



# Oxygen and hydrogen isotope compositions of paleosol phyllosilicates: Differential burial histories and determination of Middle–Late Pennsylvanian low-latitude terrestrial paleotemperatures



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## ABSTRACT

The clay mineralogy, chemistry, and stable hydrogen and oxygen-isotope compositions were measured from 20 phyllosilicate samples representing 11 Pennsylvanian-age paleosol profiles taken from three cores in the Illinois basin in order to assess their utility as proxies of low-latitude terrestrial paleotemperatures. The majority of the samples are mineralogical mixtures of illite–smectite (I/S), kaolinite, and rarely discrete illite. Samples from a shallowly-buried locality in the northern part of the basin are dominantly composed of smectite-rich I/S, with variable amounts of kaolinite, and no discrete illite. Samples from deeply-buried, interior parts of the basin are composed of illite-rich I/S, variable amounts of kaolinite, and discrete illite.

These phyllosilicate mixtures have  $\delta^{18}\text{O}_{\text{V-SMOW}}$  and  $\delta\text{D}_{\text{V-SMOW}}$  values that range from 17.2‰ to 23.0‰ and  $-56\text{‰}$  to  $-27\text{‰}$ , respectively. Assuming that the phyllosilicates preserve a record of isotopic equilibrium with Pennsylvanian meteoric waters, these oxygen and hydrogen isotope values correspond to crystallization temperatures ranging from  $22 \pm 3^\circ\text{C}$  to  $55 \pm 3^\circ\text{C}$ . The clay mineralogy, phyllosilicate  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values and calculated crystallization temperatures of  $44^\circ\text{C}$  to  $55^\circ\text{C}$  from deeply buried localities in the interior of the basin are not consistent with a pedogenic origin. Instead, these trends are considered to be the result of diagenetic recrystallization of pedogenic minerals in response to greater depths of burial (by  $\sim 1.5$  to  $3\text{ km}$ ) in the southerly, basin-center localities, as well as an interval of middle Permian elevated heat flow associated with magmatic intrusions in the southern part of the basin.

Phyllosilicate mineralogy,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values, and calculated phyllosilicate crystallization temperatures from a shallowly buried, northern locality in the Illinois basin are consistent with a pedogenic origin, and reveal a long-term warming trend from an average temperature of  $23 \pm 3^\circ\text{C}$  in the lower Desmoinesian to an average temperature of  $32 \pm 3^\circ\text{C}$  in the Missourian. This temperature change is coincident with a significant change in the composition of wetland vegetation in Euramerica, which has been attributed to a shift in low-latitude Pennsylvanian climate towards warmer and drier conditions in the Late Pennsylvanian. This study reveals the presence of a dynamic Late Paleozoic paleoequatorial icehouse climate characterized by significant low-latitude temperature variability unprecedented on modern Earth.

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## 1. Introduction

During the Late Mississippian to Late Permian the earth was entrained in the Late Paleozoic Ice Age (LPIA; Isbell et al., 2012). Recent advances in our understanding of the LPIA reveal that it consisted of multiple glaciations that waxed and waned across Gondwanaland (Frakes et al., 1992; Isbell et al., 2003; Rygel et al., 2008; Isbell et al., 2012). Global compilations of climate-sensitive sediments, mineralogic assemblages, fossil floras and geochemical proxy records have provided insight into the paleoclimate and paleoenvironments during the LPIA (Nairn and Smithwick, 1976; Phillips and Peppers, 1984; Phillips et al., 1985a,b;

Rowley et al., 1985; Ziegler et al., 1987; Parrish and Peterson, 1988; Scotese et al., 1999; Tabor and Montañez, 2005; Came et al., 2007; Tabor and Poulsen, 2008; Tabor et al., 2008; Falcon-Lang and DiMichele, 2010). However, the far-field (tropical to sub-tropical) paleoclimatic impacts of the glaciations remain controversial (Ziegler et al., 1987; Cecil, 1990; Heckel, 1994; West et al., 1997; Isbell et al., 2008; Soreghan et al., 2008, 2009; Bishop et al., 2010). Particularly, questions remain regarding the extent to which paleotropical temperatures varied throughout the waxing and waning of Gondwanan ice sheets (Angiolini et al., 2007; Poulsen et al., 2007; Soreghan et al., 2007a,b; Tabor and Poulsen, 2008).

Numerous studies have demonstrated that the isotopic composition of hydroxyl-bearing phyllosilicate minerals that form in low-temperature sub-aerial weathering environments may provide information related to weathering and environmental conditions at

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the time of formation, such as the oxygen isotope composition of local meteoric water and crystallization temperature (Savin and Epstein, 1970; Lawrence and Taylor, 1971, 1972; Bird and Chivas, 1988, 1989; Lawrence and Rashkes-Meaux, 1993; Delgado and Reyes, 1996; Stern et al., 1997; Tabor et al., 2002, 2004; Vitali et al., 2002; Tabor and Montañez, 2005). Consequently, authigenic, soil-formed (pedogenic) phyllosilicate minerals taken from paleosol profiles have the potential to provide proxies of terrestrial paleoenvironmental conditions, provided that the original isotopic signatures have not been diagenetically-altered.

Tabor and Montañez (2005) estimated crystallization temperatures of mixtures of kaolinite and 2:1 phyllosilicate minerals in Upper Pennsylvanian (Virgilian)–Lower Permian (Leonardian) paleosols in north-central Texas, U.S.A. To date, this study represents one of the few quantitative terrestrial paleotemperature estimates for the Pennsylvanian tropics (see also Lawrence and Rashkes-Meaux, 1993; Tabor, 2007). This contribution expands upon this limited data set by providing paleotropical Middle–Late Pennsylvanian terrestrial paleotemperature estimates from the Illinois basin (U.S.A.). This paper discusses the spatial and stratigraphic variations in the mineralogic, chemical and oxygen- and hydrogen-isotope compositions of 2:1 phyllosilicate and kaolinite mixtures from 11 Middle–Late Pennsylvanian (Desmoinesian–Missourian) paleosol profiles across the Illinois basin. Following the methodological approach discussed in Tabor and Montañez (2005), this work evaluates the utility of the mineralogic, chemical and isotopic properties of Illinois basin paleosol phyllosilicates as proxies for paleotemperature and Pennsylvanian soil water  $\delta^{18}\text{O}$  values. In addition, the influence of burial history and tectonic activity is considered as a potential mechanism for diagenetic alteration of the mineralogic and isotopic composition among some of these phyllosilicate mixtures. Finally, the data set provides best estimates of Pennsylvanian phyllosilicate crystallization temperatures from a shallowly-buried part of the Illinois basin. These data (1) demonstrate the isotopic composition of paleosol phyllosilicates that have experienced shallow burial and minimal post-depositional heating likely retain their original pedogenic values and provide a reliable source of paleoenvironmental proxy information and (2) provide the first quantitative paleotropical terrestrial temperature estimates across the Desmoinesian–Missourian boundary, an interval in the Pennsylvanian marked by significant paleoenvironmental changes, but whose mechanistic links to LPIA glacioeustasy remain debated (e.g., Frakes et al., 1992; Fielding et al., 2008a,b,c; Bishop et al., 2010; Gulbranson et al., 2010; Falcon-Lang et al., 2011).

## 2. Geologic background

### 2.1. Basin history

The Illinois basin is an intracratonic basin located in Illinois, Indiana, and Kentucky (Fig. 1). The basin began subsiding in the late Precambrian–Early Cambrian in response to extension in the Reelfoot rift and Rough Creek graben associated with late Paleozoic Appalachian–Ouachita tectonic activity (Kolata and Nelson, 1991, 1997). Structural features separating the Illinois basin from adjacent provinces include the Kankakee Arch to the northeast, the Wisconsin Arch to the north, the Ozark Dome to the southwest, and the Cincinnati Arch to the east (Fig. 1; Willman et al., 1975). During the Pennsylvanian, the Illinois basin was located in western equatorial Pangaea ( $\sim 0$  to  $5^\circ\text{N}$ ; Scotese et al., 1999; Blakey, 2007). Pennsylvanian biostratigraphic zonation in the basin, based on fusulinids (Dunbar and Henbest, 1942; Douglass, 1987), ostracods (Thompson et al., 1959; Thompson and Shaver, 1964), spores (Winslow, 1959; Peppers, 1964, 1970, 1996) and conodonts (Heckel and Baesemann, 1975; Swade, 1985; Heckel, 1991; Heckel and Weibel, 1991), permit regional and global correlations to Middle–Upper Pennsylvanian strata in contemporaneous basins (Ritter et al., 2002; Barrick et al., 2004; Heckel et al., 2007; Falcon-Lang et al., 2011). The sedimentary section in the Illinois basin preserves a nearly continuous record of Cambrian–Pennsylvanian strata. Pennsylvanian strata

comprise the youngest outcrops in the basin, except for abundant Quaternary sediments and Mesozoic strata at the southern margin of the basin (Willman et al., 1975). The greatest degree of Pennsylvanian subsidence and sediment accumulation occurred in the southeastern part of the Illinois basin, resulting in a maximum stratigraphic thickness of approximately 760 m (Fig. 1; Willman et al., 1975).

### 2.2. Tectonic and burial history

The upper contact of Pennsylvanian strata is erosional (Willman et al., 1975) indicating maximum burial depths in excess of modern (note that strata studied herein are from bore-hole cores). Additionally, vitrinite reflectance values for the Middle Pennsylvanian (upper Carbondale Formation) Herrin Coal suggest significantly higher thermal maturities than can be satisfactorily explained by current burial depths (Fig. 1; Damberger, 1971, 1974). To account for this inconsistency, it is estimated that 1500 to 3000 m of southeastward-thickening Permian to Lower Cretaceous strata were deposited upon the Pennsylvanian strata, and later removed by erosion, in the thickest areas of the basin (Damberger, 1971, 1974; Zimmerman, 1986; Buschbach and Kolata, 1991; Gharrabi and Velde, 1995; Rowan et al., 2002). Permian strata associated with the Rough Creek graben in western Kentucky support this post-Pennsylvanian burial scenario (Fig. 1; Schwalb, 1982; Kehn et al., 1982).

From the Cambrian through the Cretaceous the Illinois basin was intermittently affected by magmatic activity in the Reelfoot rift (Fig. 1). Radiometric ages of intrusive igneous rocks reveal a particularly substantial interval of magmatism during the middle Permian ( $\sim 270$ – $280$  Ma). This activity was concentrated in southern Illinois and resulted in the emplacement of numerous ultramafic dikes and sills in the southern part of the basin and northern Reelfoot rift (Zartman, 1977; Brannon et al., 1992; Chesley et al., 1994). Contemporaneous fluorite mineralization occurred in the Fluorspar district in the vicinity of the cryptovolcanic Hicks dome (Fig. 1; Zartman, 1977; Nelson and Lumm, 1987; Rowan and Goldhaber, 1996). Collectively, these studies indicate that the Illinois basin experienced a complex tectonic and thermal history that was primarily focused in the southern part of the basin. Estimated maximum burial depth and temperatures for basal Pennsylvanian strata in the southern part of the basin are  $\sim 3000$  m and  $>175^\circ\text{C}$ , respectively (Harris, 1979; Elliott and Aronson, 1993; Grathoff et al., 2001). However, temperature estimates from fluid inclusions in diagenetic sphalerites in Middle Pennsylvanian coals (Damberger, 1971, 1974, 1991; Cobb, 1981; Coveney et al., 1987), vitrinite reflectance values (Barrows and Cluff, 1984; Comer et al., 1994), and smectite to illite mineral transformations (Gharrabi and Velde, 1995; Grathoff et al., 2001; Rowan et al., 2002) indicate that the Pennsylvanian strata in the northern part of the basin experienced a maximum burial depth of  $\sim 1500$  m (approximately equivalent to eroded post-Pennsylvanian strata) and burial temperatures ranging from  $70$  to  $120^\circ\text{C}$ .

### 2.3. Previous work and samples used in this study

Pennsylvanian strata of the Illinois basin are characterized by a series of repeated successions of terrestrial, deltaic and marine deposits called cyclothems (Udden, 1912; Wanless and Weller, 1932). Cyclothems are commonly interpreted to result from repeated large-scale ( $\geq 100$  m), high-frequency ( $10^4$  to  $10^5$  kyr) eustatic sea-level fluctuations associated with the waxing and waning of ice sheets in Gondwanaland (Heckel, 1977, 1986, 1994; Soreghan, 1994; West et al., 1997; Soreghan and Giles, 1999; Haq and Schutter, 2008). Pennsylvanian strata contain abundant pedogenically-modified horizons (paleosols; Hopkins and Simon, 1975; Greb et al., 1992; Mastalerz and Shaffer, 2000; Rosenau et al., 2013a,b) which developed on paleolandscapes during periods of glacio-eustatic lowstand and relative landscape stability. Based upon a comprehensive study of the morphological, mineralogical and geochemical content of paleosol profiles preserved within Pennsylvanian (Atokan–Virgilian; Westphalian–Stephanian) strata

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