to values of −35‰ in petroleums of pre-Devonian age. $^{13}\delta$ values of coals lie between −18‰ and −30‰ and natural gas has a broad range of $^{13}\delta$ values from −18‰ to −74‰.

The fermentation of sugars and starches produces ethanol and CO_2 gas of high purity. In the United States, there has been a marked increase in the number of ethanol plants starting up in the Cornbelt region (Suresh & Ishikawa, 2003) because ethanol is used as an additive compound in motor fuels. Corn is a C-4 type plant and therefore the CO_2 recovered from its fermentation has a $^{13}\delta$ lighter than −13‰, near to the value of the heaviest hydrocarbons.

Summarizing, industrial CO_2 can be manufactured from diverse raw materials, the most important being fossil fuels. These materials and their derivatives show more negative $^{13}\delta$ than most of the values found in the geochemical cycle of carbon. The CO_2 recovery from fermentation plants also has light $^{13}\delta$ values. Considering the possibility of the existence of exceptions to the ranges shown in Fig. 2, nowadays it is unlikely to find on the market an industrial CO_2 with a $^{13}\delta$ heavier than −18‰. In the laboratory where the isotope analyses were performed, industrial CO_2 has been consumed over

Table 2
$^{13}C/^{12}C$ of natural CO_2-rich waters in different countries

Location	$\delta^{13}C(CO_2)$	$\delta^{13}C(DIC)$	Reference
Central Massif and Wertern Alps, France	−8 to −4		Blavoux et al. (1982)
Azerbaijan	−8 to −0.9		Blavoux et al. (1982)
Scuol-Tarasp, Lower Engandine, Suiss Alps	Around −4		Wexteen et al. (1988)
Kuzuluk/Adapazari Area, Turkey		2.42 to 6.69	Greber (1994)
Guandgdong, Southeast China	−6.8 to −8.4		Xu et al. (1997)
Kyselka Area (near Karlovy Vary), Czech Republic	Around −3	Around −7.5 (?)	Möller et al. (1998)
Jungwon Area, South Korea	−7.6 to −4.5	−5.9 to 0.3	Koh et al. (1999)
Azores Islands, Portugal, Atlantic Ocean	−5.5 to−3		Cruz et al. (1999)
Saratoga Springs, USA		−7.9 to −3.1	Lesniak and Siegel (2000)
Ischia Island, Italy	−5 to 0		Inguaggiato et al. (2000)
Northern Italian Apennines	−10.3 to −0.26		Minissale et al. (2000)
Rapolano and Rome, Central Italy	−7.95 to −1.94		Minissale et al. (2002)
Sprudel, Bad Elster Area, Germany	−4.3 to −5.0		Weinlich et al. (1999)
Eisenquelle, Bad Brambach, Germany	−4.3		Weise et al. (2001)
Eastern Carpathians, Romania	−4.7 to −2.2		Vaselli et al. (2002)
Koros Area, Pannonian Basin, Hungary		−4.2 to −2.1	Varsányi et al. (2002)
Daylesford, Victoria, Australia	−7 to −10.6	−5.9 to −0.1	Cartwright et al. (2002)

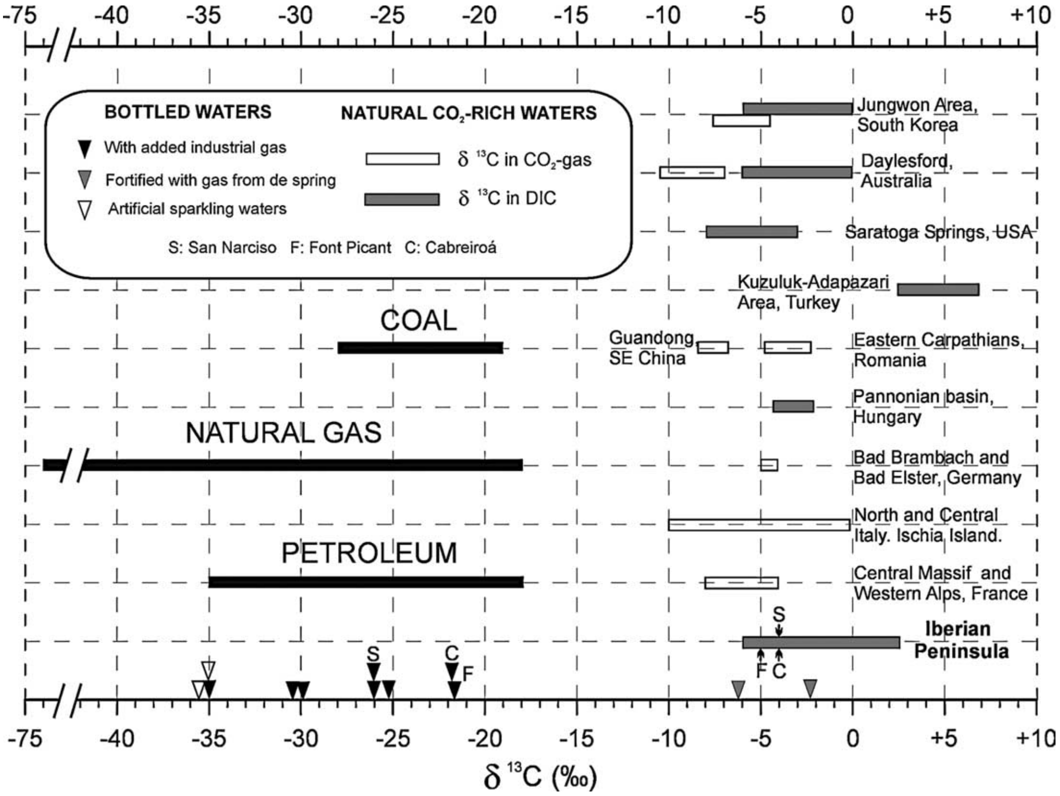

Fig. 2. General view of $^{13}C/^{12}C$ values for fossil fuels, sparkling bottled waters and natural CO_2-rich waters.

12 years. The ^{13}C measured in the CO_2 from diverse manufacturers was never heavier than −29‰. Mook (2000) estimates the global average of CO_2 from the combustion of fossil fuels to be about −27‰. Other potential sources for production of industrial CO_2 are discussed in the next section.

4. Discussión

The compiled $^{13}\delta$ data are shown in Fig. 2. There is a noticeable difference among the $^{13}\delta$ values of natural CO_2-rich waters and the industrial CO_2. It seems that there are no natural carbonic waters with $^{13}\delta$ (DIC) values lighter than −8‰, quite far from the values shown by industrial CO_2 gas. The standard deviation of the $^{13}\delta$ (DIC) analyses in most laboratories is better than 0.2‰. Therefore, as initially expected, the differences found in natural isotope ratios are larger than the uncertainties of the method.

The natural CO_2-rich waters of Daylesford (Australia) have the lowest $^{13}C/^{12}C$ ratios, but anyway they show values of $^{13}\delta$ (DIC) at least 7‰ more positive than the isotopically heaviest hydrocarbons.

As a complementary task, we collected and analyzed all sparkling waters found on the Spanish market. The $^{13}\delta$ results are shown in Table 3 and are graphically represented in Fig. 2.

Most bottled waters correspond to carbonated natural mineral waters, which are exploited from natural carbonic springs or wells. In these cases, the δ^{13} (DIC) lies between −20‰ and −35‰, which shows the use of industrial CO_2. In three cases (Cabreiroá, Font Picant and San Narciso) we have the δ^{13} (DIC) taken from the spring besides the δ^{13} (DIC) of the commercial bottled water. The differences in δ^{13} (DIC) values are more than 15 units, showing heavier ratios in natural samples.

Isotope analysis was also carried out on two French waters classified on their labels as "natural mineral water fortified with gas from the spring". In this case, the DIC of the waters keep the isotope fingerprint in the expected range of natural CO_2-rich waters. Thus, the determination of δ^{13} (DIC) does not distinguish between naturally carbonated natural mineral water and natural mineral water fortified with gas from the spring.

The injection of 1 or 2 g/l of industrial gas in order to carbonate a natural mineral water generally increases the initial amount of DIC by 50–80%. Even if the original DIC has a δ^{13} (DIC) value negative or close to 0, the addition of exogenous gas contributes largely to the isotope mass balance and it is easy to detect it.

In the 19th and part of the 20th century, some boreholes were drilled in areas with natural CO_2-rich waters in order to obtain carbon dioxide for use in the manu-

Table 3
Carbon isotopic values of effervescent bottled waters

Trade mark	Location	$\delta^{13}C_{VPDB}$ (DIC)
Spanish natural mineral waters with added industrial carbon dioxide		
Vichy Catalán	Caldas de Malavella, Gerona	−25.2
Malavella	Caldas de Malavella, Gerona	−30.5
San Narciso	Caldas de Malavella, Gerona	−26.0
Fonter	Amer, Gerona	−26.1
Font Picant	Amer, Gerona	−21.7
Cabreiroá	Verín, Orense	−21.9
Fuente Primavera	Huerta del Marque., Cuenca	−29.9
Marmolejo	Marmolejo, Jaén	−35.0
Mineral waters fortified with gas from the spring		
Perrier	Vergeze, France	−6.2
Vichy Celestins	Vichy, France	−2.3
Artificial sparkling waters		
Geiser-Sifón		−35.6
Siti-Lidl		−35.1

facture of soda pop and other carbonated drinks. This source of CO_2 is clearly not enough nowadays because of the need for CO_2 in the world market. Furthermore, the excessive number of boreholes causes a severe decrease in the flow rate of natural carbonated springs, for instance in Saratoga Springs (Back, Landa, & Meeks, 1995). Nowadays, some companies have difficulties in producing natural CO_2-rich waters for the market, and instead dispose of surplus CO_2 to produce soda drinks. In this situation, it could be that certain companies sell carbonated natural mineral water, labelling it as naturally carbonated natural mineral water.

Historically, CO_2 was obtained by pouring acid on limestone. This method was first used by the Schweppes Company, the earliest bottler of carbonated water, in a factory opened in London in 1792 (Back et al., 1995). Since the δ^{13} value of marine limestone is in the same range as that of natural CO_2-rich waters, it could be an alternative method for production of carbonated waters without isotope fingerprint.

The production of CO_2 from marine limestones is more efficient by calcination than by acid reaction. Another alternative for gas production, really a variation of that previously described, could be the recovery of the CO_2 produced in the neutralisation of acid industrial waste streams which is usually carried out using marine limestone in the acid–base reaction.

Finally, in certain cases, it is feasible to detect the addition of industrial CO_2 by analysing ^{14}C. In general it is not possible to date the carbonic waters with this isotope because the deep CO_2 contains only dead carbon, without ^{14}C. Equally, the carbon dioxide from hydrocarbons has no radioactivity. If the analysis of ^{14}C of carbonic water indicates a recent age, it implies the addition of modern biogenic CO_2, obtained from ethanol plants. Anyway, such addition can be detected by the simpler analysis of stable carbon isotope.

5. Conclusion

This work shows that a single analysis of $^{13}\delta$ carried out on sparkling bottled water distinguishes between the natural or artificial origins of the carbon dioxide. The method is valid by the analysis of $^{13}\delta$ on the DIC and by the $^{13}\delta$ analysis of the gaseous CO_2 of the water. The differences found in the $^{13}\delta$ values of sparkling waters are larger than the standard deviation of the analytical method, usually around 0.2‰.

The method has two limitations. It does not allow detection of sparkling water reinforced with the original gas from the source, nor addition of industrial carbon dioxide produced from marine limestone.

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