Meteoric sphaerosiderite lines and their use for paleohydrology and paleoclimatology

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ABSTRACT
Sphaerosiderite, a morphologically distinct millimeter-scale spherulitic siderite (FeCO₃), 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 δ¹³C and relatively stable δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O 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 (FeCO₃), 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 δ¹⁸O in 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.

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 crystalites. Note light-toned birefringent clay coatings wrap around pre-existing sphaerosiderites. Horizontal field of view is 3.2 mm.

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
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 1.011 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 13 C values and relatively invariant 18 O values (Fig. 2). Sphaerosiderite horizon SCB4B-119.6 defines a trend having a δ18O composition of −4.7‰ ± 0.2‰ and sphaerosiderite horizon SCB4A-139 defines a trend having a δ18O 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 13 C and 18 O values, and a δ18O 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 δ18O 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 δ18O of −7.3‰ ± 0.3‰ (Fig. 2).

Data for sphaerosiderite and concretionary siderite from siliciclastic mudstones and sand-
stones of the Early Triassic Rewan Group of Australia (Baker et al., 1996) also define a vertical linear trend with a δ18O of ~3.3‰ ± 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 δ18O linear trends.

DISCUSSION

The vertical linear trends in δ18O 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 18O and highly variable 13C 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 Fe2+ concentrations (Fig. 3). While marine redox sequences would lead to reduction of SO42−, and sequestering of iron in sedimentary sulfides, the typical absence of SO42− in most fresh-water environments leads to iron sequestering in siderite (FeCO3).

The relatively constant and distinct 18O composition of sphaerosiderites indicates that during sphaerosiderite formation within a single horizon, the δ18O composition of ground water as well as temperature remain relatively constant; temperature varies by no more than 1 to 2 °C. The invariant siderite δ18O values defining the meteoric sphaerosiderite lines suggest that bacteriologically 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 δ18O composition of sphaerosiderites to record precipitation in stable shallow ground-water systems at depths of a few meters, below which seasonal variability is buffered and varies within a few degrees of the mean annual temperature (Matthes, 1982; Mazor, 1991).

The δ13C compositions of the sphaerosiderites in this study showed greater variability than the δ18O data, either very negative or very positive values, than those that are commonly exhibited by calcium carbonate defining meteoric calcite lines. Sphaerosiderite δ13C 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 13C buffering by carbonate dissolution, as occurs in carbonate environments from which meteoric calcite lines are defined. The 13C composition of the Whitemud Formation sphaerosiderites indicates that they formed within or near a zone of CO2 reduction, resulting in highly enriched δ13C composition of the dissolved CO2 (Schoell, 1980; Whiticar et al., 1986) (Fig. 3).

The extremely negative δ13C values (≤–50‰) of some Dakota Formation sphaerosiderites indicate 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 δ18O values of meteoric sphaerosiderite lines can potentially be used to estimate paleotemperatures and ground-water δ18O, 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 sphärolitic 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 δ18O 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 δ18O 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 δ18O 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 δ18O composition of meteoric phreatic spherulite, 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°N, 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 δ18O values from sphaerosiderite δ18O 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 × CO2 Cretaceous simulation (Barron, 1989). These δ18O estimates are more depleted than mean annual δ18O of modern precipitation at higher mid-latitudes. PDB—Peedee belemnite; SMOW—standard mean ocean water; t—temperature.
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CONCLUSIONS
The frequently overlooked presence of sphaero siderite in continental deposits offers opportunity for extending the environmental range of continental sampling of δ18O 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 sphaero siderite lines for δ18O values from the Mesozoic and show that estimated paleotemperatures and δ18O of paleoprecipitation are reasonably consistent with the estimated paleolatitudes for the sampled horizons. Our analysis shows that the δ18O values of sphaero siderites 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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much steeper latitudinal δ18O 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 18O fractionations at higher latitudes. These observations suggest that the latitudinal δ18O 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 δ18O of paleoprecipitation, as suggested in Figure 4A. The data of Rozanski et al. (1993) show that over latitudes from 35° to 65°, the average δ18O of modern precipitation decreases by about 8‰, whereas the siderite fractionation effects on a global scale, increasing latitudinal gradients in the δ18O of paleoprecipitation, as suggested in Figure 4A. The data of Rozanski et al. (1993) show that over latitudes from 35° to 65°, the average δ18O 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 sphaero siderites could record a decrease of about 14‰ over the same latitudinal range.