METHODOLOGIES FOR EXTRACTION OF DISSOLVED INORGANIC CARBON FOR STABLE CARBON ISOTOPE STUDIES: EVALUATION AND ALTERNATIVES

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The gas evolution and the strontium carbonate precipitation techniques to extract dissolved inorganic carbon (DIC) for stable carbon isotope analysis were investigated. Theoretical considerations, involving thermodynamic calculations and computer simulation pointed out several possible sources of error in the stable carbon isotope measurements of the DIC and demonstrated the need for experimental evaluation of the magnitude of the error. An alternative analytical technique, equilibration with outgassed vapor phase, is proposed.

The experimental studies revealed that $\delta^{13}C$ of the DIC extracted from a 0.01 molar $NaHCO_3$ solution by both techniques agreed within 0.1 per mil with the $\delta^{13}C$ of the solid $NaHCO_3$. An approximate linear relationship was found between log molality of sulfate and the increase in $\delta^{13}C$ of the DIC extracted by the precipitation technique. Similar trend was observed in the gas evolution technique; however, less in magnitude. The percentages of recovered DIC decreased linearly with log molality of sulfate in the precipitation technique and were independent of sulfate concentration in the gas evolution technique.

Both the precipitation and gas evolution technique were found to be satisfactory for extraction of DIC from different kinds of natural water for stable carbon isotope analysis, provided appropriate precautions are observed in handling the samples. Laboratory tests indicated that sampling devices and laboratory preparation may alter the carbon isotope ratio of the samples.

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Afifa Afifi Hassan

ABSTRACT

The gas evolution and the strontium carbonate precipitation techniques to extract dissolved inorganic carbon (DIC) for stable carbon isotope analysis were investigated. Theoretical considerations, involving thermodynamic calculations and computer simulation pointed out several possible sources of error in the stable carbon isotope measurements of the DIC and demonstrated the need for experimental evaluation of the magnitude of the error. An alternative analytical technique, equilibration with outgassed vapor phase, is proposed.

The experimental studies revealed that $\delta^{13}C$ of the DIC extracted from a 0.01 molar $NaHCO_3$ solution by both techniques agreed within 0.1 per mil with the $\delta^{13}C$ of the solid $NaHCO_3$. Addition of 0.1 mol/L sulfate resulted in a 0.45 per mil increase in $\delta^{13}C$ of the DIC extracted by the precipitation technique, and an increase of only 0.11 per mil in that extracted by the gas evolution technique. An approximate linear relationship was found between log molality of sulfate and the increase in $\delta^{13}C$ of the DIC extracted. However, in the gas evolution technique, the increase in $\delta^{13}C$ was very small and may be ignored. The percentages of the recovered DIC decreased linearly with log molality of sulfate in the precipitation technique and were independent of sulfate concentration in the gas evolution technique. It was possible to construct curves to correct the measured values of the precipitated DIC and their $\delta^{13}C$ in presence of sulfate.

Laboratory tests indicated that $\delta^{13}C$ of DIC did not change in pyrex glass bottles with Teflon-coated screw caps, whereas diffusion of atmospheric CO_2 does alter the carbon isotope ratio of the samples contained in polyethylene bottles. Under normal laboratory conditions, glass syringes with metal Luer-lok tips did not change the $\delta^{13}C$ of the DIC extracted by the gas evolution technique. All other devices, glass samplers with stopcocks, Tygon tubing, and serum bottles, changed the $\delta^{13}C$ of the DIC. Serum bottles, were the only reliable device, among those tested, for preserving carbon-isotope ratios at high temperatures or low pressures, conditions which are likely to prevail during shipment of samples from the field to the laboratory. Sample treatment and laboratory preparation were evaluated. The results of the evaluation indicate that addition of $HgCl_2$ solution to the samples prevents biological production of CO_2 and thus preserves the original inorganic carbon-isotope ratios; filtration and drying of the precipitation-technique $SrCO_3$ should be carried out in a nitrogen-atmosphere glove box; 85 percent phosphoric acid is satisfactory for carbonate reaction for $\delta^{13}C$ measurements; and hot MnO_2 purification changes the $\delta^{13}C$ of CO_2.

Both the precipitation and gas evolution technique were found to be satisfactory for extraction of DIC from different kinds of natural water for stable carbon isotope analysis, provided appropriate precautions are observed in handling the samples.

INTRODUCTION

Variation in the ratio of ^{13}C to ^{12}C are usually reported as values of $\delta^{13}C$ in parts per thousand (per mil) relative to a standard Thus:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)\ \text{Sample}}{(^{13}C/^{12}C)\ \text{Standard}} - 1\right] 1000$$

Belemnites from the Peedee formation of South Carolina (PDB), having a $^{12}C/^{13}C=88.99$, usually serve as the standard for reporting the data.

Measurements of $\delta^{13}C$ of water requires separation of the dissolved inorganic carbon (DIC). The separation is usually done by precipitation in the form of strontium carbonate or evolution as carbon dioxide. Both techniques have advantages and disadvantages and possible sources of error. The precipitation technique is easy to carry out in the field and the samples can be stored for further investigation if needed. However, this technique requires more preparation steps in the laboratory during which extreme care must be taken to avoid possible errors. The gas evolution procedure is difficult to accomplish in the field, but is very easy to handle in the laboratory. Field sample collection for laboratory gas evolution is a simple procedure.

Literature review and personal communication with other laboratories indicated that some investigators support the precipitation technique and others support the gas evolution technique. For example, Gleason and others (1969) and Barnes and others (1978) and Barnes and others (unpublished report, 1979) support the precipitation technique. The gas evolution technique is also used to separate DIC from different types of water (Williams and Gordon, 1970; Mook, 1968 and 1970; Tan and others, 1973; Kroopnick, 1974; Games and Hayes, 1974; and Reardon and others, 1979). A variety of sampling devices are used to collect water samples by both techniques, and different methods are employed to prepare the samples in the laboratory.

Previous studies determined the precision of the techniques of DIC extraction for stable carbon-isotope analyses. For example, Tan and others (1973) determined the precision of the gas evolution technique. However, studies on the accuracy of these techniques are lacking. One study to determine the accuracy of the techniques was conducted by Gleason and others (1969). However, the factors that affect the accuracy and precision of these techniques were not determined. Also none of the previous investigators has determined the effects of the different sampling devices on the accuracy and precision of the measured ^{13}C of the DIC. Effects of laboratory preparation steps on accuracy and precision also have never been investigated.

One of the major concerns is the possibility of incomplete separation of the dissolved inorganic carbon. Accordingly, as a result of carbon-isotope fractionation the measured $\delta^{13}C$ may not represent the actual $\delta^{13}C$ of DIC. Another concern is the possible change of the carbon isotopic composition of water during shipping, storage, and laboratory preparation.

The purpose of the present investigation is to evaluate the strontium carbonate precipitation and the gas evolution, in order to determine the most suitable technique for stable carbon isotope studies of water. The evaluation includes determination of efficiency of extraction of DIC, accuracy and precision of the techniques for $\delta^{13}C$ measurements of DIC and the effect of sulfate concentrations, reliability of water sampling devices during shipping and storage, and effects of the laboratory preparation steps. The investigation involves theoretical studies, including thermodynamic calculations and computer simulations, laboratory experiments on prepared solutions, and studies on different kinds of natural waters. The present report also investigates the possibility of developing a new technique.

THEORETICAL INVESTIGATION

The Precipitation Technique

The principles of this technique involve addition of ammoniacal strontium chloride solution (amm. $SrCl_2$) in the field to the water samples which are usually collected in polyethylene bottles. The bottle caps are sealed with electrical tape and the bottles are shaken well. In the laboratory, samples are filtered and the precipitate is rinsed thoroughly with distilled water. The precipitate is dried. A portion of the precipitate is reacted with 100 percent phosphoric acid in a closed system and the evolved CO_2 is purified and analyzed.

Gleason and others (1969) used 50 mL amm. $SrCl_2$ per liter sample. Their solution was made up from 2,366 mL of NH_4OH (approx. 30 percent NH_3) and 453.6 g of $SrCl_2 \cdot 6H_2O$ (J. C. Chemerys, oral commun., 1979). Barnes and others (1978) used 20 mL of amm. $SrCl_2$ (180 g $SrCl_2 \cdot 6H_2O$ per 200 mL of NH_4OH of 25 percent NH_3) per 20 mL of water sample. In recent unpublished research, Barnes and others (1979) used 20 mL of amm. $SrCl_2$ per 100 mL sample.

Efficiency of the Technique to Extract DIC

The computer program PHREEQE (Parkhurst and others, 1980) was used to calculate molality of the dissolved carbon left in solution after addition of ammonical $SrCl_2$ solution to different types of water. The composition of 1 liter of hypothetical groundwater in equilibrium with (1) calcite and (2) calcite, dolomite, and gypsum was modeled. In order to demonstrate the interference of high concentrations of sulfate with $SrCO_3$ precipitation, the reaction of 1 liter of hypothetical water, in equilibrium with calcite, dolomite, and gypsum, with 0.1 and o.5 moles of K_2SO_4 was also modeled. In each case the P_{CO_2} was fixed at a value of log P_{CO_2} equal to -3. In the calculation, five different volumes 10 mL, 25 mL, 50 mL, 100 mL, and 200 mL were chosen. The pe was fixed at a value of -2 except in the case of the water in equilibrium with calcite.

Thermodynamic calculations suggested precipitation of strontianite ($SrCO_3$) with addition of ammonical $SrCl_2$ to the water in equilibrium with calcite. The water in equilibrium with calcite-dolomite-gypsum precipitated strontianite and celestite ($SrSO_4$) at all steps except when 200 mL of amm. $SrCl_2$ is added. In this case, thermodynamic calculations suggested precipitation of calcite ($CaCO_3$) and celestite.

The water in equilibrium with calcite-dolomite-gypsum and reacted with 0.1 mol K_2SO_4 precipitated calcite and celestite at all steps except when 10 mL of amm. $SrCl_2$ was added. In this case, strontianite and celestite precipitated. The water in equilibrium with calcite-dolomite-gypsum - and reacted with 0.5 mol K_2SO_4 precipitated strontianite and celestite at all steps.

Table 1 shows the percentages of DIC and the total dissolved inorganic sulphur (DIS) left in solution after addition of different amounts of ammoniacal $SrCl_2$ solution. At each step, the amounts of DIC and DIS were calculated after precipitation of only the mineral phases which thermodynamically were shown to precipitate. Log molalities of DIC left in solution after addition of different amounts of ammoniacal $SrCl_2$ are plotted in Figure 1.

Thermodynamic calculations indicate that most of the DIC and some of the DIS are precipitated with the addition of 10 mL of amm. $SrCl_2$. The amount of DIC left in solution decreases when more ammonical $SrCl_2$ is added (Table 1). However, the decrease in the DIC left in solution is not proportional to the added amount of the ammoniacal $SrCl_2$ (Figure 1). The amount of DIC left in solution after addition of ammoniacal $SrCl_2$ increases with the increase of the sulfate concentrations (Table 1). That increase is associated with precipitation of celestite and is attributed to the competition of sulfate with carbonate for strontium cations. After addition of 50 mL amm. $SrCl_2$, the highest amount of DIC left in solution was 7.55 percent (Table 1), in the hypothetical water in equilibrium with calcite-dolomite-gypsum to which 0.5 mol of K_2SO_4 was added. The calculations take into consideration the amount of carbon left in solution as $CaCO_3^o$, $CaHCO_3^+$. Possible formation of $SrCO_3^o$ and $SrHCO_3^+$ is not considered because thermodynamic data are unavailable.

Accuracy of the Technique for $\delta^{13}C$ Measurements of DIC

The effect of incomplete precipitation of DIC on the measured $\delta^{13}C$ was calculated. The isotope mass balance equation developed by Wigley and others (1978) was used. The equation is:

$$R = R_o \left[\frac{mC}{mC_o}\right]^{(\alpha_{ps}-1)}$$

This equation calculates the carbon isotope ratio $^{13}C/^{12}C$ in the final solution, where the initial $^{13}C/^{12}C = R_o$, the initial molality of the carbon = mC_o, the final molality is mC, and α_{ps} is the carbon isotopes fractionation factor between the solid and the solution.

The above isotope mass balance equation for zero input and one output may be written in the $\delta^{13}C$ term as follows: $\delta^{13}C + 1000 =$

$$[\delta^{13}C_o + 1000] \left[\frac{mC}{mC_o}\right]^{(\alpha_{ps}-1)}$$

(Wigley and others, 1978).

$\delta^{13}C$ of the total precipitate ($\delta^{13}C_p$) was obtained from the following mass balance equation:

$$\delta^{13}C_o mC_o - \delta^{13}C mC = \delta^{13}Cp\ mCp.$$

The equilibrium fractionation factors are obtained from Wigley and others (1978). These factors are based on Deines and others (1974) data. The values of the fractionation factors determined by Deines and others (1974) differ from those of Friedman and O'Neil (1977); however, the differences are negligible at 30°C.

Data for ^{13}C fractionation between precipitated strontianite and a carbonate solution are unavailable. Accordingly, for rough estimates, the equilibrium ^{13}C fractionation between precipitated calcite and a carbonate solution is used. The average $\delta^{13}C_p$ of $SrCO_3$ precipitated from a hypothetical water containing 10 mmol of carbon of $\delta^{13}C_o$=-10.0 per mil is calculated. The precipitation is assumed to occur at 30°C and pH 9.0. At these conditions, the equilibrium fractionation factors ξ_{sp} is approximately 2 per mil (Wigley and others, 1978: Fig. 3).

The calculations indicate that the precipitated $SrCO_3$ has an average $\delta^{13}Cp$=9.90 per mil when the final solution contains 0.1 mmol of carbon. The calculated error in the $\delta^{13}C$ of the precipitate is 0.1 per mil, however, if 99 percent of the DIC is extracted. The calculations also do not consider the formation of $SrCO_3^o$ and $SrHCO_3^+$ ion pairs, and the difference in the fractionation factor between a carbonate solution and $SrCO_3$ and that between a carbonate solution and $CaCO_3$. Accordingly, the error in the measured $\delta^{13}C_p$ could be higher.

Sample Collection and Sampling Devices - Sources of Error

The use of polythylene bottles to collect and store water samples could be a source of error. It is well known that CO_2 diffuses through plastics (Rogers, 1964; and Koros and others, 1976 and 1977). Presence of Ammoniacal $SrCl_2$ in solution will enhance diffusion of atmospheric CO_2 into the bottles containing the water samples. Thus, carbonate from atmospheric carbon will be added to the $SrCO_3$ precipitated from the water.

Exposure to air could produce erroneous $\delta^{13}C$ measurement of the sample. The error could be the result of loss of CO_2 from the water sample or addition of CO_2 from the atmosphere. The method of sample collection used by Barnes and others (1978) exposes the sample to the atmosphere for a period of 22 seconds. The time of exposure is minimal, however, it is during the addition of the ammoniacal $SrCl_2$ solution. Accordingly, there is a chance of atmospheric CO_2 contribution due to absorption by the ammoniacal $SrCl_2$. Other geochemists in the U.S. Geological Survey add the ammoniacal $SrCl_2$ solution at the bottom of the bottle which has been filled with the water sample (J.C. Chemerys, oral commun., 1979). In both methods (Barnes and others (1978) and U.S. Geological Survey there is a slight chance of loss of CO_2 from the water sample by gas evolution.

Some investigators do not filter water samples collected by the precipitation technique which could lead to erroneous $\delta\ ^{13}C$ measurements in presence of suspended carbonate minerals.

Laboratory Preparation - Sources of Error

The precipitation technique requires several steps of sample preparation in the laboratory which might contribute erroneous carbon isotope data. These steps include filtration, drying, storing, homogenizing, reacting with acid, and cleaning the evolved CO_2.

Filtering water samples in air can be a major source of error. Gleason and others (1969) found that filtration in contact with air had changed the $\delta^{13}C$ value of the $SrCO_3$ by -0.5 per mil, from -6.3 to -6.8. This is a result of the rapid absorption of atmospheric CO_2 by the alkaline ammoniacal $SrCl_2$ solution.

The filtered $SrCO_3$ is dried in the oven at 110^o overnight. As long as the $SrCO_3$ is completely free of any traces of NH_4OH, there is no contamination from CO_2 in the air (Ivan Barnes, oral commun., 1979). However, Mook (1968) found that calcite samples which were stored in a moist atmosphere had exchanged carbon and oxygen with the CO_2 in the atmosphere. Mook left one portion of finely powdered limestone for one month at room temperature in an atmosphere enriched in CO_2 that had a $\delta^{13}C$ of + 4157 per mil with a beaker of water with $\delta^{18}O$ + 297 per mil. The $\delta^{13}C$ of the limestone has increased by + 30.3 per mil and $\delta^{18}O$ by 13.3 per mil.

Previous mineralogic and carbon isotopic studies on hydroxy-carbonate-apatite (Dahllite) of fossil bone have proved that heating at 90°C introduces changes in the crystallite lattice parameters (Hassan and others, 1977), as well as surface exchange of carbon (Hassan, unpublished report, 1978). These studies were done on a mineral of a different nature, yet they support a possible atmospheric exchange during drying.

The precipitated $SrCO_3$ is isotopically inhomogeneous. This fact is a result of fractionation during precipitation. Although there are no data on the fractionation of $SrCO_3$ precipitate-solution, the published data on the calcite precipitate-solution system (Wigley and others, 1978) indicate that the fractionation during step precipitation is enormous. Another kind of inhomogeneity is due to the presence of different mineral phases in the precipitate.

Inhomogeneity of the precipitated $SrCO_3$ could be the cause of the different values of $\delta^{13}C$ of different aliquots of the same sample (Table 2). However, the variations in $\delta^{13}C$ presented in Table 2 could be explained by incomplete reaction between the precipitate and the phosphoric acid. Malfunction in the mass spectrometer could also produce different $\delta^{13}C$ values for the same sample.

Changes in the carbon isotopic composition of the $SrCO_3$ may occur during storage in unsealed bottles in a moist atmosphere. The changes could be a result of isotopic exchange, absorption of atmospheric CO_2 by the $SrCO_3$ crystals, and(or) formation of aggregates may produce variations in $\delta^{13}C$ similar to those obtained in the data presented in Table 2.

Some laboratories use liquid nitrogen and dry ice traps to purify CO_2. This procedure is not sufficient to remove contaminants such as sulfur, nitrogen, and organic compounds which might interfere with the isotope data. Other laboratories purify CO_2 by furnaces of copper and manganese dioxide at 500°C (Degens, 1969, p. 305-306), thermal treatment for 15 minutes at 475°C while pumping (Epstein and others, 1953), or gas chromatography (T. C. Hoering, oral commun., 1979). However, the effects of these purification systems on the carbon isotopic composition of CO_2 is not known.

The Gas Evolution Technique

The principles of the gas evolution technique involve reaction of the water sample with phosphoric acid in a closed system. The evolved CO_2 is pumped off slowly through cooling traps at -80°C to eliminate the water, and is frozen in a liquid nitrogen trap (Mook, 1968). During the reaction, the water sample is heated to decrease the solubility of CO_2.

Efficiency of the Technique to Extract DIC - Thermodynamic Calculations

The present capability of the computer program PHREEQEE does not allow simulation of the gas evolution technique. Accordingly, preliminary calculations of the amount of CO_2 evolved from a hypothetical water containing 1 and 10 mmoles of HCO_3 were done. The volume of the water sample and the tube for collecting the CO_2 gas were assumed to be 50 mL and 250 mL, respectively. It is assumed that the collection tube was preevacuated. The calculations were drawn from the equations

$$K = \frac{aH_2CO_3}{P_{CO_2}a_{H_2O}} = 10^{-1.47}, \text{ and } PV = nRT.$$

Calculations indicate that in both hypothetical waters, if the CO_2 evolved is collected in a 250 mL flask and is in equilibrium with the water, 10 percent of the DIC will be left in the water. However, if the evolved CO_2 is frozen with liquid nitrogen, the percentage of the DIC which is not collected should approach zero.

Accuracy of the Technique for $\delta^{13}C$ Measurements of DIC

The equilibrium ^{13}C fractionation between a CO_2 gas phase and a carbonate solution, ξgs, at 30°C and pH 5 is approximately 0.5 per mil (Wigley and others, 1978; Figure 2). Using this value in the previously mentioned equation of isotope mass balance (Wigley and others, 1978) indicates that the error in the measured $\delta^{13}C$ of DIC, as a result of incomplete evolution of CO_2, can be ignored if the yield is more than 95 percent, not 75 percent as Mook (1968) stated. If 95 percent of the DIC is evolved from a hypothetical water containing 10 mmol of carbon of $\delta^{13}C_o$=-10.0 per mil, the measured $\delta^{13}C_g$ of the evolved gas at 30°C and pH 5.0 is -9.92 per mil. The calculated error in the $\delta^{13}C$ of the evolved gas is 0.08 per mil when 95 percent of the TIC is extracted.

Sample Collection and Sampling Devices - Sources of Error

Possible loss or gain in CO_2, and exchange of carbon isotopes with the atmosphere are crucial problems in the method of gas evolution. Mook (1968) found an enrichment of approximately 0.5 per mil in $\delta^{13}C$ of dissolved bicarbonates in most freshwaters left in contact with the atmosphere for 24 hours. The enrichment is a result of depletion of the escaping CO_2 in $\delta^{13}C$ relative to the bicarbonate. Mook also found that the presence of plant and organic material changes the $\delta^{13}C$ of the bicarbonate in water due to photosynthesis and organic decay, respectively. The result is ^{13}C enrichment in the first case and ^{13}C depletion in the second case. To avoid these effects, Mook (1968) filled the sample bottles to the top, sealed, and stored in the dark at a temperature below 4°C. Mook (1968) also added iodine to the samples.

Several devices are used to sample water for the gas evolution technique; however, their accuracy has not been determined. Reardon and others (1979) used 50 mL glass syringes with metal Luer-Lok[1] tips to collect water samples. The syringes are shipped in containers with half their length emmersed in water and their tips inserted in rubber stoppers (Reardon, oral commun., 1979). The containers are covered to prevent dryness of the barrels of the syringes, thus, air leakage.

The sampling devices shown in Figure 2A and 2B resemble those of Tan and others (1973) and Pearson and others (1978), with some modifications. The volume of samples collected is 100mL for ground water and 250 mL for surface water. The sampling device has a ground ball joint at both ends. The device in Figure 2B has a side arm which has to be preevacuated. It allows for possible outgassing and changes in volume as a result of changes in temperature and(or) pressure without building excess pressure inside. A Tygon tube with two clamps is another sampling device (James O'Neil, oral commun., 1980). This device (Figure 2D) is simple, however, diffusion of CO_2 and water leakage may occur.

Another possible sampling device is suggested (Figure 2E1). It consists of a 100-mL amber-glass serum bottle with 20-mm mouth and 20-mm serum-bottle aluminum seal. A Teflon-coated silicone septum is used with the seal. A hand operated crimper is used to seal the bottle. Instead of the aluminum seal a rubber sleeve-stopper may also be used (Figure 2E2). In the laboratory, a syringe is used to withdraw and inject the water sample in the vacuum preparation line.

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[1] The mention of brand name does not constitute endorsement by U.S. Geological Survey.

Laboratory Preparation - Sources of Error

Transfer of the samples to the vacuum line without any loss of CO_2 is the crucial problem in the method of gas evolution. Another problem is the large amount of water that is collected with the evolved CO_2.

Vapor Phase Equilibration: A Proposed Technique

This technique is based on the technique used by Pearson and others (1978) to reconstruct the water chemistry and its carbon isotopic composition. Pearson and others outgassed a known volume of water sample in a preevacuated known volume. They used a sampling device resembling that in Figure 2B; however, the water chamber was 500 mL and the side arm was 50 mL. The sampling device was connected to a gas chromatographic column and the vapor phase was allowed to equilibrate for 5 minutes in the enlarged previously determined volume.

The proposed technique uses a sampling device (Figure 3) which is a modification of that of Pearson and others (1978). The gas chamber of the modified device is connected to the water chamber only at the top stopcock. In addition, a spherical trap is in the gas collecting tube immediately above the stopcock. These two features allow the gas to escape to the preevacuated chamber without water in the liquid phase. The outgassing has to be very slow in order to prevent water flow to the gas chamber.

In the laboratory the water-vapor system has to reequilibrate at known temperature. A water-bath shaker will speed the equilibration; however, the time required to attain equilibrium is expected to be long. Then the stopcock between the water and gas chambers should be closed. The vapor phase can be transferred through the lower stopcock of the gas chamber to the vacuum line. A cooling trap will eliminate the water and the volume of the pure CO_2 can be measured in the mercury manometer (Figure 4).

The dissolved CO_2 content as $(CO_{2aq}+H_2CO_3^o)$ of the sample can be calculated from the measured ${}^{P}CO_2$ and Henry's law constant. The calculations require the assumptions that CO_2 outgassed into the gas chamber comes only from dissolved CO_2 and that $aH_2CO_3={}^{M}H_2CO_3$. The stable carbon isotope abundance in the water can be calculated from the measured $\delta^{13}C$ of the outgassed CO_2 using the isotope mass balance equation by Wigley and others (1978). This equation is explained under a previous section. The water in the water chamber may also be transferred to the vacuum line. The remainder of the dissolved carbon in the water and its isotopic composition may also be measured to check the calculated values in order to confirm the validity of the technique.

The proposed technique is expected to have sources of error which affect the accuracy of $\delta^{13}C$ of the DIC. The sources of error include uncertainties involved in the aqueous model, mass balance equation, pH measurements, and the equilibrium fractionation factors.

EXPERIMENTAL STUDIES

Accuracy and Precision of $\delta^{13}C$ Determination of Dissolved Inorganic Carbon (DIC)

In order to determine the accuracy[1/] and precision[2/] of the techniques of DIC extraction, the accuracy and precision of the mass spectrometer have to be determined. The accuracy and precision of the techniques also have to be separated from those related to water chemistry, the analytical procedures, shipping and storage, and the sampling devices. Thus, it was logical to use a simple solution to determine the accuracy and precision of the techniques before evaluating the effect of water chemistry, particularly sulfate concentration, on the accuracy and precision. Sets of four samples each, unless stated differently, were used in these determinations.

The steps in the analytical procedure that might affect the accuracy and precision of the techniques were evaluated or, whenever possible, eliminated. For example, homogeneity of the samples and the standards and the effect of homogenization on the precision and accuracy was determined. Several aliquots of the sample and standards were analyzed. A nitrogen gas glove box was used during the entire sample preparation procedure to prevent any possible exchange with atmospheric CO_2. Also the automated system of loading the samples in the mass spectrometer was not used in order to eliminate sources of contamination due to possible leaks and(or) memory effects from previous samples. A 100 percent phosphoric acid was used (rather than the usual 85 percent reagent grade) to evolve CO_2 from samples until the effect of acid concentration on $\delta^{13}C$, if any, is evaluated.

The accuracy and precision of the techniques of DIC separation also have to be separated from those related to the sampling devices and shipping and storage. Based on the theoretical evaluation which was later demonstrated experimentally, Pyrex glass bottles with Teflon-coated

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[1/] The accuracy is the per mil deviation of the measured $\delta^{13}C$ values of the actual value.

[2/] The precision is the per mil standard deviation of $\delta^{13}C$ values of different analyses of the same sample (precision of the mass spectrometer), or of analyses of different preparations of the same sample (precision of the technique).

screw-caps, and glass syringes with metal Luer-lok tips were selected to sample the bicarbonate solution by the precipitation technique and the gas evolution technique. In order to eliminate the effect of shipping and storage on the measured $\delta^{13}C$, DIC was extracted less than 48 hours after preparation of the $NaHCO_3$ solution.

Precision and Accuracy of the Isotope Ratio Mass Spectrometer

The precision of the mass spectrometer was determined by analyzing the same gas sample at intervals during the entire period of the study. The standards NBS-20, and NBS-19[1/] were used for that purpose. A modified 21-491 Dupont double collector mass spectrometer was used. The precision of the mass spectrometer was less than 0.1 per mil. However, the determined precision excluded several of the analyses that did not agree with each other or with published values of $\delta^{13}C$ of the standards. The excluded analyses indicated possible instrument malfunction. Accordingly, samples analyzed during these suspected malfunction episodes were also excluded from the present study.

The accuracy of $\delta^{13}C$ measurements was determined by analyzing three international standards, NBS-20, NBS-21, and NBS-19. NBS-19 and NBS-20 are limestones and were converted to CO_2 by reacting with 100 percent phosphoric acid, whereas NBS-21 is graphite and was converted to CO_2 by combustion. The calculated mean $\delta^{13}C$ values are-1.09 ± 0.04 per mil for NBS-20, -28.10 ± 0.06 per mil for NBS-21, and 2.04 ± 0.09 per mil for NBS-19. These results agree favorably with those of other workers (Table 3).

Precision of $\delta^{13}C$ Analytical Procedure

The measured precision is influenced by the laboratory preparation of the sample, homogeneity of the sample, and the mass spectrometer. Two bottles of $NaHCO_3$ manufactured by two different companies were sampled. These samples were reacted with 100 percent phosphoric acid. The CO_2 produced was analyzed to evaluate the overall precision.

The measured $\delta^{13}C$ values of the first bottle of $NaHCO_3$ are scattered, indicating inhomogeneity of this brand. The mean $\delta^{13}C$ of the four-sample set is -6.40 ± 0.21 per mil. The second brand of

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[1/] Calcium carbonate sample obtained by Irving Friedman and others, U. S. Geological Survey, from a marble of unknown origin used as working standard (called TS-limestone) by some laboratories in the USA.

$NaHCO_3$ is manufactured by Baker. The mean $\delta^{13}C$ of the first five-sample set of this lot of Baker analytical reagent $NaHCO_3$ is -15.33 ± .07 per mil indicating that this lot of Baker $NaHCO_3$ is more homogeneous than the other brand lot because the precision of $\delta^{13}C$ of the former is less than 0.1 per mil. Also the large difference between $\delta^{13}C$ of atmospheric CO_2 (approximately -6.9 per mil) and that of Baker $NaHCO_3$ makes it easy to detect atmospheric contamination. Thus, it was concluded that this lot of Baker $NaHCO_3$ is suitable for preparing solutions of known stable carbon isotopic composition.

After a few months another four-sample set of the same lot of Baker $NaHCO_3$ was analyzed. The mean $\delta^{13}C$ of that set is -15.52 ± 0.07 per mil. The reason for the 0.2- per mil difference between the two sets is not evident. However, modification and repair of the mass spectrometer that shortly preceded the second set of analyses may be the reason. Accordingly, $\delta^{13}C$ of the DIC of the standard solutions prepared and analyzed before the modification was compared with $\delta^{13}C$ of the first set, whereas that of the solutions prepared and analyzed after the modification was compared with the second set.

Accuracy and Precision of $\delta^{13}C$ Determination of DIC Extracted by the Different Techniques

In order to determine the accuracy of $\delta^{13}C$ of DIC extracted by different techniques, samples with DIC of known $\delta^{13}C$ values are needed, whereas several aliquots taken from a big sample are needed in order to determine the precision. Baker analytical reagent $NaHCO_3$ of $\delta^{13}C$ value -15.33 ± 0.07 (or -15.52 ± 0.07) per mil was used to prepare the required samples. Deionized water was freed from dissolved CO_2 by boiling for four hours while purging with nitrogen gas. After cooling, while purging with N_2 gas, the water was used to dissolve the $NaHCO_3$.

Four and half liters of $NaHCO_3$ solution were prepared in order to minimize the effect of the solid reagent inhomogeneity on the measured $\delta^{13}C$. The prepared solution was 0.01 molar. This value is representative of bicarbonate concentrations in many natural waters. Sampling of the prepared bicarbonate solution immediately followed its preparation. A peristaltic pump was used to transfer the standard solution from the 4.5- liter stock bottle through a 0.2-μm pore-glass filter into the sampling devices.

The precipitation technique

Pyrex glass bottles, 152 mL capacity with Teflon-coated screw caps were used to sample the prepared water for the precipitation technique.

After filling the bottles, 8 ml of ammoniacal $SrCl_2$ solution was added to the bottom. The method of preparation of the ammoniacal $SrCl_2$ and the $SrCl_2$/sample ratio were the same as those used by Gleason and others (1969). The bottles were closed immediately, the caps sealed with black electrical tape, and the bottles shaken well. After two days, the samples were filtered in a nitrogen-atmosphere glove box. The precipitate was dried in a nitrogen atmosphere glove box then ground. The technique of splitting the samples to quarters was used to obtain a representative sample of the dried precipitate. The samples were reacted with 100 percent phosphoric acid in order to evolve the CO_2.

The calculated efficiency of extraction of DIC from a simple $NaHCO_3$ solution by the precipitation technique is 95 percent. The calculated efficiency of extraction considers the amount of the non-carbonate precipitates with the $SrCO_3$. The amount of the recovered precipitate and the percent of the carbonate in the precipitate are used in calculations. The $\delta^{13}C$ value of the four-sample set of the DIC extracted by the precipitation technique is -15.36 ± 0.05 per mil (Table 4). This value is in good agreement with the $\delta^{13}C$ value (-15.33 ± 0.07 per mil) of the solid $NaHCO_3$.

The gas evolution technique

Glass syringes, 50mL, with metal Luer-lok tips were used to sample the prepared water. Twenty mL of 100 percent phosphoric acid were used to evolve the CO_2 from each sample. The sample was injected into the reaction flask containing the acid (Fig. 4). The evolved CO_2 was frozen in a Horible trap while pumping. The reaction flask was also heated to 100°C.

The mean $\delta^{13}C$ value of the four-sample set of the DIC extracted by the gas evolution technique is -15.36 ± 0.02 per mil (Table 4). Even though the amount of the extracted carbonate as calculated from the volume of the evolved CO_2 was only 90 percent of the DIC, the measured $\delta^{13}C$ is accurate and precise. It was possible to extract more than 90 percent of the DIC by allowing longer periods for the extraction, which led to collection of more water with the CO_2. However, the efficiency of extraction of DIC never reached 100 percent.

Effect of Sulfate Concentration on Accuracy and Precision of $\delta^{13}C$ determination of DIC extracted by the different techniques

In order to determine the effect of sulfate concentration in water on the precision and accuracy of $\delta^{13}C$ of DIC, $\delta^{13}C$ of DIC should be measured before and after addition of known amounts of sulfate. Five samples of 0.01 molar $NaHCO_3$ were prepared as described in the previous sections. Analytical reagent Na_2SO_4 was used to prepare 0.001, 0.005, 0.01, and 0.1 molar sulfate solutions.

The precipitation technique

The procedure described in the previous section was used to prepare the samples. However, in the presence of sulfate, two different amounts of amm.$SrCl_2$, 8 and 18 mL, were added in order to determine the effect of the amount of ammoniacal $SrCl_2$ on the amount of DIC extracted. Weights of the sulfate-containing precipitates analyzed were adjusted to evolve the desired volume of CO_2.

It was found that strontium sulfate ($SrSO_4$) precipitates with strontium carbonate ($SrCO_3$). The increase in sulfate concentration increases the total amount of solid precipitated. Accordingly, the percent yield of CO_3 in the total precipitate decreases. Additional amounts of amm.$SrCl_2$ precipitate more of the sulfate and also increase the efficiency of DIC extraction. However, the increase in the amount of DIC extracted is very small and does not vary linearly with the amount of the ammoniacal $SrCl_2$ added. This finding is in agreement with the theoretical calculations obtained by computer simulation. The increase in the sulfate concentration to 0.01 molar also decreases the efficiency of DIC extraction from 95 ± 3 to 90 ± 5 percent (Table 4). The amount of the decrease is small; however, presence of 0.1 molar sulfate decreases the efficiency of extraction to 70 ± 3 percent.

The relationship between the percentages of the recovered DIC and log molality of sulfate is approximately linear (Fig. 5). The relationship is:

$$\text{percent recovered DIC} = \frac{\text{Log } M_{SO4}}{a} + b \ .$$

The constants a and b are −0.08 and 60.5, respectively, for water containing 0.01 molar $NaHCO_3$ and 0.001 to 0.1 molar $Na_2 \ SO_4$ at 25°C. This equation may be used to correct the measured amounts of the DIC in water samples of known sulfate concentrations. Similar equations may be developed for water containing different amoungs of DIC and SO_4.

The relationship between the change in $\delta^{13}C$ of the extracted DIC and log molality of sulfate also is approximately linear (Fig. 6). The relationship is:

$$\text{per mil } \Delta^{13}C_{MSO_4} = \frac{\text{Log } M_{SO4}}{a} + b$$

where $\Delta^{13}C_{MSO_4} = \delta^{13}C_{measured(MSO_4)} - \delta^{13}C_{true(zero\ SO_4)}$,

a = 4.88 and b = 0.61 at 25°C. This relationship may be used to correct the measured $\delta^{13}C$ of the DIC in water samples of known sulfate concentrations. However, the concentration of the DIC of the water samples and their $\delta^{13}C$ value may change the constants of the equation.

The increase in sulfate concentration to 0.1 mole resulted in a 0.45 per mil increase in the $\delta^{13}C$ value of the DIC extracted by the precipitation technique. This trend of $\delta^{13}C$ increase agrees with the conclusions obtained from theoretical calculations. However, based on the theoretical calculations of carbon isotope fractionation during precipitation, magnitude of the increase in $\delta^{13}C$ should be higher. More positive values of $\delta^{13}C$ of the DIC also correlate with decreases in the amount of DIC extracted (Table 4).

The increase in sulfate concentration required a ball mill, as Barnes suggested, to homogenize the sample to obtain 0.1 per mil precision (oral commun., 1979).

The gas evolution technique

The procedure described in the previous section was used to prepare the samples. The data in Table 4 indicate that the efficiency of extraction of DIC by the gas evolution technique is 90 percent and is not affected by the concentration of sulfate in the water. However, $\delta^{13}C$ of the DIC show a slight increase with the increase in sulfate concentration. The trend of the increase is similar to that observed in the precipitation technique but less in magnitude and may be ignored. The increase in sulfate concentration to 0.1 mole/L corresponds to 0.11 per mil increase in the $\delta^{13}C$ value of the DIC.

Reliability of Sampling Devices During Shipping and Storing

In order to determine the effect of various devices on the accuracy and precision of the measured $\delta^{13}C$ of the sampled water, a $NaHCO_3$ solution with known $\delta^{13}C$ was prepared and sampled as previously described. The water sampling devices in figure 3 were used.

The sampling devices were tested after storing under normal laboratory conditions for one to two days and after two weeks. Intensified conditions of vacuum, heat, and high concentrations of atmosphere CO_2 were used to simulate the effects of air shipping and long storage.

The vacuum simulated air shipping of water samples in an unpressurized baggage compartment. After subjecting the sampling devices containing the 0.01 molar bicarbonate solutions to each test, DIC was extracted and analyzed. The method of preparation and the necessary precautions, described above, were followed.

Reliability of Sampling Devices Stored Under Normal Laboratory Conditions for One to Two Days

The precipitation technique

The measured $\delta^{13}C$ values of the DIC indicates that the $\delta^{13}C$ of the prepared solutions did not change after storage in pyrex, whereas the measured $\delta^{13}C$ of the prepared solutions stored in polyethylene increased by .2 per mil (Table 5). Because the atmospheric CO_2 has higher $\delta^{13}C$ than the standard solution, the increase in the mean $\delta^{13}C$ of the precipitate in the polyethylene bottles could result from contamination with atmospheric CO_2. The CO_2 contamination is due to diffusion through the polyethylene. Ammonia absorbs CO_2, consequently, the rate of diffusion of CO_2 through the polyethylene increases due to the presence of the ammoniacal $SrCl_2$ reagent.

The 0.2 per mil increase in the measured $\delta^{13}C$ of the water stored in ployethylene bottles is small. However, if the time of storage was considered, it is disturbing that 0.2 per mil increase in $\delta^{13}C$ had occurred in less than 48 hours. The time from collecting the samples until they are analyzed, in most cases, is considerably more than 48 hours. A long laboratory back-log would further lengthen the storage time and permit more serious contamination of carbon isotope samples.

The gas evolution technique

The measured $\delta^{13}C$ values of the DIC of the standard solutions stored in all sampling devices, except the syringes, had changed (Table 5). The observed increase in $\delta^{13}C$ values in some of the samples could be explained by outgassing of CO_2. For example, the measured $\delta^{13}C$ of the water in the glass tubes (Figure 2) is -15.19 ± 0.05 per mil (Table 5), whereas the determined value for the solid $NaHCO_3$ is -15.33 ± 0.07 per mil. The difference (0.14 per mil could result from outgassing of CO_2 during the transfer of the water sample to the reaction flask (figure 4). The outgassed CO_2 remains in the sampling tube and cannot be drawn into the reaction flask due to the higher pressure in the flask.

Substantially increased $\delta^{13}C$ values are observed in the waters contained in Tygon tubes (Table 5). Possibly. diffusion of the outgassed CO_2 through the tubing walls contributed to the higher $\delta^{13}C$ results. Incomplete transfer of light vapor-phase CO_2 to the reaction flask as well as diffusion of atmospheric CO_2 through the tubing walls during the transfer could also contribute to higher $\delta^{13}C$ results.

The serum bottles remained very well sealed to the atmosphere while withdrawing the sample with a syringe. The transfer of the sample and the outgassed CO_2 was complete, however, it was a difficult process. Another experimental method to transfer the samples was tried. A syringe needle was glued to the reaction flask and a rubber stopper was used to seal the needle to the atmosphere. The sample was transferred by pushing the serum bottle so that the needle penetrated the stopper and the septum. It is impossible to transfer all of the outgassed CO_2 due to the reasons previously explained.

The average $\delta^{13}C$ of samples stored in rubber-stoppered serum bottles was less than one standard deviation greater than that of the analyzed solid $NaCHO_3$ (Table 5). On the other hand, results of isotope analyses of samples in serum bottles with Teflon-coated silicone septa indicate a definite decrease in the $\delta^{13}C$ of these samples. The reason for this change in isotope composition is not evident.

The glass syringes with metal Luer-lok tips (Figure 3) were the easiest sampling devices to use. The measured $\delta^{13}C$ values of the water in these containers were accurate and precise (Table 5). The measured mean $\delta^{13}C$ (-15.36 ± 0.02 per mil) agrees very well with that of the solid $NaHCO_3$ (-15.33 ± 0.07 per mil).

Effect of storing sampling devices under laboratory conditions for two weeks

The precipitation technique

The $\delta^{13}C$ of the prepared solutions in glass bottles did not change, while those in polyethylene bottles increased by 0.4 per mil after two weeks of storing (Table 5). This test confirms the unreliability of polyethylene bottles for sampling and storing water for $\delta^{13}C$ measurements.

The gas evolution technique

The unreliability of all sampling devices, except glass syringes, exists during the sample transfer into the vacuum line. Thus, these samples are unreliable and there is no need to also evaluate the effect of long storage.

After two weeks, $\delta^{13}C$ of the prepared solution in the glass syringes decreased by 0.2 per mil. The change in $\delta^{13}C$ is small, however, is in the opposite direction of what is expected due to outgassing. Furthermore, there was no indication of air leakage around the barrels. The syringes were stored with half their length emersed in water in a covered beaker. The tips were also inserted in rubber stoppers.

Effect of storing sampling devices in a CO_2 atmosphere under a bell jar for one week

This test was conducted in order to evaluate the extent of CO_2 diffusion through polyethylene bottles and thus to determine the reliability of polyethylene bottles as sampling devices. Pure CO_2 with a $\delta^{13}C = -44.95$ per mil was the atmosphere of a bell jar under which the prepared water samples were stored.

The data in Table 5 indicate that the pyrex bottles are reliable. The measured mean $\delta^{13}C$ (-15.44 ± 0.08 per mil) agrees with the mean $\delta^{13}C$ of the solid $NaHCO_3$ within the limit of accuracy and precision of the mass spectrometer. However, the measured mean $\delta^{13}C$ of the samples stored in polyethylene bottles ($-39.08 + 0.32$ per mil) is close to that of the surrounding CO_2 (-44.95 per mil) (Table 5). Furthermore, the amount of the precipitated $SrCO_3$ in the polyethylene bottles is four times that in the glass bottles. Weights of precipitate in the glass bottles are in agreement with the calculated values. These results indicate rapid diffusion of CO_2 through the polyethylene. The diffusion rate is affected by the variation in the wall thickness of the polyethylene bottles as indicated by the scattered $\delta^{13}C$ values of the same set (Table 5).

Effect of storing sampling devices under vacuum in a bell jar

This test was conducted in order to evaluate the reliability of the sampling devices of the gas evolution technique. The samples were stored in bell jar under an evacuated condition in order to intensify the effect of air shipping in unpressurized luggage compartment.

Immediately upon evacuating the bell jar, air bubbles formed inside the Tygon tubing. After three hours, the barrels of the syringes and the stopcocks of the glass sampling tubes had leaked. After 24 hours, it was obvious that all the sampling devices, except the serum bottles, had leaked.

The volume of the water samples in all devices except the serum bottles decreased due to evaporation. Accordingly, there was no need to measure $\delta\ ^{13}C$ of the samples, in order to confirm the unreliability of these devices. The $\delta^{13}C$ of the samples in the serum bottles, which passed the vacuum test for a period of one week, only were measured. The values recorded in Table 5 indicate the reliability of the serum bottles. It is noteworthy to mention that the measured mean $\delta^{13}C$ of that test of the samples in the bottles with the two different kinds of septa are closer to the solid $NaHCO_3$ $\delta^{13}C$ than those of the earlier test (Table 5). It is possible that, due to repetition, the author's technique of withdrawing the sample from the bottles had improved.

Effect of storing sampling devices at 60°C

The water sampling devices for the gas evolution technique were tested at an elevated temperature in order to evaluate their reliability under extreme shipping or storage conditions. A heat lamp was used as a heat source. The devices containing the samples were inside a beaker lined with aluminum foil. The temperature inside the beaker was controlled by adjusting the distance from the heat lamp until the desired temperature, as measured by a thermometer, was obtained.

Reaction of the differnt sampling devices under high temperature was similar to that under vacuum. After 48 hours, serum bottles were the only sampling device to pass the heat test, whereas some water evaporated from other devices.

Evaluation of Sample Treatment and Laboratory Preparation on $\delta^{13}C$ Values

Effect of Addition of $HgCl_2$ to Water Samples

Three of 4-sample sets were collected in 50 mL glass syringes from each of 4 types of water. A peristaltic pump was used to transfer the samples through a 0.2- µm-pore-glass filter into the syringes.

Approximately 0.2 mL of saturated $HgCl_2$ per sample was added to one set. The other two sets were left free of $HgCl_2$. The DIC in one of the $HgCl_2$-free sets was extracted after one week and the second after four weeks. The carbon isotope analyses of the three sets are recorded in Table 6.

All the samples without $HgCl_2$, except those from the ocean, are lighter in the carbon isotopes, indicating production of CO_2 by organic decay (Table 6). The $\delta^{13}C$ of the samples analyzed became more negative after four weeks indicating more production of the organic CO_2. The magnitude of the change in $\delta^{13}C$ is greatest in the samples from Sudley Spring. These samples showed approximately -2 and -3 per mil change in $\delta^{13}C$ respectively, after one and four weeks (Table 6). The water from Sudley Spring has brownish yellow color that remained after filtration.

The ocean water without $HgCl_2$ became heavier in the carbon isotopes, possibly due to micro plant photosynthesis. Each of the two sets without $HgCl_2$ showed a positive trend for the change in $\delta^{13}C$ when compared with those with $HgCl_2$ (Table 6). However, $\delta^{13}C$ values are -4.45, + 0.89, and -3.65 per mil respectively, for the set with $HgCl_2$, and without $HgCl_2$ analyzed after one week, and analyzed after four weeks. The reason for the inconsistency of the trend is not evident.

Effect of Filtering and(or) Drying the $SrCO_3$ Precipitate in the Air

Four 4-sample sets of 0.01 molar $NaHCO_3$ standard solution were sampled by the $SrCO_3$ precipitation technique as previously described. One set was filtered and dried in a nitrogen-atmosphere glove box, the second was filtered in the glove box but dried in an oven at 90°C. Samples were analyzed and the $\delta^{13}C$ values are recorded in Table 7.

The mean $\delta^{13}C$ value of the $SrCO_3$ filtered and dried in the nitrogen-atmosphere, -15.51 ± 0.1 per mil, agreed with that of the $NaHCO_3$ used to prepare the solution. However, $\delta^{13}C$ of the $SrCO_3$ filtered or dried in the air changed by approximately +0.3 per mil indicating atmospheric contamination. The contamination results from absorption of atmospheric CO_2 by the alkaline solution during filtration, or isotopic exchange between CO_2 and the precipitate while drying. Although the precipitate is rinsed thoroughly with distilled water, absorption of CO_2 on the alkaline surfaces of the $SrCO_3$ grains is also possible. The $\delta^{13}C$ of the $SrCO_3$ filtered in the air and dried in oven changed by +0.5 indicating the cumulative effect of both processes.

Effect of the Phosphoric Acid Concentration

Strontium carbonate precipitates from three natural water samples were reacted with 85 and 100 percent phosphoric acid. The $\delta^{13}C$ values of the $SrCO_3$ samples reacted with 85 percent phosphoric acid agreed with those of the same samples reacted with 100 percent acid within the standard deviation (Table 7). Completion of the reaction was slow with the 100 percent acid. Insufficient reactions time might result in errors in routine $\delta^{13}C$ determinations using the 100 percent H_3PO_4. The 85 percent acid reacted with NBS-19(TS) yielded a $\delta^{13}C$ value of 2.02 per mil, in agreement with the value obtained with the 100 percent acid.

This test indicated that the commercially available 85 percent phosphoric acid is suitable for $\delta^{13}C$ measurements. This acid is much less expensive than the 100 percent acid, which must be specially prepared in the laboratory. The suitability of the 85 perent phosphoric acid for $\delta^{13}C$ measurement does not imply its suitability for $\delta^{18}O$ measurement.

Effect of Purification on Cu and MnO_2 Furnaces at 450°C

A set of $SrCO_3$ samples precipitated from 0.01 molar $NaHCO_3$ solution containing 0.1 molar Na_2SO_4 was prepared as previously described, and analyzed. After further purification, the separated CO_2 was reanalyzed. The purification consisted of passing the gas through furnaces containing Cu and MnO_2 at 450°C. The results indicate that the change in $\delta^{13}C$ of the CO_2 samples due to purification on hot Cu is 0.1 per mil, whereas that due to purification on hot MnO_2 is more than 0.7 per mil (Table 7). The MnO_2 furnace also produced large changes in $\delta^{18}O$ of the CO_2 samples. The changes in $\delta^{13}C$ and $\delta^{18}O$ may result from memory effect of previous samples. It is noteworthy to mention that allowing one hour to purify each sample and pumping between samples for longer periods did not eliminate the problem.

Comparison Between Carbon Isotope Analysis of DIC Extracted from Various Natural Waters by the Precipitation and Gas Evolution Techniques

Four-sample sets of four types of natural water were collected. A peristaltic pump was used to transfer the samples through 0.2-µm-pore glass filter into the sampling devices. Glass syringes with metal Luer-lok tips and pyrex glass bottles with Teflon-coated screw caps were used to collect samples for the gas evolution and the precipitation techniques, respectively. Approximtely 0.2 mL of saturated $HgCl_2$ was added to each 50-mL syringe, and 8 mL amm.$SrCl_2$ were added to each 152-mL bottle.

The surface waters were collected at approximately 1.5 meter depth. The Potomac River represented the low salinity type while, the Atlantic Ocean represented the high salinity type. Springs represented the ground water; Sudley Spring has high sulfate content (1100 mg/L) and Chinn Spring has low sulfate content (100 mg/L). Both springs are at Manassas, Virginia.

The $SrCO_3$ samples were filtered and dried in a nitrogen-atmosphere glove box. After homogenizing the precipitate, a representative sample weighing approximately 50 mg was reacted with 5 mL of 85 percent phosphoric acid. For the surface water, the entire sample was used. The high salinity samples were reacted with 10 mL volume of acid. Due to the large amounts of non-carbonate containing salts, the reaction tubes were left over night to ensure completion of the reaction. X-ray diffraction of the precipitate from the ocean water indicated presence of celestite ($SrSO_4$), and brucite ($Mg(oH)_2$); however, carbonate minerals were below detection limits. The precipitates from the water of the Potomac River and Sudley Spring indicated presence of strontianite.

Each of the samples collected for the gas evolution technique was injected into the reaction flask containing 30 mL of 85 percent phosphoric acid (Figure 4). The flask was heated. The CO_2 evolved from both techniques was separated from water by passing through several dry ice traps. No other purification steps were employed.

The carbon isotope analyses are recorded in Table 8. The carbon analyses of the different types of natural water collected by both techniques agreed within the limit of precision of the mass spectrometer (Table 8).

CONCLUSIONS

The efficiency of separation of DIC is more crucial in the precipitation technique than in the gas evolution technique. The higher fractionation factor between the precipitate and the carbonate solution than between the evolved CO_2 and the carbonate solution is the main reason.

The precipitation technique is capable of extracting more than 90 percent of the DIC in presence of sulfate up to 0.01 molar. However, when the sulfate concentration increases to 0.1 molar the efficiency of extraction drops to 70 percent. On the other hand, the efficiency of DIC extraction by the gas evolution technique is independent of sulfate concentration. On the average, 90 percent of the DIC could be easily extracted by the gas evolution technique. However, 100 percent extraction of the DIC as predicted theoretically and as Mook (1968) stated could not be obtained.

Carbon isotope fractionation during precipitation may explain the 0.45 per mil increase in $\delta^{13}C$ of the DIC extracted by the precipitation technique from 0.01 molar $NaHCO_3$ standard solution in the presence of 0.1 mole/L Na_2SO_4. The measured increase in $\delta^{13}C$ is less than the theoretically calculated increase if 30 percent of the DIC is left in solution as a result of interference of sulfate with carbonate precipitation. The discrepancy between the calculated and measured increase is a result of assuming equilibrium during precipitation to obtain the calculated $\delta^{13}C$. However, it is possible that the process of precipitation occurs fast and before reaching equilibrium. High sulfate concentrations may slightly slow the precipitation of DIC.

The reason for the 0.11 per mil increase in $\delta^{13}C$ of the DIC extracted by the gas evolution technique in the presence of 0.1 mole/L $NaSO_4$ is not evident. It is possible that sulfate interferes with the distribution of carbon species; however, addition of the acid to evolve the CO_2 should cancel that effect. However, it is also possible that the change is because of analytical or instrumental error.

The approximate linear relationship between log molality of sulfate and the increase in $\delta^{13}C$ of the precipitated DIC suggests possible correction curves for the measured $\delta^{13}C$. Similar curves to correct the measured amounts of DIC are also possible. Thus, it is recommended to associate sulfate concentrations and total alkalinity with $\delta^{13}C$ measurements of water samples until such correction curves are well established. The present investigation documents the effect of sulfate concentration on stable carbon isotope fractionation; however, further studies to evaluate the effect of other components and the total water chemistry are needed.

The study indicates that both techniques, the precipitation and gas evolution are accurate and precise for extracting DIC for stable carbon isotope analysis from natural waters. However, the gas evolution technique seems to be more suitable than the precipitation technique for high sulfate and high salinity waters because of the difficulties involved in preparing these precipitates for isotope analyses. Erroneous $\delta^{13}C$ values of DIC were generally not the result of failure of the extraction technique; but were more often caused by the methods employed in handling and preparing the samples.

For example, atmospheric CO_2 diffuses into polyethylene bottles producing error in the measured $\delta^{13}C$ of the DIC extracted by the precipitation technique. Glass bottles with Teflon-coated screw caps should be used to eliminate that error. Another problem is absoption of atmospheric CO_2 and(or) carbon isotopic exchange during filtering and drying the precipitate. To eliminate this problem, samples should be filtered and dried inside a nitrogen-atmosphere glove box. In the precipitation technique, it was also found that inhomogeneity of the precipitate from high-sulfate waters affect the precision of the measured $\delta^{13}C$. However, this problem can also be overcome by homogenizing the sample very well.

The most serious problem in the gas evolution technique is the lack of a perfect sampling device. Glass syringes with metal Luer-lok tips are shown to be the only reliable sampling device among those tested. However, they are not suitable for geothermal samples, or for long storage, air shipping, and heat. In these situations, serum bottles with aluminum seals lined with Teflon-coated septa seem to be satisfactory. The incomplete transfer of outgassed CO_2 from the serum bottles into the vacuum line produces some error in the measured $\delta^{13}C$. Another problem in handling the samples collected for the gas evolution technique is production of CO_2 from decay of organic matter after sample collection. Addition of saturated $HgCl_2$ overcomes this problem.

The methods employed to purify the CO_2 samples also introduce errors in the measured $\delta^{13}C$. For example, hot MnO_2 furnaces produced more than a 0.7 per mil change in $\delta^{13}C$. Hot Cu furnaces produced only a 0.1 per mil change in $\delta^{13}C$ and may be suitable for purifying CO_2 samples. Both types of furnaces change $\delta^{18}O$. The change $\delta^{18}O$ is approximately 1 per mil in the Cu furnaces, and greater changes occurred in the MnO_2 furnaces. The natural samples prepared by the gas evolution and precipitation techniques did not require purification other than dry ice traps. However, if additional purification is needed, it is recommended to use only hot Cu traps or gas chromotographic columns.

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Figure 1.- -Log molality of dissolved inorganic carbon in Hypothetical waters after addition of different volumes of ammoniacal $SrCl_2$.

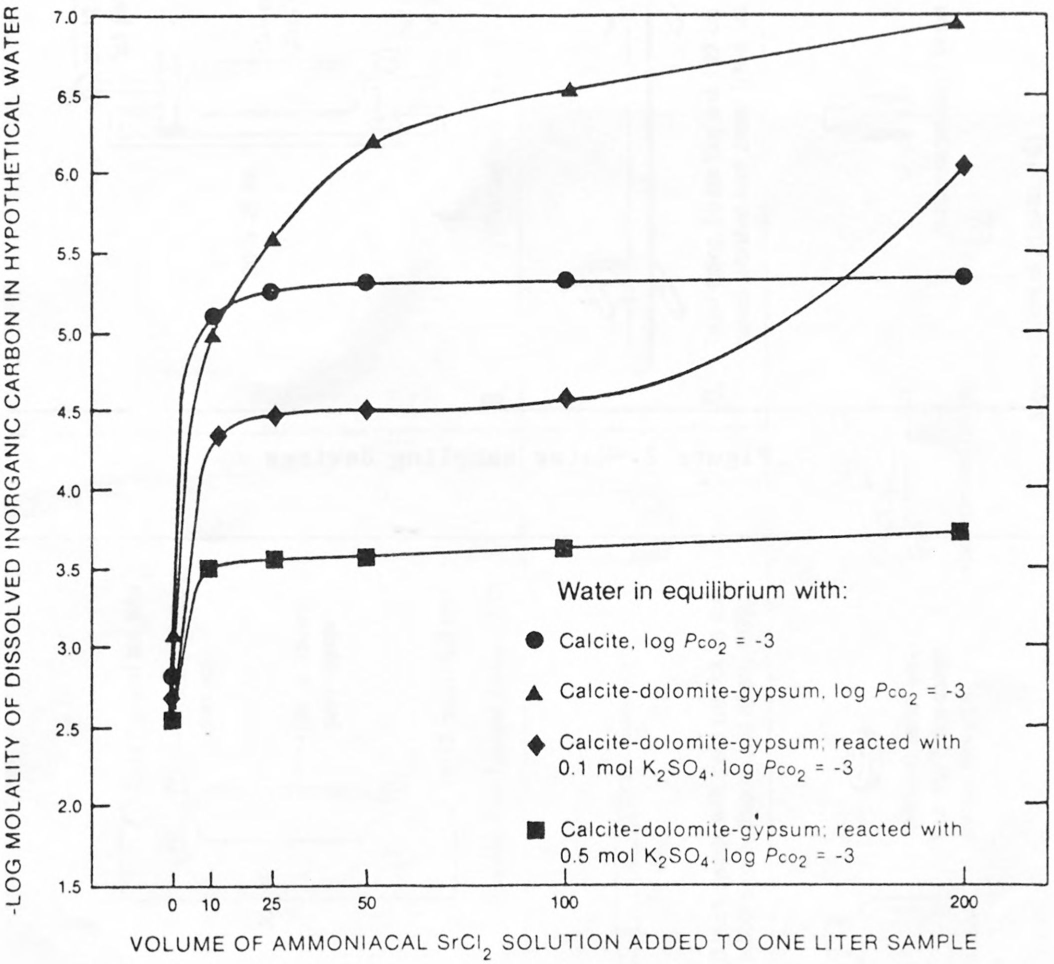
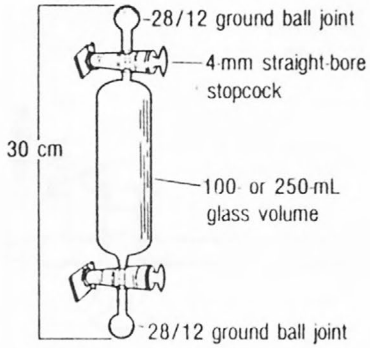
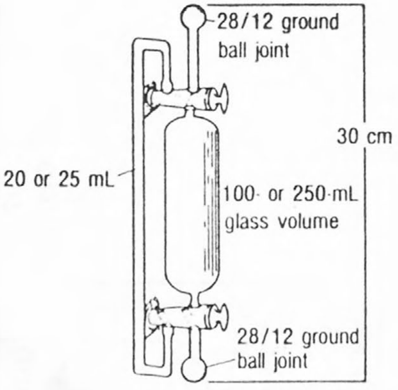

-LOG MOLALITY OF DISSOLVED INORGANIC CARBON IN HYPOTHETICAL WATER
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
0
10
25
50
100
200
VOLUME OF AMMONIACAL $SrCl_2$ SOLUTION ADDED TO ONE LITER SAMPLE
Water in equilibrium with:
● Calcite, log P_{CO_2} = -3
▲ Calcite-dolomite-gypsum, log P_{CO_2} = -3
◆ Calcite-dolomite-gypsum; reacted with 0.1 mol K_2SO_4, log P_{CO_2} = -3
■ Calcite-dolomite-gypsum; reacted with 0.5 mol K_2SO_4, log P_{CO_2} = -3

Figure 2.-Water sampling devices



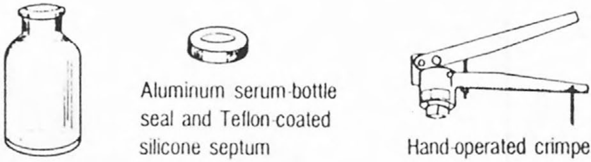
A. (Modified from Tan and others, 1973)



B. (Modified from Pearson and others, 1978)

C. B-D glass syringe with metal Luer-lok tip and a rubber stopper (Readon and others, 1979)

D. Tygon tubing, 90 cm long and 1.27 cm ID, and two Hoffman clamps (Modified from James O'Niel, oral commun., 1980)



100-mL amber-glass serum bottle with 20-mm ID neck

Aluminum serum-bottle seal and Teflon-coated silicone septum

Hand-operated crimper

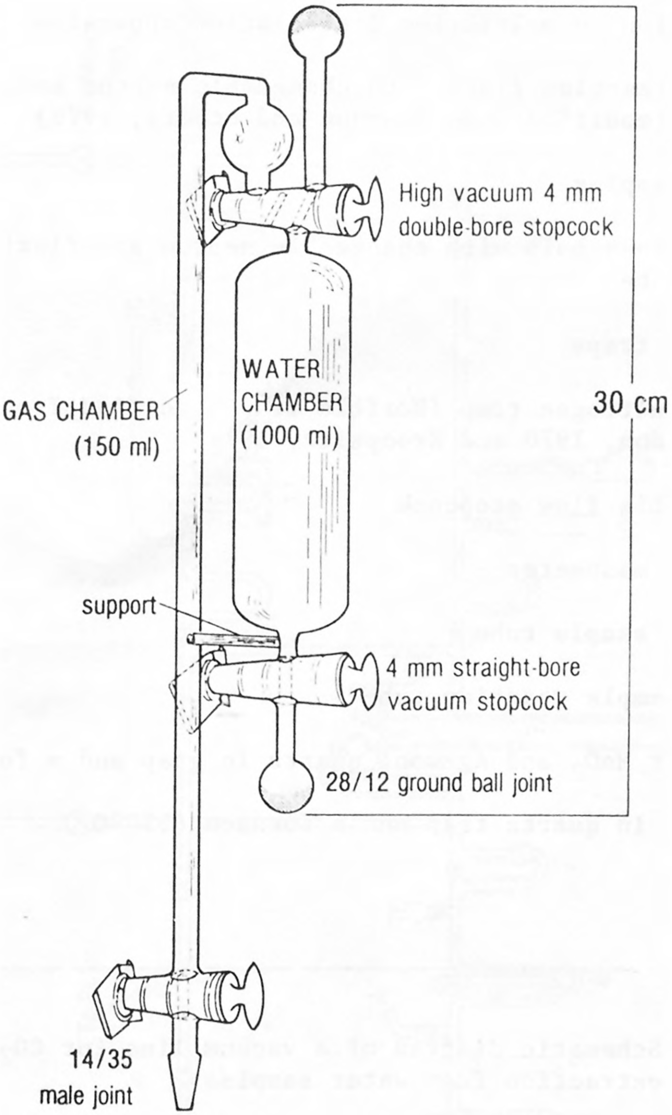
E1.

Rubber serum-bottle sleeve-stopper

E2.

suggested devices (Hassan, n.d.)

Figure 3.-Water sampling apparatus for DIC determination by the proposed vapor phase equilibration technique.


High vacuum 4 mm double-bore stopcock
WATER CHAMBER (1000 ml)
GAS CHAMBER (150 ml)
30 cm
support
4 mm straight-bore vacuum stopcock
28/12 ground ball joint
14/35 male joint

T.C.	Thermocouple gauge
"A"	Connection to a line for soil-gas separation by the gas chromatographic technique
"B"	Connection to multibrine distillation apparatus
1	500-mL reaction flask with changeable septum and heating mantle (modified from Reardon and others, 1979)
2	Water sampler
3	20-mL glass bulb with changeable septum and flexible metal tube
4,5,6	Dry ice traps
7	Liquid nitrogen trap (Horible trap, modified from Williams and Gordon, 1970 and Kroopnick, 1974)
8	Adjustable flow stopcock
9	Mercury manometer
10a	CO_2 gas sample tube
10b	$SrCO_3$ sample reaction tube
11	Granular MnO_2 and Ag-wool quartz in grap and a furnace (550°C)
12	Cu wire in quartz trap and a furnace (550°C

Figure 4.-Schematic diagram of a vacuum line for CO_2 extraction from water samples.

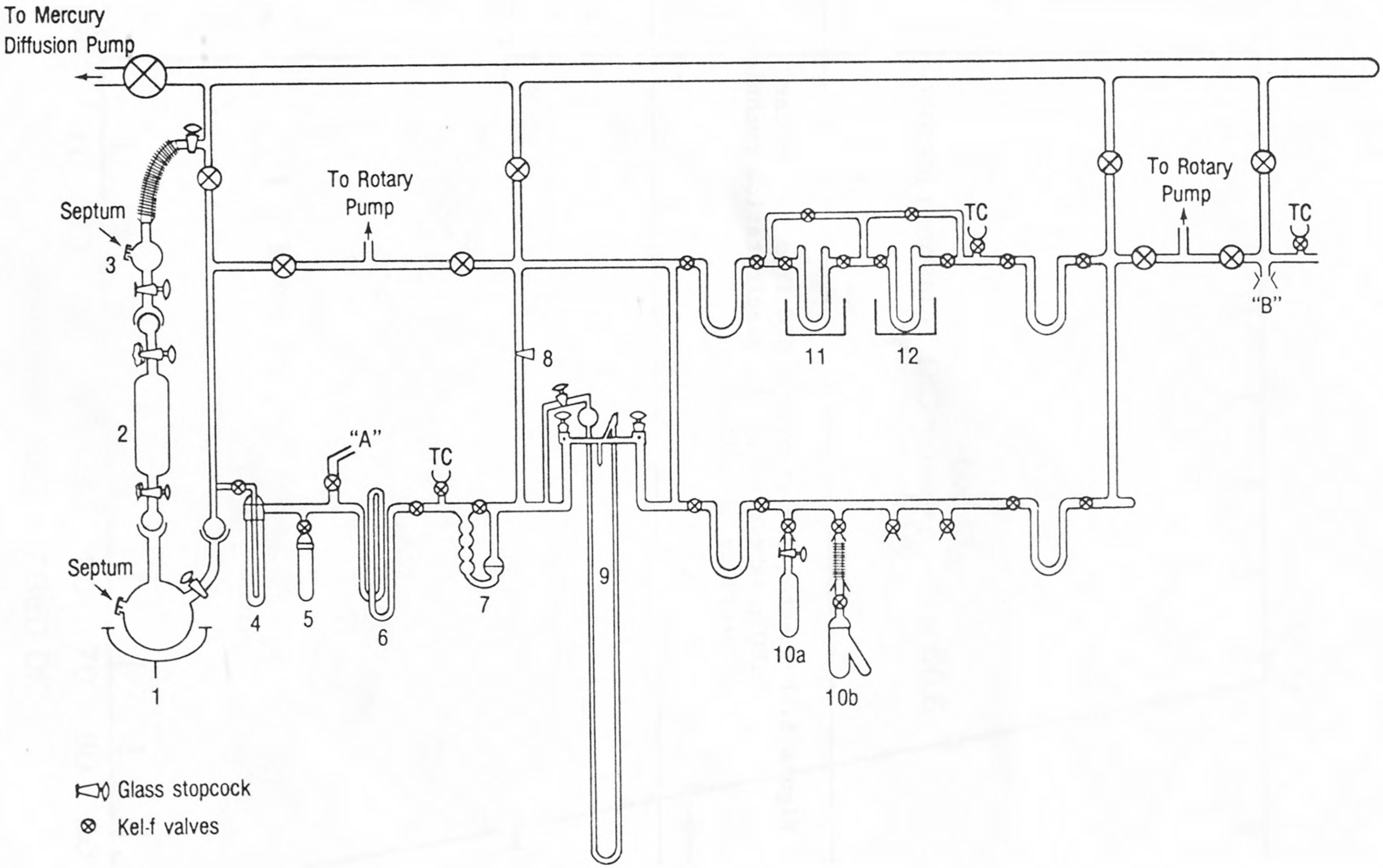

To Mercury
Diffusion Pump
To Rotary
Pump
To Rotary
Pump
TC
TC
TC
Septum
3
2
Septum
1
4
5
6
"A"
7
8
9
10a
10b
11
12
"B"
Glass stopcock
Kel-f valves

Figure 5.-Percentage of recovered DIC from 0.01 molar $NaHCO_3$ extracted by the precipitation technique in presence of sulfate

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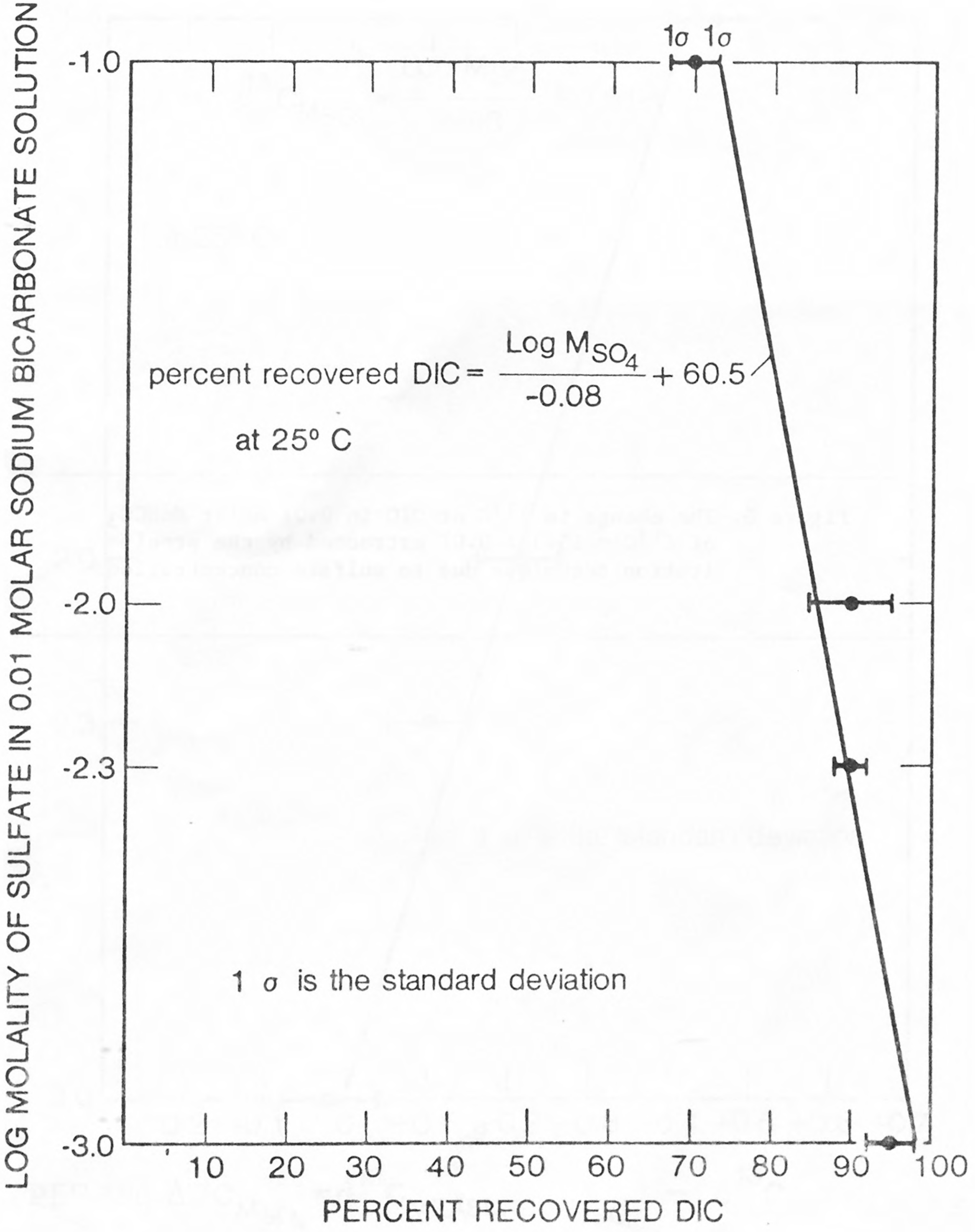
1σ 1σ
-1.0
-2.0
-2.3
-3.0
LOG MOLALITY OF SULFATE IN 0.01 MOLAR SODIUM BICARBONATE SOLUTION
percent recovered DIC = $\frac{\text{Log } M_{SO_4}}{-0.08} + 60.5$
at 25° C
1 σ is the standard deviation
10
20
30
40
50
60
70
80
90
100
PERCENT RECOVERED DIC

Figure 6.-The change in $\delta^{13}C$ of DIC in 0.01 molar $NaHCO_3$ of $\delta^{13}C = 15.33 \pm 0.07$ extracted by the precipitation technique due to sulfate concentration

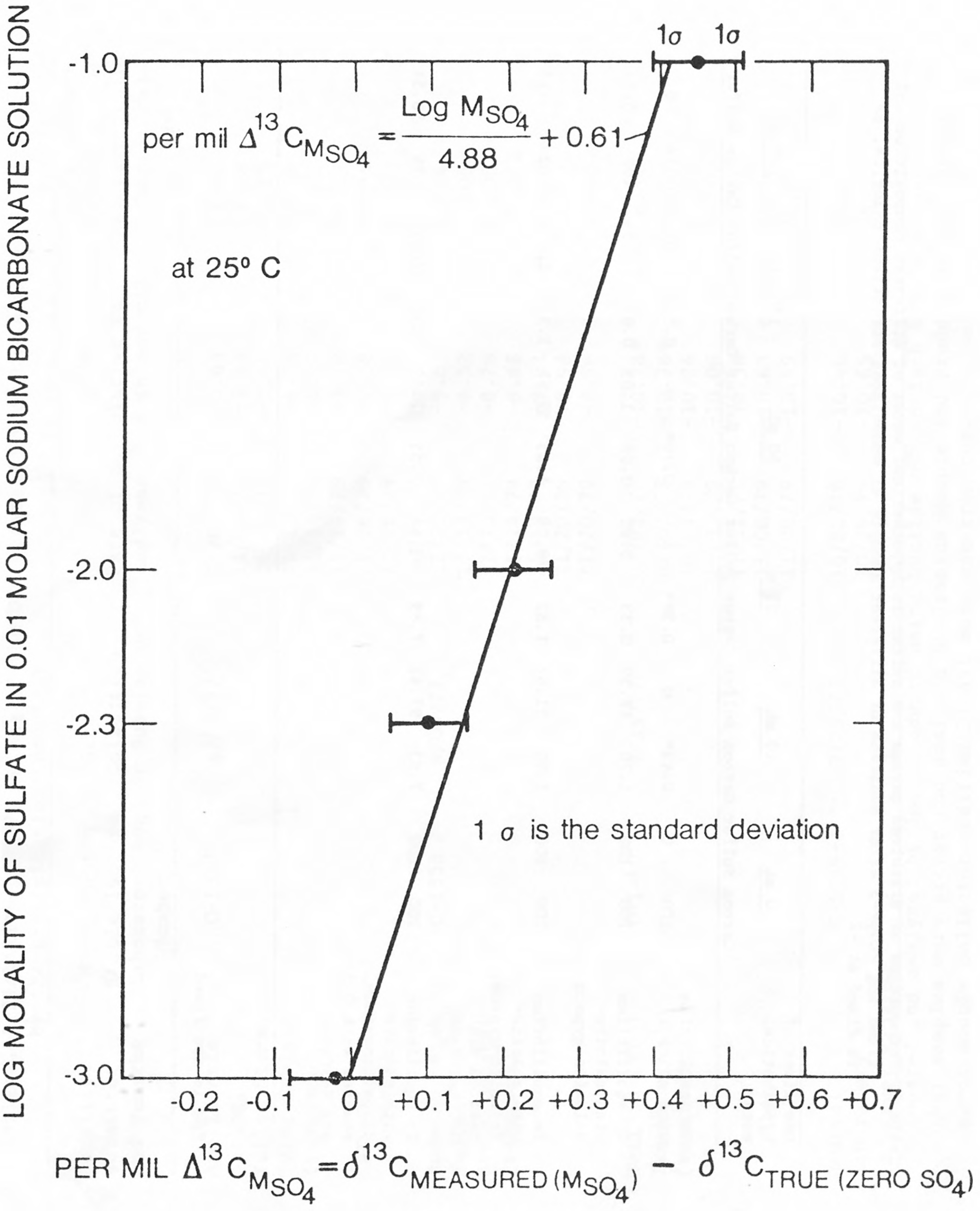LOG MOLALITY OF SULFATE IN 0.01 MOLAR SODIUM BICARBONATE SOLUTION
-1.0
-2.0
-2.3
-3.0
1σ
1σ
per mil Δ13 C MSO4 = Log MSO4 / 4.88 + 0.61
at 25° C
1 σ is the standard deviation
-0.2
-0.1
0
+0.1
+0.2
+0.3
+0.4
+0.5
+0.6
+0.7
PER MIL Δ13 C MSO4 = δ13 C MEASURED (MSO4) − δ13 C TRUE (ZERO SO4)

Table 1.-Percentages of dissolved carbon and sulfur in hypothetical water of different composition and fixed $\log P_{CO_2}=-3$ after addition of different amounts of ammoniacal strontiaum chloride, pe is fixed at -2

One liter of hypothetical water	0 mL		10 mL		25 mL		50 mL		100 mL		200 mL	
	Carbon	Sulfur	Carbon	Sulfur	Carbon	Sulfur	Carbon	Sulfur	Carbon	Sulfur	Carbon	Sulfur
In equilibrium with calcite	100	0	0.43*	0	0.38*	0	0.36*	0	0.34*	0	0.31*	0
In equilibrium with calcite-dolomite-gypsum	100	100	1.20	48.39	0.33	3.96	0.07	1.05	0.03	0.56	.02	0.34
In equilibrium with calcite-dolomite-gypsum, reacted with 0.1 mol K_2SO_4	100	100	1.95	91.62	1.82	79.29	1.65	59.51	1.32	22.77	0.02	.15
In equilibrium with calcite-dolomite-gypsum, reacted with 0.5 mol K_2SO_4.	100	100	7.83	97.41	7.69	93.64	7.55	87.59	7.31	76.28	6.79	56.51

*pe is not fixed

Table 2.-Reliability of $\delta^{13}C$ values of the DIC separated from the same water samples by the precipitation technique

Locality, submitter and remarks	USGS, Reston Stable Isotope Laboratory Log Number	Date of Collection or Submission	Date of Analyses	$\delta^{13}C$ Relative to PDB in per mil	In Percentage Yield/ of CO_2 Relative to the Theoretical Value
Apollinaris Spring, Yellow Stone, Tyler Coplen (reseived)	C-1317	6/14/77	11/05/79	-3.64	91.01
			11/05/79	-3.34	93.28
			11/09/79	-3.46	85.23
			11/12/79	-4.48	82.58
			11/14/79	-4.77	90.81
			11/14/79	-3.12	88.82
(ground and reseived)			11/26/79	-4.88	84.94
			11/26/79	-4.62	83.02
Bozeman, Fish H. Madison Bruce Hanshaw (reseived)	C-1358	9/09/77	12/20/77	-9.83*	80.14
			11/13/79	-8.52	88.06
			11/13/79	-8.76	87.00
			11/14/79	-8.66	88.37
			11/19/79	-9.01	81.10
			11/20/79	-8.98	82.98
			11/20/79	-8.96	82.81
Well 5B (NTS) Ike Winograd (reseived)	C-1450	1/15/77	02/02/77	-10.78*	78.54
			02/02/77	-10.78*	73.88
			10/31/79	-10.26	83.62
			10/31/79	-10.06	85.35
			11/21/79	-10.56	79.44
			11/08/79	-10.63	76.14
			11/08/79	-10.49	78.75
Central Laboratory in Denver #251703	C-1719-1	9/25/79	10/22/79	-10.46	38.07
			10/29/79	-10.65	38.26

*Prepared and analyzed by Joan Woodward using Nuclide 60°, 6 inch RMS mass spectrometer. Other samples were prepar and analyzed by Jessica Hopple and Freddie Leighty using Depont double collector modified 21-491 mass spectrometer.

Table 3.-Values of carbon isotope ratios of the international standards used in the present study

Standard	δ^{13}C PDB ± 1 σ per mil	Reference
NBS-20	-1.06 ± 0.02	Tan and others (1973)
	-1.17 ± 0.04	Tan and others (1973)
	-1.09 ± 0.04	Present study
	-1.03	Mook (1968)
NBS-21	-27.79	Craig (1957)
	-28.00	Eckelman and others (1967)
	-28.19	Mook (1968)
	-27.22	Farmer (1972, after Tan and others, 1973)
	-28.36	Tan (1972, after Tan and others, 1973)
	-28.22 ± 0.04	Tan and others (1973)
	-28.10	Friedman and O'Neil (1977)
	-28.10 ± 0.06	Present study
NBS-19(TS-limestone)	1.96	Eric Olson (University of California at Riverside, 1977)
	1.64	Irving Friedman (U. S. Geological Survey)
	2.04 ± 0.09	Present study

Table 4.-Accuracy and precision of $\delta\ {}^{13}C$ determination of total inorganic dissolved carbon (DIC) in 0.01 molar $NaHCO_3$ of $\delta^{13}C = -15.33 \pm 0.07$ extracted by the different techniques and the effect of sulfate concentration.

		The precipitation technique			The gas evolution technique		
Sulfate moles/ liter	Log MSO_4	Efficiency of DIC Extraction in Percentage	$\delta^{13}C_{PDB}$ per mil	$\Delta^{13}C$ * per mil	Efficiency of DIC Extraction in Percentage	$\delta\ {}^{13}C_{PDB}$ per mil	$\Delta^{13}C$ * per m
0.0	0.0	95 ± 3	-15.36 ± 0.05	0.0	90 ± 2	-15.36 ± 0.02	0.0
0.001	-3.0	95 ± 3	-15.38 ± 0.04	-0.02 ± 0.06	90 ± 3	n.d.	0.0 ± 0.02
0.005	-2.3	90 ± 5	-15.26 ± 0.02	+0.10 ± 0.05	n.d.	n.d.	n.d.
0.01	-2.0	90 ± 2	-15.25 ± 0.02	+0.21 ± 0.05	90 ± 2	-15.24 ± 0.04	+0.12 ± 0.04
0.1	-1.0	70 ± 3	-14.91 ± 0.03	+0.45 ± 0.06	90 ± 5	-15.25 ± 0.07	+0.11 ± 0.07

n.d. = not determined

* $\Delta^{13}C_{MSO_4} = \delta^{13}C_{Measured(MSO_4)} - \delta^{13}C_{True(zero\ SO_4)}$

Table 5.-Reliability of sampling devices and their effect on $\delta^{13}C$ of total inorganic dissolved carbon (DIC) in 0.01 molar $NaHCO_3$ of $\delta^{13}C = -15.33 \pm 0.07$ stored under laboratory conditions and intensified conditions simulating air shipping, heat, and very long storing $\delta^{13}C$ relative to PDB in per mil

Technique and sampling device	Stored under normal laboratory conditions for one to two days	Stored under normal laboratory conditions for two weeks	Stored in CO_2 atmosphere of $\delta^{13}C$ -44.95 per mil under a bell jar for one week	Stored under vacuum in a bell jar for one week	Stored at 60°C for two days
A. <u>Precipitation</u>					
1. Pyrex glass bottles with teflon coated caps	-15.36 ± 0.05	-15.58 ± 0.04*	-15.44 ± 0.08	n.d	n.d
2. Polyethylene bottles	-15.16 ± 0.04	-15.11 ± 0.1*	-39.08 ± 0.32	n.d	n.d
B. <u>Gas Evolution</u>					
1. Serum bottles with sleeve stoppers	-15.23 ± 0.13	n.d.	n.d.	-15.42 ± 0.17	n.d.
2. Serum bottles	-15.76 ± 0.12	n.d.	n.d.	-15.22 ± 0.06	n.d.
3. Glass sampling tube with two stopcocks	-15.19 ± 0.05	n.d.	n.d	Leaked around the stopcocks	Leaked around the stopcocks
4. Tygon tubing with two clamps	-14.90 ± 0.02	n.d.	n.d.	Air bubbles formed on the walls	Air bubbles formed on the walls
5. Glass syringe with metal Luer-lok tip	-15.36 ± 0.02	-15.72 ± 0.1*	n.d.	Leaked around the barrels	Leaked around the barrels

n.d. = not determined.

* $\delta^{13}C$ of the solid $NaHCO_3$ is -15.52 ± 0.07 per mil

Table 6.-Effect of $HgCl_2$ on $\delta^{13}C$ of DIC ($\delta^{13}C$ relative to PDB in per mil)

Type of water and locality	$HgCl_2$ added to sample	Without $HgCl_2$	
		Analyzed after one week	Analyzed after four weeks
1. Surface water			
a. Low salinity Potomac River Alexandria, VA	-9.83 ± 0.14	-10.85 ± 0.02	-10.81 ± 0.97
b. High Salinity Atlantic Ocean Ocean City, MD	-4.40 ± 0.04	+ 0.89 ± 0.64	- 3.65 ± 0.69
2. Groundwater			
a. High sulfate Sudley Spring Manassas, VA	-9.69 ± 0.06	-11.60 ± 0.18	-12.63 ± 0.08
b. Low sulfate Chinn Spring Manassas, VA	-15.57 ± 0.05	-15.67 ± 0.03	-16.06 ± 0.60

Table 7.-Effects of Laboratory preparation of samples on $\delta^{13}C$ values

Treatment	Set Number	$\delta^{13}C_{PDB}$ in per mil
Filtered and dried in nitrogen-atmosphere glove box	1	-15.51 ± 0.1
Filtered in nitrogen atmosphere glove box, dried in oven at 90°C	1	-15.17 ± 0.07
Filtered in atmosphere dried in nitrogwen-atmosphere glove box	1	-15.18 ± 0.03
Filtered in atmosphere, dried in oven at 90°C	1	-15.03 ± 0.05
Reacted with 100 percent phosphoric acid	2	-8.62 ± 0.14@
	3	-8.70 ± 0.03@
	4	-10.08 ± 0.06@
Reacted with 85 percent phosphoric acid	2	-8.74 ± 0.02@
	3	-8.65 ± -.05@
	4	-10.07 ± 0.04@
No treatment	5	-14.89 ± 0.0
Passed through hot Cu at 450°C	5	-14.99 ± 0.0
Passed through hot Cu then through MnO_2 at 450°C	5	-15.76 ± 0.17

1. 4-samples each from the same 0.01 molar $NaHCO_3$ solution of $\delta^{13}C$ = 15.52 ± 0.07 per mil.

2,3,4. Three natural samples prepared in duplicates.

5. 2 samples from 0.01 molar $NaHCO_3$ solution containing 0.1 mole Na_2SO_4.

@. Prepared and analyzed by Ronald Schienhaus.

Table 8.-Comparison of $\delta^{13}C$ values of various water samples collected by the precipitation and gas evolution techniques

Type of water and locality	DIC extracted by the precipitation techniques	DIC extracted by the gas evolution techniques
	$\delta^{13}C_{PDB}$ per mil	$\delta^{13}C_{PDB}$ per mil
1. Surface water a - Low salinity Potomac River, Alexandria, VA	-9.97 ± 0.09	-9.83 ± 0.14
b - High salinity Atlantic Ocean, Ocean City, MD	-4.39 ± 0.07	-4.40 ± 0.04
2. Ground water a - High sulfate (1100 mg/L) Sudley Spring, Manassas, VA	-9.77 ± 0.02	-9.69 ± 0.06
b - Low sulfate (100 mg/L) Chinn Spring, Manassas, VA	-15.51 ± 0.1	-15.57 ± 0.05

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