Meteoric sphaerosiderite lines and their use for paleohydrology and paleoclimatology

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ABSTRACT

Sphaerosiderite, a morphologically distinct millimeter-scale spherulitic siderite ($FeCO_3$), forms predominantly in wetland soils and sediments, and is common in the geologic record. Ancient sphaerosiderites are found in paleosol horizons within coal-bearing stratigraphic intervals and, like their modern counterparts, are interpreted as having formed in water-saturated environments. Here we report on sphaerosiderites from four different stratigraphic units, each of which has highly variable ^{13}C and relatively stable ^{18}O compositions. The unique isotopic trends are analogous to well-documented meteoric calcite lines, which we define here as meteoric sphaerosiderite lines. Meteoric sphaerosiderite lines provide a new means of constraining ground-water $\delta^{18}O$ and thus allow evaluation of paleohydrology and paleoclimate in humid continental settings.

INTRODUCTION

Pedogenic carbonates from vadose soils form in areas of net water deficit, have $\delta^{18}O$ values that are highly correlated with that of local meteoric water, and have been widely used as paleoclimate proxy records (Cerling and Quade, 1993). Paleoclimatic and paleohydrologic studies in humid continental settings, however, have been limited by the lack of suitable early diagenetic mineral phases that can serve as paleoclimatic and paleohydrologic proxy records. Sphaerosiderite, a morphologically distinct millimeter-scale spherulitic variety of siderite (Fig. 1), is an early diagenetic product that forms in siliciclastic mudstones in continental environments. The formation of modern sphaerosiderite in reducing wetland soils (e.g., Stoops, 1983; Landuyt, 1990) and their common occurrence in the geologic record (e.g., Tucker, 1981; Retallack, 1981; Leckie et al., 1989) provide the opportunity for extending the range of continental sampling for $\delta^{18}O$ of carbonates into humid areas that have been widely presumed to lack suitable study materials.

Reported Holocene sphaerosiderites range from 20 to 200 mm in diameter, and we suggest that these materials have been widely overlooked in modern environments because (1) compared to vadose soils, wetland soils have received less attention from soil scientists, (2) the small size of Holocene sphaerosiderites precludes accidental detection, and (3) the utility of stable isotopic data from sphaerosiderite has not been recognized until now. Little is known of Holocene sphaerosiderite chemistry, although it is safe to assume that their formation and chemistry are controlled by reducing conditions that prevail in wetland soils.

Sphaerosiderites have been reported from many localities in pre-Holocene deposits, and like their modern counterparts, few studies have focused on their chemistry. Here we report on our studies of sphaerosiderite isotope chemistry from the Cretaceous Dakota and Swan River Formations and review the isotopic data reported for sphaerosiderites sampled from other nonmarine intervals in coastal plain successions.

RESEARCH METHODS

Samples from the Dakota Formation were obtained from cores at Sergeant Bluff, Iowa (Witzke and Ludvigson, 1994). Samples from the Swan River Formation of Manitoba were obtained from unit 1 of outcrop section 57 of McNeil and Caldwell (1981, p. 349–350). Samples were impregnated with epoxy, and thin slabs and thin sections were cut perpendicular to bedding. Powdered

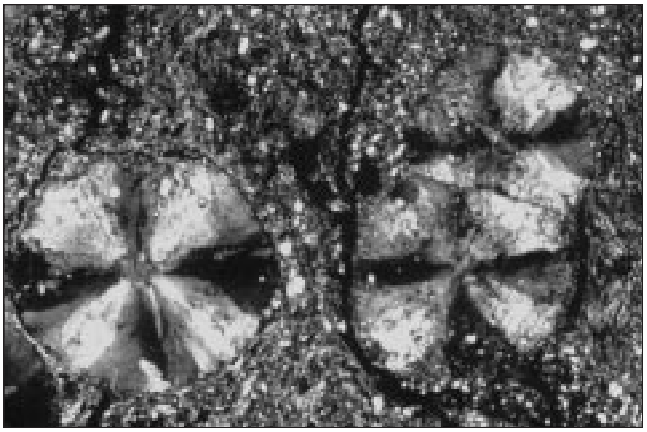

Figure 1. Cross-polarized thin section photomicrograph of sphaerosiderites in silty mudstone paleosol of Cretaceous Dakota Formation (sample SCB4-91.5). Optical extinction patterns (black) in nodules show spherulitic structure of radially elongated siderite crystallites. Note light-toned birefringent clay coatings wrap around preexisting sphaerosiderites. Horizontal field of view is 3.2 mm.

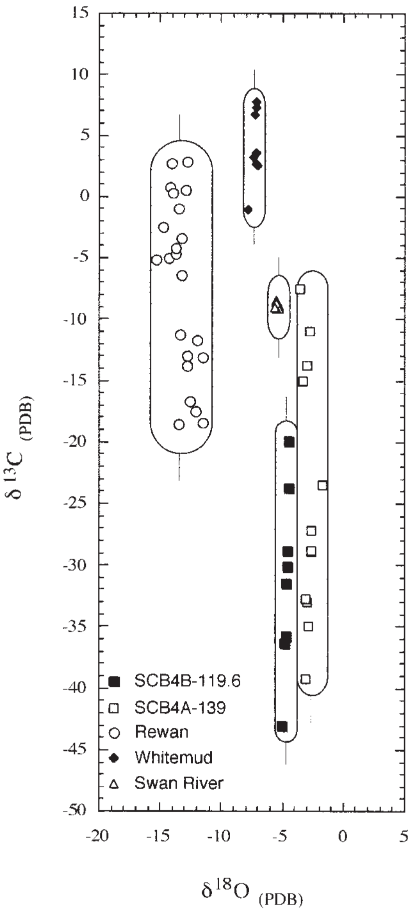

Figure 2. Stable isotopic geochemistry of Mesozoic sphaerosiderites in Dakota (SCB4B-119.6 and SCB4A-139), Swan River, and Whitemud (Fritz et al., 1971) Formations, and Rewan Group (Baker et al., 1996). PDB—Peedee belemnite.

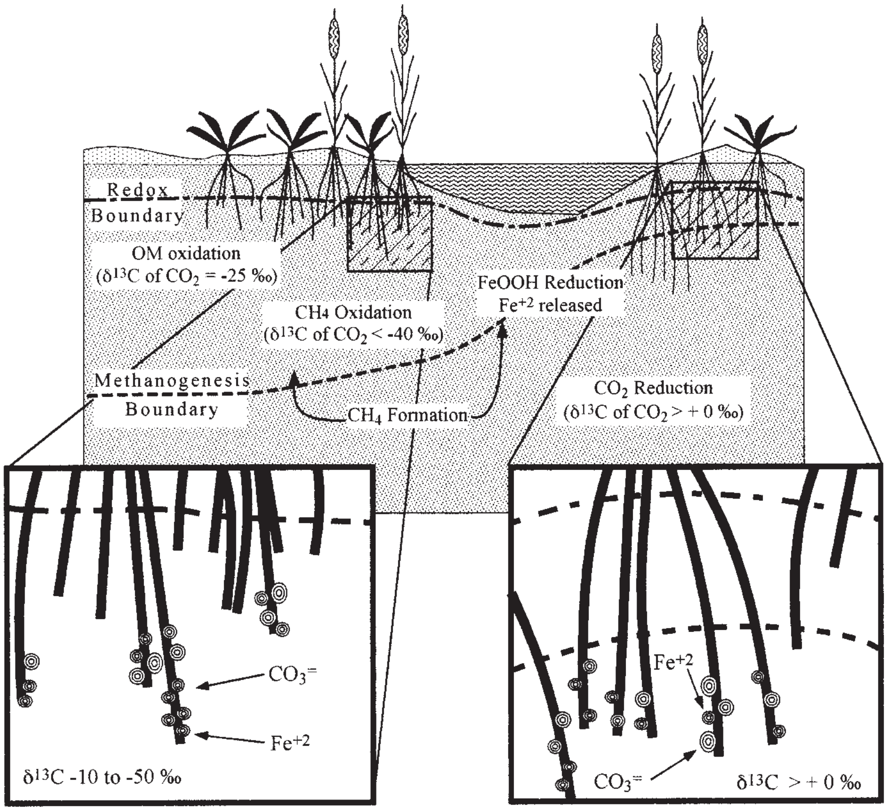

Figure 3. Formation of sphaerosiderites in wetland setting, and geomicrobiological processes responsible for δ^{13}C variations in meteoric sphaerosiderite lines.

samples of a few tens of micrograms were extracted with a microscope-mounted drill assembly with a 0.5 mm bit. Stable isotopic analyses were performed at the University of Michigan Stable Isotope Laboratory. Samples were roasted in vacuum at 380 °C for 1 hr and reacted with anhydrous phosphoric acid at 72 °C in a CarboKiel reaction device coupled to the inlet of a Finnigan MAT 251 ratio mass spectrometer. All values are reported relative to the Peedee belemnite (PDB) standard, with reported precision better than ±0.05‰ for both carbon and oxygen.

All siderite isotopic data were corrected to account for the temperature-dependent oxygen isotope fractionation between phosphoric acid and siderite, using data in Carothers et al. (1988). Siderite from the Dakota and Swan River Formations (reacted at 72 °C) and siderite from the Rewan Group (Baker et al., 1996) (reacted at 75 °C) have all been corrected with a fractionation factor of 1.008 675. Siderite from the Whitemud Formation was reacted at 25 °C, and Fritz et al. (1971) corrected their own δ^{18}O data with a fractionation factor of 1.011 69, which is consistent with the fractionation factors derived by Carothers et al. (1988).

NEW ISOTOPIC INFORMATION FROM CRETACEOUS PALEOSOLS

Dakota Formation

Sphaerosiderite in the mid-Cretaceous Dakota Formation of the midwestern United States occurs in discrete horizons contained in successions of multiple amalgamated kaolinitic mudstone paleosols, and is arrayed along clay-filled horizontal root traces. These sphaerosiderites are largely free of detrital inclusions, and it appears that they crystallized as void-filling phreatic nodules in open root channels. Dakota sphaerosiderites within individual horizons are characterized by unique patterns of constructive concentric zonation, and no other diagenetic carbonates (i.e., post–sphaerosiderite formation) are present. Petrographic observations indicate that Dakota Formation sphaerosiderites are primary features and thus provide proxy records of primary pore-fluid chemistry in mid-Cretaceous coastal wetland soils.

The Dakota Formation ^{13}C and ^{18}O data from two discrete sphaerosiderite horizons, each only 1 cm thick, define vertical linear trends with highly variable δ^{13}C values and relatively invariant δ^{18}O values (Fig. 2). Sphaerosiderite horizon SCB4B-119.6 defines a trend having a δ^{18}O composition of –4.7‰ ± 0.2‰ and sphaerosiderite horizon SCB4A-139 defines a trend having a δ^{18}O composition of –2.9‰ ± 0.5‰ (Fig. 2).

Swan River Formation

Sphaerosiderite occurs in rooted kaolinitic mudstone paleosols of the mid-Cretaceous Swan River Formation of western Manitoba. The ^{13}C and ^{18}O data from a single sphaerosiderite horizon a few centimeters thick also define a vertical linear trend with relatively invariant δ^{13}C and δ^{18}O values, and a δ^{18}O composition of –5.5‰ ± 0.1‰ (Fig. 2).

ISOTOPIC INFORMATION FROM OTHER SPHAEROSIDERITE LOCALES

Similar trends are defined by the data reported for sphaerosiderite from kaolinitic mudstones of the Late Cretaceous Whitemud Formation of Saskatchewan (Fritz et al., 1971). Although siderite-water ^{18}O fractionation data were not available at the time, Fritz et al. (1971) noted that the sphaerosiderite δ^{18}O values suggested a freshwater origin and were consistent with other indicators of continental deposition. The Whitemud Formation data were derived from samples in the top 5 m of the formation. The data of Fritz et al. (1971) define a vertical linear trend with δ^{18}O of –7.3‰ ± 0.3‰ (Fig. 2).

Data for sphaerosiderite and concretionary siderite from siliciclastic mudstones and sandstones of the Early Triassic Rewan Group of Australia (Baker et al., 1996) also define a vertical linear trend with a δ^{18}O of –13.3‰ ± 1.0‰ (Fig. 2). The light δ^{18}O compositions of the siderite were attributed to deposition of the Rewan Group at high latitudes (65°S) coupled with drainage derived from highland precipitation from adjacent mountain ranges (Baker et al., 1996). Whereas Rewan Group data show a notable consistency in δ^{18}O values, they have a greater variability than the data from the Dakota, Swan River, and Whitemud Formations (Fig. 2). The 22 siderite analyses reported for the Rewan Group were obtained from various positions in over 30 m of stratigraphic section. In comparison, the 25 analyses from two individual sphaerosiderite horizons from the Dakota Formation have a standard deviation of ±1.0‰, and a range in compositions that span ~3.3‰. These values are nearly identical to the standard deviation and range exhibited by Rewan Group siderites, ±1.0‰ and 3.5‰, respectively, and suggests that if studied in greater detail, each Rewan Group sphaerosiderite horizon might reveal distinct vertical δ^{18}O linear trends.

DISCUSSION

The vertical linear trends in δ^{18}O of the siderites discussed here are similar to the meteoric calcite lines defined by meteoric phreatic calcite (Lohmann, 1988), and we define them as meteoric sphaerosiderite lines. The distinct trends defined by invariant ^{18}O and highly variable ^{13}C values are controlled by the composition of the ground waters from which they formed. Sphaerosiderites form under conditions favorable for the microbial reduction of iron oxyhydroxides that result in increased Fe^{2+} concentrations (Fig. 3). While marine redox sequences would lead to reduction of $SO_4^{=}$, and sequestering of iron in sedimentary sulfides, the typical absence of $SO_4^{=}$ in most fresh-water environments leads to iron sequestering in siderite ($FeCO_3$).

The relatively constant and distinct ^{18}O composition of sphaerosiderites indicates that during sphaerosiderite formation within a single horizon, the δ^{18}O composition of ground water as well as temperature remain relatively constant; temperature varies by no more than 1 to 2 °C. The invariant siderite δ^{18}O values defining the meteoric sphaerosiderite lines suggest that bacterially mediated fractionation effects (Mortimer and Coleman, 1997) are not significant, or that bacterial activity is not a major factor in sphaerosiderite formation. We interpret the invariant δ^{18}O composition of sphaerosiderites to record precipitation in stable shallow groundwater systems at depths of a few meters, below which seasonal variability is buffered and varies within a few degrees of the mean annual temperature (Matthess, 1982; Mazor, 1991).

The δ^{13}C compositions of the sphaerosiderites in this study show greater variability than the δ^{18}O data, either very negative or very positive values, than those that are commonly exhibited by calcium carbonate defining meteoric calcite lines. Sphaerosiderite δ^{13}C data are consistent with formation within or in close proximity to methanogenic environments (Fig. 3), and a paucity of calcium carbonate in the hosting strata precludes ^{13}C buffering by carbonate dissolution, as occurs in carbonate environments from which meteoric calcite lines are defined. The ^{13}C composition of the Whitemud Formation sphaerosiderites indicates that they formed within or near a zone of CO_2 reduction, resulting in highly enriched δ^{13}C composition of the dissolved CO_2 (Schoell, 1980; Whiticar et al., 1986) (Fig. 3). The extremely negative δ^{13}C values (<–50‰) of some Dakota Formation sphaerosiderites indicates that formation took place in a zone of microbial methane oxidation (Whiticar and Faber, 1986) (Fig. 3).

Paleoclimatologic Applications

As early meteoric phreatic diagenesis integrates the mean annual oxygen isotopic composition of local precipitation and the mean annual temperature (Swart et al., 1993; Hays and Grossman, 1991), the δ^{18}O values of meteoric sphaerosiderite lines can potentially be used to estimate paleotemperatures and ground-water δ^{18}O, in particular when coexisting early diagenetic calcite can be found in associated horizons. Studies by our group (e.g., Murillo et al., 1997) of early spherulitic siderite and poikilotopic calcite cements in estuarine deposits of the middle Turonian Codell Sandstone Member of the Carlile Formation demonstrate that reasonable temperature estimates can be obtained using mineral-pair (siderite-calcite) paleothermometry when these early diagenetic phases are carefully selected.

Although they are derived from deposits of widely different ages and global climate systems, the δ^{18}O values of sphaerosiderites from the Dakota Formation, Swan River Formation, Rewan Group, and Whitemud Formation nevertheless show values that decrease with increasing paleolatitude (Fig. 4A), and are the same order of magnitude as the latitudinal changes observed in δ^{18}O of continental meteoric calcite cements (Hays and Grossman, 1991). The curve derived from these Mesozoic deposits, however, shows a

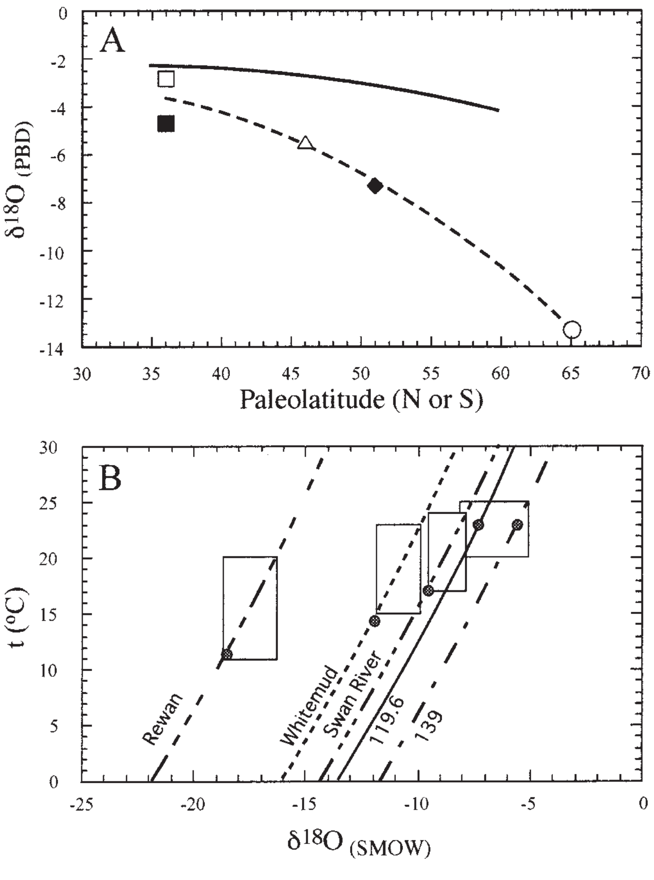

Figure 4. Paleoclimatologic implications of meteoric sphaerosiderite lines from Mesozoic sphaerosiderites. A: Paleolatitudinal gradient of δ^{18}O values of Mesozoic sphaerosiderites. Symbols as in Figure 2. Dashed curve is second-order polynomial on data, showing paleolatitudinal variability similar to that in continental meteoric calcite cements (Hays and Grossman, 1991). Solid curve shows theoretical δ^{18}O composition of modern meteoric phreatic siderite, based on regressions of data in Rozanski et al. (1993) for stations less than 300 m above sea level. Modern theoretical curve is terminated at latitude 60°, where mean annual temperatures drop below 0 °C. Paleolatitudes for Dakota, Swan River, and Whitemud Formations are based on reconstructions in Scotese (1991), and that of Rewan Group is based on paleomagnetic data (Baker et al., 1996). B: Estimates of ground-water δ^{18}O values from sphaerosiderite δ^{18}O values shown in A. Rectangles show ranges of minimum and maximum estimates for mid-Cretaceous mean annual temperatures at respective paleolatitudes for each sedimentary deposit, based on Barron et al. (1989). Shaded circles show mean annual temperatures at paleolatitudes of each deposit, based on a 4 × CO_2 Cretaceous simulation (Barron, 1989). These δ^{18}O estimates are more depleted than mean annual δ^{18}O of modern precipitation at higher mid-latitudes. PDB—Peedee belemnite; SMOW—standard mean ocean water; t—temperature.

much steeper latitudinal $\delta^{18}O$ gradient than a theoretical curve for modern siderite (Fig. 4A). The modern gradient is buffered, in part, by a much steeper gradient in mean annual temperatures, increasing water-siderite ^{18}O fractionations at higher latitudes. These observations suggest that the latitudinal $\delta^{18}O$ gradients of paleoprecipitation in the Mesozoic were steeper than those of today. Barron et al. (1989) proposed that the continental paleoprecipitation flux in the mid-Cretaceous climate system was 28% greater than present. Such increases in precipitation flux could possibly have led to increased “rainout effects” on a global scale, increasing latitudinal gradients in the $\delta^{18}O$ of paleoprecipitation, as suggested in Figure 4A. The data of Rozanski et al. (1993) show that over latitudes from 35° to 65°, the average $\delta^{18}O$ of modern precipitation decreases by about 8‰, whereas the siderite fractionation factors of Carothers et al. (1988) combined with paleotemperature estimates derived from paleoclimatic proxies and model simulations (Barron and Washington, 1985; Barron, 1989) (Fig 4B) suggest that greenhouse world sphaerosiderites could record a decrease of about 14‰ over the same latitudinal range.

CONCLUSIONS

The frequently overlooked presence of sphaerosiderite in continental deposits offers opportunity for extending the environmental range of continental sampling of $\delta^{18}O$ in soil-formed carbonates into humid regions that have been presumed to lack suitable study materials. In this paper we establish the concept of meteoric sphaerosiderite lines for $\delta^{18}O$ values from the Mesozoic and show that estimated paleotemperatures and $\delta^{18}O$ of paleoprecipitation are reasonably consistent with the estimated paleolatitudes for the sampled horizons. Our analysis shows that the $\delta^{18}O$ values of sphaerosiderites preserve records of ancient rainfall, an atmospheric tracer with great potential for reconstructing the paleohydrology and paleoclimatology of ancient continental environments.

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REFERENCES CITED

Baker, J. C., Kassan, J., and Hamilton, P. J., 1996, Early diagenetic siderite as an indicator of depositional environment in the Triassic Rewan Group, southern Bowen Basin, eastern Australia: Sedimentology, v. 43, p. 77–88.

Barron, E. J., 1989, Studies of Cretaceous climate, *in* Berger, A., Dickinson, R. E., and Kidson, J. W., eds., Understanding climate change: American Geophysical Union Geophysical Monograph 52, p. 149–157.

Barron, E. J., and Washington, W. M., 1985, Warm Cretaceous climates: High atmospheric CO_2 as a plausible mechanism, *in* Sundquist, E. T., and Broecker, W. S., eds., The carbon cycle and atmospheric CO_2: Natural variations Archean to present: American Geophysical Union Geophysical Monograph 32, p. 546–553.

Barron, E. J., Hay, W. W., and Thompson, S. L., 1989, The hydrologic cycle: A major variable during Earth history: Global and Planetary Change, v. 1, p. 157–174.

Carothers, W. W., Adami, L. H., and Rosenbauer, R. J., 1988, Experimental oxygen isotope relation between siderite-water and phosphoric acid liberated CO_2-siderite: Geochimica et Cosmochimica Acta, v. 52, p. 2445–2450.

Cerling, T. E., and Quade, J., 1993, Stable carbon and oxygen isotopes in soil carbonates, *in* Swart, P. K., Lohmann, K. C, McKenzie, J., and Savin, S., eds., Climate change in continental isotopic records: American Geophysical Union Geophysical Monograph 78, p. 217–231.

Fritz, P., Binda, P. L., Folinsbee, F. E., and Krouse, H. R., 1971, Isotopic composition of diagenetic siderites from Cretaceous sediments in western Canada: Journal of Sedimentary Petrology, v. 41, p. 282–288.

Hays, P. D., and Grossman, E. L., 1991, Oxygen isotopes in meteoric calcite cements as indicators of continental paleoclimate: Geology, v. 19, p. 441–444.

Landuydt, C. J., 1990, Micromorphology of iron minerals from bog ores of the Belgian Campine area, *in* Douglas, L. A., ed., Soil micromorphology: A basic and applied science: Elsevier, Amsterdam, Developments in Soil Science, v. 19, p. 289–294.

Leckie, D. A., Fox, C., and Tarnocai, C., 1989, Multiple paleosols of the Late Albian Boulder Creek Formation, British Columbia, Canada: Sedimentology, v. 36, p. 307–323.

Lohmann, K. C., 1988, Geochemical patterns of meteoric diagenetic systems and their application to studies of paleokarst, *in* James, N. P., and Choquette, P. W., eds., Paleokarst: New York, Springer-Verlag, p. 58–80.

McNeil, D. H., and Caldwell, W. G. E., 1981, Cretaceous rocks and their foraminifera in the Manitoba Escarpment: Geological Association of Canada Special Paper 21, 439 p.

Matthess, G., 1982, The properties of groundwater: New York, John Wiley and Sons, 406 p.

Mazor, E., 1991, Applied chemical and isotopic groundwater hydrology: New York, Halsted Press, 274 p.

Mortimer, R. J. G., and Coleman, M. L., 1997, Microbial influence on the oxygen isotopic composition of diagenetic siderite: Geochimica et Cosmochimica Acta, v. 61, p. 1705–1711.

Murillo, A. P., Brenner, R. L., González, L. A., Ludvigson, G. A., Witzke, B. J., and Hammond, R. H., 1997, Paleohydrologic and paleoclimatic evaluation of early carbonate cements in the Codell Sandstone, middle Turonian, eastern margin of the Western Interior Seaway: Geological Society of America Abstracts with Programs, v. 29, no. 6, p. A270.

Retallack, G. J., 1981, Fossil soils: Indicators of ancient terrestrial environments, *in* Niklas, K. J., ed., Paleobotany, paleoecology, and evolution, Volume 1: New York, Praeger Publishers, p. 55–102.

Rozanski, K., Araguás-Araguás, L., and Gonfiantini, R., 1993, Isotopic patterns in modern global precipitation, *in* Swart, P. K., Lohmann, K. C, McKenzie, J., and Savin, S., eds., Climate change in continental isotopic records: American Geophysical Union Geophysical Monograph 78, p. 1–36.

Schoell, M., 1980, The hydrogen and carbon isotopic composition of methane from natural gases of various origins: Geochimica et Cosmochimica Acta, v. 44, p. 649–661.

Scotese, C. R., 1991, Jurassic and Cretaceous plate tectonic reconstructions: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 87, p. 493–501.

Stoops, G., 1983, SEM and light microscopic observations of minerals in bog-ores of the Belgian Campine: Geoderma, v. 30, p. 179–186.

Swart, P. K., McKenzie, J. A., and Lohmann, K. C, 1993, Introduction, *in* Swart, P. K., Lohmann, K. C, McKenzie, J., and Savin, S., eds., Climate change in continental isotopic records: American Geophysical Union Geophysical Monograph 78, p. xi–xiii.

Tucker, M. E., 1981, Sedimentary petrology—An introduction: Oxford, Blackwell Scientific Publications, Geoscience Texts, v. 3, 252 p.

Whiticar, M. J., and Faber, E., 1986, Methane oxidation in sediment and water column environments—Isotope evidence: Organic Geochemistry, v. 10, p. 759–768.

Whiticar, M. J., Faber, E., and Schoell, M., 1986, Biogenic methane formation in marine and freshwater environments: CO_2 vs. acetate fermentation—Isotope evidence: Geochimica et Cosmochimica Acta, v. 50, p. 693–709.

Witzke, B. J., and Ludvigson, G. A., 1994, The Dakota Formation in Iowa and the type area, *in* Shurr, G. W., Ludvigson, G. A., and Hammond, R. H., eds., Perspectives on the Eastern Margin of the Cretaceous Western Interior Basin: Geological Society of America Special Paper 287, p. 43–78.

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