

Article

Exploring the Deuterium Excess of Cretaceous Arctic Paleoprecipitation Using Stable Isotope Composition of Clay Minerals from the Prince Creek Formation (Maastrichtian) in Northern Alaska

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Abstract: We report estimated stable isotope compositions of Arctic paleoprecipitation using phyllosilicates sampled from three paleosols and two bentonites in the Prince Creek Formation (Maastrichtian) in northern Alaska. Previous studies reported a deuterium excess in estimates of Arctic paleoprecipitation from the Late Cretaceous by combining hydrogen and oxygen proxy sources, including pedogenic minerals, dinosaurian tooth enamel phosphates, pedogenic siderites, and *n*-alkane biomarkers. The new dataset produced in this study removes uncertainty on possible explanations (photosynthetic and transpiration) of the deuterium excess by producing stable hydrogen and oxygen isotopic signatures from the same source material. The δD of the phyllosilicates range from -171‰ to -72‰ VSMOW and $\delta^{18}O$ ranges from 5.0 to 11.8‰ VSMOW. By assuming a MAT of 6.3 °C and calculating uniquely derived fractionation equations for each phyllosilicate, we report estimated isotopic composition of Late Cretaceous paleoprecipitation with an average δD value of -133‰ VSMOW, corresponding to an average $\delta^{18}O$ value of -20.3‰ VSMOW. The estimates of Late Cretaceous paleoprecipitation do not intersect the Global Meteoric Water Line and reveal a reported deuterium excess ranging from 7 to 46 per mil. These results confirm the presence of a deuterium excess in Late Cretaceous Arctic paleoprecipitation and provide new insight to assessing possible explanations for this phenomenon.

Keywords: Cretaceous; hydrogen and oxygen isotopes; paleoprecipitation; pedogenic phyllosilicates



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1. Introduction

The Cretaceous period has been the focus of a substantial amount of paleoclimate research, given its status as an ancient greenhouse world with higher atmospheric pCO_2 levels, warmer global temperatures, and reduced equator-to-pole temperature gradients [1,2]. However, gaps in our understanding of the Cretaceous greenhouse still exist, particularly surrounding the polar regions. This is often expressed as a conflict between resolving paleoclimate proxy data, which suggests a warm Cretaceous Arctic, and that of climate model simulations [3]. In an effort to resolve this conflict, new research has focused on collecting and analyzing samples that can reveal the relationship of paleotemperature and stable isotopic ($\delta^{18}O$ and δD) composition of paleoprecipitation. This work includes studies on pedogenic siderite, dinosaurian tooth enamel phosphates, and pedogenic clay minerals producing $\delta^{18}O$ data and *n*-alkane biomarkers producing δD data from terrestrial deposits that capture the Cretaceous record in the Arctic [4,5].

The results from this previous research revealed low $\delta^{18}O$ of paleoprecipitation corresponding to higher δD than would be expected, given modern relationships of $\delta^{18}O$ and δD plotting along the Global Meteoric Water Line [5]. However, the question became if this deuterium excess recorded in *n*-alkane biomarkers was the result of photosynthetic and

transpiration fractionation events occurring within plants producing higher δD values or if it was related to the paleoprecipitation. Here, we address this concern by producing both $\delta^{18}O$ and δD data from pedogenic clays and bentonites, thus removing any photosynthetic or transpiration fractionation components from arctic vegetation. These data not only allow us to address the question of the existence and magnitude of the deuterium excess but also allow us to discuss the possible mechanisms that could contribute to its existence.

2. Materials and Methods

Samples from the Prince Creek Formation used in this study were previously collected from three field localities on the North Slope of Alaska. The Colville Basin of northern Alaska formed in the Aptian to Albian as a result of subsidence to the north of the Brooks Range orogenic belt [6,7]. Uplift and erosion of the Brooks Range drove clastic wedges, including the Prince Creek Formation, into the basin during the Late Cretaceous and Paleogene [8]. Bluffs of the Prince Creek Formation along the Colville, Kogosukruk, and Kikiakrorak rivers dip to the northeast ($<3^\circ$), exposing alluvial sandstone, siltstone, shale, coal and bentonites [9,10]. The entire Prince Creek Formation is known to range in age from Campanian to Paleocene; however, the samples used in this study are thought to be early Maastrichtian, based on palynological and geochronological constraints [11]. Plate reconstructions indicate that the Prince Creek Formation was deposited at a paleolatitude of $82\text{--}85^\circ N$ [12,13].

Flaig et al. [9,10] interpreted the strata of the Prince Creek Formation to record deposits of meandering fluvial channels, levees, crevasse splays, and associated floodplains (which include lakes, ponds, swamps, and paleosols). Soil-forming processes on floodplains were continually interrupted by alluvial input, resulting in weakly developed paleosols similar to modern aquic Entisols and Inceptisols [10]. At least some of these paleosols were influenced by the presence of volcanic ash [14]. Macro- and micromorphological features in the paleosols indicate repeated, possibly seasonal, wetting and drying of floodplains [10,11]. Overall, the Prince Creek Formation preserves a Cretaceous, paleopolar low-gradient, muddy coastal plain succession [9,10]. The Prince Creek Formation also contains the densest concentration of high-latitude dinosaur bones of any high-latitude location in the Northern or Southern Hemisphere [15], making it an important ancient greenhouse ecosystem for continuing study [16].

With respect to samples collected and analyzed for this study, locality 06SH is located downriver and up-stratigraphic section from localities PFDV 17 and KKT, and is presumed to contain slightly younger sediments. Samples 06SH9.2, 06SH14.4, and 06SH15.1 were collected from a series of stacked, compound-cumulative paleosols exposed along the modern Colville River (Figures 1 and 2). Detailed description and analyses of the paleosols by Flaig et al. [10] identified the paleosols as having characteristics similar to Aquic Inceptisols and Entisols. Sample 06SH9.2 was collected from a dark organic rich B-horizon (10YR 2/1) measuring approximately 70 cm thick. Flaig et al. [10] noted several features within the paleosol, including platy structure, organic fragments, high amounts of bioturbation, common Fe-oxide nodules/coatings, and root traces. Sample 06SH14.4 was collected from a dark olive gray (5Y 3/2) B-horizon measuring approximately 60 cm thick. Noted features included blocky structure and organic fragments [10]. Sample 06SH15.1 was collected from an olive gray (5Y 4/1) B-horizon measuring approximately 80 cm thick. Noted features included blocky structure, micro-sphaerosiderite, root traces, common Fe-oxide nodules/coatings, and papules [10]. Samples PFDV 17 and KKT were collected from bright olive-green bentonite layers measuring approximately 45 cm and 30 cm thick. Bulk samples from each locality and their exact stratigraphic position are indicated by blue stars in Figure 2.

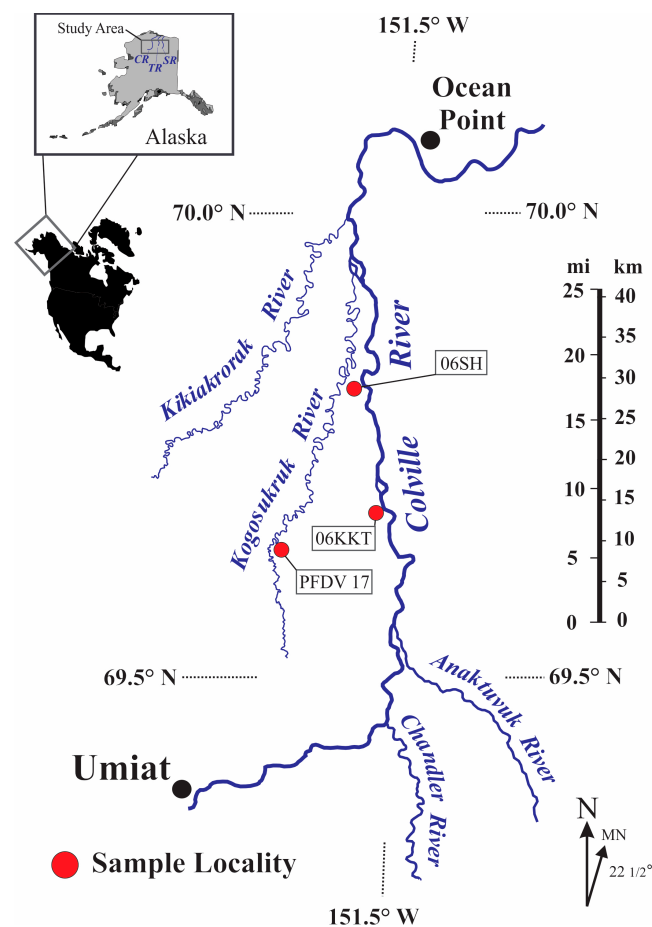


Figure 1. Sample locations from the Prince Creek Formation along the Colville and Kogosukruk Rivers in northern Alaska.

Bulk paleosol material was disaggregated and centrifuged to isolate the $<0.2\ \mu\text{m}$ fraction, regarded to be dominated by pedogenic clays in paleosol profiles [17–23]. The isolated $<0.2\ \mu\text{m}$ -size fraction samples were then treated using the following solutions to remove non-phyllsilicate materials: (1) 10% acetic acid solution for 24 h to remove calcite [24,25], (2) sodium citrate–bicarbonate–dithionite solution to remove secondary iron oxy-hydroxides, and (3) 30% H_2O_2 solution to remove organic matter.

Mineralogy of the chemically treated $<0.2\ \mu\text{m}$ fraction samples was determined using X-ray diffraction (XRD). Three oriented aggregates were created for each sample: (1) potassium saturation at room temperature, (2) magnesium saturation at room temperature, and (3) magnesium saturation followed by glycerol solvation at room temperature. Oriented aggregates were analyzed at the Roy M. Huffington Department of Earth Sciences at Southern Methodist University (SMU: Dallas, TX, USA) using a Rigaku Ultima III X-ray diffractometer with a step scan of 0.05° over a spectrum of $2\text{--}30^\circ\ 2\theta$. Relative abundance of clay minerals in each sample was determined using the area of the background-subtracted intensities of the 001 peak for glycerol-solvated samples ($17\text{--}20\ \text{\AA}$ for smectite, $9.9\text{--}10.1\ \text{\AA}$ for illite, $7.1\text{--}7.2\ \text{\AA}$ for kaolinite) [18,22,23,26]. The chemically treated samples were then split into three aliquots for stable isotope and elemental analysis.

The first aliquot was prepared as a pressed powder pellet using $0.25\ \mu\text{m}$ polished hardened steel disks and coated with $\sim 150\text{-\AA}$ layer of high-purity carbon in a carbon evaporator. The pressed pellets were analyzed for major and minor elemental composition using a Cameca SXFive electron microprobe housed at the Texas A&M Materials and Characterization Facility.

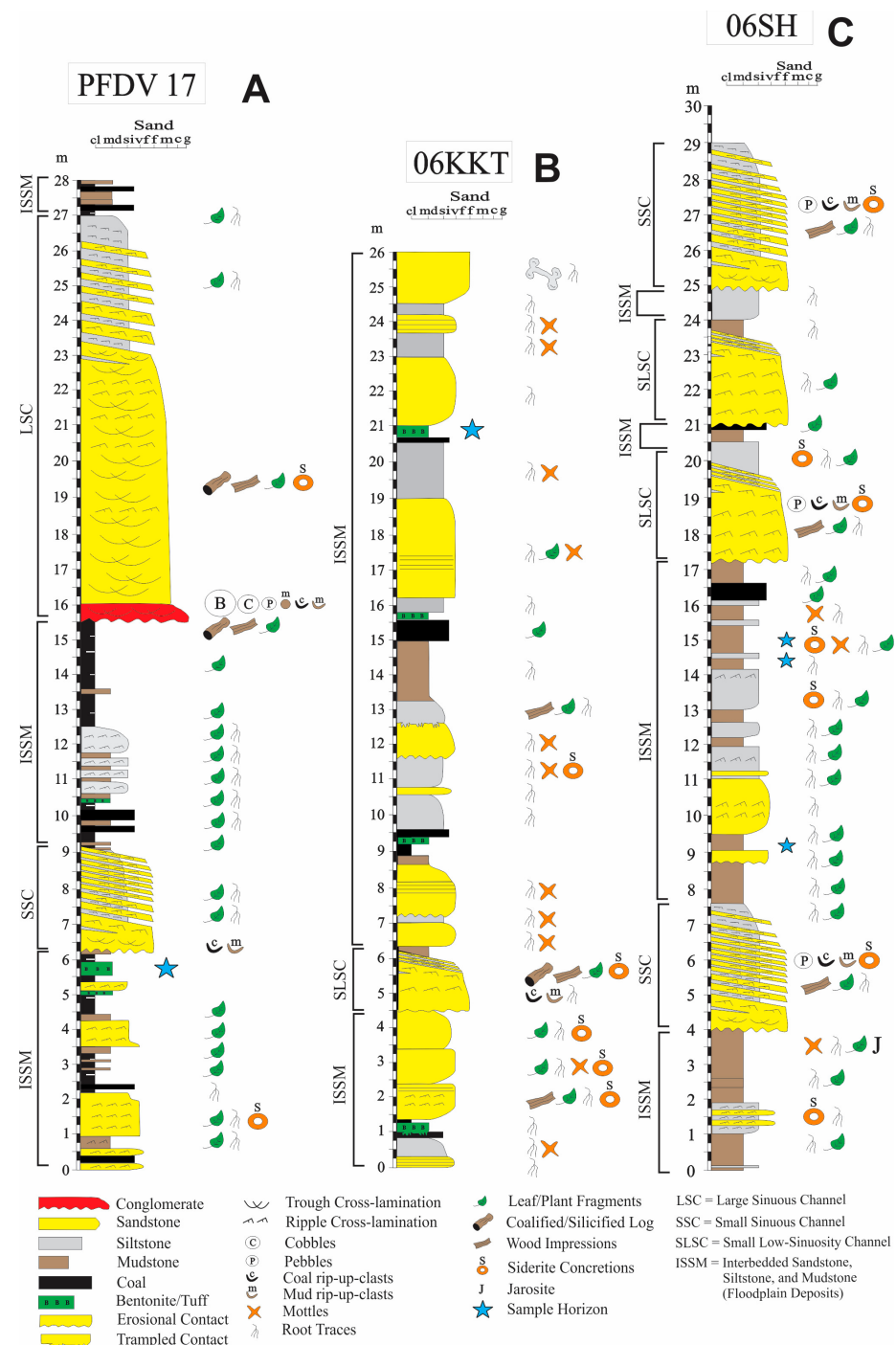


Figure 2. Measured stratigraphy including all stratigraphic features and sample horizons from the Prince Creek Formation in northern Alaska. Figure includes the stratigraphic location of samples analyzed for this study, indicated by blue stars. (A) Representative stratigraphic column and paleoenvironmental interpretations for the PFDV 17 sample locality along the Kogosukruk River. (B) Representative stratigraphic column and paleoenvironmental interpretations for the 06KKT sample locality along the Colville River. (C) Representative stratigraphic column and paleoenvironmental interpretations for the 06SH sample locality along the Colville River.

The second and third aliquots were analyzed for stable oxygen and hydrogen isotope composition at extraction laboratories housed at the Roy M. Huffington Department of Earth Sciences at Southern Methodist University (SMU: Dallas, TX, USA). Oxygen isotope analyses were conducted following the methods of Clayton and Maydada [27]. Samples

were heated overnight in nickel-rod bombs connected to a gas extraction line while kept at 100–150 °C to remove sorbed and interlayer water. Samples were then reacted with BrF₅ at ~560 °C overnight to produce O₂ gas. The O₂ gas was converted to CO₂ using heated graphite rods in high-vacuum glass extraction lines. The CO₂ gas was then cryogenically captured and measured on a Finnigan MAT 252 isotope ratio mass spectrometer (IRMS) operating in dual inlet mode. Repeated oxygen isotope analyses of the 3 pedogenic phyllosilicate samples yield an analytical error of 0.2‰.

Hydrogen isotope analyses were conducted following the methods of Savin and Epstein [24]. Samples were initially outgassed at 150 °C for a minimum of 1 h under closed-system conditions in 0.16 bar of O₂ gas to remove sorbed and interlayer water and destroy any recalcitrant organic matter not destroyed by previous H₂O₂ treatment. The samples were then dehydroxylated at 850 °C under closed-system conditions in 0.16 bar O₂ gas. The low- and high-temperature water fractions were then converted to H₂ gas by passage over depleted uranium metal at 760 °C as two separate fractions. H₂ gas yields were measured on a mercury manometer with an uncertainty of ±1 µmol, and the δD values were measured on a Finnigan MAT 252 IRMS operating in dual inlet mode at SMU. Replicate hydrogen isotope analyses of phyllosilicate samples yield an analytical error of ±4‰. The oxygen and hydrogen isotopic composition of the <0.2 µm fraction are reported in conventional delta notation (δ) in parts per thousand (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW; [28]).

Sample 06KKT-20.5 was collected from a bentonite layer along the Colville River and sample PFDV 17 was collected from a bentonite layer along the Kogosukruk River (Figures 1–3). Previous work by Salazar-Jaramillo et al. [14,29] analyzed mineralogy and oxygen isotope composition of the clay fraction of both bentonite samples. We obtained bulk samples and separated the clay size fraction <2 µm. The isolated <2 µm-size fraction samples were then treated using the following solutions to remove non-phyllosilicate materials: (1) 10% acetic acid solution for 24 h to remove calcite [24,25], (2) sodium citrate–bicarbonate–dithionite solution to remove secondary iron oxyhydroxides, and (3) 30% H₂O₂ solution to remove organic matter. Mineralogy of the chemically treated <2 µm fraction samples was determined using X-ray diffraction (XRD). Three oriented aggregates were created for each sample and analyzed at the Geology Department at the University of Kansas (KU: Lawrence, KS) using a Bruker D2 Phaser diffractometer with a step scan of 0.05° over a spectrum of 2–30° 2θ. Results from XRD analyses were used to confirm previous mineralogical analyses reported by Salazar-Jaramillo et al. [14].

Hydrogen isotope analyses of the clay fraction from the two bentonite samples were conducted at the Laboratory for Stable Isotope Science (LSIS), University of Western Ontario, London, Ontario, Canada following methods described by Sharp et al. [30]; VanDeVelde and Bowen [31]; Bauer and Venemann [32]; Qi et al. [33]; and Kanik et al. [34]. Approximately 2 mg of each sample was weighed into 3.5 × 5 mm silver capsules. Duplicates of each sample were run as well as three standards: USGS 57, USGS 58, and in-house biotite standard (GBS). Capsules were folded shut and dried in a vacuum oven at 200 °C for 18 h. Samples were then immediately transferred to a helium (He)-flushed, Costech Zero-Blank autosampler attached to the furnace port of the TCEA. The autosampler was then immediately purged under helium flow of 0.85 bar to limit clay mineral rehydration by atmospheric moisture. The samples and standards were maintained under He flush in the autosampler for 4 h prior to isotopic analyses. The H-isotope data are reported in delta (δ) notation relative to VSMOW-SLAP (Standard Light Antarctic Precipitation) calibrated scale [35]. Phyllosilicate standards USGS 57 (biotite δD = −91.5‰ VSMOW) and USGS 58 (muscovite δD = −28.4‰ VSMOW) were used to calibrate the H-isotope measurements to VSMOW [33].

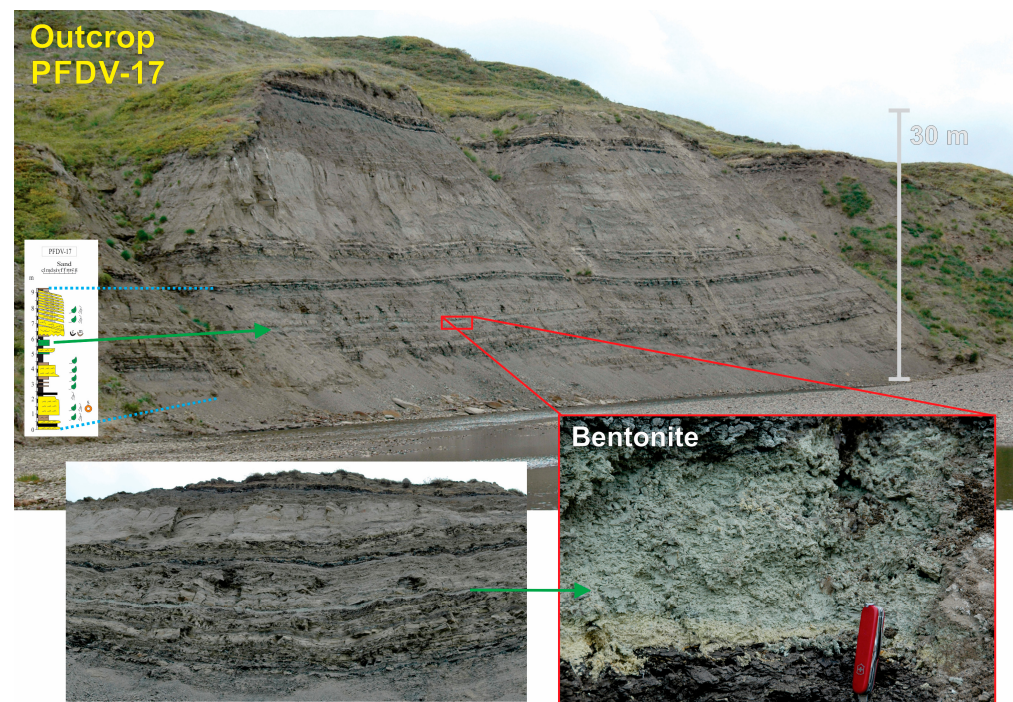


Figure 3. Outcrop imagery of locality PFDV 17 located along the Kogosukruk River showing the sedimentologic, stratigraphic and stratal architecture framework of the site. Figure includes part of the PFDV 17 stratigraphic chart. Outlined red box and green arrow show the location of the sampled bentonite layer along the outcrop belt and a closeup image of the bentonite. Pocketknife is 9 cm for scale.

3. Results

3.1. Clay Mineralogy and Chemical Composition

X-ray diffraction analyses of the $<0.2\ \mu\text{m}$ -size fraction from paleosol samples collected from locality 06SH revealed a mixture of smectite (001) peak ($18.5\ \text{\AA}$), illite/mica (001) peak ($10\ \text{\AA}$), and kaolinite (001) peak ($7.2\ \text{\AA}$) (Figure 4, Table 1). The average kaolinite content of the three paleosol samples was $\sim 21\%$, with the remainder accounted for by 2:1 phyllosilicates. The chemical composition of end-member 2:1 phyllosilicates was calculated using wt% oxide data collected from the $<0.2\ \mu\text{m}$ -size fraction (Table 1). The wt% kaolinite of each sample was taken into account based on results from X-ray diffraction spectra. The mole fraction of Al_2O_3 and SiO_2 within mineralogical mixtures of each sample was calculated from the wt% oxide data in Table 1. Estimated mole fractions of Al and Si from kaolinite were subtracted from the phyllosilicate mixtures to calculate an end-member 2:1 phyllosilicate chemical formula for each sample. X-ray diffraction analyses of the $<2\ \mu\text{m}$ -size fraction of the bentonite samples 06KKT-20.5 and PFDV 17 confirmed the results of Salazar-Jaramillo et al. [14], revealing a monomineralic signature (pure montmorillonite; Supplementary Table S1).

3.2. $\delta^{18}\text{O}$ and δD of Meteoric Water from Pedogenic Phyllosilicates

To calculate the $\delta^{18}\text{O}$ and δD of meteoric water from which the pedogenic phyllosilicates precipitate requires known fractionation factors for both oxygen and hydrogen for each sample as well as crystallization temperature. Given the mineralogical mixture present in the three paleosol samples, unique oxygen and hydrogen fractionation factors were calculated for each sample based on mineralogy and end-member chemical composition (Table 2).

Table 1. Electron microprobe and X-ray diffraction data for the <0.2 µm-size fraction of phyllosilicates for paleosol samples (this study) and the <2 µm-size fraction of bentonite samples [14]. Weight percentage (wt. %) of clay mineralogy was calculated using X-ray diffraction data, and results reported have an analytical error of ±5%.

Sample	Formation	Na ₂ O	MgO	MnO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂	Total	2:1 Phyllosilicate (wt.%)	Kaolinite (wt.%)
Paleosol													
06 SH 9.2	Prince Creek	2.51	1.68	0.01	24.57	56.99	2.56	0.03	5.56	1.04	94.95	77	23
06 SH 14.4	Prince Creek	2.28	1.67	0.02	23.40	57.39	2.50	0.03	6.51	1.01	94.81	85	15
06 SH 15.1	Prince Creek	2.01	2.18	0.04	24.29	57.23	3.21	0.11	5.25	1.09	95.41	75	25
Bentonite													
* PFDV 17	Prince Creek	2.24	1.82	0.02	19.31	66.96	0.49	1.37	4.71	0.19	97.11	100	0
** 06 KKT-20.5	Prince Creek	0.19	1.84	0.01	20.67	60.78	0.07	1.91	6.04	0.21	91.72	100	0

* Geochemical analyses produced from XRF data reported in Salazar-Jaramillo et al. [14] ** Geochemical analyses produced from microprobe data reported in Salazar-Jaramillo et al. [14].

Table 2. Calculated chemical formulae for end-member 2:1 phyllosilicate mixtures.

Sample	Formation	Chemical Formulae
Paleosol		
06 SH 9.2	Prince Creek	(K _{0.26} Na _{0.39})(Al _{1.37} Fe _{0.33} Mg _{0.20} Ti _{0.06})(Si _{3.61} Al _{0.39})O ₁₀ (OH) ₂
06 SH 14.4	Prince Creek	(K _{0.23} Na _{0.32})(Al _{1.37} Fe _{0.36} Mg _{0.18} Ti _{0.06})(Si _{3.67} Al _{0.33})O ₁₀ (OH) ₂
06 SH 15.1	Prince Creek	(K _{0.33} Na _{0.31} Ca _{0.01})(Al _{1.33} Fe _{0.32} Mg _{0.26} Ti _{0.07})(Si _{3.61} Al _{0.39})O ₁₀ (OH) ₂

Chemical formulae were calculated from the oxide data reported in Table 1, based on the presence of twelve oxygen atoms and two hydrogen atoms in each unit-cell [26].

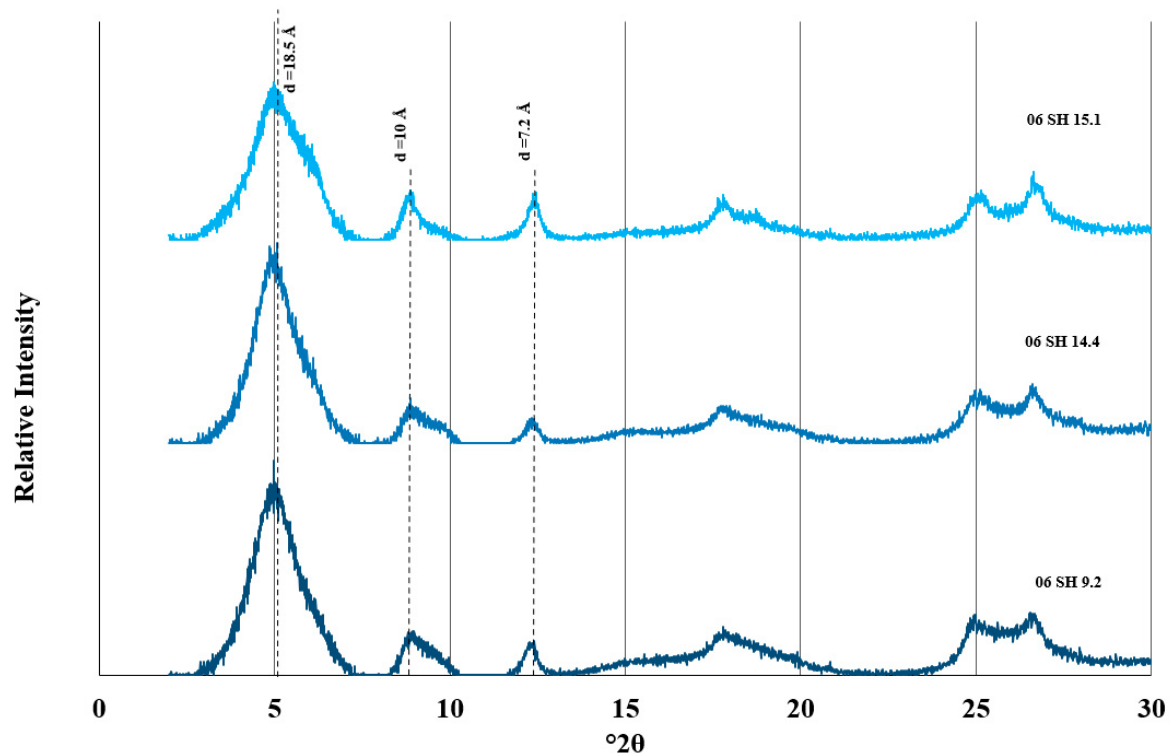


Figure 4. X-ray diffraction of glycerol-solvated clays in the <0.2 µm size fraction from paleosols sampled at site 06 SH in the Prince Creek Formation, shown in stratigraphic order. Spectra show the samples are dominated by smectite (001; 18.5 Å) with smaller amounts of illite/mica (10 Å) and kaolinite (001; 7.2 Å).

Oxygen fractionation factors for 2:1 phyllosilicates were calculated using the bond-model approach of Savin and Lee [36]. Hydrogen fractionation factors for 2:1 phyllosilicates were calculated using Equation (1), which was developed by Tabor and Montañez [20]:

$$1000\ln^D\alpha = -2.2 \times 10^6/T^2 - 7.7 + (2X_{Al} - 4X_{Mg} - 68X_{Fe}) \quad (1)$$

where X_{Al} , X_{Mg} , and X_{Fe} are the mole fractions of aluminum, magnesium, and iron present in the octahedral layer of the 2:1 phyllosilicate mineral.

The calculated hydrogen and oxygen fractionation factors for the 2:1 phyllosilicates were then weighted and combined with oxygen and hydrogen fractionation factors for kaolinite, proposed by Sheppard and Gilg [37] (Equations (2) and (3)):

$$1000\ln^{18}\alpha_{\text{kaolinite-water}} = 2.76 \times 10^6/T^2 - 6.75 \quad (2)$$

$$1000\ln^D\alpha_{\text{kaolinite-water}} = -2.2 \times 10^6/T^2 - 7.7 \quad (3)$$

The $\delta^{18}\text{O}$ of meteoric water reported for the bentonite samples by Salazar-Jaramillo et al. 2019 was calculated using the smectite fractionation factor proposed by Sheppard and Gilg [37]. This was chosen due to its monomineralic composition (pure montmorillonite) and close alignment to the Fe-rich end member of the fractionation curve [29]. To calculate the δD of meteoric water, this study calculated unique hydrogen fractionation factors by using chemical data reported by Salazar-Jaramillo et al. [29] and applying the equation developed by Tabor and Montañez [20] (Equation (1)).

A crystallization temperature of 6.3 °C was assumed for all samples based on estimates produced by Spicer and Herman [38]. This temperature has also been assumed by previous attempts to calculate the $\delta^{18}\text{O}$ of meteoric water [4,29,39].

The stable oxygen isotope composition of the pedogenic phyllosilicates from the paleosol samples ranges from 10.3‰ to 11.8‰ VSMOW with a reported analytical error of ± 0.2 ‰, while hydrogen ranges from −72‰ to −93 ‰ VSMOW with a reported analytical error of ± 4 ‰ (Table 3). When combined with their respective unique fractionation factors and an assumed crystallization temperature of 6.3 °C, the estimated $\delta^{18}\text{O}$ meteoric water values range from −17.2‰ to −18.8‰ VSMOW and the estimated δD meteoric water values range from −86‰ to −106‰ VSMOW (Table 3, Figure 5).

The stable hydrogen isotope composition of the clay fraction from the bentonite samples ranges from −131‰ to −172‰ VSMOW with a reported analytical error of ± 4 ‰. When combined with previous $\delta^{18}\text{O}$ data from Salazar-Jaramillo et al. [29], the respective unique hydrogen fractionation factors, and an assumed crystallization temperature of 6.3 °C, the estimated $\delta^{18}\text{O}$ meteoric water values average −23.6‰ [29] and the estimated δD meteoric water values range from −142‰ to −179‰ VSMOW (Table 3, Figure 5).

Table 3. Measured phyllosilicate oxygen and hydrogen isotope compositions, oxygen and hydrogen isotope fractionation equations, and estimated meteoric water isotopic compositions.

Sample	Formation	$\delta^{18}\text{O}_{\text{mix}}$ V-SMOW ($\pm 0.3\%$)	$\delta\text{D}_{\text{mix}}$ V-SMOW ($\pm 4\%$)	Wt. % Kaolinite ($\pm 5\%$)	^a $10^3 \ln^{18}\alpha_{2:1\text{-water}}$	^b $10^3 \ln^{\text{D}}\alpha_{2:1\text{-water}} =$ $-2.2 \times 10^6 T^{-2} +$	^c $10^3 \ln^{18}\alpha_{\text{mix-water}}$	^d $10^3 \ln^{\text{D}}\alpha_{\text{mix-water}} =$ $-2.2 \times 10^6 T^{-2} +$	^e $\delta\text{D}_{\text{meteoric water}}$ V-SMOW	^f $\delta^{18}\text{O}_{\text{meteoric water}}$ V-SMOW
<i>Paleosol</i>										
06 SH 9.2	Prince Creek	11.8	−3	23	$2.84 \times 10^6 \times T^{-2} - 7.03$	−18.51	$2.82 \times 10^6 \times T^{-2} - 6.96$	−13.40	−106	−17.2
06 SH 14.4	Prince Creek	10.3	−83	15	$2.83 \times 10^6 \times T^{-2} - 6.90$	−19.43	$2.82 \times 10^6 \times T^{-2} - 6.87$	−15.48	−95	−18.8
06 SH 15.1	Prince Creek	11.5	−72	25	$2.81 \times 10^6 \times T^{-2} - 7.00$	−18.28	$2.80 \times 10^6 \times T^{-2} - 6.93$	−12.97	−86	−17.3
<i>Bentonite</i>										
PFDV 17	Prince Creek	5.03	−136	0	$2.55 \times 10^6 \times T^{-2} - 4.05$	−19.38	$2.55 \times 10^6 \times T^{-2} - 4.05$	−19.38	−147	−23.6
PFDV 17 duplicate	Prince Creek	5.03	−132	0	$2.55 \times 10^6 \times T^{-2} - 4.05$	−19.38	$2.55 \times 10^6 \times T^{-2} - 4.05$	−19.38	−142	−23.6
06KKT-20.5	Prince Creek	4.96	−169	0	$2.55 \times 10^6 \times T^{-2} - 4.05$	−15.44	$2.55 \times 10^6 \times T^{-2} - 4.05$	−15.44	−177	−24.6
06KKT-20.5 duplicate	Prince Creek	4.96	−172	0	$2.55 \times 10^6 \times T^{-2} - 4.05$	−15.44	$2.55 \times 10^6 \times T^{-2} - 4.05$	−15.44	−179	−24.6

^a Calculated oxygen isotope fractionation equations between the <0.2 μm phyllosilicate and water. Fractionation equations were calculated using the bond-model data of Savin and Lee [36] in conjunction with the calculated chemical composition end-member 2:1 phyllosilicates presented in Table 2. ^b Calculated hydrogen isotope fractionation equations between the <0.2 μm phyllosilicate and water. Fractionation equations were calculated based on the molar fraction of Al, Mg, and Fe in the octahedral layer, as proposed by Gilg and Sheppard [40] and Tabor and Montañez [20]. ^c Calculated oxygen isotope fractionation equations between mixed phyllosilicate mineralogies in the <0.2 μm phyllosilicate fraction and water. Fractionation equations were calculated based on the molar fraction of oxygen contributed by kaolinite and 2:1 phyllosilicates in each sample [37]. ^d Calculated hydrogen isotope fractionation equations between mixed phyllosilicate mineralogies in the <0.2 μm phyllosilicate fraction and water. Fractionation equations were calculated based on the molar fraction of hydrogen contributed by kaolinite and 2:1 phyllosilicates in each sample [37]. ^e Calculated δD of meteoric water in equilibrium with the phyllosilicate mixture, assuming a crystallization temperature of 6.3 °C. ^f Calculated $\delta^{18}\text{O}$ of meteoric water in equilibrium with the phyllosilicate mixture, assuming a crystallization temperature of 6.3 °C.

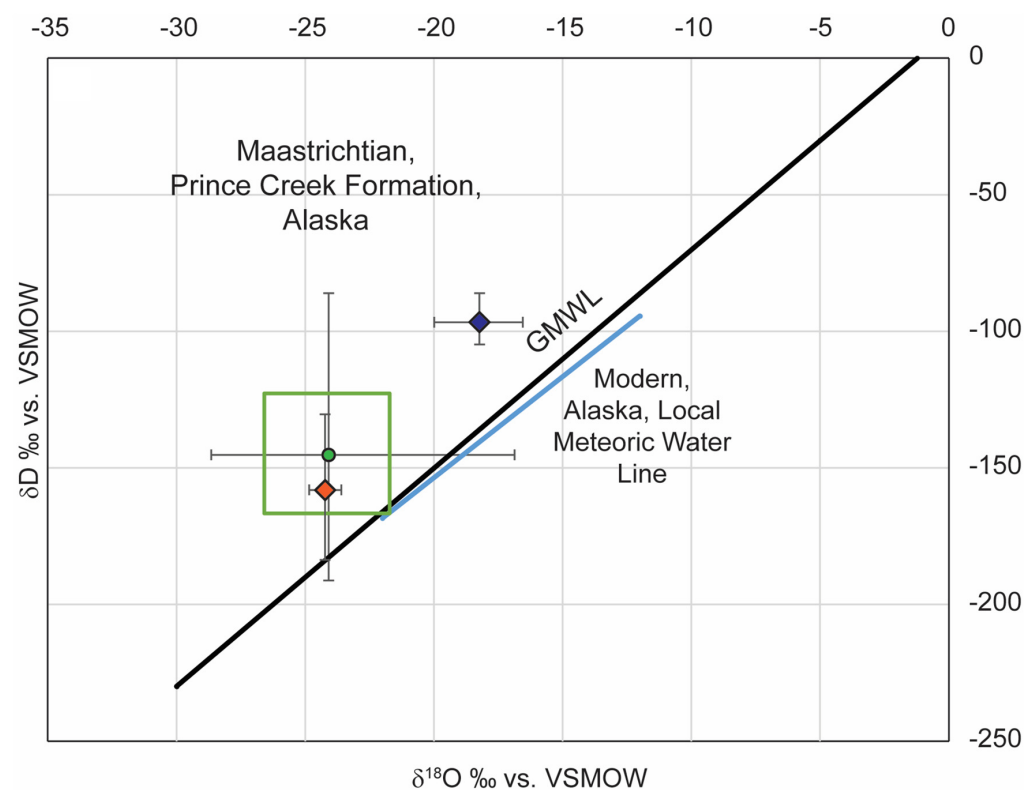


Figure 5. Hydrogen and oxygen isotope plot of estimated ranges of meteoric water isotope compositions from the Prince Creek Formation. The single dot and diamonds represent average composition, with the whiskers showing the full range of $\delta^{18}\text{O}$ and δD . Results are compared to the modern Global Meteoric Water Line (black line) and local meteoric water line for Alaska (blue line; Rozanski, K. et al. [41]). The green dot represents average $\delta^{18}\text{O}$ (estimated from dinosaur tooth enamel phosphate, pedogenic siderite, and pedogenic clays) and of δD (estimated from n-alkanes extracted from carbonaceous mudstones) presented in Ludvigson et al. [5]. The open green box surrounding the green dot is the 1 sigma of the dataset. The blue diamond represents the average $\delta^{18}\text{O}$ and δD estimated from pedogenic clays sampled from site 06 SH (this study). The orange diamond represents the average $\delta^{18}\text{O}$ and δD estimated from bentonites sampled from sites PFDV 17 and 06 KKT-20.5 (this study).

4. Discussion

4.1. Stable Isotope Composition of Phyllosilicates and Use as Paleoclimate Proxies

Materials collected from paleosols can contain a variety of components, including pedogenic clays, detrital and burial authigenic clays, and diagenetically altered pedogenic clays. In order to ensure a true paleoclimate signal is being recovered from analyzed paleosol materials, several conditions need to be met, including:

1. Phyllosilicates analyzed from a paleosol are authigenic.
2. Phyllosilicates have not been diagenetically altered since the time of formation.
3. The relationship between the oxygen and hydrogen isotope compositions of soil water is known.

In order to satisfy condition 1, paleosol samples analyzed in this study were separated and chemically treated in an effort to isolate a fraction thought to be the best representation of a mineral fraction derived from pedogenesis (see Section 2). The fine clay fraction, $<0.2\ \mu\text{m}$, is regarded as dominated by pedogenic clays in a paleosol profile [17–20]. Furthermore, mineralogical analyses show the $<0.2\ \mu\text{m}$ fraction is dominated by 2:1 smectite and I/S clay minerals with no detrital material such as quartz present. Therefore, we argue the $<0.2\ \mu\text{m}$ fraction is pedogenic in origin. The two bentonite samples are argued to have formed in situ as the result of weathering of primary ashfall deposits, resulting in a

monomineralic signature. Given its mineralogical composition, we are satisfied with the $<2\ \mu\text{m}$ size fraction for paleoclimate analyses.

Several lines of evidence are also presented to satisfy condition 2. Evidence presented by Burns et al. [42] suggests the Prince Creek Formation experienced relatively shallow burial depths of approximately 600 to 2000 m based on downhole vitrinite reflectance profiles and sonic-porosity logs along the Colville River. Vitrinite reflectance values ($n = 4$, avg. 0.3825; [43,44]) indicate a maximum burial temperature of $48\ ^\circ\text{C}$, which is too low to have caused substantial diagenetic changes in paleosol mineralogy [45]. This is also confirmed by studies conducted by Ludvigson et al. [5], which indicated organic matter sampled from the Prince Creek Formation had very low thermal maturity and the n -alkane biomarkers were suitable for δD and $\delta^{13}\text{C}$ isotopic analyses as their values had not been thermally altered. Additionally, there are well-preserved micromorphological features present in the paleosols [14] and the paleosols remain unlithified. Clay mineral analyses by Salazar-Jaramillo et al. [14] showed no ordering of illite during I/S interstratification analyses of paleosols in the Prince Creek Formation, suggesting little or no diagenetic transformations of illite [46]. Furthermore, the results presented in Figure 5 indicate reasonable oxygen and hydrogen isotopic values of estimated meteoric water that are within the range of previously published isotopic estimates of meteoric water from the Prince Creek Formation using alternative proxies, including pedogenic siderite, dinosaurian tooth enamel phosphates, and n -alkane biomarkers [5].

The bentonites sampled for this study are argued to be the products of in situ weathering of volcanic ash [14,29]. The $<2\ \mu\text{m}$ -size clay fraction from the bentonite samples contains pure montmorillonite with no I/S mixed layer clays, indicating that illitization in the Prince Creek Formation is purely a low-temperature pedogenic process [14].

The third condition is met with the assumption that processes that govern the global meteoric water line have been constant for well-developed soils throughout geologic history [41,47,48]. This, combined with uniquely derived oxygen and hydrogen fraction factors for each sample and crystallization temperatures, allows for calculations of meteoric water. The possibility does exist that the authigenic phyllosilicates collected from each paleosol may be composed of several different fractions crystallized under different climate regimes throughout the development of the soil. This scenario cannot be ruled out, and therefore soil-water $\delta^{18}\text{O}$ and δD estimates are considered to represent average paleoclimatic conditions that persisted throughout the interval(s) of pedogenesis that included phyllosilicate crystallization.

4.2. Implications of $\delta^{18}\text{O}$ and δD of Meteoric Water from Pedogenic Phyllosilicates

When the calculated $\delta^{18}\text{O}$ and δD of meteoric water are compared to the Global Meteoric Water Line, all the samples show a deuterium excess, plotting above the expected relationship (Figure 5). This deuterium excess measures between 7–46 per mil, with an average deuterium excess of 28 per mil. There is a significant difference in the estimated $\delta^{18}\text{O}$ of meteoric water between the paleosol (average -17.8‰ VSMOW) and bentonite samples (-24.1‰ VSMOW). This could be the result of geographic, orographic, or geochronological differences between the paleosol and bentonite localities. Regardless, these oxygen isotope estimates of meteoric water fall within previously reported data from paleosol siderites, dinosaur tooth enamel phosphate, and pedogenic clay minerals [4,5], and both the bentonite and paleosol localities record deuterium excess despite the large shift in oxygen isotopic composition of meteoric water.

Previous studies using oxygen isotopes from pedogenic siderites, dinosaur tooth enamel phosphate, and pedogenic clay minerals to calculate $\delta^{18}\text{O}$ of meteoric water and hydrogen isotopes from n -alkane biomarkers to calculate δD of meteoric water first reported an apparent deuterium excess of 40–60 per mil in the Cretaceous Prince Creek Formation [5]. However, the hydrogen isotopes measured from n -alkane biomarkers of plants living in an arctic environment with continuous photosynthetic activity and transpiration during the growing season could produce an apparent deuterium excess due to kinetic fractionation

that preferentially concentrates deuterium (^2H) over protium (^1H) in the leaf tissue [5]. Although it appears that part of the deuterium excess reported from *n*-alkane biomarkers may be the result of photosynthetic and transpiration fraction components given the larger reported deuterium excess in Ludvigson et al. [5], this study has confirmed the deuterium excess by measuring both oxygen and hydrogen isotopes from phyllosilicates, thus removing any photosynthetic or transpiration fractionation components of Arctic vegetation.

With the exclusion of photosynthetic/transpiration fractionation, Ludvigson et al. [5] proposed two other possible processes that could contribute to the deuterium excess, the first being changes in the zonal patterns of evaporation and precipitation at lower latitudes. This includes relationships between D-excess based on relative humidity, precipitation recycling, seasonality, air mass trajectory, and others [49–54]. The second proposed process is the potential influence of hydrogenotrophic methanogenesis occurring in Cretaceous soils. Carbon isotopic data from paleosol siderites collected at localities throughout the Prince Creek Formation have $\delta^{13}\text{C}$ values that are characteristic of environments in which hydrogenotrophic methanogenesis is the dominant anaerobic CH_4 -producing pathway [5,55,56]. During hydrogenotrophic methanogenesis, the preferential uptake of ^1H can enrich the source water in deuterium without impacting the oxygen isotopic composition [57–59]. In order to evaluate the degree of influence of hydrogenotrophic methanogenesis on the deuterium excess, the next step would be to use previously collected data to quantitatively evaluate methane fluxes from Cretaceous Arctic soils. This would be further aided by additional phyllosilicate stable isotopic data from Cretaceous paleosols to determine the extent both temporally and geographically of the deuterium excess persisting during the Cretaceous and aid in the development of new climate models.

5. Conclusions

Our data confirm the presence of an apparent deuterium excess of Cretaceous Arctic paleoprecipitation first reported by Ludvigson et al. [5]. Results of stable oxygen and hydrogen isotopic analyses combined with elemental and chemical data of pedogenic clays reveal an average $\delta^{18}\text{O}$ of paleoprecipitation of -20.3‰ VSMOW and average δD values of -122‰ VSMOW. The data produced from three paleosol samples and two bentonite samples reveal a deuterium excess ranging from 7 to 46 per mil with an average reported deuterium excess of 28 per mil. These results exclude any influence from photosynthetic and transpiration fractionation components in Arctic vegetation that could plague previous attempts to define the deuterium excess using *n*-alkane biomarker data. This leaves two processes that could explain the observed deuterium excess: (1) mass-balance changes in zonal patterns of evaporation and precipitation at lower latitudes, and/or (2) concentration of ^2H in the groundwaters of methane-emitting Arctic soils. Further research is needed to constrain the influence of each of these processes and to understand the extent to which both temporally and geographically the deuterium excess was present during the Cretaceous and how this knowledge can aid future climate modeling.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/geosciences13090273/s1>. Table S1 Raw X-ray diffraction data for $<0.2\text{ }\mu\text{m}$ fraction of pedogenic phyllosilicates from locality 06SH and the $<2\text{ }\mu\text{m}$ size fraction for bentonite samples from localities PFDV 17 and 06KKT. Table S2 Bond model equations used to calculate 2:1 end-member oxygen isotope fractionation for pedogenic phyllosilicates from locality 06SH.

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