

# Oxygen and hydrogen isotope compositions of Permian pedogenic phyllosilicates: Development of modern surface domain arrays and implications for paleotemperature reconstructions

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## Abstract

Mineralogic, chemical, and oxygen and hydrogen isotope compositions of 15 different phyllosilicate samples from Permo–Pennsylvanian-age paleosols of the eastern shelf of the Midland basin of Texas and the southern Anadarko basin are presented. Mixtures of 2:1 phyllosilicates and kaolinite dominate most samples, although some samples consist of relatively pure 2:1 phyllosilicates. Chemical and mineralogic data are used in conjunction with published thermodynamic data to calculate hydrogen and oxygen isotope fractionation factors for each sample. In turn, application of measured oxygen and hydrogen isotope compositions of the phyllosilicates to temperature-dependent fractionation equations are used to calculate paleotemperatures of crystallization.

The  $\delta D$  values of the phyllosilicates range from  $-69\text{‰}$  to  $-55\text{‰}$ . The  $\delta^{18}O$  values range from  $19.5\text{‰}$  to  $22.7\text{‰}$ . If these samples preserve a record of equilibrium with paleo-meteoric waters, the isotopic compositions of the phyllosilicates correspond to paleotemperatures of phyllosilicate crystallization ranging from  $22 \pm 3\text{ °C}$  to  $35 \pm 3\text{ °C}$ . In particular, the stratigraphic trend of calculated temperatures from Midland basin samples suggests that Early Permian surface temperatures may have been up to  $10\text{ °C}$  warmer than those of the latest Pennsylvanian.

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## 1. Introduction

Climate plays an important role in the deposition and distribution of many terrestrial lithologies such as coals, laterites, kaolins, red beds, calcretes, and eolianites (e.g., Parrish, 1993; Sellwood and Price, 1993; Ziegler et al., 1996; Barron and Moore, 1994). As

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such, the terrestrial sedimentary record provides insight into the evolution of climate through the Phanerozoic. However, temperature, which is an integral component of climate and a strong influence on the distribution of climate zones, is poorly approximated by the character and morphology of terrestrial lithologies (e.g., Parrish, 1993). One potential quantitative proxy of paleotemperature is combined oxygen and hydrogen isotope ratios of ancient soil-formed (hereafter pedogenic) hydroxyl-bearing minerals. The potential of the isotopic compositions of these minerals to provide paleotemperature estimates is particularly attractive given their widespread occurrence in soils. In this regard, paleothermometry could be broadly applied to pedogenic systems of any age.

The potential utility of pedogenic phyllosilicates as isotopic archives of paleoenvironmental conditions and paleotemperature has been recognized since the early work of Savin and Epstein (1970). More recent work has demonstrated that combined study of the oxygen and hydrogen isotopic composition of hydroxyl-bearing minerals from pedogenic environments can yield more environmental information than either  $\delta^{18}\text{O}$  or  $\delta\text{D}$  values alone (Yapp, 1987, 1993, 2000; Delgado and Reyes, 1996; Savin and Hsieh, 1998; Vitali et al., 2002). With few notable exceptions, this approach has seldom been applied in isotopic studies of phyllosilicate minerals (Bird and Chivas, 1988, 1989; Lawrence and Rashkes-Meaux, 1993; Vitali et al., 2002). These studies elucidate the challenge in isotopic analysis of pedogenic phyllosilicates in which (1) mixtures of authigenic and detrital minerals were analyzed together and end-member isotope compositions of the authigenic phases were calculated assuming the abundance and isotopic composition of the detrital phase, or (2) chemical variability among phyllosilicate samples, and attendant variability of the oxygen and hydrogen isotope fractionation factors associated with it, were largely unknown or ignored.

Although soils with pedogenic 2:1 phyllosilicate minerals are geographically and geologically more abundant than kaolinite-rich weathering profiles (e.g., Wilson, 1999), very few studies have applied combined oxygen and hydrogen isotopic studies of these minerals to paleoclimate and paleotemperature reconstructions (Delgado and Reyes, 1996; Vitali et al., 2002; Tabor et al., 2004). This primarily reflects the variable chemistry of 2:1 phyllosilicates, and the

corresponding variability of thermodynamic isotopic fractionation factors for these minerals, relative to chemically invariant minerals such as kaolinite.

Based on profile-scale mineralogic analysis of the clay-size fraction ( $<2\ \mu\text{m}$ ) of the Permo–Pennsylvanian weathering profiles, Tabor et al. (2002) asserted that those paleosols preserve profile-scale mineralogic trends in phyllosilicate composition and abundance that are similar to modern pedogenic signatures and therefore isotopic compositions of the soil-formed minerals may have paleoenvironmental significance. This paper builds on the earlier work of Tabor et al. (2002) by presenting combined oxygen and hydrogen isotope compositions of paleopedogenic 2:1 phyllosilicates and kaolinite from 15 Permo–Pennsylvanian paleosol profiles that formed in the Eastern Shelf of the Midland basin (herein referred to as Eastern Midland basin) of Texas and the Anadarko basin of Oklahoma. Utilizing the concept of surface domain arrays defined by Yapp (1993, 2000), we assert that these paleopedogenic phyllosilicates preserve isotopic compositions similar to those expected in modern soil forming environments. These data provide new constraints that help to refine our understanding of Late Paleozoic climate and the role that climate may have played in the terrestrial sedimentary record.

### 1.1. Sample set and previous work

The stratigraphic distribution and geographic location of the samples are presented in Table 1. Fossil soils (paleosols) include Late Pennsylvanian (Virgilian) and Early Permian (Wolfcampian and Leonardian) examples from the Eastern Midland basin and Early Permian (Wolfcampian and Leonardian) samples from the extreme southern rim of the Anadarko basin in south-central Oklahoma. Chronostratigraphic constraints for all sections include fluvial marker beds and correlated marine limestones with good fusulinid and ammonite biostratigraphic control (Dunbar, 1960; Hentz, 1988; Donovan, 1986).

The Permo–Pennsylvanian strata of the Eastern Midland and Anadarko basins were deposited along the western coastal zone of equatorial Pangea (Ziegler et al., 1996; Golonka et al., 1994; Scotese, 1984; Loope et al., 2004). Major tectonic elements that influenced Late Paleozoic sedimentation within these two basins, such as the Muenster Arch and the

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