STABLE ISOTOPE ANALYSES OF CARBONATE COMPLICATED BY NITROGEN OXIDE CONTAMINATION: A DELAWARE BASIN EXAMPLE[1]

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ABSTRACT: Whole rock subsurface samples from the Cherry Canyon Formation, Delaware Basin, were used to document the presence of a contaminant gas affecting the isotopic composition of acidified carbonate. The whole rock material, when reacted in purified phosphoric acid using the McCrea (1950) method, produces a contaminant mass-46 gas (nitrogen dioxide, NO_2). This mass-46 gas contributes to the $^{18}O/^{16}O$ ratio (mass 46/44), artificially enriching the $\delta^{18}O$ value and masking the true isotope signature of the CO_2 derived from the carbonate minerals. Acidified whole rock samples containing low carbonate (< 5%) tend to yield more positive $\delta^{18}O$ (PDB) values, some greater than +30‰. Conversely, samples with higher carbonate (> 5%) have $\delta^{18}O$ values ranging from +5‰ to −8‰, hence diluting the effects of the contaminant gas on the mass 46/44 ratio. After purifying the CO_2 produced by the McCrea (1950) method with a reduction furnace, all of the $\delta^{18}O$ values fall in the range of 0‰ to −12‰ regardless of carbonate content. The $\delta^{13}C$ (PDB) values remain unchanged after reduction furnace purification, indicating no effect on mass 45/44 ratio.

The inferred source of the contaminant NO_2 gas is from inorganic ammonium adsorbed to interlayer sites of alumina silicates such as illite and mica. This source is supported by the detection of ammonium and clays in the whole rock material and the lack of correlation between percent organic carbon and $\delta^{18}O$ values influenced by NO_2. To eliminate the effect of the contaminant gas on $\delta^{18}O$ values, we describe a simple procedure that removes the contaminant NO_2 gas, yielding the true isotopic signal from the carbonate minerals in whole rock material.

INTRODUCTION

Stable isotope studies of carbonate-bearing sediments and rocks have been used in numerous studies for documenting diagenetic and depositional processes. The $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios are obtained by reacting carbonate mineral separates or whole rock samples in purified phosphoric acid. This process of carbonate acidification is commonly referred to as the McCrea (1950) method. Since publication of the McCrea (1950) paper, there have been many modifications to the technique to obtain more accurate isotopic results. Epstein et al. (1951, 1953) discussed the importance of heat treatment (roasting) to remove organic impurities from shell calcium carbonate prior to acidification. Organic impurities can affect the isotopic composition of CO_2 derived from carbonate acidification. Epstein et al. (1951) found it necessary to purify samples by roasting to eliminate the possibility of molecules or radicals forming within the mass spectrometer ionization chamber, which can contribute to masses 43 to 47. These compounds and radicals can be organic or inorganic, including such examples as C_2H_5OH, CS, CH_3COOH, BCl, NO_2 and N_2O (Epstein et al. 1951). Epstein et al. (1964) developed a chemical separation technique which allows the correction of isotope results for physically inseparable mixtures of calcite and dolomite. Sharma and Clayton (1965) modified these procedures to include the kinetic isotope effects for mixtures of calcite and dolomite.

Additional factors that influence isotopic results include particle size and reaction rates of carbonate minerals (Walters et al. 1972). Wachter and Hayes (1985) measured the exchange rate of isotopes of oxygen between solutions of phosphoric acid as a function of temperature, acid strength, CO_2 pressure, and reaction vessel surface area. Although these methods are well established and widely used, no method currently corrects for contaminant gases produced during the acidification of whole rock material.

Whole rock samples analyzed using the standard acidification technique can produce anomalous $\delta^{18}O$ values that do not reflect the correct isotopic composition of carbonate minerals. Instead, $\delta^{18}O$ values may include an artificial contribution to the $\delta^{18}O$ signal caused by a contaminant gas of mass-46. The source of this mass-46 contaminant could be organically or inorganically derived from the constituents in the whole rock. Suess (1973) discusses the process of adsorbed organic compounds in the form of carbon, nitrogen and phosphorous on calcium carbonate as a function of grain size. Both organic and inorganic matter can be adsorbed to other non-carbonate minerals such as illite, mica and other clays (Stevenson and Cheng 1972; Müller 1977). As discussed by Epstein et al. (1951, 1953), organic and inorganic compounds or radicals with masses 44 to 46 associated with CO_2 from carbonate acidification can affect the true isotopic composition. Whole rock samples in this study produce a contaminant mass–46 gas during the acidification procedure even after using standard roasting treatment. $\delta^{18}O$ values influenced by the contaminant mass-46 gas will hereafter be referred to as contaminated $\delta^{18}O$ values.

A technique using a reduction furnace with copper shavings (Epstein et al. 1951; Sackett and Thompson 1963) in conjunction with the standard acidification method was implemented to remove the contaminant mass-46 gas. The combination of these two techniques will remove the contaminant gas from CO_2 produced by acidification of carbonate and yield a true $\delta^{18}O$ value. To demonstrate the effect of this contaminant mass-46 gas on $\delta^{18}O$ values, only contaminated $\delta^{18}O$ values less than +10‰ will be

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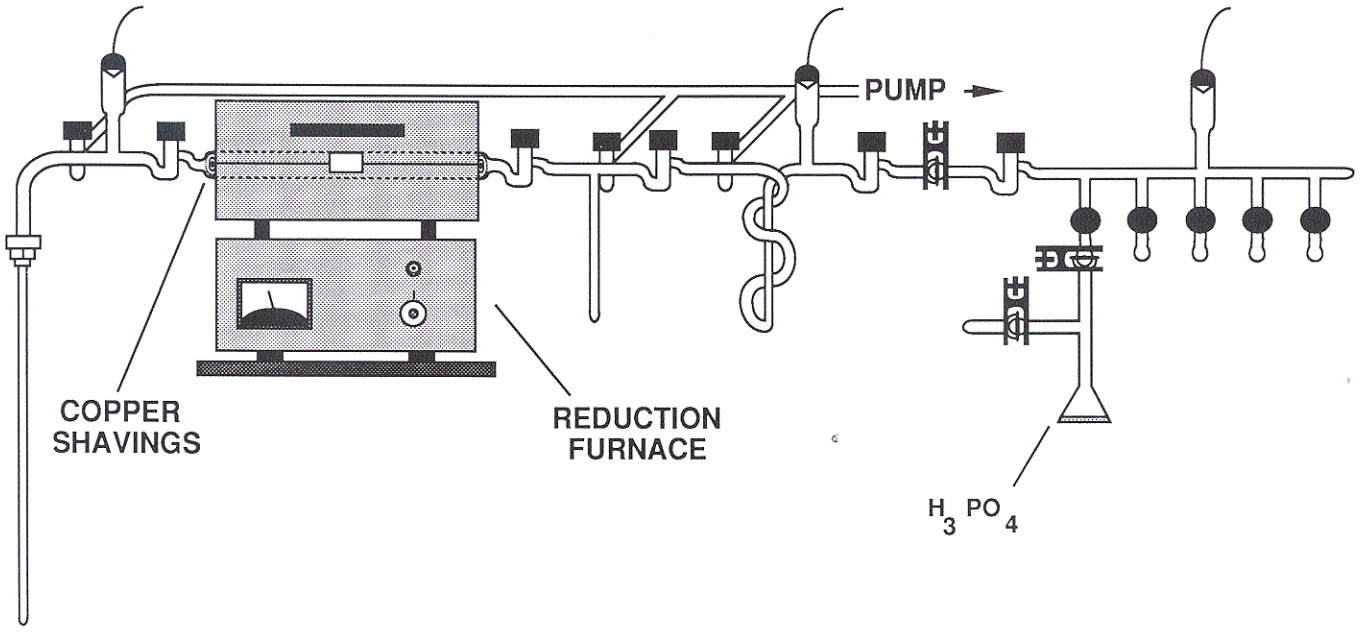

FIG. 1.—Carbonate extraction line used for the generation and purification of CO_2 from whole rock material before mass spectrometry.

discussed in this study, since most published carbonate $\delta^{18}O$ values fall negative of this limit. Carbonate $\delta^{18}O$ values in this range (< 10‰) are generally not considered anomalous. Unless there is some other indication of contamination, such as discoloration in the sample gas when frozen with liquid nitrogen, these samples are not tested for the presence of contaminants. Extreme $\delta^{18}O$ values (> 10‰) for carbonate cements are unusual and normally would be further investigated. No sample gas discoloration was observed in any of the Delaware Basin samples; both the McCrea (1950) and reduction furnace methods yield gases which produce white rings when frozen. The objectives of this study are to 1) identify the contaminant mass-46 gas, 2) discuss the effect this contaminant gas has on the isotopic composition of acidified carbonates using whole rock samples from the Delaware Basin, and 3) offer a plausible explanation for the source of contaminant gas.

METHODS

Whole rock material from the Cherry Canyon Formation, Delaware Basin, west Texas was obtained from two subsurface cores ranging in depth from 1880 to 1920 m. Lithologies sampled in the two cores consist of sandstones, siltstones, and limestones. The fine- to medium-grained massive sandstones and laminated sandstones contain 0.05 to 1.25% total organic carbon (TOC) with varying amounts of carbonate (1 to 30%). Massive sandstones regardless of grain size have lower TOC (< 0.5%) than laminated sandstones. Medium- to coarse-grained siltstones on average contain more TOC (0.1 to 2.3%) than either massive or laminated sandstones but are lower in carbonate content (< 10%). Limestone is a minor constituent in the two cores, comprising less than 2.5 m in one core and 0.5 m in the other. The limestones observed in thin section contain silt and poorly preserved fossils. The carbonate and TOC contents in these limestones range from 35 to 85% and 0.1 to 2.0%, respectively.

Total organic carbon was measured by acidifying whole rock material to remove carbonate and combusted using an HP185 CHN Analyzer. Percent carbonate was determined using a gasometric technique modified after Jones and Kaiteris (1983). Mineralogy was determined by thin section petrography and X-ray diffraction.

After being lightly ground with a carbide mortar and pestle, whole rock samples were sieved to < 63 μm. Sieved samples ranging from 10 to 30 mg were roasted under vacuum at 380°C, then reacted in purified phosphoric acid (H_3PO_4) at 50°C until all carbonate was completely digested (Fig. 1). Resultant CO_2 was purified of contaminant water vapor and passed through a reduction furnace containing copper shavings at 250°C (Fig. 1). Purified CO_2 was analyzed on a VG Isogas SIRA 24 mass spectrometer.

A pure carbonate laboratory standard was used to test the reproducibility of the technique using the reduction furnace (Fig. 1) with respect to the McCrea (1950) method. The mean for the laboratory standards using the McCrea (1950) method and reduction furnace technique were the same with a precision of ±0.11‰ for $\delta^{18}O$ and ±0.09‰ for $\delta^{13}C$. This indicates that there is no isotopic difference in the pure carbonate laboratory standard using either technique. All of the data are expressed in the conventional delta (δ) notation,

$$\delta‰ = \frac{(\text{Ratio}_{\text{standard}} - \text{Ratio}_{\text{reference}})}{(\text{Ratio}_{\text{reference}})} \times 1000$$

where the isotope ratios of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ are reported relative to the international PBD standard (Craig 1957).

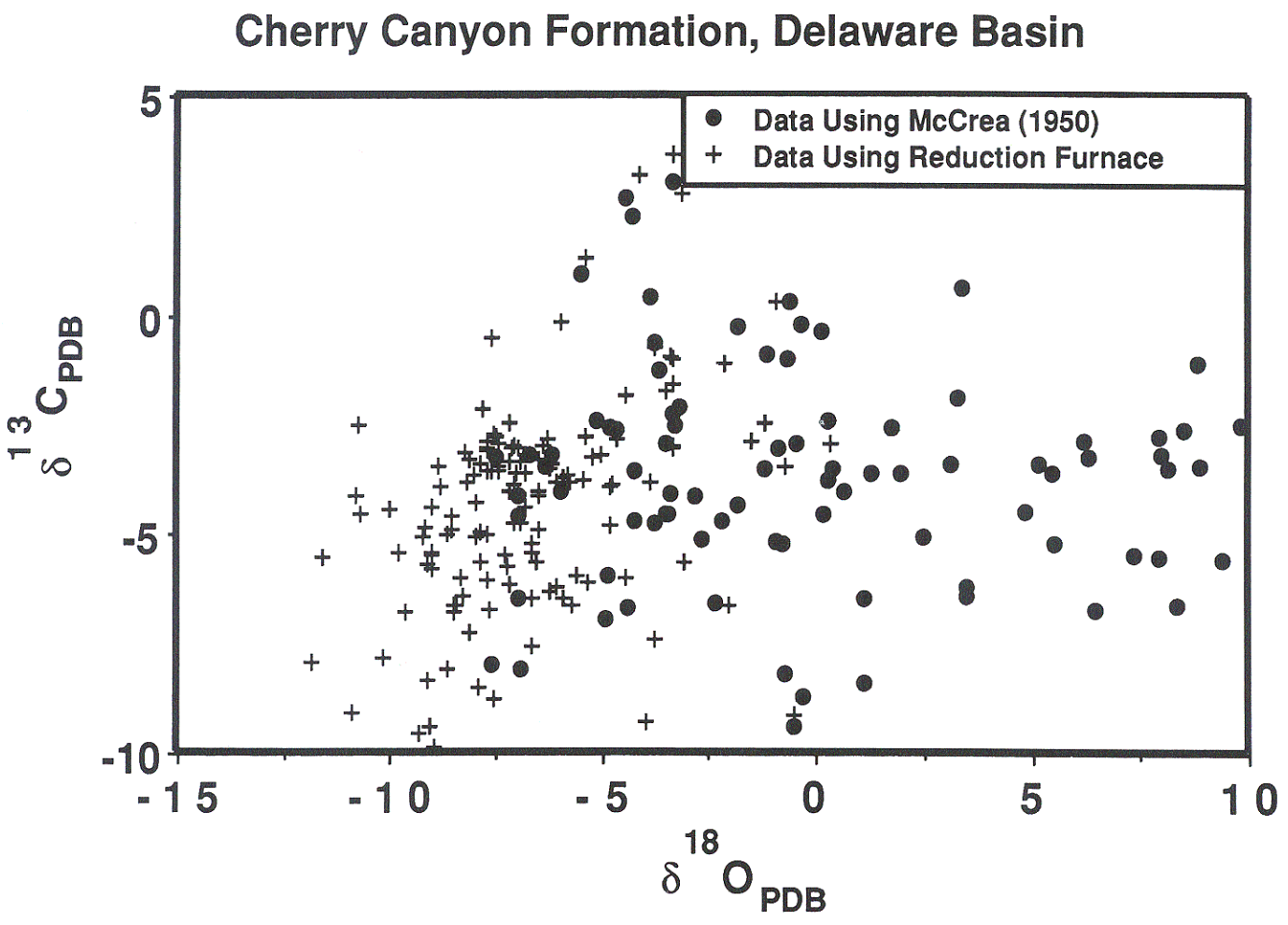

FIG. 2.—Stable isotope values using the McCrea (1950) method indicated by dots and the reduction furnace method indicated by plus symbols for whole rock $\delta^{18}O$ and $\delta^{13}C$ values in the range of −14 to +10‰.

RESULTS AND DISCUSSION

Isotope analysis of whole rock samples from the Cherry Canyon Formation, Delaware Basin was complicated by the presence of a contaminant mass-46 gas that obscures the isotopic composition of carbonate phases. Some acidified whole rock samples, especially siltstones and laminated sandstones containing less than 5% carbonate, have produced $\delta^{18}O$ values greater than +30‰ (Mucciarone et al. 1987; Mucciarone 1988). The majority of contaminated $\delta^{18}O$ values for all lithologies range from −7 to +10‰ with associated $\delta^{13}C$ values in the range of −10 to +3‰ (dots, Fig. 2; Table 1). The $\delta^{18}O$ and $\delta^{13}C$ values designated by dots in Figure 2 were generated using the McCrea (1950) method. Isotope values denoted by plus signs in Figure 2 are for the same samples after reduction furnace purification.

To determine the cause of more positive $\delta^{18}O$ values using the McCrea (1950) method (dots, Fig. 2), the relative mass distribution of sample gas derived from whole rock material via the McCrea (1950) method was scanned from mass 41 to 50 (Fig. 3A). Although carbon dioxide gas has a mass distribution ranging from mass 44 to 49, 99.995% of CO_2 is represented by masses 44, 45 and 46 (McCrea 1950). The natural abundance of CO_2 species with masses 47, 48 and 49 is so low that they are usually below mass spectrometer detection limit. The mass scan from a whole rock sample (Fig. 3A) illustrates the presence of significant amounts of masses 47 and 48 which do not appear in the mass scan of CO_2 from a pure carbonate laboratory standard (Fig. 3B).

The sample that produced the scan peaks in Figure 3A was reacted again using the same amount of material and then passed through a reduction furnace to remove oxides of nitrogen. The mass scan of this purified CO_2 gas (Fig. 3C) was then compared with the previous mass scan of unpurified gas (Fig. 3A) measured at the same pressure and beam current. The gas scan in Figure 3C shows the absence of peaks 47 to 48 and the reduction of peak 46 relative to the scan in Figure 3A.

Since the reduction furnace procedure is designed to remove oxides of nitrogen, specifically N_2O and NO_2 (Epstein et al. 1951; Sackett and Thompson 1963), inferences can be made on the type of contaminating gas. The removal of NO_2 would explain the reduction of the mass-

TABLE 1.—*A subset from 90 Cherry Canyon Formation, Delaware Basin Cores 1 and 2, chosen to represent the variability range of contaminated (Con) and uncontaminated (Unc) $\delta^{18}O$ and $\delta^{13}C$ values, $\delta^{18}O_{diff}$ and $\delta^{13}C_{diff}$ results, weight percent organic carbon (TOC), and percent carbonate (CO_3) (modified from Mucciarone, 1988)*

	McCrea (1950) Method		Reduction Furnace					
Depth (m)	$\delta^{18}O_{Con}$	$\delta^{13}C_{Con}$	$\delta^{18}O_{Unc}$	$\delta^{13}C_{Unc}$	$\delta^{18}O_{diff}$	$\delta^{13}C_{diff}$	Wt.% TOC	% CO_3
Core 1:								
1,883.65	−0.55	−9.39	−0.53	−9.13	0.02	0.26	0.11	85.2
1,883.87	−3.81	−0.59	−3.39	−0.98	0.42	−0.39	2.31	8.1
1,885.54	−4.91	−5.93	−8.52	−6.79	−3.61	−0.86	0.79	3.5
1,887.97	1.50	−43.40	0.00	−43.27	−1.50	0.13	0.05	28.9
1,889.01	−6.43	−3.55	−7.00	−4.05	−0.57	−0.50	1.11	2.4
1,897.08	−3.46	−4.51	−7.10	−4.73	−3.64	−0.22	0.12	2.3
1,901.03	8.83	−3.39	−4.84	−3.87	−13.67	−0.48	0.26	2.1
1,912.32	1.26	−3.57	−8.25	−3.12	−9.51	0.45	0.26	2.0
1,914.77	5.42	−3.55	−6.53	−4.07	−11.95	−0.52	0.45	2.1
1,915.97	0.24	−3.74	−6.19	−3.36	−6.43	0.38	0.17	1.4
Core 2:								
1,885.65	−6.92	−8.05	−8.66	−8.06	−1.74	−0.01	0.07	3.8
1,889.76	9.39	−5.57	−11.57	−5.52	−20.96	0.05	0.23	2.6
1,899.48	7.90	−5.53	−7.99	−5.03	−15.89	0.50	0.55	4.9
1,901.29	4.80	−4.45	−7.98	−4.24	−12.78	0.21	0.23	4.1
1,903.02	−0.66	0.33	−3.78	−0.70	−3.12	−1.03	2.11	4.1
1,903.69	−3.35	3.07	−4.13	3.21	−0.78	0.14	0.37	73.1
1,904.70	−5.52	0.95	−5.39	1.32	0.13	0.37	0.72	35.7
1,908.08	−4.81	−2.55	−0.73	−3.43	4.08	−0.88	0.14	3.4
1,912.92	−4.67	−2.58	−7.55	−2.67	−2.88	−0.09	0.14	2.1
1,917.05	8.47	−2.59	−7.78	−3.34	−16.34	−0.75	0.40	2.8

46 peak and the elimination of mass-47 and -48 peaks in the scan of the uncontaminated or purified gas. Therefore, the most likely contaminant gas, in this case, is NO_2 with the dominant species being mass-46 (99.17%).

The nitrogen oxide, N_2O, can be excluded as a contributing species in these samples, even though it contains masses 44 to 46. The removal of N_2O from the sample gas by reduction furnace treatment would produce a change in the mass 45/44 ratio ($^{13}C/^{12}C$). The correlation coefficient between $\delta^{13}C$ values before and after reduction purification is 0.97, indicating that N_2O contribution to the $\delta^{13}C$ signal is negligible.

The contaminant NO_2 gas originates from an inorganic rather than an organic nitrogen source. Total organic carbon (TOC) does not correlate with contaminated $\delta^{18}O$ values ($r = 0.10$). In fact, samples with high TOC (> 1.0%) have more negative $\delta^{18}O$ values than samples containing low TOC (< 1.0%). In addition, nitrogen peaks were not discernible from CHN analysis. A plot of $\delta^{18}O_{diff}$ ($\delta^{18}O$ values using the McCrea (1950) method minus $\delta^{18}O$ values using reduction furnace purification; Fig. 4) illustrates that any carbonate and total organic carbon content occurs with both small or large changes in $\delta^{18}O_{diff}$ after reduction furnace purification. This indicates something other than organic material is affecting the $^{18}O/^{16}O$ ratio (Fig. 4).

Although organic content shows no relationship to contaminated $\delta^{18}O$, there is an apparent correlation between TOC and grain size. Siltstones (< 62 μm) have the highest TOC (0.4–2.3%) with laminated sandstones (63–225 μm) containing higher TOC (< 1.25%) than massive sandstones (< 0.5%) of the same grain size. However, grain size is not linked to the occurrence of the contaminated $\delta^{18}O$ values ($r = -0.14$).

After identifying the contaminant gas NO_2, the whole rock material was analyzed for nitrogen content. Results from six samples reveal the presence of nitrogen in the form of ammonium which ranges from 20.6 to 95.8 μg/g. Nitrogen occurs in soils and sedimentary rocks in ammonium-bearing minerals such as illite and mica (Stevenson and Cheng 1972; Müller 1977; Sterne et al. 1982; Juster et al. 1987). Ammonium ions are adsorbed within interlayer sites of alumina silicates such as clays and mica which possess high layer charges (Stevenson and Cheng 1972; Müller 1977). Both illite and mica are present in varying abundance in all lithologies except for the massive sandstones, which are virtually devoid of illite but contain mica (< 3.0%). Siltstones have the highest mica content (> 20%) with laminated sandstones containing 3 to 20%.

All lithologies with less than 5% carbonate have approximately the same range of $\delta^{18}O_{diff}$ values. However, samples with carbonate content greater than 5% exhibit less change in $\delta^{18}O$ values after reduction furnace purification (i.e., smaller $\delta^{18}O_{diff}$ values). This implies that higher carbonate contents could have the ability to mask, but not eliminate, the influence of the ammonium-bearing minerals capable of producing the contaminant gas. For example, if ammonium content remains the same and carbonate content is increased, the effect of the contaminant gas on the derived CO_2 will be diluted, thereby reducing the effect on contaminated $\delta^{18}O$ values. Exactly how much of these ammonium-bearing minerals is required to affect the $\delta^{18}O$ value of a given sample is un-

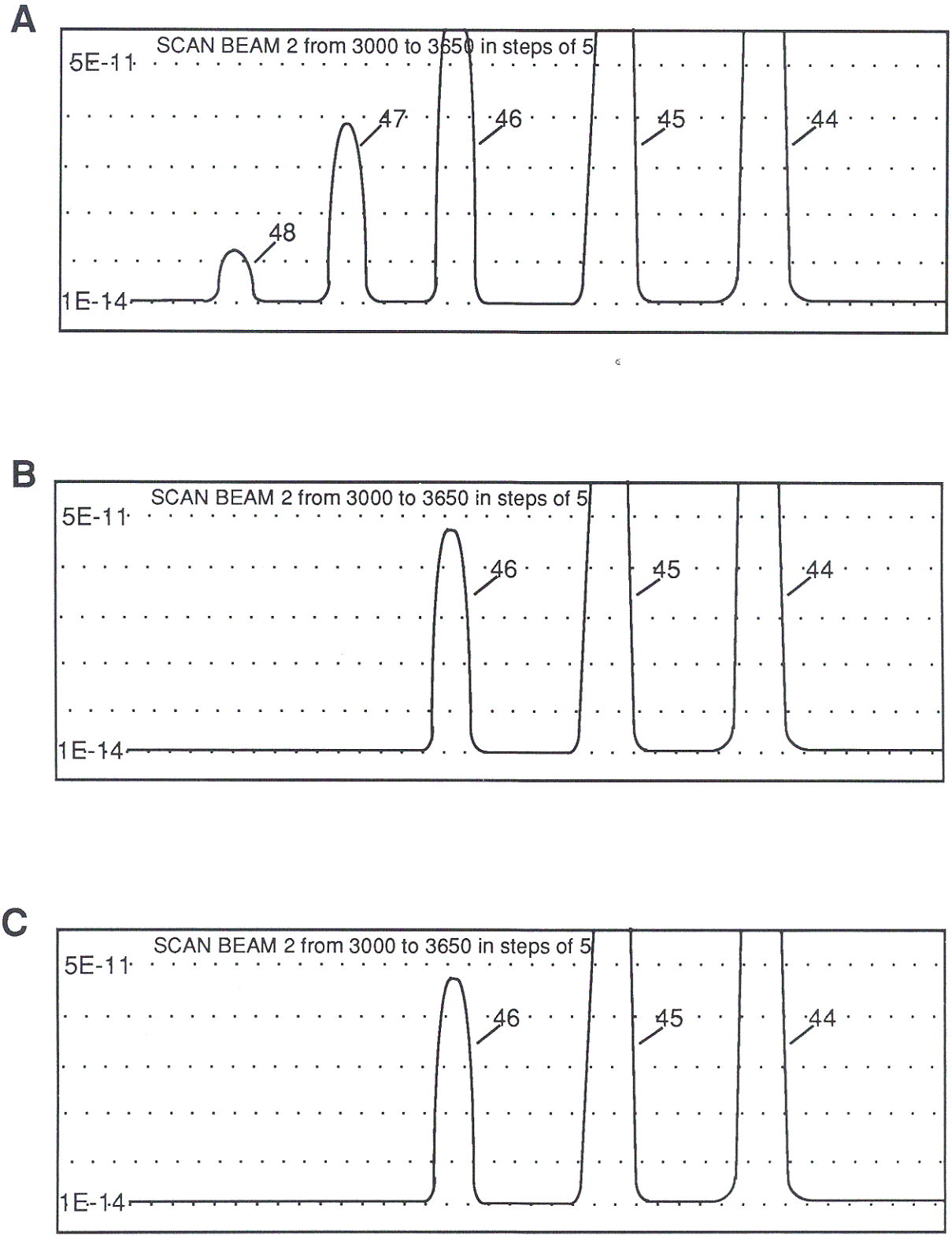

FIG. 3.—Mass spectrometer scans of gas generated from (A) a whole rock sample using the McCrea (1950) method, (B) a calcite standard using the McCrea (1950) method and (C) a whole rock sample after reduction furnace purification. All of the mass scans were analyzed at the same gas pressure.

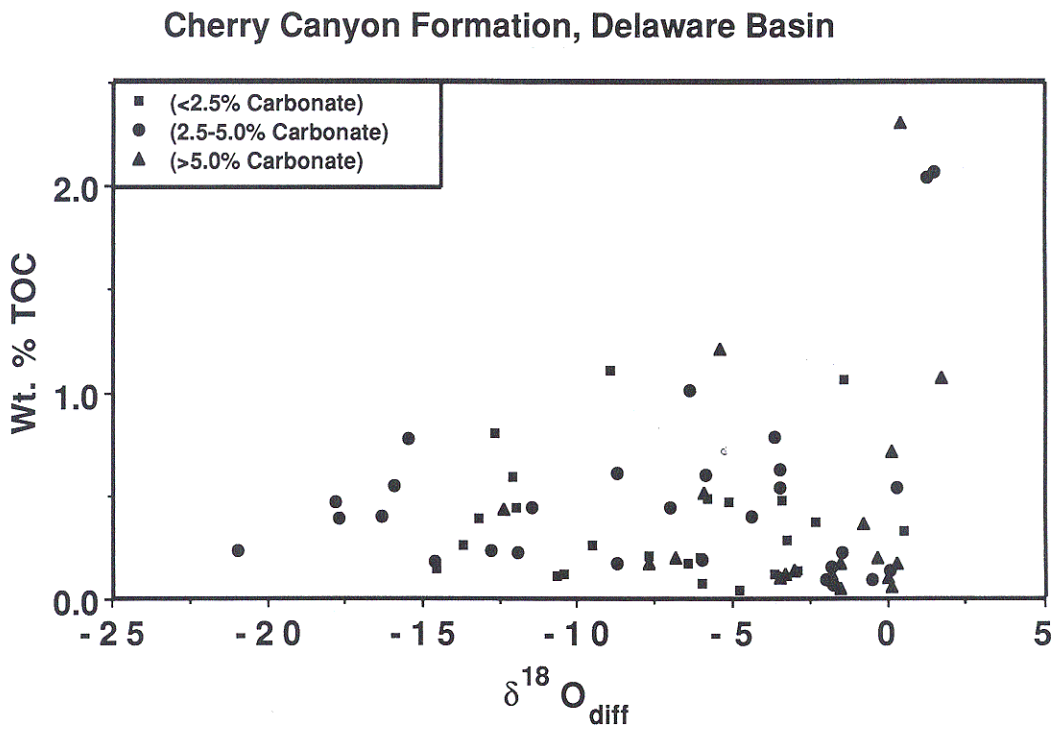

FIG. 4.—Weight percent total organic carbon (TOC) plotted against $\delta^{18}O_{diff}$ values ($\delta^{18}O$ using the McCrea (1950) method minus $\delta^{18}O$ using reduction furnace). The square, circle and triangle symbols represent the carbonate content range for each sample. The carbonate and TOC contents are not related to $\delta^{18}O_{diff}$ (r = −0.12 and 0.10 respectively).

known. Only a direct measurement of NH_4 content will answer this question. Unfortunately the detection of NH_4 or ammonium-bearing minerals in whole rock samples will only identify the potential source of contaminants. Routine use of a reduction furnace will prevent NO_2 or N_2O produced by acidifying nitrogen-bearing matter from affecting $\delta^{18}O$ or $\delta^{13}C$ values of carbonates in whole rock material.

CONCLUSIONS

Roasted whole rock material when acidified using the McCrea (1950) method can produce a contaminant gas which contributes to the isotopic composition of the derived CO_2. This contaminant gas is NO_2, with ammonium-bearing micaceous minerals determined as the most plausible inorganic source of nitrogen. Contaminated $\delta^{18}O$ values show no relationship to total organic carbon (TOC) or grain size. The amount of organic material does not correlate with the change in $\delta^{18}O$ ($\delta^{18}O_{diff}$) values after reduction furnace purification. This indicates that organic material when acidified does not produce contaminant NO_2 gas.

Contaminated $\delta^{18}O$ values (Table 1; Fig. 2) presented in this study are within the range of most carbonate $\delta^{18}O$ in the published literature. The $\delta^{18}O$ results after reduction furnace purification substantiate that the presence of NO_2 can drastically affect the $\delta^{18}O$ values of carbonates in whole rock material, where isotope results obtained without reduction furnace purification yield more positive $\delta^{18}O$ values (Fig. 2). After reduction furnace treatment, more positive $\delta^{18}O$ values change considerably, in some cases by more than 10‰. Conversely, negative $\delta^{18}O$ values (−12 to 0‰) change less than extremely positive $\delta^{18}O$ values (Fig. 2). The $\delta^{13}C$ values remain virtually unchanged after reduction furnace purification, demonstrating no effect on the mass 45/44 ratio ($^{13}C/^{12}C$) by the contaminant gas. In addition, there is no coloration difference between contaminated and purified gas frozen by liquid nitrogen; all sample gases were white when frozen.

Elimination of the contaminant mass-46 gas by reduction furnace purification produces a pure CO_2 representative of the carbonate fraction in whole rock material. Results of this study illustrate that even whole rock $\delta^{18}O$ values in the range of −12 to +10‰ could contain enough contaminant gas to bias isotopic results and subsequent interpretations (Fig. 2). Considering the range of $\delta^{18}O$ values over which this effect occurs, steps should be taken to test for the presence of this contaminant gas regardless of $\delta^{18}O$ values and to further purify the gas samples, if necessary, or routinely use a reduction furnace.

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REFERENCES

CRAIG, H., 1957, Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide: Geochim. Cosmochim. Acta, v. 12, p. 133–149.

EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H., AND UREY, H. C., 1951, Carbonate-water isotopic temperature scale: G. S. A. Bull., v. 62, p. 417–426.

EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H., AND UREY, H. C., 1953, Revised carbonate-water isotopic temperature scale: G. S. A. Bull., v. 64, p. 1315–1326.

EPSTEIN, S., GRAF, D. L., AND DEGENS, E. T., 1964, Oxygen isotope studies on the origin of dolomites, *in* Craig, H., Miller, S. L., and Wasserburg, G. J., eds., Isotopic and Cosmic Chemistry: Amsterdam, North Holland, p. 169–180.

JONES, G. A., AND KAITERIS, P., 1983, A vacuum-gasometric technique for rapid and precise analysis of calcium carbonate in sediments and soils: Jour. Sed. Petrology, v. 53, p. 655–660.

JUSTER, T. C., BROWN, P. E., AND BAILEY, S. W., 1987, NH_4-bearing illites in very low grade metamorphic rocks associated with coal, northern Pennsylvania: Am. Mineralogist, v. 72, p. 555–565.

MCCREA, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: Jour. Chem. Phys., v. 18, p. 849–857.

MUCCIARONE, D. A., 1988, The effect of anomalous $\delta^{18}O$ values on stratigraphic interpretations: Delaware Basin, West Texas [unpubl. M.S. thesis]: Columbia, Univ. South Carolina, 93 p.

MUCCIARONE, D. A., TRAINOR, D. M., AND WILLIAMS, D. F., 1987, Whole rock stable isotope geochemistry for correlation and diagenetic interpretation: Delaware Basin and Monterey Formation examples: A. A. P. G. Bull. (abstr.), v. 71, p. 596.

MÜLLER, P. J., 1977, C/N ratios in Pacific deep-sea sediments: effect on inorganic ammonium and organic nitrogen compounds absorbed by clays: Geochim. Cosmochim. Acta, v. 41, p. 765–776.

SACKETT, W. M., AND THOMPSON, R. R., 1963, Isotopic organic carbon composition of recent continental derived clastic sediments of eastern Gulf of Mexico: A. A. P. G. Bull., v. 47, p. 525–527.

SHARMA, T., AND CLAYTON, R. M., 1965, Measurements of $^{18}O/^{16}O$ ratios of total oxygen of carbonates: Geochim. Cosmochim. Acta, v. 29, p. 1347–1353.

STERNE, E. J., REYNOLDS, R. C., AND ZANTOP, H., 1982, Natural ammonium illites from black shales hosting a stratiform base metal deposit, Delong Mountains, northern Alaska: Clays and Clay Minerals, v. 30, p. 161–166.

STEVENSON, F. J., AND CHENG, C.-N., 1972, Organic geochemistry of the Argentine Basin sediments: carbon-nitrogen relationships and Quaternary correlations: Geochim. Cosmochim. Acta, v. 36, p. 653–671.

SUESS, E., 1973, Interaction of organic compounds with calcium carbonate-II. Organo-carbonate association in recent sediments: Geochim. Cosmochim. Acta, v. 37, p. 2435–2447.

WACHTER, E. A., AND HAYES, J. M., 1985, Exchange of oxygen isotopes in carbon dioxide-phosphoric acid systems: Isot. Geosci., v. 52, p. 365–374.

WALTERS, L. J., CLAYPOOL, G. E., AND CHOQUETTE, P. W., 1972, Reaction rates and ^{18}O variations for the carbonate-phosphoric acid preparation method: Geochim. Cosmochim. Acta, v. 36, p. 129–140.