

# PALEOCLIMATIC APPLICATIONS AND MODERN PROCESS STUDIES OF PEDOGENIC SIDERITE

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**ABSTRACT:** Pedogenic siderite is a carbonate mineral that forms in the reducing groundwaters of poorly drained soils and paleosols in zonal climatic belts with strongly positive precipitation–evaporation balances. Microcrystalline and spherulitic forms of siderite are commonly recognized in micromorphologic studies of hydromorphic paleosols. Ancient paleosol sphaerosiderites commonly occur with diameters in excess of 1 mm, while modern pedogenic siderite crystal dimensions in excess of 100  $\mu\text{m}$  are rare. Pedogenic siderites have been widely reported from Late Paleozoic, Mesozoic, and Cenozoic paleosols. The carbon and oxygen isotopic compositions of pedogenic siderites have been widely used as proxies for the oxygen isotopic composition of paleoprecipitation for their respective paleosols. Modern process studies of historic pedogenic siderites are yielding a more refined understanding of the stable isotopic systematics of low-temperature siderite. These works will lead to a future change in usage of published siderite–water  $^{18}\text{O}$  fractionation equations.

**KEY WORDS:** siderite, paleosols, carbon isotopes, oxygen isotopes, Cretaceous, Holocene

## INTRODUCTION

Pedogenic siderite ( $\text{FeCO}_3$ ) is a common authigenic mineral that forms in reducing water-saturated soil systems (Retallack 1981). It has been widely used as a proxy record for the  $\delta^{18}\text{O}$  values of paleogroundwaters and paleoprecipitation in paleosols (Baker et al. 1996; Ludvigson et al. 1998; Ufnar et al. 2001, 2002, 2004a, 2004c, 2005, 2008; White et al. 2001, 2005; Choi et al. 2003; Ufnar 2007; Robinson et al. 2010; Suarez et al. 2010b, 2011b). Paleoclimatologic studies employing this paleoclimate proxy have been applied to warm periods in Earth history, with special emphasis on the mid-Cretaceous (Ufnar et al. 2001, 2002, 2004a, 2004b, 2004c, 2005, 2008; White et al. 2001, 2005; Ufnar 2007; Robinson et al. 2010; Suarez et al. 2010b, 2011b). As emphasized by Ludvigson et al. (1998, 2002), pedogenic siderite opens a much wider paleogeographic distribution of climatic belts to obtain estimates of the  $\delta^{18}\text{O}$  of paleoprecipitation than would be available from the study of semiarid or arid climates alone.

Ancient pedogenic siderites have been noted from a number of geologic time periods (Sheldon and Tabor 2009). Published Permian–Carboniferous examples include Brown and Kingston (1993), Faure et al. (1995), Ludvigson et al. (2002), and Driese and Ober (2005).

Published Triassic examples include Retallack (1976) and Baker et al. (1996). Some other published Cretaceous examples include McCarthy and Plint (1998, 1999) and Ludvigson et al. (2010b). Jacobs et al. (2005) published descriptions of pedogenic siderite from Paleogene deposits.

Ancient and modern pedogenic siderites remain a very fertile topic for active scientific study, with new results continuing to accumulate. Here, we review major topics and current sets of scientific inquiry related to pedogenic siderite for the benefit of our colleagues in paleopedologic community.

## ZONAL CLIMATIC BELTS AND THEIR CHARACTERISTIC PEDOGENIC CARBONATES

The formation of nodular calcareous soils is generally well documented in the soil science and geologic literature (Birkeland 1999, p. 127–132). Well-drained calcareous soils accumulate in regions of precipitation–evaporation deficit, where groundwater infiltration is insufficient to leach calcite from the soil profile, and there is net evaporative accumulation (Goudie and Kenneth 1983). The term “pedogenic carbonate” is frequently used as a synonym for

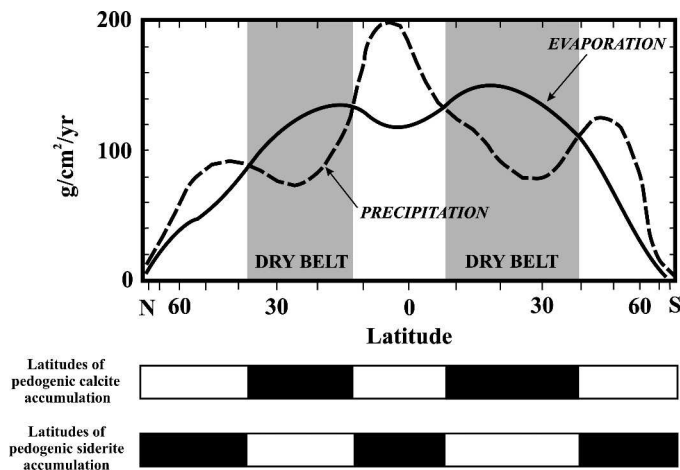


FIG. 1.—Zonal distribution of climatic belts (in black) that are dominated by the accumulation of pedogenic calcite and siderite. The zonally averaged precipitation and evaporation rates are from the modern climate system, and are modified from Barron and Moore (1994). From Ludvigson et al. (2002).

pedogenic calcite, but such usage fails to account for the common occurrence of siderite as a pedogenic mineral, and the broad geographic extent in which it accumulates in soils. Hard-cemented calcareous soils, or calcretes, accumulate in continental deposits that are largely confined to the subtropical dry belts (Fig. 1), with notable local exceptions that are related to “rain shadow” orographic effects. The zonal dry belts that typify pedogenic calcite accumulation do cover a substantial land surface area, but they are not ubiquitous to the terrestrial paleoenvironments that are preserved in the sedimentary record (Fig. 1).

Over the remainder of the globe that is characterized by zonal belts of precipitation excess, detrital matrix or nodular calcite commonly is chemically leached from soil profiles. Within the humid belts, in soils that are at least seasonally saturated, the oxidation of soil organic matter frequently leads to development of strong vertical redox gradients within soil waters, and the presence of reducing groundwaters near the land surface. In these settings, dissolved  $\text{Fe}^{2+}$  released from the chemical cannibalization of detrital or pedogenic ferric oxides by reducing groundwaters is taken up by the formation of siderite (Ufnar 2007), especially in settings with locally rising base levels (McCarthy and Plint 1998). These conditions often develop in the case of polygenetic paleosols with well-drained profiles overprinted by late-stage hydromorphism. The zonal belts of precipitation excess are the areas where siderite typically accumulates in water-saturated surface soils (Fig. 1). Local exceptions of wet soils in dry climates and drier soils in wetter climates certainly do occur in nature, but these generalizations are a useful organizing principle for describing the zonal climatic patterns of pedogenic carbonates. Our research experience has shown that terrestrial stratigraphic units with well-documented descriptions of coal deposits also contain pedogenic siderites in mudstone paleosols.

### SPHAEROSIDERITE AND METEORIC SPHAEROSIDERITE LINES

Sphaerosiderite, a morphologically distinct millimeter-scale spherulitic form of siderite (Fig. 2), is commonly preserved in buried soils in the ancient geologic record (Retallack 1981). Spherulitic forms are commonly represented, but microcrystalline and twinned micron-scale



FIG. 2.—Photograph of millimeter-scale sphaerosiderites weathering out in positive relief from an exposed mudstone paleosol in the mid-Cretaceous Dakota Formation, Sioux City Brick claypit, Sergeant Bluff, Iowa. This locality is described in Ludvigson et al. (1998) and White et al. (2005). Photo courtesy of Dr. Brian Witzke, Iowa Geological Survey.

crystals also commonly occur (Fig. 3A, B). Ludvigson et al. (1998) showed that sphaerosiderites from a given paleosol have a characteristic carbon and oxygen isotopic signature arrayed along vertical linear trends in carbon–oxygen isotope space, which they referred to as *meteoric sphaerosiderite lines* (MSLs; Fig. 4). This early diagenetic trend, analogous to the *meteoric calcite lines* (MCLs) of Lohmann (1988), is characterized by relatively invariant  $\delta^{18}\text{O}$  values, either with or without more variable  $\delta^{13}\text{C}$  values. Ludvigson et al. (1998) argued that the invariant  $\delta^{18}\text{O}$  values in MSLs are determined by the  $\delta^{18}\text{O}$  values of soil waters (i.e., the weighted mean annual  $\delta^{18}\text{O}$  of local paleoprecipitation) and local mean annual soil temperatures. They also argued that highly variable  $\delta^{13}\text{C}$  values in pedogenic siderites are determined by the differing biogeochemical processes that produce dissolved inorganic carbon in the groundwaters of wetland soils. These include methanogenic microbial environments that result in positive  $\delta^{13}\text{C}$  values, and methanotrophic microbial environments that result in  $\delta^{13}\text{C}$  values less than  $-40\text{‰}$  VPDB, where VPDB is the Vienna Pee Dee Belemnite standard (Ludvigson et al. 1998).

Micromorphologic studies of siderite-bearing paleosols are always recommended to confirm the mineralogical identity of contained carbonates. Electron microprobe analyses of the Fe, Mg, and Ca contents of pedogenic siderites are useful for discriminating paleosols that formed in purely freshwater systems from those that formed in brackish water systems in coastal plain deposits (Mozley 1989; Ufnar et al. 2001, 2004c; White et al. 2005; Ufnar 2007). Petrographic studies are also needed to assure that ancient pedogenic siderites have not been overprinted by later diagenetic carbonates. Even in those cases where later overprinting carbonate components are present, it is possible to isolate microsamples of early and later diagenetic products to interpret syndepositional paleohydrology (Ufnar et al. 2004a).

### MODERN EXAMPLES OF PEDOGENIC SIDERITE

Siderite has not been commonly reported as a pedogenic mineral in modern hydromorphic soils, but this is a general oversight that is related to the microscopic size of siderite crystals found in modern

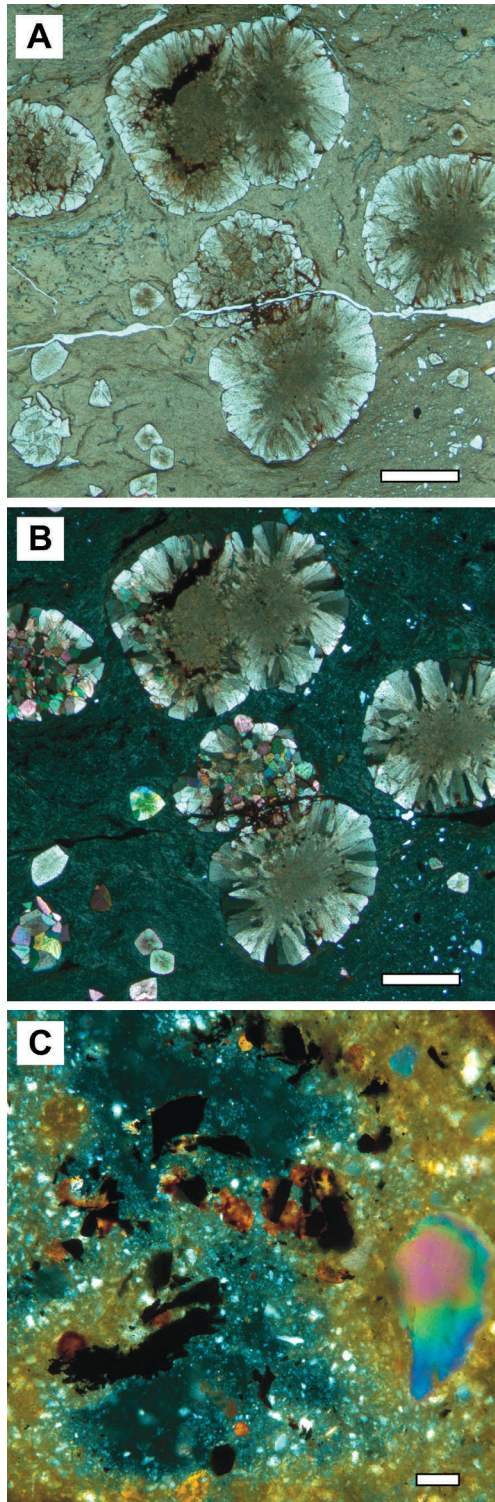


FIG. 3.—Photomicrographs of pedogenic siderite. **A)** Sphaerosiderite from the Los Mangos 4 core at the 957.5 m level in the Cretaceous Caballos Formation of Colombia (Suarez et al. 2010b). These siderites consist of microcrystalline cores with more coarsely crystalline spherulitic cortices. Note smaller microcrystalline siderites with euhedral and twinned siderite overgrowths. Plane-polarized light. Scale bar is 1 mm in length. **B)** Same field of view

occurrences, and also a sampling problem posed by the rapid chemical oxidation of reduced iron mineral crystals in wet soil samples once they are exposed to the oxidizing atmosphere. Modern pedogenic siderites cannot be recognized unless routine micromorphologic studies are undertaken, as their crystal size dimensions are generally less than 100  $\mu\text{m}$  (Fig. 3C).

Stoops (1983) and Landuydt (1990) provided some of the first micromorphologic descriptions of Holocene sphaerosiderites, with maximum spherulite diameters in the 200  $\mu\text{m}$  range. Pedogenic siderite is often associated with the chemically unstable reduced iron phosphate mineral vivianite, and also fine-grained pyrite in wetland settings influenced by infiltration of brackish fluids. Kim et al. (1999) reported on sphaerosiderites in Early Holocene paleosols with diameters up to 300  $\mu\text{m}$ . Other reports of siderite accumulation in Holocene wetland sediments include Dirven et al. (1976), Postma (1981), Pye et al. (1990), Moore et al. (1992), Virtanen (1994), McMillan and Schwertmann (1998), Aslan and Autin (1999), Choi et al. (2003), Kaczorek and Sommer (2003), Lim et al. (2004), Choi (2005), Driese et al. (2004), Ashley et al. (2004), Wilamowski and Boski (2005), Vulava et al. (2007), and Driese et al. (2010).

An examination of the global distribution of published Holocene pedogenic siderite occurrences (Fig. 5) shows that most reported locales are in the humid belts of the temperate latitudes in the Northern Hemisphere, and also the equatorial humid belt. There are also reports from humid coastal localities in the subtropical dry belts in the Northern Hemisphere (Dirven et al. 1976, Moore et al. 1992, Aslan and Autin 1999).

#### PROTOCOLS FOR THE GENERATION AND TREATMENT OF STABLE ISOTOPIC DATA FROM PEDOGENIC SIDERITES

The extraction of early diagenetic MSL trends in carbon–oxygen isotope space from pedogenic siderite requires application of micro-sampling techniques to document the micro-scale variability in stable isotopic compositions of pedogenic siderites from each studied paleosol. In examples from ancient paleosols, microsampling is done by the milling siderite powders from counterpart polished billets from paleosol thin sections using a microscope-mounted microdrill assembly with 0.3- to 0.5-mm-diameter carbide dental burrs. In modern examples, siderites are concentrated from dry crushed soil samples by gravimetric separation techniques as in Driese et al. (2010). Siderite powder samples of 0.5 to 2.0 mg will produce sufficient volumes of  $\text{CO}_2$  at 75° C to carry out carbon and oxygen isotope analyses, which were conducted using the Thermo-Finnigan Kiel III device coupled to a dual-inlet Thermo-Finnigan MAT 253 stable isotope mass spectrometer at the University of Kansas W.M. Keck Paleoenvironmental and Environmental Stable Isotope Laboratory. Reported  $\delta^{18}\text{O}$  values are corrected for the siderite–acid fractionation factor following Carothers et al. (1988), and are expressed in standard

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as in A under cross-polarized light. Note pseudo-uniaxial cross extinction pattern in the coarsely crystalline spherulites. Scale bar is 1 mm in length. **C)** Historic pedogenic siderite from the CCP2 soil core at the 92–96 cm level (Driese et al. 2010). Birefringent brown siderite crystals nucleated on broken fragments of opaque coal clinker. Note small siderite spherulite ( $\sim 40 \mu\text{m}$  in diameter) in lower center of micrograph. Cross-polarized light. Scale bar is 100  $\mu\text{m}$  in length.

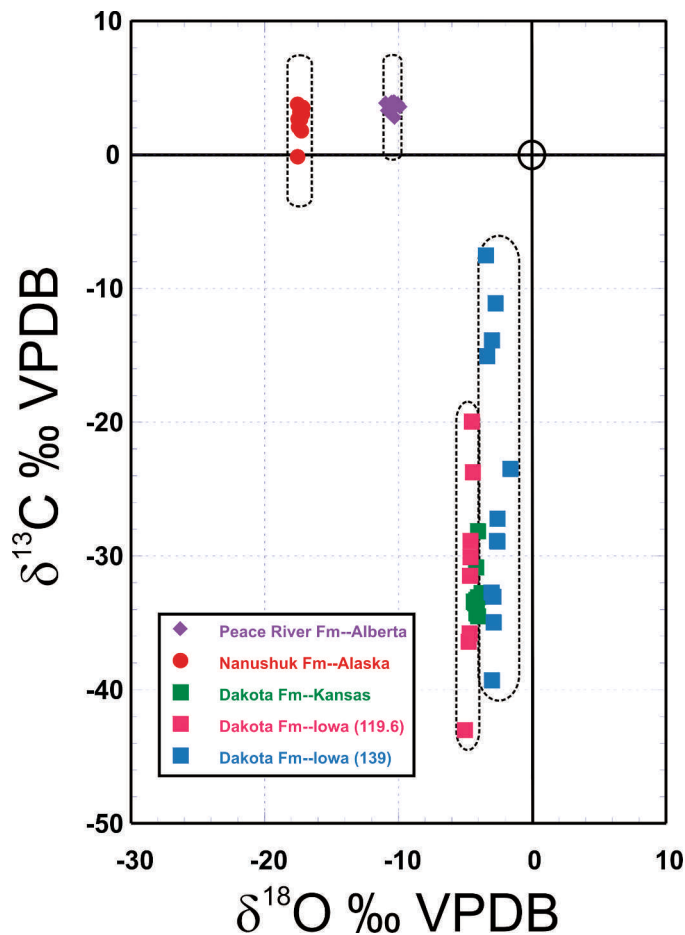


FIG. 4.—Carbon and oxygen isotope plot of meteoric sphaerosiderite lines from selected Cretaceous paleosol horizons. Siderites from the Peace River Formation are from the 1653.2 m level horizon in the Amoco Wapiti core of Ufnar et al. (2005). Siderites from the Nanushuk Formation are from the 171.19 m level horizon in the Grandstand #1 core of Ufnar et al. (2004c). Siderites from the Dakota Formation in Kansas are from the 270.6 ft level horizon in the KGS Jones #1 core of Macfarlane et al. (1994) and Ludvigson et al. (2010). Siderites from the Dakota Formation in Iowa are from the SCB-4B-119.6 and SCB4A-139 ft level horizons from the Sioux City Brick claypit locality of Ludvigson et al. (1998) and White et al. (2005).

delta ( $\delta$ ) notation in per mil deviations from the VPDB isotope standard.

#### APPLICATIONS TO STUDIES OF THE CRETACEOUS HYDROLOGIC CYCLE

The principal application of stable isotopic data from pedogenic siderites to date involves reconstructions of the oxygen isotope compositions of soil waters and their relation to the mass balance of the mid-Cretaceous hydrologic cycle. Ludvigson et al. (1998) first pointed out the apparent difference in the latitudinal  $\delta^{18}\text{O}$  gradients between the modern and Mesozoic climate systems, and attributed the difference to accelerated rainout of  $^{18}\text{O}$  during poleward transport of tropical air masses. The concept of an amplified Cretaceous hydrologic

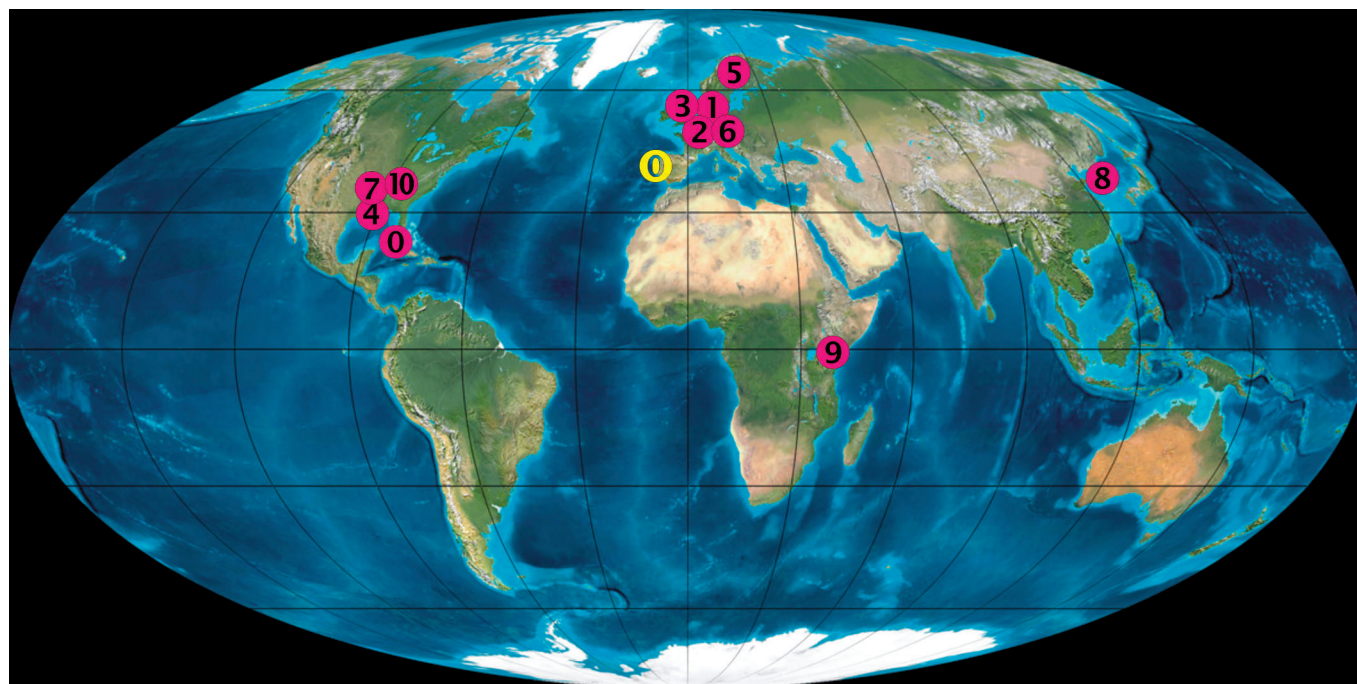
cycle was further explored by White et al. (2001) and Ufnar et al. (2002, 2008). The idea of major mass-balance changes in Cretaceous precipitation–evaporation balances was proposed by Ufnar et al. (2004b) to account for major increases in latent heat fluxes from the tropics, and a possible mechanism for polar warmth in the Cretaceous greenhouse world. The most recent iterations of the Cretaceous precipitation  $\delta^{18}\text{O}$  gradient appear in Suarez et al. (2009, 2010b, 2011b) and Robinson et al. (2010), with data spanning from the paleoequator to the high Arctic (Fig. 6A, B). An equator-to-pole transect of the Cretaceous Northern Hemisphere requires the integration of data from the humid and dry zonal belts (Fig. 1). These include MSL  $\delta^{18}\text{O}$  data from equatorial and high-latitude pedogenic siderites, and MCL  $\delta^{18}\text{O}$  data from subtropical pedogenic calcites (Fig. 6A). This newly revised data set was the subject of an updated iteration of the oxygen isotope mass balance model of Ufnar et al. (2002), presented by Suarez et al. (2011b). This more comprehensive data set (Fig. 6A) clearly shows that Cretaceous paleolatitudes higher than  $50^\circ$  N currently are sampled far more sparsely than is the case in the tropics and midlatitudes. The importance of these high-latitude data is likely to come into sharper focus in the coming years.

Poulsen et al. (2007) evaluated the Cretaceous precipitation  $\delta^{18}\text{O}$  gradient of Ufnar et al. (2002) using an Earth system model with a stable isotope module for the  $\delta^{18}\text{O}$  values of precipitation. They found that greenhouse warming forced by higher  $\text{pCO}_2$  levels led to model simulations of higher, rather than lower,  $\delta^{18}\text{O}$  values for precipitation in the polar regions (Fig. 6A). The simulations of Poulsen et al. (2007) do not support the idea of an amplified Cretaceous hydrologic cycle to the extent that was postulated by Ufnar et al. (2002). The model–data misfit (Fig. 6A) between the North Slope Alaskan siderite  $\delta^{18}\text{O}$  data of Ufnar et al. (2002, 2004c) and the Earth system model  $\delta^{18}\text{O}$  simulations of Poulsen et al. (2007) are central to these contrasting views of the Cretaceous climate system. Poulsen et al. (2007) suggested that the siderite isotopic data from the Grandstand #1 drill core of Ufnar et al. (2002, 2004c) were produced from an anomalous paleogeographic site located very close to the ancestral Brooks Mountain Range, so that the reported  $\delta^{18}\text{O}$  values were biased by local orographic effects, and thus were not representative of zonal Arctic climate.

Did the  $\delta^{18}\text{O}$  values of Cretaceous Arctic paleoprecipitation decrease (Ufnar et al. 2002, 2004b, 2004c, 2008; Suarez et al. 2011) or increase (Poulsen et al. 2007) relative to the modern climate system? In order to address this question, there is an urgent need to expand the paleogeographic and temporal distribution of paleosol and other terrestrial paleoclimatic  $\delta^{18}\text{O}$  data sets from the Cretaceous Arctic. Model–data paleoprecipitation  $\delta^{18}\text{O}$  misfits in the high Arctic highlight a glaring scarcity of Cretaceous terrestrial paleoclimatic data from paleolatitudes north of  $50^\circ$  N (Fig. 6A). Efforts to address this need are currently under way (Lollar et al. 2010; Ludvigson et al. 2010a; Suarez et al. 2010a, 2011a).

#### MODERN PROCESS STUDIES OF PEDOGENIC SIDERITE

One philosophical challenge that has restrained paleoclimatic applications of pedogenic siderite  $\delta^{18}\text{O}$  values involves a lack of modern baseline studies to validate first-principle assumptions behind the original formulation of this tool (Ludvigson et al. 1998). One basic assumption is that the groundwaters from which pedogenic siderites form have  $\delta^{18}\text{O}$  values equivalent to mean annual precipitation at the paleosol sites. A second basic assumption for the sphaerosiderite paleoclimate proxy is that pedogenic siderite forms in oxygen isotopic equilibrium with soil groundwaters, following the experimental results of inorganically precipitated siderite, and the experimental temperature-dependent  $^{18}\text{O}$  fractionation relationship (abiotic laboratory synthesis experiments from  $33$  to  $197^\circ$  C) of



- |                                 |                                |   |
|---------------------------------|--------------------------------|---|
| 0 Dirven et al., 1976           | 4 Moore et al., 1992           | 8 Kim et al., 1999; Choi et al., 2003; Lim et al., 2004; Choi, 2005 |
| 1 Postma, 1981                  | 5 Virtanen, 1994               | 9 Driese et al., 2004; Ashley et al., 2004                          |
| 2 Stoops, 1983; Llanduydt, 1990 | 6 McMillen & Schwertmann, 1998 | 10 Vulava et al., 2007; Driese et al., 2010                         |
| 3 Pye et al., 1990              | 7 Aslan & Autin, 1999          | 0 Wilamowski & Boski, 2005  |

FIG. 5.—Global distribution of field sites with published descriptions documenting Holocene freshwater to brackish siderites. Most reported occurrences are within the Northern Hemisphere temperate humid belt. Some humid coastal localities in the western hemisphere along the US Gulf Coast and Cuba extend southward into the zonal subtropical dry belt. Mollweide projection is courtesy of Dr. Ron Blakey.

Carothers et al. (1988). This relationship was expressed by Carothers et al. (1988) as:

$$10^3 \ln \alpha = 3.13(10^6 T_K^{-2}) - 3.50$$

where  $T_K$  is the temperature of siderite precipitation in Kelvin and  $\alpha$  is the siderite–water  $^{18}\text{O}$  fractionation factor.

This siderite–water  $^{18}\text{O}$  fractionation relationship was utilized by Ludvigson et al. (1998), who extrapolated from the original lower-bounding experimental conditions at 33° C down to even lower sedimentary temperatures. This same  $^{18}\text{O}$  fractionation relationship has since been used by all subsequent workers using the pedogenic siderite proxy.

The concept of isotopic equilibrium siderite precipitation at low sedimentary temperatures was challenged by Mortimer and Coleman (1997), based on experimental results with biogenic siderites that formed at 18 to 40° C in bacterial culture. However, Zhang et al. (2001) carried out experiments on formation of biogenic siderites in bacterial cultures over the temperature range from 10 to 75° C, and determined that oxygen isotopic equilibrium was attained, with a temperature-dependent equilibrium fractionation relationship as follows:

$$10^3 \ln \alpha = 2.56(10^6 T_K^{-2}) + 1.69$$

The changes in constants between these two fractionation equations

produce water  $\delta^{18}\text{O}$  values that are closely similar at higher experimental conditions but significantly diverge at temperatures lower than 30° C. Estimated water  $\delta^{18}\text{O}$  values at low sedimentary temperatures are a few per mil higher using the Zhang et al. (2001) equation than those using the Carothers et al. (1988) equation.

We have undertaken actualistic studies of siderite–water  $^{18}\text{O}$  fractionations at a site of historic pedogenic siderite formation in Chattanooga, Tennessee, first described by Vulava et al. (2007), and more recently described by Driese et al. (2010). Pedogenic siderite at this site formed in anthropogenic landfill deposits (Fig. 3C). Driese et al. (2010) discussed the various biogeochemical processes involved in the formation of siderite and presented siderite carbon and oxygen isotopic data from soil cores, along with estimates of the likely soil temperatures and groundwater  $\delta^{18}\text{O}$  values at the site. Driese et al. (2010) noted that the fractionation equation of Carothers et al. (1988) produces calculated groundwater  $\delta^{18}\text{O}$  values that are lower than those estimated for the CCP site using the Online Isotopes in Precipitation Calculator (OIPC; Bowen 2009).

Using the full range of measured siderite  $\delta^{18}\text{O}$  values (–5.4 to –4.1‰ VPDB), we have calculated equilibrium water  $\delta^{18}\text{O}$  values for the CCP site siderites over a temperature range from 4 to 50° C, using the equations of both Carothers et al. (1988) and Zhang et al. (2001) (Fig. 7). As noted already, both fractionation equations calculate

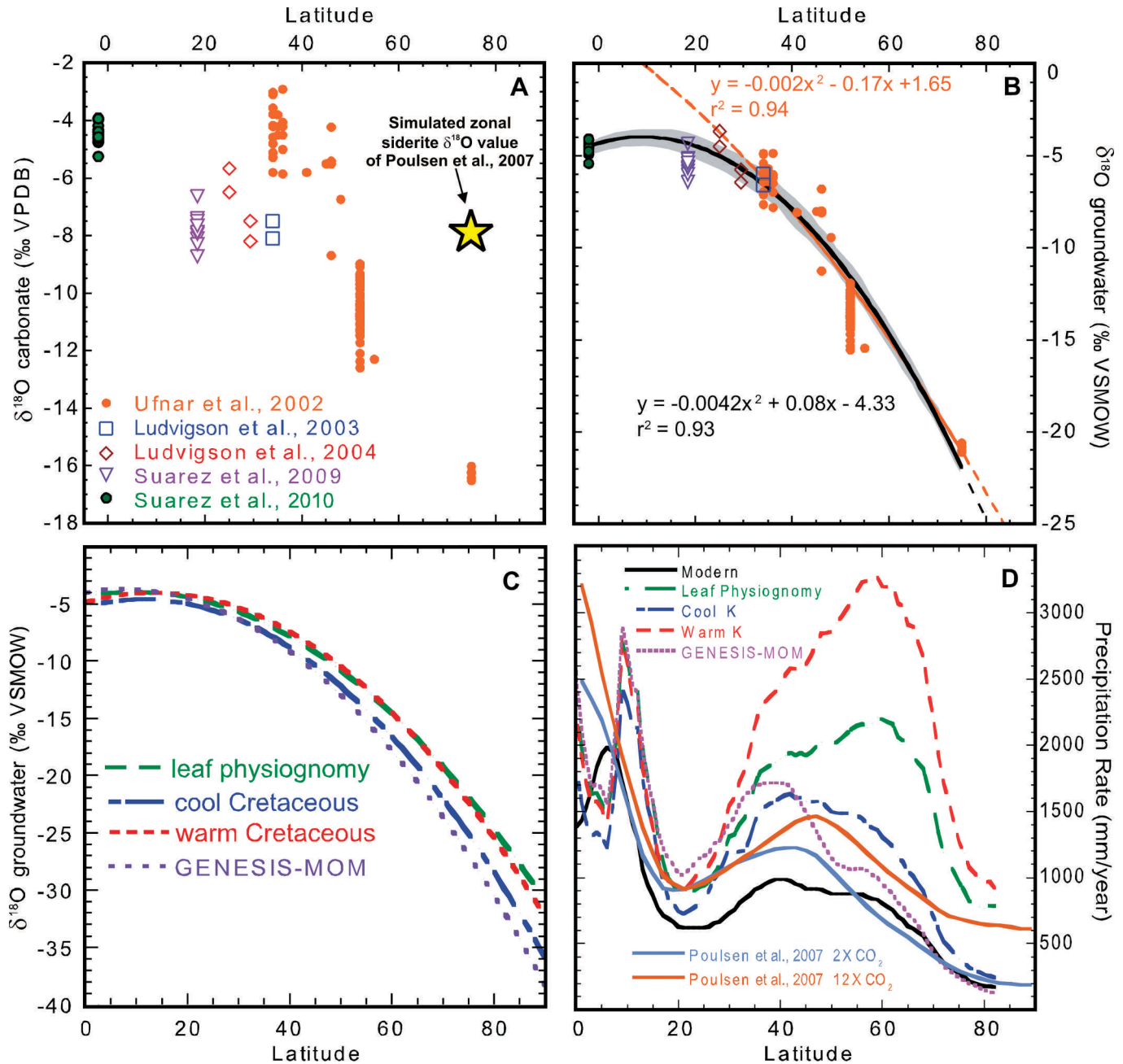


FIG. 6.—Latitudinal gradient for  $\delta^{18}\text{O}$  of mid-Cretaceous meteoric water estimated from the isotopic composition of pedogenic siderites and calcites, and resultant oxygen isotope mass balance modeling of the Cretaceous hydrologic cycle, modified from Suarez et al. (2011b). **A)** Latitudinal distribution of Cretaceous carbonate  $\delta^{18}\text{O}$  data. Data from pedogenic siderites are shown as closed symbols, and data from pedogenic calcites are shown as open symbols. Calcite data from the Cedar Mountain Fm of Utah were reported by Ludvigson et al. (2003), and calcite data from the Glen Rose Fm of Texas were reported by Ludvigson et al. (2004). Note the misfit between Earth system model simulated pedogenic siderite  $\delta^{18}\text{O}$  values at 75° N (Poulsen et al. 2007) and the empirical data from this same paleolatitude (Ufnar et al., 2002). **B)** The paleolatitudinal gradient of groundwater  $\delta^{18}\text{O}$  data derived from the carbonate data in (A), using the temperature-dependent fractionation equations for calcite–water (Friedman and O’Neil 1977) and siderite–water (Carothers et al. 1988). Temperatures used for these calculations are based on the leaf physiognomy data of Wolfe and Upchurch (1987), compiled by Spicer and Corfield (1992). The orange curve and equation are a second-order polynomial fit to the data of Ufnar et al. (2002). The black curve and equation are a second-order polynomial fit to all of the data. The shaded region encompasses 1 $\sigma$  standard deviations from the polynomial regression shown by black curve. Dashed parts of the curves are extrapolations beyond the ranges of the empirical data. **C)** Groundwater  $\delta^{18}\text{O}$  gradients using three additional equator-to-pole temperature gradients estimated for the Cretaceous, and the carbonate  $\delta^{18}\text{O}$  data from (A). Cool Cretaceous and warm Cretaceous gradients are from the temperature range estimates of Barron (1983), and the GENESIS-MOM temperature estimates are from the Earth system model outputs of Zhou et al. (2008). **D)** Modern and Cretaceous zonal precipitation rates calculated for alternative equator-to-pole temperature gradient scenarios in (C). Light blue and orange solid lines show Cretaceous precipitation rates from GENESIS GCM simulations based on 2 $\times$  and 12 $\times$  modern  $\text{CO}_2$  concentrations, from Poulsen et al. (2007).

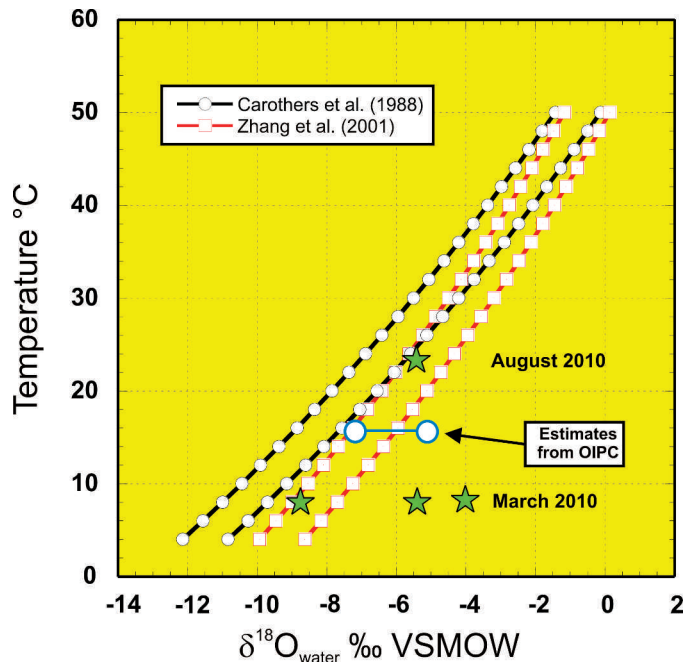


FIG. 7.—Comparison of the siderite–water  $^{18}\text{O}$  fractionation equations of Carothers et al. (1988) and Zhang et al. (2001), with estimates of groundwater temperatures and  $\delta^{18}\text{O}$  values from the CCP site in Chattanooga from Driese et al. (2010), using the OIPC of Bowen (2009). The two curves for each fractionation equation are calculated from the minimum ( $-5.4\text{‰}$  VPDB) and maximum ( $-4.1\text{‰}$  VPDB) siderite  $\delta^{18}\text{O}$  values reported from the CCP site by Driese et al. (2010). Shallow soil temperatures and groundwater  $\delta^{18}\text{O}$  values measured from field studies in March and August 2010 are shown by green star symbols. This analysis clearly shows that the  $^{18}\text{O}$  fractionation relationship of Zhang et al. (2001) is more appropriate for estimating equilibrium siderite–water  $^{18}\text{O}$  fractionations for low-temperature siderites.

closely similar groundwater  $\delta^{18}\text{O}$  values at  $50^\circ\text{C}$ , but they diverge to differences of a few per mil at  $4^\circ\text{C}$ . At the estimated mean annual soil temperature of  $15.8^\circ\text{C}$  for the CCP site, the mean annual precipitation  $\delta^{18}\text{O}$  values of  $-7.2$  to  $-5.1\text{‰}$  VSMOW (where VSMOW is Vienna standard mean ocean water) estimated from the OIPC clearly overlap with the higher water  $\delta^{18}\text{O}$  values calculated from the Zhang et al. (2001) equation, but not with the lower  $\delta^{18}\text{O}$  values calculated from the Carothers et al. (1988) equation.

Figure 7 also shows the results from March and August 2010 field studies at the CCP site in the alluvium of Chattanooga Creek. Shallow soil temperatures taken at a depth of 1 m showed a seasonal temperature range from  $7.3$  to  $23^\circ\text{C}$ . Green star symbols in Figure 7 show the combined soil temperature and shallow phreatic groundwater  $\delta^{18}\text{O}$  values from the alluvium at Chattanooga Creek. March 2010 groundwater  $\delta^{18}\text{O}$  values ranged between  $-8.7$  and  $-3.4\text{‰}$  VSMOW, while August 2010 groundwater  $\delta^{18}\text{O}$  values ranged between  $-5.5$  and  $-5.4\text{‰}$  VSMOW. The three differing groundwater  $\delta^{18}\text{O}$  values from the March 2010 field sampling came from three different soil core sites reoccupied from those originally described by Vulava et al. (2007). Each soil core appears to have sampled phreatic groundwater parcels that were recharged in differing seasons, but were very poorly mixed in the highly heterogeneous anthropogenic fill deposits. According to the

OIPC of Bowen (2009), mean monthly precipitation  $\delta^{18}\text{O}$  values at the CCP site in Chattanooga range from a February minimum of  $-13.8\text{‰}$  to a June maximum of  $-4.8\text{‰}$  VSMOW.

Our actualistic studies clearly show that the siderite–water  $^{18}\text{O}$  fractionation relationship of Zhang et al. (2001) is a more appropriate equation for low-temperature siderite than that of Carothers et al. (1988), which produces estimates of water  $\delta^{18}\text{O}$  values that are too low to fit any of our field measurements or estimates from the OIPC. Our findings will force new changes in the calculated latitudinal gradient of  $\delta^{18}\text{O}$  values for Cretaceous paleoprecipitation (Fig. 6B, C), and yet newer iterations of the oxygen isotope mass balance models of the Cretaceous hydrologic cycle (e.g., Ufnar et al. 2002, Suarez et al. 2011b).

## SUMMARY

Pedogenic siderites are commonly preserved in the sedimentary rock record. They are a characteristic mineral precipitate from reducing groundwaters in poorly drained, water-saturated soils that form in the humid climatic belts of precipitation–evaporation excess. Published descriptions of modern pedogenic siderites in surface soils are less well known than the more abundant literature on calcitic nodules, the pedogenic carbonates that are characteristic of climatic belts with net evaporative losses. Modern pedogenic siderite is never recognized by macroscopic features in water-saturated surface soils. Micromorphologic studies are always required for the recognition of pedogenic siderite in modern hydromorphic soils, and they also are required to confirm the identification and state of preservation of pedogenic siderite in ancient paleosols.

Ancient pedogenic siderites have been described from Late Paleozoic, Mesozoic, and Cenozoic paleosols. The principal paleoclimatic application of pedogenic siderite has been utilization as a proxy for the  $\delta^{18}\text{O}$  values of paleoprecipitation during the formation of paleosols. Applications to the Cretaceous greenhouse climate system have been a major area of published work on pedogenic siderites. At present, misfits between empirical pedogenic siderite  $\delta^{18}\text{O}$  data and Earth system model simulations of the  $\delta^{18}\text{O}$  values of Cretaceous Arctic paleoprecipitation are focusing attention on the Arctic region as a priority area for future work.

Modern process studies on the formation of pedogenic siderite are needed to reduce uncertainties in the paleoclimatic applications of  $\delta^{18}\text{O}$  data from pedogenic siderites in the sedimentary rock record. Actualistic studies on a site of historic pedogenic siderite accumulation in Chattanooga, Tennessee, have resolved a fundamental question concerning the most appropriate siderite–water  $^{18}\text{O}$  fractionation equation for mineral precipitation at low sedimentary temperatures. Up to now, the abiotic laboratory synthesis experiments and fractionation equation of Carothers et al. (1988) have been used in all published treatments of pedogenic siderite  $\delta^{18}\text{O}$  data. Our continuing work will supplant the siderite–water  $^{18}\text{O}$  fractionation equation of Carothers et al. (1988) with a second  $^{18}\text{O}$  fractionation equation by Zhang et al. (2001) that is more appropriate for isotopic equilibrium precipitation at low sedimentary temperatures.

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