Geofísica Internacional
ISSN: 0016-7169
silvia@geofisica.unam.mx
Universidad Nacional Autónoma de México
México

Favara, Rocco; Grassa, Fausto; Inguaggiato, Salvatore; Pecoraino, Giovannella; Capasso, Giorgio
A simple method to determine the δ13C content of total dissolved inorganic carbon
Geofísica Internacional, vol. 41, núm. 3, july-september, 2002, pp. 313-320
Universidad Nacional Autónoma de México
Distrito Federal, México

Geofísica Internacional (2002), Vol. 41, Num. 3, pp. 313-320

A simple method to determine the $\delta^{13}C$ content of total dissolved inorganic carbon

Rocco Favara, Fausto Grassa, Salvatore Inguaggiato, Giovannella Pecoraino and Giorgio Capasso
[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy*

Received: September 4, 2001; accepted: April 26, 2002

RESUMEN

Un método sencillo para la determinación de $\delta^{13}C$ del TDIC (Carbón inorgánico total disuelto) en agua fue desarrollado y probado. El método propuesto está basado en la extracción química y física de CO_2 de la muestra de agua. El aparato de muestreo es una botella de vidrio (alrededor de 100 ml) llenada completamente de agua durante el muestreo de campo y cerrada con una tapa de teflón. En el laboratorio se introducen 10 ml de argón como gas huésped en la botella y se quita la misma cantidad de agua. Se inyecta aproximadamente 0.5 ml de HCl superpuro al 37% en la botella. El pH del agua disminuye hasta el valor de 1 y como consecuencia la única especie de carbón presente es el CO_2 tanto como fase disuelta como gaseosa. Posteriormente la botella se conecta a la línea de vacío para extraer el CO_2 gaseoso y purificarlo utilizando las técnicas estandares de purificación del CO_2. Para probar este método se prepararon y analizaron varias muestras de agua de mar, así como una serie de soluciones estándar de Na_2CO_3 de composición isotópica conocida. La precisión de estas medidas fue de ± 0.2 por mil vs V-PDB y la reproducibilidad fue major de 0.2 por mil vs V-PDB.

PALABRAS CLAVE: Isótopos de carbono, TDIC, CO_2, HCO_3, interacción agua - CO_2.

ABSTRACT

A simple method for determining the $\delta^{13}C$ of TDIC (Total Dissolved Inorganic Carbon) in natural waters was developed and tested. The proposed method is based on chemical and physical stripping of CO_2 from water samples. The sampling apparatus consists of a glass bottle (ca 100 ml) totally filled with water sample in the field and sealed by gas-tight rubber/teflon plug. In the laboratory, we introduce 10 ml of pure Ar as host gas into the bottles and draw out an equal volume of water. About 0.5 ml of 37% extra-pure HCl is then injected into the bottle. Water pH decreases to values close to 1 and, therefore, the only carbon species present is CO_2 both as dissolved and gaseous phase. Then the bottle is connected to a vacuum line to extract CO_2 gas and to purify it by means of standard techniques for CO_2 purification. In order to test this method, several sea water samples were prepared and analysed, as well as a series of standard solutions of Na_2CO_3 at known isotopic composition of carbon. The accuracy of these measurements was ± 0.2 ‰ vs V-PDB and their reproducibility was better than 0.2 ‰ vs V-PDB.

KEY WORDS: Carbon isotopes, TDIC,CO_2, HCO_3 , CO_2- water interaction.

INTRODUCTION

In the past, several methods of sample preparations to determine the $\delta^{13}C_{TDIC}$ have been proposed. All methods imply the use of chemical reagents, and time consuming sampling and analytical procedures. The most used techniques are based on two main methods. The first consists in the precipitation of total dissolved inorganic carbon (TDIC) as precipitated carbonates by using $Ba(OH)_2$ or $Sr(OH)_2$. The second is performed by acidification with phosphoric acid of samples so as to shift the chemical equilibrium among dissolved carbon species towards CO_2, which can be easily removed from water.

The most used precipitation techniques (Gleason *et al.*, 1969; Barnes *et al.*, 1978) consist in the addition of an ammoniacal $SrCl_2$ alkaline solutions in the water samples in order to precipitate $SrCO_3$. Subsequently, by using standard techniques, this carbonate reacts with H_3PO_4 in a vacuum line and liberates CO_2 (McRea, 1950; Rosembaum and Sheppard, 1986). These methods imply the use of large amounts of sample (about 1000 ml) and several steps of sample preparation, such as filtering and drying under a controlled (carbon-free) atmosphere, homogenization of the precipitate and its reaction with acids to form a CO_2 gas phase.

Further TDIC extraction techniques based on gas evolution have been proposed (Games and Hayes, 1976; Hassan, 1982) aimed to simplifying the sampling and analytical operations. Water samples are collected in glass syringes or bottles, filled totally, with no head space. Samples react with 100% phosphoric acid in a closed system. The CO_2 gas liberated is pumped off slowly through an ice cold trap (-80°C) and then collected in a liquid nitrogen cooled trap (-196°C).

However, dynamic flow conditions do not ensure the complete trapping of vapour water within the ice cold trap.

A rapid procedure has been recently proposed (Mc Nicol *et al*., 1994) for preparation of seawater TDIC for radiocarbon analysis, by using a gas evolution technique. Unlike other methods, CO_2 stripping does not occur under vacuum conditions, but under a re-circulating flow of high-purity N_2 gas. The average analysis time depends on the TDIC content. A seawater sample (*ca.*1 mmol CO_2) requires about 45 min for preparation.

A modification of the gas evolution technique (Atekwana and Krisnamurthy, 1998), which involves the use of glass septum tubes (VACUTAINER®) as sampling apparatus has been recently proposed. Before sampling, 0.5 ml 85% H_3PO_4 and a magnetic stir bar are introduced in the tubes. Then tubes are connected to a vacuum line and evacuated. In the field, water samples are injected into vacutainer tubes by use of a syringe. The amount of samples that has to be injected into the tubes is inversely proportional to TDIC content. In the laboratory, the septum tubes are placed in a water bath (50°C) on a magnetic stirrer and then connected to a vacuum line. CO_2 extraction proceeds for 5 minutes with constant stirring. The extracted CO_2 is then cryogenically purified. In our opinion, this method is not suitable with water samples characterized by large amounts of TDIC because of very high CO_2 pressures derived from the reaction between phosphoric acid and water. In the following section, we propose a method for collection and purification of $\delta^{13}C_{TDIC}$ in water samples, which we describe in detail together with a theoretical application on natural water samples.

SAMPLING AND EXTRACTION PROCEDURES

The proposed method is based on acidification of water samples and consequent physical stripping of yielded CO_2. On the field, water samples are collected in glass bottles (ca 100 ml) and quickly sealed by gas tight rubber/teflon plugs. In the laboratory, about 10 ml of pure Ar, or another carbon-free host gas, are introduced with a syringe in the upturned bottles. An equal volume of water is drawn out simultaneously (Figure 1), so that a head space is produced in the bottle. This space hosts the gas phase that separates from the liquid phase. Then the bottles are connected to a vacuum line for CO_2 extraction and purification (Figure 2). Up to four samples can be connected to the line.

The vacuum system consists of an EDWARDS® RV5 rotary pump coupled with an oil diffusion pump.

Before the stripping of the gas phases, a needle is partially inserted in the plug and the volume of line between the stopcock at level 1 (Figure 2) and the end of the needle is evacuated. Finally it is necessary to exclude the vacuum pump by closing the stopcocks at level 2 and the needle is entirely introduced within the sampling bottle and the apparatus is now ready to strip.

Chemical stripping is performed by injecting about 0.5 ml of 37% Suprapure HCl into the sample bottle so that the pH of water closes to 1. At this step, the samples begin to bubble because the only carbon species in solution are transformed in CO_2 by the chemical reaction.

The separated gas phase, that is composed mainly of CO_2 gas produced by the reacting solution, water vapour and other gases such as Ar, He and N_2, is statically stripped into the vacuum line. Yielded CO_2 and water vapour are captured as solid phases into a liquid nitrogen trap (-196°C), while Ar, He and N_2 are non-condensable at the temperature of the liquid nitrogen and consequently they will remain as gas phases in the vacuum line. In order to restore the initial vacuum conditions in the purification line and to ensure the total extraction of CO_2 from the sample, non-condensable gases need to be removed every three minutes. This is done by closing the stopcock at level 1, in order to connect the

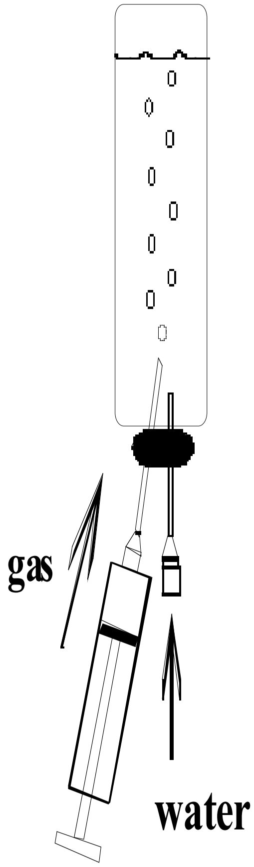

Fig. 1. Sampling apparatus (glass bottle) and handling treatments to obtain the head-space.

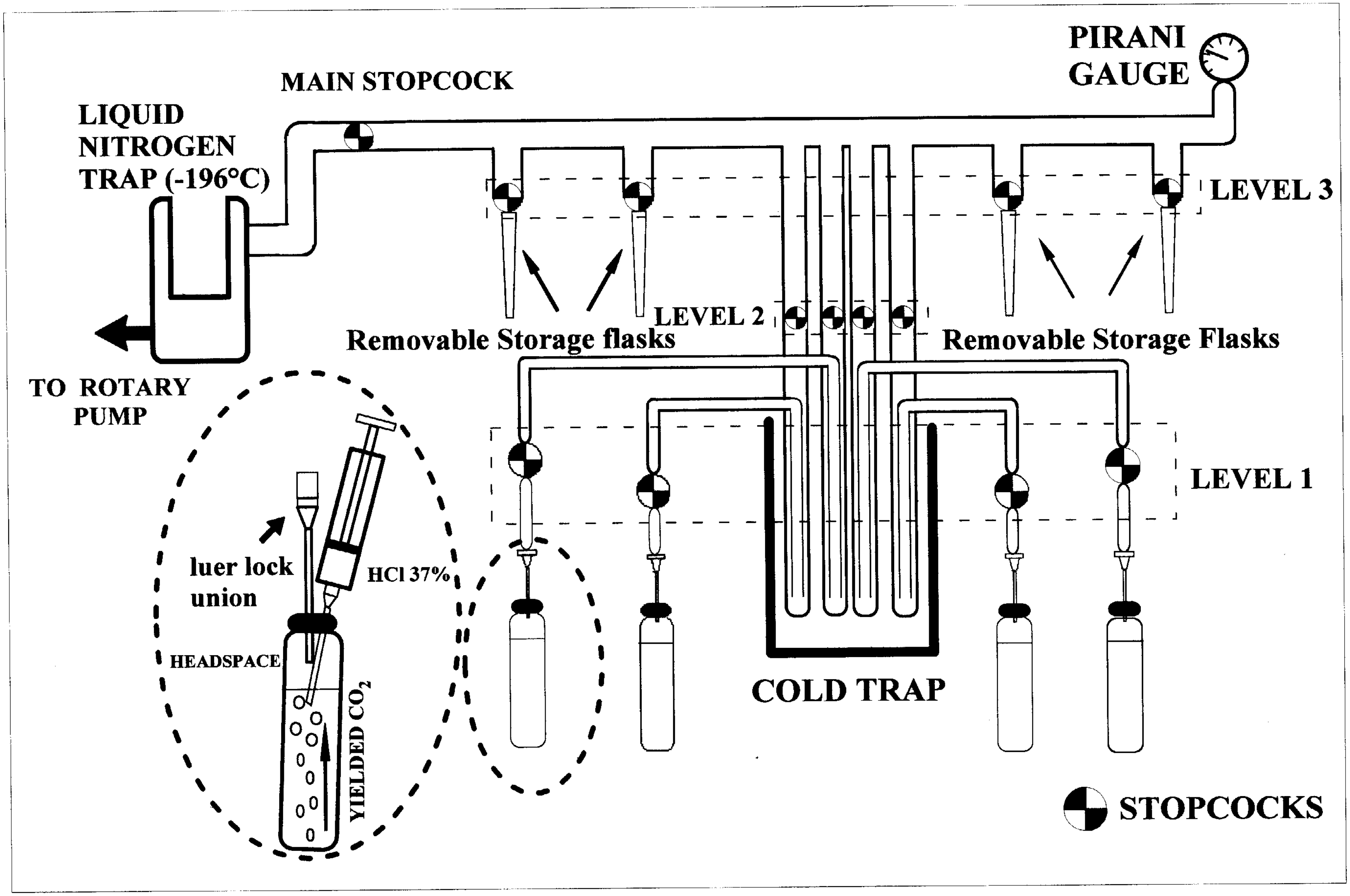

Fig. 2. Vacuum line for CO_2 purification. The vacuum system consists of an EDWARD rotary pump coupled with an oil diffusion pump. The CO_2 gas produced by the reacting solution and water vapour are captured as solid phases into a liquid nitrogen trap (-196°C), while non-condensable gases need to be removed from the line every three minutes. When the CO_2 gas is totally stripped from the samples, the nitrogen liquid trap is replaced with a trichloroethylene cold trap (about -85°C). About 10 minutes are necessary to ensure that the solid CO_2 is completely converted to the gaseous phase. Then, the CO_2 is collected into the storage flasks for isotopic analysis.

purification line to the vacuum pump, and by opening the stopcock at level 2. This step has to be repeated at least five times until no more CO_2 bubbles are produced from the samples.

When the CO_2 gas is totally stripped, the nitrogen liquid trap is replaced with a trichloroethylene cold trap (-80°C). About 10 minutes are necessary to ensure that the solid CO_2 is completely converted to the gaseous phase. Then, the CO_2 is collected into the storage flasks for isotopic analysis. The average time for the preparation of every group of 4 samples is less than 40 min.

Small amounts of acid gases (for example H_2S) dissolved in the water samples could be transferred into the storage flasks together with gas samples. These gases could produce interfering signals during measurements and they could damage the mass spectrometer ion source. For these reasons, it is necessary to further purify the gas by passing the samples through a tube filled with lead acetate basic anhydrous powder, so as to trap H_2S and any residual vapours (H_2O and HCl) if present.

The isotopic measurements were carried out with a Finnigan Delta Plus mass-spectrometer. The standard deviation of $^{13}C/^{12}C$ ratios measurements is about ± 0.2 ‰. In order to test the accuracy and reproducibility of the proposed method in the laboratory, a series of Na_2CO_3 samples with known carbon isotopic composition and at various concentrations (2.5mM, 10mM, and 40mM) were prepared. $\delta^{13}C_{TDIC}$ values of these samples were close to the isotopic composition of solid Na_2CO_3 (Table 1). To test the proposed method also on natural waters, five Mediterranean seawater samples were measured and the $\delta^{13}C_{TDIC}$ values are reported in Table 2.

The isotopic composition of total dissolved inorganic carbon (TDIC) in surficial seawater is the result of the steady-state quasi-equilibrium between water and atmospheric CO_2 (Tan, 1980). The equilibrium reaction can be written as follows:

$$\delta^{13}C_{CO2atm} + H_2O = H^+ + \delta^{13}C_{HCO3^-(aq)} + \varepsilon_{CO2g\,-HCO3}\ . \qquad (1)$$

The isotope fractionation factor between CO_2 gas and HCO_3^- depends strongly on temperature. At 25°C, the $\delta^{13}C_{HCO3^-}$ is enriched by about 8 ‰ with respect to the $\delta^{13}C$ of the interacting CO_2 gas (Mook *et al.*, 1974). The average isotopic composition of atmospheric CO_2 is about –7.5 ‰ vs. V-PDB (Inoue and Sugimura, 1985). The theoretical isotopic composition of TDIC of seawater in full-equilibrium with atmospheric CO_2 at temperature of 25 °C would then be close to +0.5 ‰ vs. V-PDB. The average $\delta^{13}C$ values of the measured seawater samples (~0 ‰ vs. V-PDB, Table 2) are in good agreement with the theoretical isotopic composition. These are the firsts $\delta^{13}C$ values of Total Dissolved Inorganic Carbon carried out for the Mediterranean Sea. The repeatability of the new proposed procedure of TDIC extraction is better than 0.2 ‰ vs V-PDB.

Table 1

Isotope composition of carbon of Na_2CO_3, both solid and dissolved in water at different concentrations (2.5 mM, 10 mM, 40 mM.). The isotopic values of C of TDIC are expressed in δ‰ vs. V-PDB

Sample	$\delta^{13}C$ TDIC
solid Na_2CO_3	
	-10.76
	-10.71
	-10.72
mean	-10.73
σ	0.03
dissolved Na_2CO_3	
2.5 mmol/l	-10.66
2.5 mmol/l	-10.51
2.5 mmol/l	-10.35
10 mmol/l	-10.61
10 mmol/l	-10.42
10 mmol/l	-10.44
40 mmol/l	-10.70
40 mmol/l	-10.38
40 mmol/l	-10.33
mean	-10.49
σ	0.14

For comparison, we tested our method in other eight Mediterranean seawater samples using H_3PO_4 85% instead of HCl to extract TDIC, as often done by other authors (Hassan, 1982; Mc Nicol *et al.*, 1994; Atekwana and Krisnamurthy, 1998). Use of this weak acid implies the introduction of 5 ml of H_3PO_4. Consequently, in order to have enough head space into the sampling bottles, up to 20 ml of host gas have to be introduced in the sample.

By comparing the obtained results (Table 2), we noted that use of HCl is preferable to that of H_3PO_4, for the following reasons:

- The kinetics of the acidification reaction when using HCl is much faster and no device or other means (ultrasonic

Table 2

Isotopic composition of TDIC from Mediterranean seawater samples both using HCl and H_3PO_4. The isotopic values of C of TDIC are expressed in δ‰ vs. V-PDB

Sample		$\delta^{13}C$ TDIC
Seawater 0,5 ml HCl		
		0.10
		-0.12
		-0.33
		0.01
		0.01
	mean	-0.07
	σ	0.17
Seawater 5 ml H_3PO_4		
		0.20
		0.00
		0.18
		0.31
		0.35
		-0.27
		-0.48
		-0.50
	mean	-0.03
	σ	0.34

bath or stirring of samples by means of magnetic bars) is required to ease the extraction procedure.

- Very low amounts of HCl are required;
- When using HCl, measurements are more accurate and their reproducibility is better.

On the other hand, HCl vapour pressure is several orders of magnitude higher than that of H_3PO_4. This property could cause high contents of HCl to be released in the gas phase. This inconvenient, however, is easily avoided by further purifying the sample using lead acetate-based traps, as above described.

GEOCHEMICAL APPLICATIONS

Carbon is one of the most abundant elements in nature. It occurs in the crust, in the mantle, in the hydrosphere and in the atmosphere as carbonate minerals, carbonate ions in aqueous solution and carbon dioxide. The stable isotope values of carbon, expressed as $\delta^{13}C$ ‰ vs. the V-PDB standard, show a wide compositional range in nature (Figure 3).

In the last years, several authors have focused their attention on the role played by $\delta^{13}C_{TDIC}$ measurements in natural waters. The isotopic composition of TDIC has been widely used as a geochemical tracer of natural processes that occur among dissolved carbon species. In order to evaluate the sources, sinks and fluxes of carbon, $\delta^{13}C_{TDIC}$ was applied in studies of carbon geochemistry and biogeochemistry of natural waters (Atekwana and Krisnamurthy, 1998). In active volcanic areas, the interpretation of isotopic data regarding the $\delta^{13}C_{CO2gas}$ coming from fumaroles and/or soil emanations takes into account all possible isotope fractionation processes between CO_2 gas and other carbon species present in shallow natural fluids.

In natural waters, dissolved carbon exists as inorganic species as the result of different reaction processes that take place among gaseous CO_2, water and carbonate rocks. The relative concentrations of inorganic carbon species in solution (CO_{2aq}, HCO_3^- and CO_3^{2-}) are strongly pH-dependent, and the enrichment factors control the isotopic composition of each inorganic carbon species as a function of temperature.

The isotopic composition of TDIC represents the average of the isotopic composition of the relevant carbon species, weighted on the respective contents of the inorganic carbon compounds involved.

Therefore, the $\delta^{13}C_{TDIC}$ can be expressed as an isotopic balance of dissolved carbon species and it can be written as follows:

$$\delta^{13}C_{TDIC} = (\delta^{13}C_{CO2aq} * M_{CO2\,aq} + \delta^{13}C_{HCO3} * M_{HCO3} + \delta^{13}C_{CO3} * M_{CO3})/M_{Tot}, \quad (2)$$

where M expresses molality.

Because the relative abundance of dissolved carbon species depends on pH values, Equation 2 can be simplified. At pH lower than 8.3, CO_3^{2-} activity can be assumed negligible, so the isotopic balance can be written as follows:

$$\delta^{13}C_{TDIC} = (\delta^{13}C_{CO2aq} * M_{CO2\,aq} + \delta^{13}C_{HCO3} * M_{HCO3})/M_{Tot}\ . \quad (3)$$

By utilising the enrichment factors ε_a and ε_b

$\varepsilon_a = \delta^{13}C_{HCO3} - \delta^{13}C_{CO2g} = 9552/T_K - 24.1$ (Mook *et al.*, 1974)

$\varepsilon_b = \delta^{13}C_{CO2aq} - \delta^{13}C_{CO2g} = -0.91 + 0.0063 * 10^6/T^2_K$ (Deines, 1970)

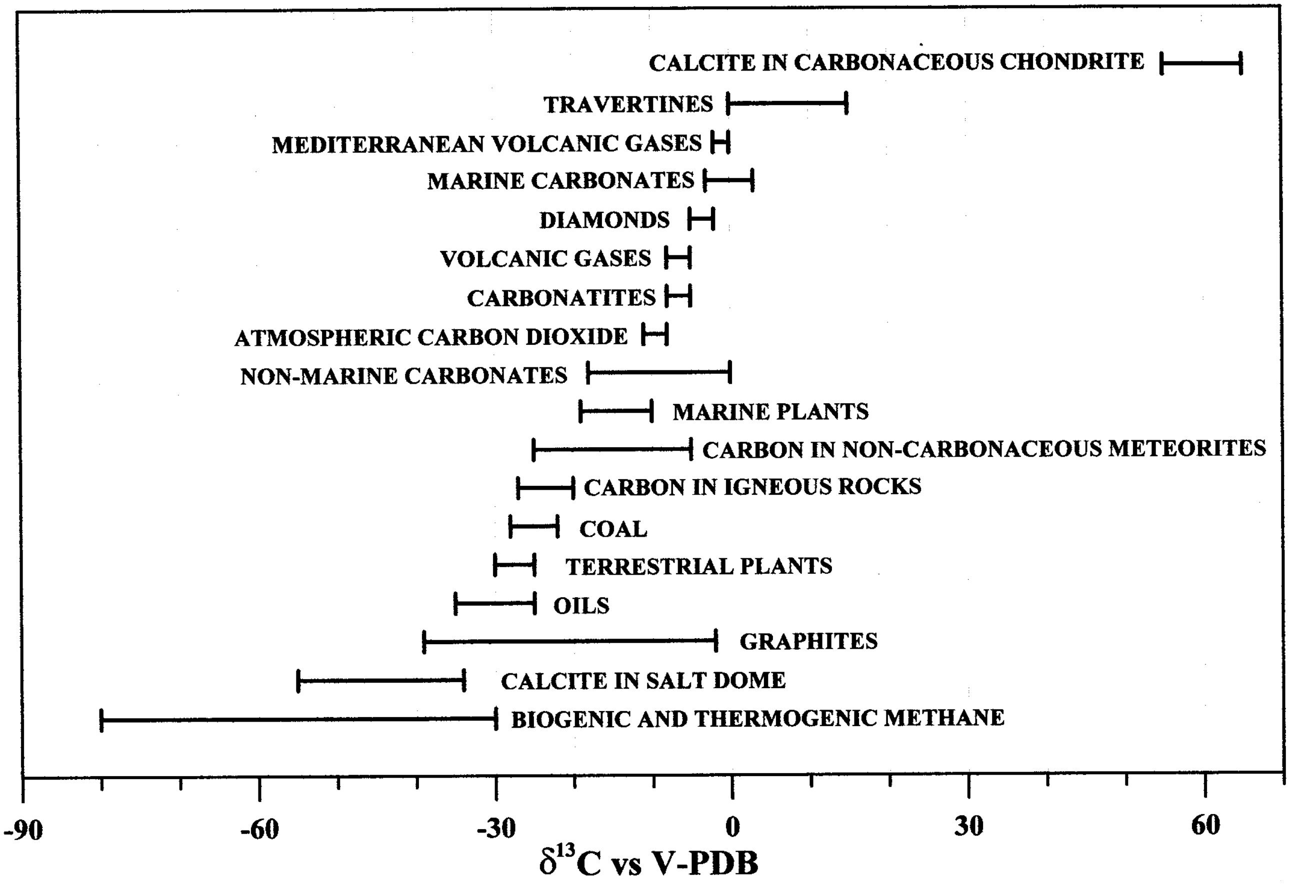

Fig. 3. Isotope composition of carbon in several natural environments. Data from Fornaseri (1984), Faure (1986), Hoefs (1987) Favara *et al.* (1999), Inguaggiato *et al.* (2000) and Favara and Inguaggiato (2000).

Eq. (3) can be written as follows:

$$\delta^{13}C_{TDIC}=\delta^{13}C_{CO2\,g} + [\varepsilon_b * (M_{CO2\,aq})/M_{Tot} + \varepsilon_a*(M_{HCO3})/M_{Tot}] \quad (4)$$

When pH is higher than 8.3 the activity of CO_{2aq} is negligible; the isotopic balance of the dissolved carbon species can thus be expressed by the following equation:

$$\delta^{13}C_{TDIC} = (\delta^{13}C_{CO3} * M_{CO3} + \delta^{13}C_{HCO3} * M_{HCO3})/ M_{Tot}\,. \quad (5)$$

By utilising the enrichment factors ε_a reported above and factor ε_c, that is expressed as

$$\varepsilon_c = \delta^{13}C_{CO3} - \delta^{13}C_{CO2g} = -3.4 + 0.87*10^6/T^2_K$$

(Deines, 1970)

Eq. (5) can also be expressed as follows:

$$\delta^{13}C_{TDIC} = \delta^{13}C_{CO2g} + [\varepsilon_a * (M_{HCO3})/M_{Tot} + \varepsilon_c * (M_{CO3})/M_{Tot}] \quad (6)$$

In Figures 4a and 4b are reported the curves representing the theoretical $\delta^{13}C_{TDIC}$ values as a function of T° C and HCO_3/TDIC and CO_3/TDIC ratios, respectively, assuming an initial value of $\delta^{13}C_{CO2gas} = 0$ ‰.

On the basis of the carbon isotope balance among dissolved carbon species, the variation observed in the isotopic composition of TDIC of geothermal waters of Ischia Island was applied to volcanic surveillance (Caliro *et al.*, 1999).

On the basis of estimated equilibrium temperatures and the molar fraction of dissolved carbon species, Equations 4 and 6 were used for the estimation of the carbon isotopic composition of CO_2 that interacts with ground-waters both in geothermal and active volcanic areas (Favara *et al.*, 1999; Inguaggiato *et al.*, 2000; Favara and Inguaggiato, 2000).

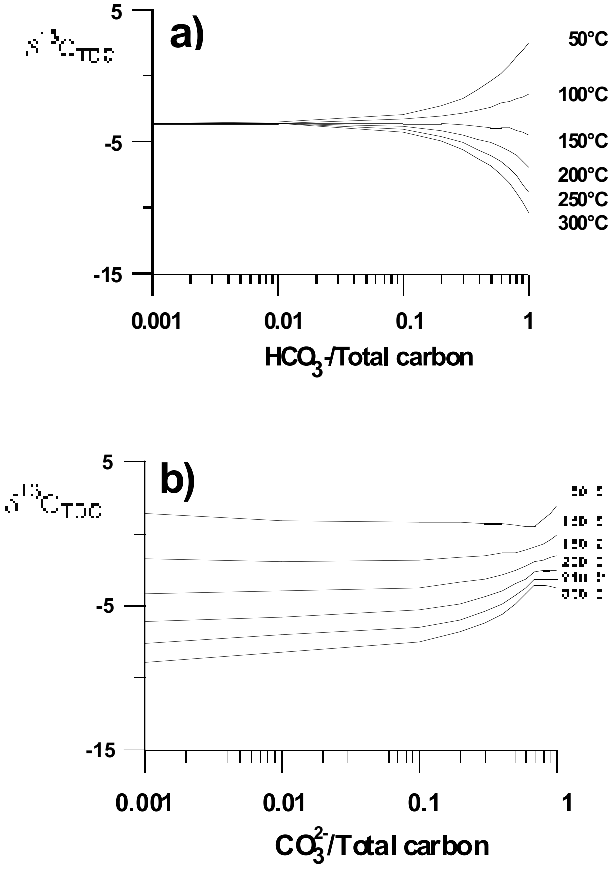

Fig. 4. Theoretical curves representing the isotopic composition of TDIC as function of HCO_3^-/Total carbon ratio (a) and $CO_3^=$/Total carbon ratio (b) in the range 50-300°C assuming a $\delta^{13}C_{CO2gas}$=-3 ‰.

In conclusion, the study of the stable carbon isotopic composition of TDIC in natural waters is a useful tool that allows to estimate the pristine carbon isotopic composition of CO_2 interacting with groundwater. Also, when the isotopic composition of CO_2 gas is known, the isotope balance among dissolved carbon species can be used to estimate the equilibrium temperature of the involved natural fluids.

CONCLUDING REMARKS

A simple method for the collection and extraction of CO_2 for $\delta^{13}C_{TDIC}$ (Total Dissolved Inorganic Carbon) measurements in natural waters is proposed.

The advantages induced by this proposed technique can be briefly summarized as follows:

- use of a simple and recyclable sampling device, with very low costs;
- rapid sample collection (less than 1 minute);
- easy preparation procedures, thus reducing to the minimum the handling of samples and consequently every possible source of error (e.g., gain/loss of free CO_2);
- very short average preparation and analysis time;
- possibility of storage of samples for a long time, ensured by gas tight rubber/teflon plug.

ACKNOWLEDGEMENTS

We are indebted to Salvatore Giammanco for his helpful suggestions and to Salvatore Francofonte for his support during field operations. This study was financially supported from the National Group for Volcanology, Italy.

BIBLIOGRAPHY

ATEKWANA, E. A. and R. V. KRISHNAMURTHY, 1998. Seasonal variations of disslved inorganic carbon and $\delta^{13}C$ of surface waters: application of a modified gas evolution technique. *J. Hydrol., 205,* 265-278.

BARNES, I., C. T. DOWNES and R. J. HULTSON, 1978. Warm springs South Island, New Zealand, and their potentials to yield lanmotite. *Am. J. Sci.,* 1412-1427.

CALIRO, S., C. PANICHI and D. STANZIONE, 1999. Variation in the total dissolved carbon isotope composition of thermal waters of the Island of Ischia (Italy) and its implication for volcanic surveillance. *J. Volcanol. Geot. Res., 90,* 219-240.

DEINES, P. 1970. The carbon and oxygen isotopic composition of carbonates from the Oka Carbonatite complex, Quebec, Canada. *Geochim. Cosmochim. Acta*, 34, 1199-1225.

FAURE, G., 1986. Principles of Isotope Geology. 2nd edition. Ed. J. Wiley & Sons. New York. 590p.

FAVARA, R., F. GRASSA and S. INGUAGGIATO, 1999. Chemical and isotopic features of dissolved gases from thermal springs of Sicily. Proceedings of The Fifth International Symposium on the Geochemistry of the Earth's Surface, GES-5 Reykjavik, Iceland, 495-498.

FAVARA, R. and S. INGUAGGIATO, 2000. Proceedings of the IAVCEI General Assembly 2000, Bali, Indonesia, 83.

FORNASERI, M., 1984. Lezioni di geochimica. Veschi Ed. 824p

GAMES, L. M. and J. M. HAYES, 1976 Isolation and quantitative anlysis of the major carbon fractions in water samples. *Anal. Chem.*, *48,* 130-135.

GLEASON, J. D., I. FRIEDMAN and B. B. HANSHAW, 1969. Extraction of dissolved carbonate species from natural water for carbon-isotope analysis. U.S. Geol. Survey Professional Paper 650-D, D248-250D.

HASSAN, A. A., 1982. Methodologies for extraction of dissolved inorganic carbon for stable carbon isotope studies: evaluation and alternative. U.S. Geol. Survey. Water-Resources Investigations 82-6, 1-51.

HOEFS, J., 1987. Stable isotopes geochemistry. 3rd edition. Ed. Springer-Verlag. New York. 224p.

INGUAGGIATO, S., G. PECORAINO and F. D'AMORE, 2000 Chemical and isotopical characterisation of fluid manifestations of Isshia Island (Italy) *J. Volcanol. Geot. Res.,* 99 (1-4), 151-178.

INOUE, H. and Y. SUGIMURA, 1985. Carbon isotopic fractionation during the CO2 exchange process between air and sea water under equilibrium and kinetic conditions. *Geochim. Cosmochim. Acta 49,* 2453-2460

MCNICOL, A. P., G. A. JONES, D. L. HUTTON, A. R. GAGNON and R. M. KEY, 1994. The rapid preparation of seawater ΣCO_2 for radiocarbon analysis at the national ocean sciences AMS facilities. *Radiocarbon*, *36-2,* 237-246.

MCREA, J. M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chim. Phys. 63 (4),* 563-568.

MOOK, W. G., J. C. BOMMERSON and W. H. STAVERMAN, 1974. Carbon Isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett. 22 (2),* 169-176.

ROSEMBAUM, J. and S. M. F. SHEPPARD, 1986. An isotopic study of siderites, dolomites and ankerites at high temperatures. *Analyst 95,* 817-822.

TAN, F. C., 1980. Stable carbon isotopes in dissolved inorganic carbon in marine and estuarine environmentals. *In:* Fritz, P. and Fontes, J.C. (Eds). Handbook of Environmental Isotope Geochemistry. Elsevier, Amsterdam, 3, 171-190.

Rocco Favara, Fausto Grassa, Salvatore Inguaggiato*, Giovannella Pecoraino and Giorgio Capasso

[1]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa,153, 90146 Palermo, Italy.

* *Corresponding author:*
Email: inguagg@pa.ingv.it; Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo Via Ugo La Malfa,153, 90146 Palermo, Italy. Fax:+ 39 0916809449