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ISOTOPIC AND TRACE ELEMENT COMPOSITIONS OF PENNSYLVANIAN BRACHIOPODS FROM NORTHERN NEW MEXICO

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Abstract—Stable isotope analyses of well preserved brachiopod shells collected from Missourian and Virgilian cyclic deposits in New Mexico yield information about paleoenvironmental variations in Late Pennsylvanian seas of North America. Samples were collected from shales or shales interbedded within limestones, found in the Manzano and Jemez Mountains of northern New Mexico. The brachiopods *Crurithyris*, *Composita* and *Neospirifer* were analyzed—genera which have been used extensively in studies of Pennsylvanian brachiopods in North America. Well preserved shells were recognized by (1) the presence of original microstructure under plane-light microscope, (2) the absence of luminescence under cathodoluminescence microscope, and (3) the absence of detectable Mn and Fe concentrations for non-luminescent areas as measured by electron microprobe. Biological differences in Sr, Na and S concentrations (*Crurithyris* > *Neospirifer* > *Composita*) are preserved in the New Mexico samples and apparently record the original chemical signals. Isotopic analyses of non-luminescent areas of 77 New Mexico shells yield $\delta^{18}O$ values from -4.5‰ to -2.1‰ and $\delta^{13}C$ values from 2.2‰ to 4.8‰. The average $\delta^{13}C$ value of *Composita* is about 1‰ higher than that of co-occurring *Crurithyris* and *Neospirifer*, suggesting vital or microhabitat effects. Changes in $\delta^{18}O$ and $\delta^{13}C$ values generally do not correlate with water depth variations in these depositional cycles. Average $\delta^{13}C$ and $\delta^{18}O$ values of New Mexico Pennsylvanian brachiopods are lower than values of brachiopods in Texas or Kansas (Grossman et al., 1991, 1993). The lower $\delta^{18}O$ values suggest warmer temperatures in New Mexico compared to Texas seas.

INTRODUCTION

Stable isotopes of carbon and oxygen are used in the study of paleoenvironments because these isotopes are sensitive to changes in environmental conditions (e.g., Popp et al., 1986; Grossman et al., 1991). The $\delta^{13}C$ of marine carbonates reflects the $\delta^{13}C$ of dissolved inorganic carbon (DIC) of seawater ($\delta^{13}C_{DIC}$), which varies with changes in primary productivity, water depth, oceanic circulation, and burial rate of organic carbon. Within a basin, changes in $\delta^{13}C_{DIC}$ of seawater may be recorded by marine carbonates, so the $\delta^{13}C$ values of marine carbonates can be utilized for stratigraphic correlation (e.g., Holser et al., 1986). The oxygen isotopic composition of $CaCO_3$ is a function of temperature and the $\delta^{18}O$ of ambient water. Therefore, paleotemperature can be calculated from $\delta^{18}O$ values of $CaCO_3$ fossil shells when the isotopic composition of ancient seawater is estimated.

Other factors affecting the isotopic composition of carbonates include diagenetic alteration and biological modifications. Most occurrences of diagenetically-altered marine carbonates can be recognized by petrographic and trace element studies (e.g., Popp et al., 1986; Adlis et al., 1988), and the influence of vital effects and difference in habitats on skeletal carbonate can be minimized by studying biogenic carbonates from the same species of organism. Brachiopod fossils are used for the isotopic study of paleoenvironment because they are the best preserved and least altered shell material available from Paleozoic strata, due to their low-magnesium calcite mineralogy, and brachiopods generally form shell carbonate in approximate isotopic equilibrium with the surrounding water (Lowenstam, 1961; Carpenter and Lohmann, 1995).

Adlis et al. (1988) and Grossman et al. (1991, 1993) produced detailed isotope stratigraphies of Late Pennsylvanian shales from Texas and Kansas, based on isotopic analyses of brachiopods from five sections in Texas and eight sections in Kansas. They observed stratigraphic variations in $\delta^{13}C$ and $\delta^{18}O$ values, concluding that the $\delta^{18}O$ values reflect a decrease in bottom temperature with increased water depth while the $\delta^{13}C$ values do not show any change with water depth. A ^{13}C depletion in *Crurithyris* and *Eridmatus* relative to *Composita* was suggested to reflect differences in the $\delta^{13}C$ of the ambient water of semi-infaunal and epifaunal genera. Grossman et al. (1993) showed that paleogeographic differences in $\delta^{13}C$ existed, suggesting that the Late Pennsylvanian ocean off eastern Laurussia was enriched in ^{13}C by at least 1‰ relative to the ocean off western Laurussia.

STUDY AREA

Samples were collected from the Jemez Springs and Hot Springs sections in San Diego Canyon of the Jemez Mountains, exposing the Jemez Springs Shale Member of the Madera Formation (Virgilian), and Manzano Mountains section in the Manzano Mountains, exposing the Sol se Mete Member of the Wild Cow Formation (early Missourian). These strata contain well preserved brachiopods (Sutherland and Harlow, 1967).

The Jemez Springs section is located beside NM-4, just north of the town of Jemez Springs, about 80 km north of Albuquerque (Fig. 1). Strata of the Jemez Springs Member of the Madera Formation (Virgilian) are 20.4 m thick, occurring in two well-defined cycles of deposition (lower Jemez Spring cycle and upper Jemez Springs cycle) that contain red beds at the base, transgressive limestone, calcareous offshore shales, and regressive limestones at the top (Fig. 2). The upper cycle contains abundant brachiopods, described by Sutherland and Harlow (1967). Usable samples were obtained from interbedded shales at 250, 350, and 600 cm above the base of the lower Jemez Springs cycle, and at 10, 100, and 180 cm above the base of the upper Jemez Springs cycle.

The Hot Springs section is located beside NM-4, 1.9 km north of Battleship Rock, in the upper part of San Diego Canyon (Fig. 2) and exposes 13.3 m of Jemez Springs Member strata. The thin sandstone and the top regressive limestone bed of the Hot Springs section are correlated with the upper thin transgressive limestone and top regressive limestone of the Jemez Springs Member in the Jemez Springs section, respectively. Correlation is based on matching limestone beds and exposure surfaces

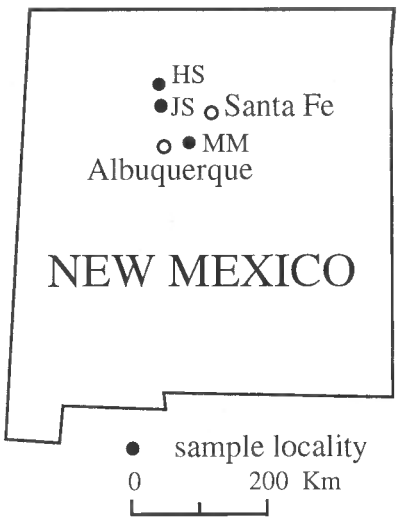

FIGURE 1. Study area and sampling localities of the Hot Springs section (HS), Jemez Springs section (JS), and Manzano Mountains section (MM).

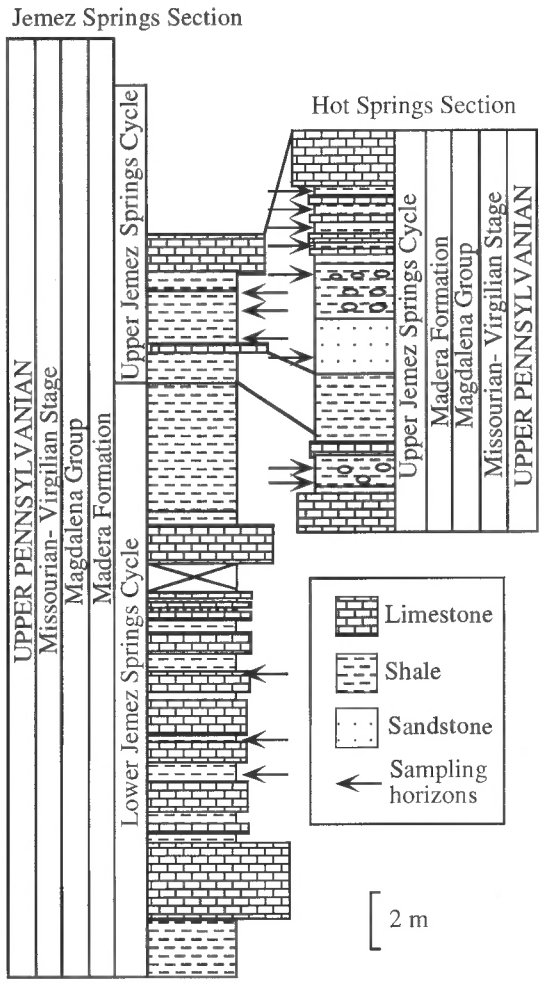

FIGURE 2. Stratigraphy and sample horizons of cycles in the Jemez Mountains, New Mexico.

and on the presence of a similar succession of marine environments within cycles. Usable samples were collected from interbedded shales at 500, 800, 900, 1000, and 1130 cm above the base of the section.

The Manzano Mountains section is a 7.7 m interval of Sol se Mete Member, basal Wild Cow Formation (early Missourian; Myers, 1973), Madera Group, exposed at a quarry off Chilili Road, south of Escabosa and east of Albuquerque. Usable samples were obtained from two shale intervals near the base of the section.

METHODS

Superficially well-preserved brachiopod shells and shell fragments were identified and embedded in pre-evacuated epoxy. Embedded shells were cut longitudinally with an Isomet™ saw and thin sectioned. Each thin section was examined under a petrographic microscope with a TECHNOSYN Model 8200 MKII cathodoluminescence stage for preservation of microstructure and luminescence. Shells with thick non-luminescent areas were photographed in plane light and under cathodoluminescence. Based on these photographs, carbonate powders from non-luminescent areas of shell were micro-sampled from thin sections using a stainless steel dental pick. The diameter of the sampled area generally was about 0.7 mm. Carbonate powders were reacted with concentrated phosphoric acid at 50°C. The CO_2 gas generated was isotopically analyzed using a Finnegan MAT 251 isotopic ratio mass spectrometer. The carbonate standards NBS-19 and NBS-20 were used to calibrate to the Peedee belemnite (PDB) standard. Average precision of the NBS standard analyses are ±0.1‰ for $\delta^{18}O$ and $\delta^{13}C$.

To evaluate preservation and diagenesis, thin sections of 50 different shells of *Crurithyris, Composita* and *Neospirifer* were analyzed by a Cameca SX50 electron microprobe for Ca, Mg, Fe, Mn, Sr, Na and S contents of the carbonate. Lower limits of detection (LLD) were 0.4, 0.7, 1.2, 0.7, and 0.5 (mmol/mol Ca) for Mg, Fe, Mn, Sr, Na, and S, respectively (using equation published in Williams, 1987). Al and Si concentrations were also analyzed as a check for silicate inclusions. The beam current was 10 nA at an accelerating potential of 15 KV; the spot diameter was about 20 mm. Counting times were 20 seconds (Ca, Al, Si), 60 seconds (Sr, Na), 70 seconds (Mn, Fe), or 120 seconds (Mg, S). The points for analysis were selected under SEM, reflected light, and transmitted light using photographs taken under plane light and cathodoluminescence. Twenty points were chosen for each specimen. The first ten points were on a transect from the exterior to interior of the shell and the next ten were on another transect in the reverse direction, parallel to and several hundred microns from the first transect.

RESULTS AND DISCUSSION

From the fossil collections made in the three sections sampled, 128 shells of the brachiopod genera *Crurithyris, Composita, Neospirifer, Hystriculina* and *Derbyia* and a few specimens of the calcitic gastropod *Amphiscapha* were thin sectioned and examined. Shells of 77 specimens of *Crurithyris, Composita*, and *Neospirifer*, the most common brachiopods among the samples collected, were used for isotope stratigraphy.

Shell preservation evaluation

Seventy-seven of the shell samples examined show petrographic evidence of good shell preservation, based on the presence of original microstructure with no diagenetic recrystallization fabric. Shells were then examined and photographed under cathodoluminescence microscope to check for luminescence. Of the thin-sectioned shells, 5 of 22 *Crurithyris*, 23 of 29 *Composita*, and 25 of 26 *Neospirifer* shells are non-luminescent, indicating good shell preservation. *Crurithyris* has the lowest preservation potential and *Neospirifer* has the highest preservation potential, which may be due to differences in crystal size and microstructure, although it also correlates strongly with average size of the brachiopod shell. Overall, the preservation of the New Mexico brachiopods is not as good as that of Midcontinent (Texas and Kansas) brachiopods.

Table 1 and Figure 3 show the average trace element concentrations of non-luminescent (NL) and luminescent to partial luminescent (PL) calcite

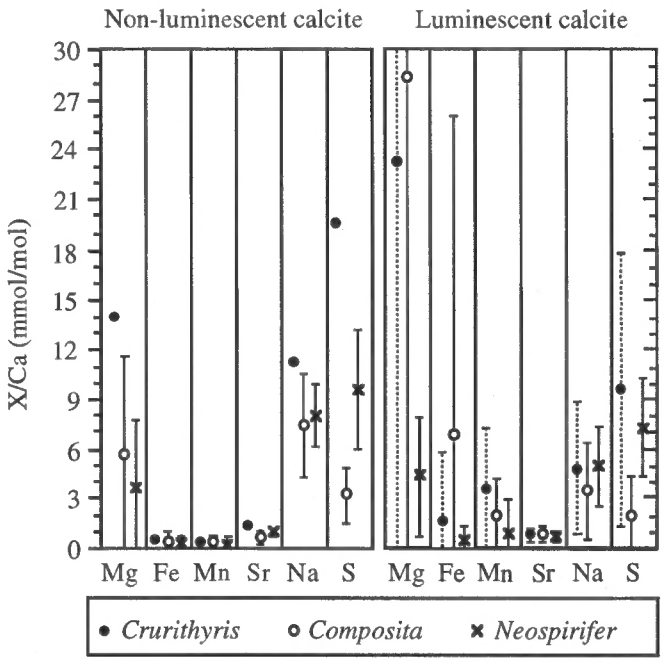

FIGURE 3. Trace element variations of different genera of Pennsylvanian brachiopods. Error bars represent ±1 times the standard deviation of the mean. Where only two shells were analyzed, smaller symbols are used and dotted lines show the range in values. When only one shell was analyzed, only smaller symbols are used.

TABLE 1. Average concentrations of elements from brachiopods (means ±1 times the standard deviation). Data are reported as mmol/mol Ca. Numbers in parentheses represent the number of analyses and number of different specimens, respectively. * = concentration below the detection limit.

New Mexico	Non-luminescent calcite			Luminescent to possible luminescent calcite		
	Crurithyris (15; 1)	*Composita* (110; 9)	*Neospirifer* (112; 7)	*Crurithyris* (28; 2)	*Composita* (66; 7)	*Neospirifer* (60; 4)
Mg	13.9 ±7.0	5.6 ±5.9	3.5 ±4.2	23.2 ±51.1	28.3 ±35.6	4.3 ±3.6
Fe	0.4 ±0.4*	0.3 ±0.6*	0.2 ±0.4*	1.7 ±4.2	6.8 ±19.2	0.4 ±0.9*
Mn	0.3 ±0.3*	0.2 ±0.5*	0.2 ±0.5*	3.5 ±3.8	1.8 ±2.4	0.8 ±2.1*
Sr	1.2 ±0.4	0.6 ±0.4*	0.9 ±0.3	0.8 ±0.4	0.8 ±0.5	0.7 ±0.3
Na	10.7 ±1.8	3.4 ±2.9	4.5 ±1.9	4.8 ±3.7	2.1 ±3.9	5.1 ±2.4
S	19.6 ±4.3	3.1 ±1.7	9.5 ±3.6	9.6 ±8.3	1.9 ±2.4	7.3 ±3.0

of *Crurithyris, Composita* and *Neospirifer*. For *Composita*, the Mg concentrations of NL calcites are lower than those of PL calcites. NL calcites of *Crurithyris* contain higher Mg concentrations than those of *Composita* and *Neospirifer*, whereas the PL calcites do not show the same relationship. This suggests that the biological control on concentration of Mg was retained in NL shells. The Fe and Mn contents of NL calcites are statistically lower than those of PL calcites ($p < 0.05$) for all genera except *Crurithyris* (only Mn is lower). This indicates that the NL calcites used for isotopic analysis contain low concentrations of Mn and Fe and that non-luminescence was not caused by Fe quenching, and provides further evidence that the original isotopic signals should be preserved in these brachiopod shells. The Sr, Na and S contents of NL *Composita* are lower than those of NL *Crurithyris* and *Neospirifer*. The same relationship was reported by Zhang et al. (1990) and was interpreted as a result of vital effects. Zhang et al. (1990) also suggested that retention of these vital effects can be used as evidence for good preservation. In conclusion, the isotopic data used for this paleoenvironmental study are from well preserved brachiopod shells; that is, either non-luminescent calcite or dominantly non-luminescent calcite with some fine luminescent spots or streaks (SP, ST). In addition to the non-luminescent calcite, nine luminescent calcite samples of *Crurithyris, Composita* and *Neospirifer* were analyzed to establish the diagenetic trends in isotopic composition.

Isotopic values of Pennsylvanian brachiopods

Isotopic values of non-luminescent calcite in *Crurithyris, Composita* and *Neospirifer* are plotted in Figure 4. The $\delta^{18}O$ range is between -4.5‰ and -2.1‰ and the $\delta^{13}C$ range is from 2.2‰ to 4.8‰. New Mexico samples generally are depleted in ^{18}O relative to samples from the central Midcontinent (Kansas) (Grossman et al., 1993), while samples from the two areas have roughly the same range in $\delta^{13}C$.

The overall isotopic variations of brachiopods reported in this study are in good agreement with many other isotopic studies of Carboniferous carbonates, except for the average $\delta^{13}C$ of brachiopods analyzed by Popp et al. (1986). Lowenstam (1961) found that the $\delta^{18}O$ of the brachiopod *Chonetes* from the Upper Mississippian of Oklahoma averaged -2.4 ±0.6‰ (N = 3). Brand (1982) reported isotopic values of three Mississippian brachiopods from New Mexico of -2.0 ±0.3‰ for $\delta^{18}O$ and 3.3 ±0.3‰ for $\delta^{13}C$. Late Carboniferous brachiopods from Spain (Popp et al., 1986) have average $\delta^{18}O$ and $\delta^{13}C$ values of -2.1 ±0.4‰ and 5.6 ±0.4‰, respectively, for Moscovian *Choristites* samples (N = 22), and average $\delta^{18}O$ and $\delta^{13}C$ values of -3.2 ±0.4‰ and 6.2 ±0.3‰, respectively, for Kasimovian samples (N = 11). Texas specimens (Grossman et al., 1991) of the brachiopods *Crurithyris, Eridmatus* and *Composita* have average isotopic values of -2.5, -1.8, and -2.2‰ for $\delta^{18}O$ and 3.2, 3.6, and 4.9‰ for $\delta^{13}C$, respectively. These data show that late Paleozoic brachiopods have average $\delta^{18}O$ values generally in the range of modern tropical brachiopods (e.g., -3 to -1 ‰; Carpenter and Lohmann, 1995).

Eight different shells of *Composita* and *Neospirifer* were microsampled two or three times for isotopic analyses. The $\delta^{13}C$ differences between two different areas of a single shell average 0.3 ±0.2‰ for *Composita* (N = 9) and 0.3 ±0.2‰ for *Neospirifer* (N = 19) (see Appendix). The $\delta^{18}O$ differences between two different areas of the same shell average 0.3 ±0.2‰ for *Composita* (N = 9) and 0.3 ±0.3‰ for *Neospirifer* (N = 19). The intrashell isotopic variability is far greater than analytical error (0.1‰ for $\delta^{13}C$ and $\delta^{18}O$) and probably represents the seasonal variation observed by Mii and Grossman (1994).

The mean standard deviations for $\delta^{13}C$ and $\delta^{18}O$ values of three or more specimens from the same stratigraphic interval are 0.3‰ (n = 49) and 0.3‰ (n = 49) for $\delta^{13}C$ and $\delta^{18}O$, respectively. The magnitude of this intershell isotopic variability for the same species is roughly the same as that within single specimens. This variability also can be attributed to environmental variability and to differences in microhabitats. Compston (1960) and Brand (1982) reported an interspecimen $\delta^{18}O$ range of 0.6‰ and 0.3‰, respectively, for Mississippian brachiopods.

Taxonomic differences in isotopic compositions of *Crurithyris, Composita* and *Neospirifer*, first noted for Texas brachiopods (Grossman et al., 1991), are also observed here. The $\delta^{13}C$ values of *Composita* are 1.5 ±0.5‰ higher than those of *Crurithyris* ($p = 0.03$, N = 3) and 0.6 ±0.5‰ higher than those of *Neospirifer* ($p = 0.01$, N = 8) (Fig. 5). Grossman et al. (1991) attributed this variation to microhabitat effects. Based on the morphology of *Crurithyris* and *Composita*, they suggested that *Crurithyris* was a semi-infaunal mud dweller, living largely buried in the substrate, whereas *Composita* lived attached and largely surrounded by sea water. Therefore, the *Crurithyris* shell would incorporate bottom water DIC plus ^{13}C-depleted DIC from the oxidation of organic matter in sediments, and the *Composita* shell would incorporate only bottom water DIC. It is also possible that metabolic differences caused the isotopic differences. Oxygen isotopic differences between *Composita, Crurithyris* and *Neospirifer* are not statistically significant.

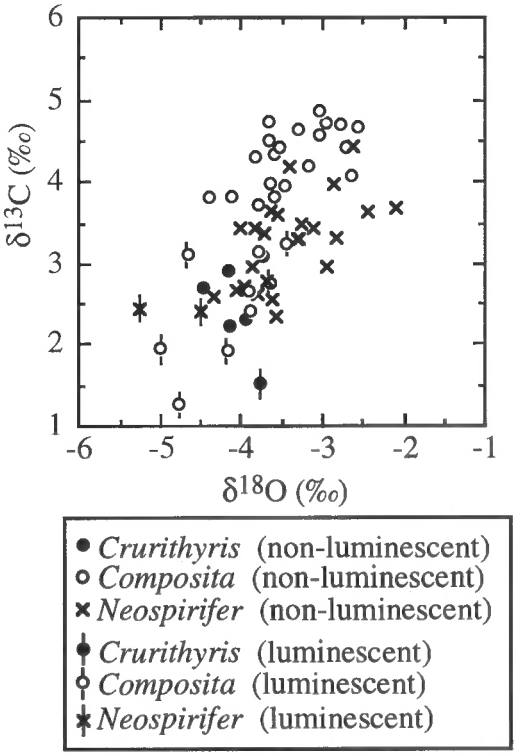

FIGURE 4. Isotopic values of non-luminescent and luminescent calcite of brachiopods from New Mexico.

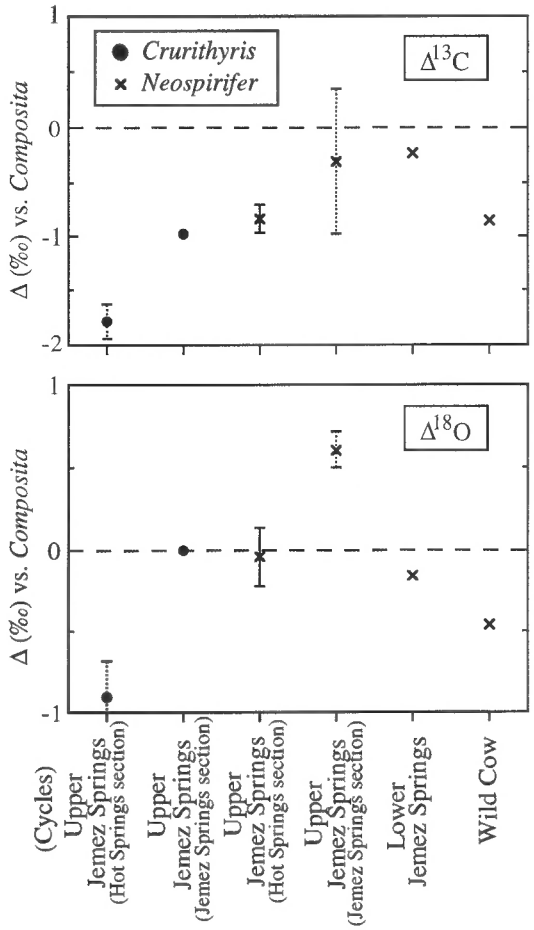

FIGURE 5. $\delta^{13}C$ vs. $\delta^{18}O$ difference between *Composita* and co-occurring species in the New Mexico cycles. Error bars represent ±2 times the standard errors of the mean. Where only two shells were analyzed, smaller symbols are used and dotted lines show the range in values. When only one shell was analyzed, only smaller symbols are used.

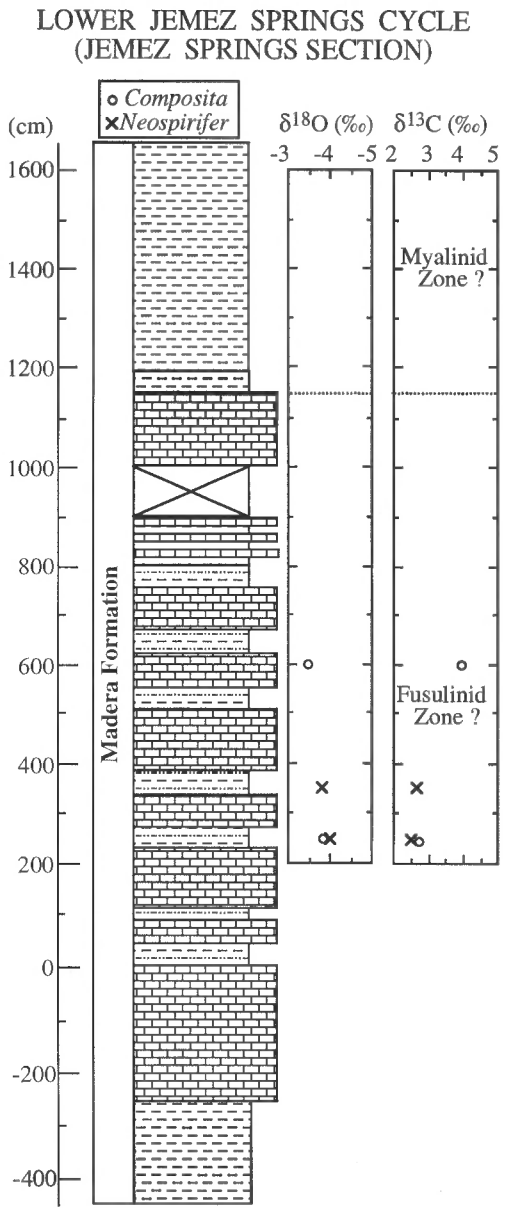

FIGURE 6. Isotope stratigraphies based on interval mean values of brachiopod shells from part of the lower Jemez Springs cycle. Where less than three shells were analyzed, smaller symbols are used. The $\delta^{18}O$ values are plotted negative to the right.

Isotope stratigraphy

Figures 6 to 9 combine lithologic and fossil depth zone information with the isotope stratigraphy for the cycles sampled. The criteria for depth zones are defined by Adlis et al. (1988). Only average values for a given horizon and taxon will be mentioned in the following discussion for the purpose of clarity. The paucity of data for the lower Jemez Springs cycle (Fig. 6) and Wild Cow cycle (Fig. 9) preclude stratigraphic analysis of these cycles.

Upper Jemez Springs cycle (Jemez Springs section)

Brachiopod-bearing samples were collected from the ammonoid zone of this cycle. Both the average $\delta^{18}O$ and $\delta^{13}C$ trend of *Composita* and *Neospirifer* do not significantly vary from interval to interval (Fig. 7).

Upper Jemez Springs cycle (Hot Springs section)

Brachiopod-bearing samples were collected from deposits of the fusulinid zone and ammonoid zone, with the boundary at 8.5 m above the base of the measured section at this locality. *Crurithyris* data are insufficient to discuss a stratigraphic trend. *Composita* data yield insignificant changes from 800 cm to 1000 cm. The $\delta^{18}O$ of *Neospirifer* linearly decrease from about -2.8‰ at 800 cm to about -3.8‰ at 1300 cm (Fig. 8). The $\delta^{13}C$ values of *Composita* and *Neospirifer* remain essentially constant at 4.4‰ and 3.5‰ respectively.

Variation in oxygen and carbon isotopes between cycles and sections

To examine stratigraphic variation in the isotopic record, the average isotopic compositions of *Crurithyris, Composita* and *Neospirifer* from each cycle have been illustrated in Figure 10. The different genera do not yield statistically significant variations in oxygen isotope stratigraphy. The average $\delta^{13}C$ values of *Composita* and *Neospirifer* tend to increase upsection from a low in the lower Jemez Springs cycle, similar to trends in ^{13}C stratigraphy seen in Midcontinent (Kansas) sections.

Cause of isotopic variations

Variations in the isotopic compositions of brachiopod shells may be caused by changes in the temperature and isotopic compositions of ambient seawater, vital effects, and diagenesis. It is unlikely that the variations observed in this study were caused by diagenetic alteration without evidence of textural or chemical change. Any variation resulting from vital effects was minimized by comparing individuals of the same species or genus.

Variations in brachiopod $\delta^{18}O$ can be interpreted as arising from changes in temperature and the $\delta^{18}O$ of seawater, which is controlled by changes in regional salinity and global ice volume. For the open ocean, the ratio of the $\delta^{18}O$ of surface water to salinity ($\Delta\delta/\Delta S$) varies from 0.1 in tropic

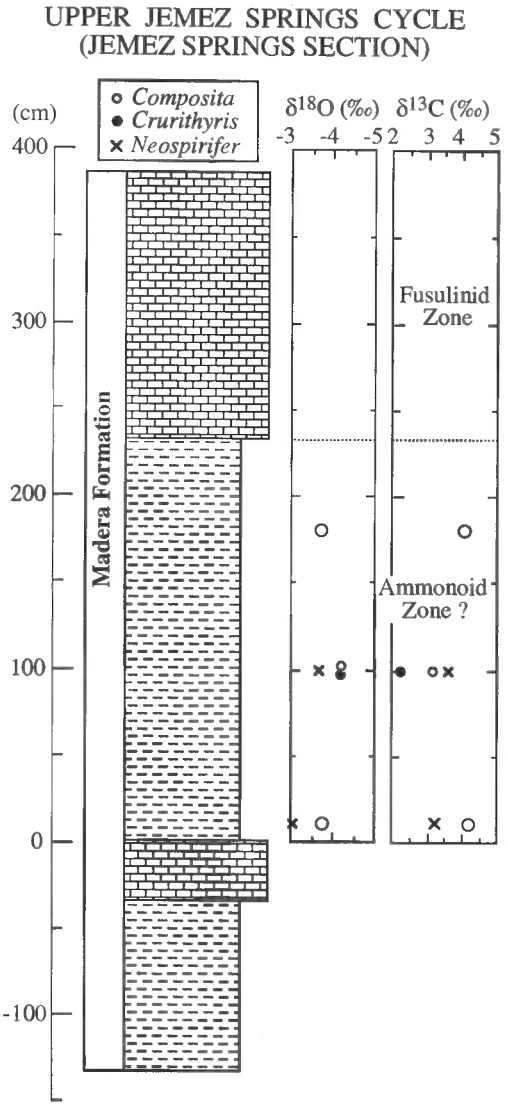

FIGURE 7. Isotope stratigraphies based on interval mean values of brachiopod shells from the upper Jemez Springs cycle (Jemez Springs section). Where less than three shells were analyzed, smaller symbols are used. The $\delta^{18}O$ values are plotted negative to the right.

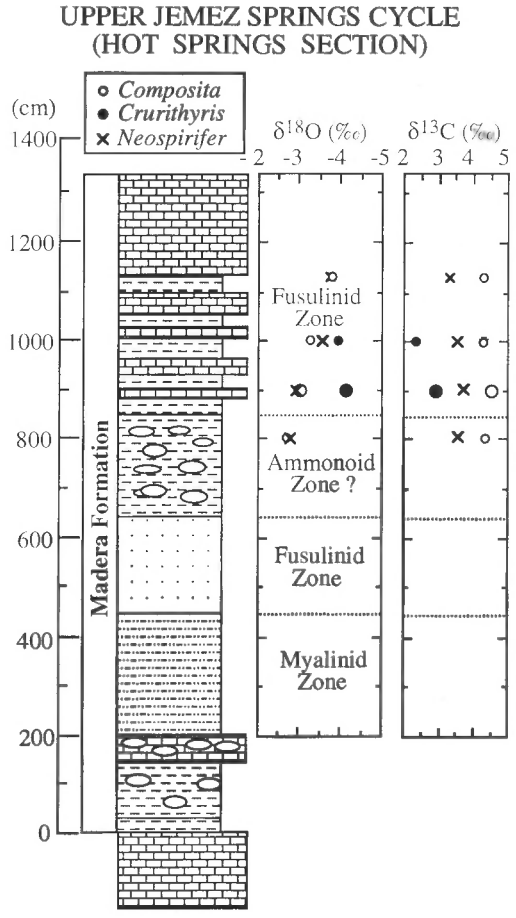

FIGURE 8. Isotope stratigraphies based on interval mean values of brachiopod shells from the upper Jemez Springs cycle (Hot Springs section). Where less than three shells were analyzed, smaller symbols are used. The $\delta^{18}O$ values are plotted negative to the right.

and subtropic trade wind regions to 0.6 in temperate regions (Craig and Gordon, 1965). The $\Delta\delta/\Delta S$ ratio of the Pennsylvanian epicontinental sea was probably less than the 0.3 to 0.4 values for the closest available analog, continental shelf and slope water in the New York Bight and Gulf of Maine (Fairbanks, 1982). Thus, a 1 ppt change in the salinity of North American epicontinental sea water probably would have produced a 0.1 to 0.3‰ change in the $\delta^{18}O$ of surface seawater, and an equivalent change in brachiopod $\delta^{18}O$ values. Therefore, salinity effects can account for small variations in the $\delta^{18}O$ of brachiopod shells.

Because the Pennsylvanian was a period of continental glaciation (Crowell, 1978; Veevers and Powell, 1987), the isotopic composition of sea water should have varied with continental ice volume. For the Pleistocene, it is estimated that a 100 m lowering of sea level due to ice accumulation corresponds to a 1‰ increase in sea water $\delta^{18}O$ (Fairbanks and Matthews, 1978). Sea level rise caused by the melting of glacial ice will result in lower $\delta^{18}O$ values for marine carbonates. Unfortunately, $\delta^{18}O$ values of New Mexico brachiopods do not show a $\delta^{18}O$ difference between different depth zones, perhaps because both fossil depth zones occurred within the mixed layer of the water column.

Variations in brachiopod $\delta^{13}C$ can be interpreted as resulting from changes in the $\delta^{13}C_{DIC}$ of seawater because the $\delta^{13}C$ of calcite is relatively insensitive to changes in temperature between 10 °C and 40 °C (Romanek et al., 1992). The depth zonation of New Mexico and Midcontinent samples shows no relation to $\delta^{13}C$ of *Composita* and *Crurithyris*, in agreement with the conclusions of Grossman et al. (1991). This suggests that the $\delta^{13}C$ of DIC was relatively constant with depth over the depth interval represented by these fossils. The stratigraphic variations in $\delta^{13}C$ may reflect regional changes in circulation or productivity, or global changes in the burial rate of organic carbon. Unfortunately, our data are not sufficient to determine the dominant factor.

Isotopic variations with paleogeography

The average $\delta^{18}O$ and $\delta^{13}C$ of Late Pennsylvanian *Crurithyris*, *Composita* and *Neospirifer* of Kansas, New Mexico and Texas (data from Grossman et al., 1991, 1993) show significant differences. For all three genera, $\delta^{18}O$ values are highest in Kansas, intermediate in Texas, and lowest in New Mexico (Fig. 11). The $\delta^{18}O$ of Kansas specimens are about 0.4‰ higher than those of Texas specimens for all three genera. The $\delta^{18}O$ of Texas *Crurithyris*, *Composita*, and *Neospirifer* are respectively 1.6, 1.2, and 1.1‰ enriched relative to New Mexico samples.

For all three genera the average $\delta^{13}C$ are highest in Texas, intermediate in Kansas, and lowest in New Mexico (Fig. 11). These regional differences in $\delta^{13}C$ are statistically significant ($p < 0.05$) except for the differences between Kansas and Texas *Crurithyris*, New Mexico and Texas *Crurithyris*, Kansas and New Mexico *Composita*, and Kansas and New Mexico *Neospirifer*. The average $\delta^{13}C$ value of *Crurithyris* from Kansas is 0.6‰ enriched in ^{13}C relative to *Crurithyris* from New Mexico. The average $\delta^{13}C$ values of *Composita* from Texas are respectively 0.6‰ and 0.8‰ higher than those from Kansas and New Mexico. The average $\delta^{13}C$ values of *Neospirifer* from Texas are respectively 0.4‰ and 0.6‰ higher than those from Kansas and New Mexico.

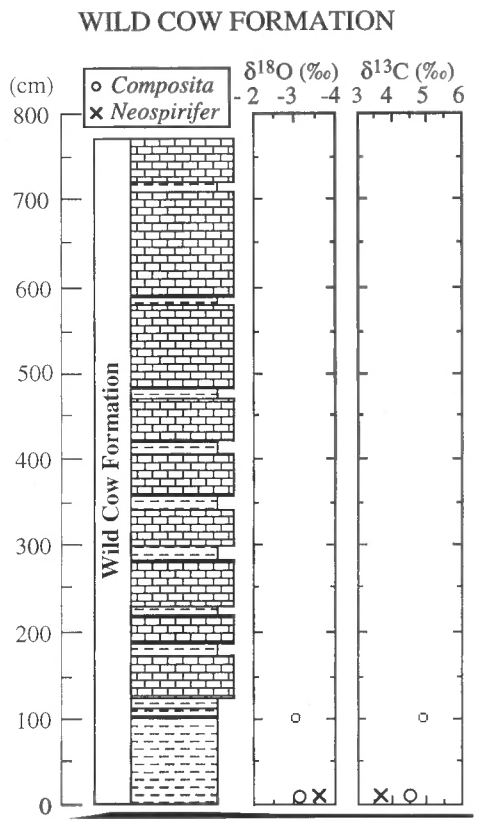

FIGURE 9. Isotope stratigraphies based on interval mean values of brachiopod shells from the Wild Cow Formation, New Mexico. Where less than three shells were analyzed, smaller symbols are used. The $\delta^{18}O$ values are plotted negative to the right.

Differences in $\delta^{18}O$ and $\delta^{13}C$ for different localities may represent variations in regional paleoenvironment. Paleogeographic reconstructions of North America during the Pennsylvanian show that New Mexico, Kansas and Texas lay within the tropics (Heckel, 1980; Scotese et al., 1979), suggesting that temperatures in the seas of New Mexico, Kansas and

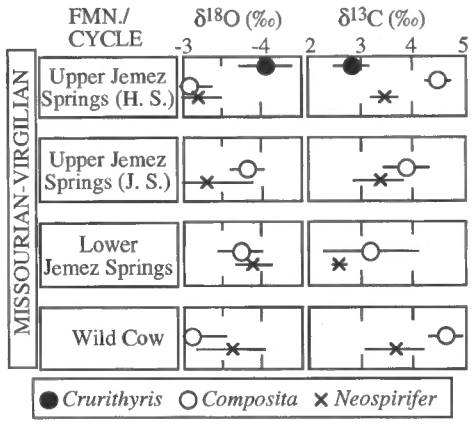

FIGURE 10. Average isotopic composition of *Crurithyris*, *Composita* and *Neospirifer* from different cycles in New Mexico. Error bars represent ±2 times the standard error of the mean. Where only one shell was analyzed for a section, the data have been omitted. The Hot Springs section (HS) and the Jemez Springs (JS) of the upper Jemez Springs cycle are stratigraphically equivalent. The $\delta^{18}O$ values are plotted negative to the right.

Texas were similar. The Kansas sea may have been more restricted than the Texas sea and differences in the average $\delta^{18}O$ of brachiopod shells from different areas may result from differences in the $\delta^{18}O$ of the sea waters in each region.

The average water depth of study areas in Kansas and New Mexico may be shallower than that of Texas. In the Texas study, 59 different specimens from three cycles were collected from the deepest fossil depth zone, the gondolellid zone, whereas no gondolellid zone samples were obtained in New Mexico. Thus, higher $\delta^{18}O$ values are expected for the Texas sea compared to the Kansas and New Mexico seas. This is observed for New Mexico seas, but the $\delta^{18}O$ values for the Kansas sea are about 0.4‰ higher than those for the Texas sea. The 0.4‰ difference in $\delta^{18}O$ may indicate 1 to 4 ppt higher salinity in Kansas, 2°C warmer temperatures in Texas, or some combination of the two. New Mexico oxygen isotope values are about 1.3‰ lower than those for Texas. This may indicate a New Mexico sea of 4 to 13 ppt less salinity than the Texas sea during the Late Pennsylvanian, 6 to 7°C warmer temperatures in New Mexico, or some combination of the two. Lower Na and S contents in

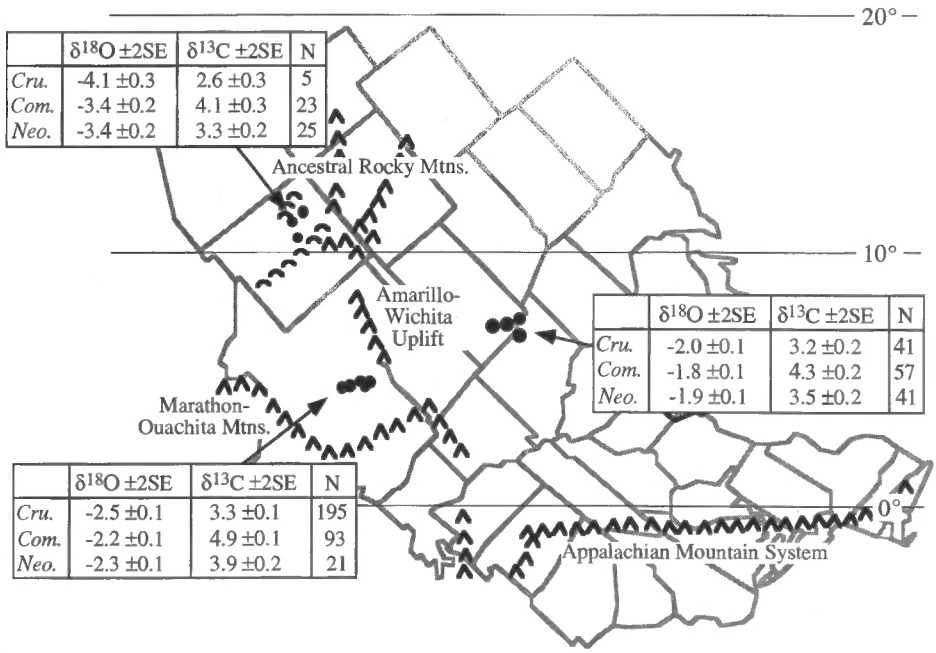

FIGURE 11. Paleogeographic map (modified from Heckel, 1980) showing sample localities and average oxygen and carbon isotopic compositions (in ‰ with ±2 x standard error, 2SE) of *Crurithyris* (*Cru.*), *Composita* (*Com.*), and *Neospirifer* (*Neo.*) shells from Kansas, New Mexico, and Texas. Texas data are from Grossman et al. (1991), with additional data from the Lower Salesville cycle (from Grossman et al., 1993).

Crurithyris shells from Kansas, intermediate contents in Texas shells, and high contents in New Mexico samples argue that temperature differences cause regional $\delta^{18}O$ variations (Grossman et al., in press, 1996). Thus, warmer temperatures for New Mexico seas and cooler temperatures for Kansas seas are suggested. Nevertheless, salinity effects may also contribute to $\delta^{18}O$ variations.

Although the factors causing geographic $\delta^{13}C$ variations are not clear, differences in the $\delta^{13}C$ of brachiopod shells suggest that the $\delta^{13}C_{DIC}$ of the Texas sea was higher than those of the Kansas and New Mexico seas. It is likely that dissolved O_2 concentrations, which covaries with $\delta^{13}C$, was highest in Texas seawaters. As mentioned earlier, there was no correlation between $\delta^{13}C$ of brachiopod shells and water depth in this study, thus, difference in water depth does not appear to cause the variation in $\delta^{13}C$. The relation between $\delta^{13}C_{DIC}$ and productivity is complex because upwelling is associated with high productivity and low $\delta^{13}C_{DIC}$. However, geographic differences in the $\delta^{13}C$ of brachiopod shells indicate that temporal trends in carbon isotope stratigraphies may reflect regional variation.

SUMMARY AND CONCLUSIONS

The original carbon and oxygen isotope signals of brachiopod shells from the Late Pennsylvanian were determined. The $\delta^{18}O$ values of *Crurithyris, Composita* and *Neospirifer* average -4.1‰ ±0.3‰ (N = 5), -3.4‰ ±0.5‰ (N = 23), and -3.4‰ ±0.4‰ (N = 25), respectively. The $\delta^{13}C$ values of *Crurithyris, Composita* and *Neospirifer* average 2.6‰ ±0.4‰, 4.1‰ ±0.7‰, and 3.3‰ ±0.5‰, respectively. The average $\delta^{13}C$ values of *Composita* are about 1‰ higher than those of concurrent *Crurithyris* and *Neospirifer*, suggesting microhabitat or vital effects. The $\delta^{18}O$ and $\delta^{13}C$ values do not significantly correlate with water depth, as indicated by fossil content and lithology, but the data are too sparse to test this relationship adequately.

Average trace element concentrations of non-luminescent (NL) and partly luminescent (PL) calcite in *Crurithyris, Composita* and *Neospirifer* suggest retention of biological signals and indicate that the original isotopic signals should be preserved in these brachiopod shells. Mg concentrations in NL calcites of *Crurithyris* are higher than in *Composita* and *Neospirifer*, a relationship not seen in the PL calcites. The Fe and Mn content of NL calcites are statistically lower than those of PL calcites ($p < 0.05$) for all three genera except *Crurithyris* (only Mn is lower). Therefore, NL calcites contain low concentrations of Mn and Fe and non-luminescence was not caused by Fe quenching. The Sr, Na and S contents of NL *Composita* are lower than those of NL *Crurithyris* and *Neospirifer*.

This study shows the degree of regional variation that can be expected in isotope stratigraphies. Average $\delta^{18}O$ values are highest in Kansas, intermediate in Texas (using data from Grossman et al., 1991), and lowest in New Mexico. $\delta^{18}O$ and trace element data suggest cooler Kansas seas, intermediate Texas seas, and warmer New Mexico seas. Salinity variations may also contribute to isotope variations. Average $\delta^{13}C$ is highest in Texas, intermediate in Kansas, and lowest in New Mexico. Thus, the $\delta^{13}C_{DIC}$ values of Texas seawater were higher than those of the Kansas and New Mexico seawaters. Consequently, the dissolved oxygen concentration of the water, which covaries with $\delta^{13}C_{DIC}$, was likely highest in Texas seawaters.

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APPENDIX

Stable isotopic compositions of brachiopod shells (in ‰ vs. PDB) from New Mexico. SP = specimen. LC = luminescent character of sampled area of brachiopod shells (key at end of appendix). s = standard deviation which is calculated only when three or more shells of each species are analyzed in an interval. Isotopic differences between replicates is indicated in the parentheses when only two specimens of a species are analyzed in an interval. ZONE = the fossil depth zone where sample was collected.

INT. (cm)	GENUS	SP[1]	$\delta^{13}C$	$\delta^{18}O$	LC	avg. $\delta^{13}C \pm 1s$	avg. $\delta^{18}O \pm 1s$	ZONE
UPPER JEMEZ SPRINGS CYCLE (HOT SPRINGS SECTION), NEW MEXICO								
1130	*Composita*	a1	4.29	-3.82	NL	4.29	-3.82	F
	Neospirifer	a	3.62	-3.58	NL	3.29 (0.66)	-3.74 (0.31)	F
		b	2.96	-3.89	NL			F

INT. (cm)	GENUS	SP[1]	$\delta^{13}C$	$\delta^{18}O$	LC	avg. $\delta^{13}C \pm 1s$	avg. $\delta^{18}O \pm 1s$	ZONE
1000	*Composita*	a	3.81	-3.59	NL-ST	4.26 (0.90)	-3.27 (0.64)	F
		b	4.89	-2.66	NL			F
		b1	4.52	-3.24	NL			F
		c	*3.13*	*-4.67*	NL-ST			F
	Crurithyris	a	2.33	-3.85	NL-SP	2.31	-3.95	F
		a1	2.28	-4.04	NL-SP			F
	Neospirifer	a	3.66	-3.66	NL	3.50 ±0.14	-3.55 ±0.36	F
		b	3.42	-3.15	NL			F
		c	3.42	-3.85	NL			F
900	*Composita*	a	4.40	-2.71	NL-SP	4.52 ±0.10	-3.01 ±0.30	F
		b	4.55	-3.03	NL			F
		c	4.60	-3.30	NL			F
	Crurithyris	a	2.69	-4.49	NL-ST	2.89 ±0.20	-4.14 ±0.37	F
		b	2.90	-4.17	NL+L			F
		c	3.08	-3.75	NL-ST			F
	Neospirifer	a	3.49	-3.28	NL	3.75 ±0.60	-2.92 ±0.33	F
		b	4.43	-2.64	NL			F
		c	3.40	-2.85	NL			F
		c1	3.25	-2.85	NL			F
800	*Composita*	a	4.68	-2.79	NL-ST	4.37 (0.63)	-2.72 (0.15)	A
		b	4.05	-2.64	NL			A
		c	*2.74*	*-3.65*	NL-ST			A
		d	*1.92*	*-4.17*	NL-ST			A
	Neospirifer	a	3.97	-2.89	NL	3.52 ±0.52	-2.77 ±0.27	A
		b	3.63	-2.46	NL			A
		c	2.95	-2.95	NL			A
500	*Derbyia*	a	3.16	-2.64	NL-SP	3.16	-2.64	
		b	*3.61*	*-4.15*	NL-BR			
		c	*3.37*	*-7.07*	BR			
UPPER JEMEZ SPRINGS CYCLE (JEMEZ SPRINGS SECTION), NEW MEXICO								
180	*Composita*	a	3.95	-3.64	NL-BD	4.03 ±0.40	-3.69 ±0.09	A
		b	3.68	-3.79	NL-SP			A
		c	4.47	-3.64	NL			A
	Crurithyris	a	*1.51*	*-3.80*	DL			A
100	*Composita*	a	3.79	-4.39	NL	3.22 (1.14)	-4.16 (0.47)	A
		b	2.65	-3.92	NL			A
		c	*2.36*	*-4.78*	NL-SP			A
		c1	*1.57*	*-5.25*	BR			A
	Crurithyris	a	2.24	-4.16	NL	2.24	-4.16	A
	Derbyia	a	*-0.20*	*-3.95*	BR-NL			
	Hystriculina	a	*0.83*	*-4.06*	NL-L			
		a1	*-1.65*	*-6.88*	BR			
	Neospirifer	a	3.53	-3.56	NL-BD	3.58 (0.41)	-3.66 (0.17)	A
		a1	4.03	-3.59	NL-BD			A
		b	3.10	-4.04	NL			A
		b1	3.37	-3.60	NL			A
		b2	3.65	-3.58	NL			A
		c	*2.40*	*-4.52*	NL-SP			A
10	*Composita*	a	4.31	-3.58	NL+LMF	4.17 ±0.33	-3.73 ±0.32	A
		b	3.80	-4.10	NL-SP			A
		c	4.41	-3.51	NL-SP			A
		d	*2.79*	*-3.06*	FL-BR			A
		d1	*3.70*	*-3.84*	FL-BR			A
		e	*-1.11*	*-5.57*	BR			A
		e1	*1.04*	*-3.85*	FL			A
		e2	*1.59*	*-4.93*	NL-ST			A
	Derbyia	a	*-0.55*	*-4.66*	BR			
		a1	*-0.20*	*-6.44*	FL-ST			
	Neospirifer	a	*2.44*	*-5.26*	vFL-SP	3.19 ±0.57	-3.02 ±0.79	A
		b	2.57	-3.63	FL-ST			A
		c	3.70	-2.12	NL-SP			A
		d	3.35	-3.35	NL			A
		d1	3.27	-3.14	NL			A
		d2	3.30	-3.40	NL			A
LOWER JEMEZ SPRINGS CYCLE, NEW MEXICO								
600	*Composita*	a	3.92	-3.45	NL	3.92	-3.45F	
350	*Derbyia*	a	2.31	-3.90	NL-SP	2.31	-3.90	
	Neospirifer	a	2.81	-3.90	NL	2.69 ±0.08	-3.82 ±0.15	F
		a1	2.40	-3.72	NL			F
		b	2.77	-3.68	NL-SP			F
		c	2.69	-3.97	NL			F
250	*Composita*	a	3.12	-3.80	NL	2.75 (0.74)	-3.84 (0.07)	F
		b	2.38	-3.87	NL			F
	Derbyia	a	1.72	-3.93	NL	1.72	-3.93	F

INT. (cm)	GENUS	SP[1]	$\delta^{13}C$	$\delta^{18}O$	LC	avg. $\delta^{13}C \pm 1s$	avg. $\delta^{18}O \pm 1s$	ZONE
	Neospirifer	a	2.34	-3.58	NL	2.52 ±0.16	-4.00 ±0.39	F
		b	2.21	-4.73	NL			F
		b1	2.92	-3.97	NL			F
		c	2.66	-4.08	NL			F
WILD COW FM., NEW MEXICO								
100	*Composita*	a	4.84	-3.05	NL	4.84	-3.05	
10	*Composita*	a	4.17	-3.17	NL	4.51 ±0.30	-3.12 ±0.53	
		b	4.67	-2.57	NL			
		c	4.70	-3.63	NL			
	Neospirifer	a	3.31	-3.32	NL-SP	3.64 ±0.47	-3.59 ±0.38	
		b	3.96	-3.85	NL			
		b1	4.41	-3.01	NL			
		c	3.43	-4.03	NL			

KEY

DEGREE: BL= bright luminescence
L = luminescence
FL= faint luminescence
vFL= very faint luminescence
NL= completely non-luminescent

FEATURES: ST= luminescent streaks, usually on the order of 100 μ long
SP= luminescent specks
MF= microfractures
BD= luminescent bands

ZONES: M = myalinid zone
F = fusulinid zone
A = ammonoid zone
G = gondolellid zone

Footnote: [1] each shell is given a different letter; multiple analyses of the same shell are denoted a1, a2, etc.
[2] Isotopic values in italics do not meet criteria for non-luminescence and are not included in calculation of mean values and isotope stratigraphy.