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Abstract

Decades of space exploration have shown that surface environments on Mars were habitable billions of years ago. Ancient, buried surface environments, or paleosols, may have been preserved in the geological record on Mars, and are considered high-priority targets for biosignature investigation. Studies of paleosols on Earth that are compositionally similar to putative martian paleosols can provide a reference frame for constraining their organic preservation potential on Mars. However, terrestrial paleosols typically preserve only trace amounts of organic carbon, and it remains unclear whether the organic component of paleosols can be detected with Mars rover-like instruments. Furthermore, the study of terrestrial paleosols is complicated by diagenetic additions of organic carbon, which can confound interpretations of their organic preservation potential. The objectives of this study were a) to determine whether organic carbon in ~30-million-year-old Mars-analog paleosols can be detected with thermal and evolved gas analysis, and b) constrain the age of organic carbon using radiocarbon (^{14}C) dating to identify late diagenetic additions of carbon. Al/ Fe smectite-rich paleosols from the Early Oligocene (33 Ma) John Day Formation in eastern Oregon were examined with a thermal and evolved gas analyzer configured to operate similarly to the Sample Analysis at Mars Evolved Gas Analysis (SAM-EGA) instrument onboard the Mars Science Laboratory *Curiosity* rover. All samples evolved CO_2 with peaks at ~400 °C and ~700° C from the thermal decomposition of refractory organic carbon and small amounts of calcium carbonate, respectively. Evolutions of organic fragments co-occurred with evolutions of CO_2 from organic carbon decomposition. Total organic carbon (TOC) ranged from 0.002 - 0.032 ±

0.006 wt. %. Like modern soils, the near-surface horizons of all paleosols had significantly higher TOC relative to subsurface layers. Radiocarbon dating of four samples revealed an organic carbon age ranging between ~6,200 – 14,500 years before present, suggesting there had been inputs of exogenous organic carbon during diagenesis. By contrast, refractory carbon detected with EGA and enrichment of TOC in near-surface horizons of all three buried profiles were consistent with the preservation of trace amounts of endogenous organic carbon. This work demonstrates that near-surface horizons of putative martian paleosols should be considered high priority locations for *in-situ* biosignature investigation and reveals challenges for examining organic matter preservation in terrestrial paleosols.

1. Introduction

Paleosols are ancient, buried soils that are commonly lithified into sedimentary rocks. Terrestrial paleosols are a geological record of the atmospheric composition, climate, topography and organisms present before soil burial [1]. On Mars, paleosols may have formed in sediments such as basaltic sand or volcanic ash that were subject to subaerial weathering by surface waters [2] and were subsequently buried and preserved in the geological record. Orbital remote sensing of the global martian surface has detected minerals within Noachian-age (4.1-3.7 Ga) layered sedimentary rocks that are consistent with precipitation-driven pedogenic weathering of mafic sediments [3–5]. Noachian sedimentary rocks with spectral signatures of subaerial weathering have been detected in thousands of locations across the surface of Mars. One hypothesis is that these deposits are paleosols [3] which are the common products of pedogenic alteration followed by burial. Mounting evidence of global-scale aqueous alteration of the Martian surface during the Noachian [3,6] suggests that pedogenesis could have been a critical process early in the planet's history. As such, paleosols have been recently named a high priority location for biosignature investigation [7] and Mars Sample Return [8], but the biosignature preservation potential of paleosols with Mars-like mineralogy remains poorly constrained [9].

On Earth, soils are highly habitable environments. Modern soils are teeming with microbial biomass, often averaging 10^{10}–10^{11} bacterial cells and 10^3 and 10^4 species per gram of soil [10]. Modern soils also contain more organic carbon than global vegetation and the atmosphere combined [11,12]. Similarly, Earth's oldest soils also appear to have been highly habitable environments. Many Precambrian (> 541 Ma) paleosols contain organic carbon and other chemical biosignatures that are thought to be remnants of surface biomass [13–16]. Furthermore, Archean (> 2 Ga) paleosols contain filamentous organic carbon and organo-mineral complexes possibly derived from cyanobacterial mats on the soil surface [17,18].

Many terrestrial paleosols preserve only trace amounts of organic carbon, especially compared to modern soils, marine shales, and lacustrine rocks [1]. Organic carbon losses during diagenesis can reduce the organic carbon content of paleosols by up to two orders of magnitude relative to their modern soil counterparts [13]. Severe losses of organic carbon are most common in paleosols that originally formed under oxidizing, well-drained conditions [19]. In general, oxidized paleosols typically contain only low amounts (< 0.1 wt. %) of organic carbon [13]. Diagenetic losses of organic carbon in oxidized terrestrial paleosols poses major challenges for detection of chemical and isotopic biosignatures preserved within the organic matter fraction. However, this is not the case for all paleosols. Those that originally formed under reducing conditions, such as Permian (~250 Ma) Histosols (poorly drained organic soils), preserve organic carbon with abundances > 25 wt. % [20], implying that redox state before burial may provide a first-order control on the preservation of organic carbon in ancient soils [21].

An additional concern for the study of terrestrial paleosol organic matter is that diagenetic alterations ranging from groundwater alteration to precipitation-driven leaching of dissolved organic carbon can result in the addition of exogenous organic molecules, so caution is necessary for interpreting whether the organic fraction has indeed been "preserved" over geological time scales. In other words, terrestrial paleosols can be contaminated by organic molecules that were not original to the soil, thereby complicating efforts to interpret their biosignature preservation potential.

One way to constrain the biosignature preservation potential of putative paleosols on Mars is to examine the organic fraction of paleosols from Earth that share compositional and morphological similarities to layered sedimentary rocks on Mars. Examination of oxidized paleosols with Mars-like mineralogy can help determine if low amounts of organic molecules within natural pedogenic mineral matrices can be detected with Mars flight-analog instruments. Furthermore, cosmogenic nuclide dating of these analog paleosols can also identify potential diagenetic additions of organic carbon.

This study builds on and combines previous results from an established Mars-analog paleosol sequence (**Broz et al, 2021, in review).** The focus here is to determine if organic molecules in oxidized paleosols are detectable with Mars flight-analog instrumentation, and to determine if there have been post-depositional additions of exogenous organic carbon. The objectives of this study were a) to determine whether organic carbon in ~30-million-year-old Mars-analog paleosols can be detected with thermal and evolved gas analysis, and b) constrain the age of organic carbon using radiocarbon (^{14}C) dating to identify late diagenetic additions of carbon.

1.1 Paleosols at John Day Fossil Beds National Monument in eastern Oregon, USA

Eocene and Oligocene (42-28 Ma) sedimentary rocks at John Day Fossil Beds National Monument in eastern Oregon are a thick sequence of volcaniclastic paleosols which altogether span over 400 meters of vertical stratigraphy. [22–25]. The paleosol sequence contains over 500 clay mineral-rich (30-95 wt. %) paleosols formed over ~15 Myr through the Eocene-Oligocene boundary (Figure 1) [23,26]. Each of the individual profiles formed from pedogenic alteration of andesitic to rhyodacitic volcanic ash and/or tuff, followed by rapid burial via emplacement of an additional layer of tephra onto the soil surface. This process of soil formation and burial repeated for nearly 15 million years, and as such, the paleosol sequence provides a unique record of Cenozoic climate change in eastern Oregon. Changes in mineralogy throughout the paleosol sequence reflect the Eocene-Oligocene cooling and drying of the climate [27].

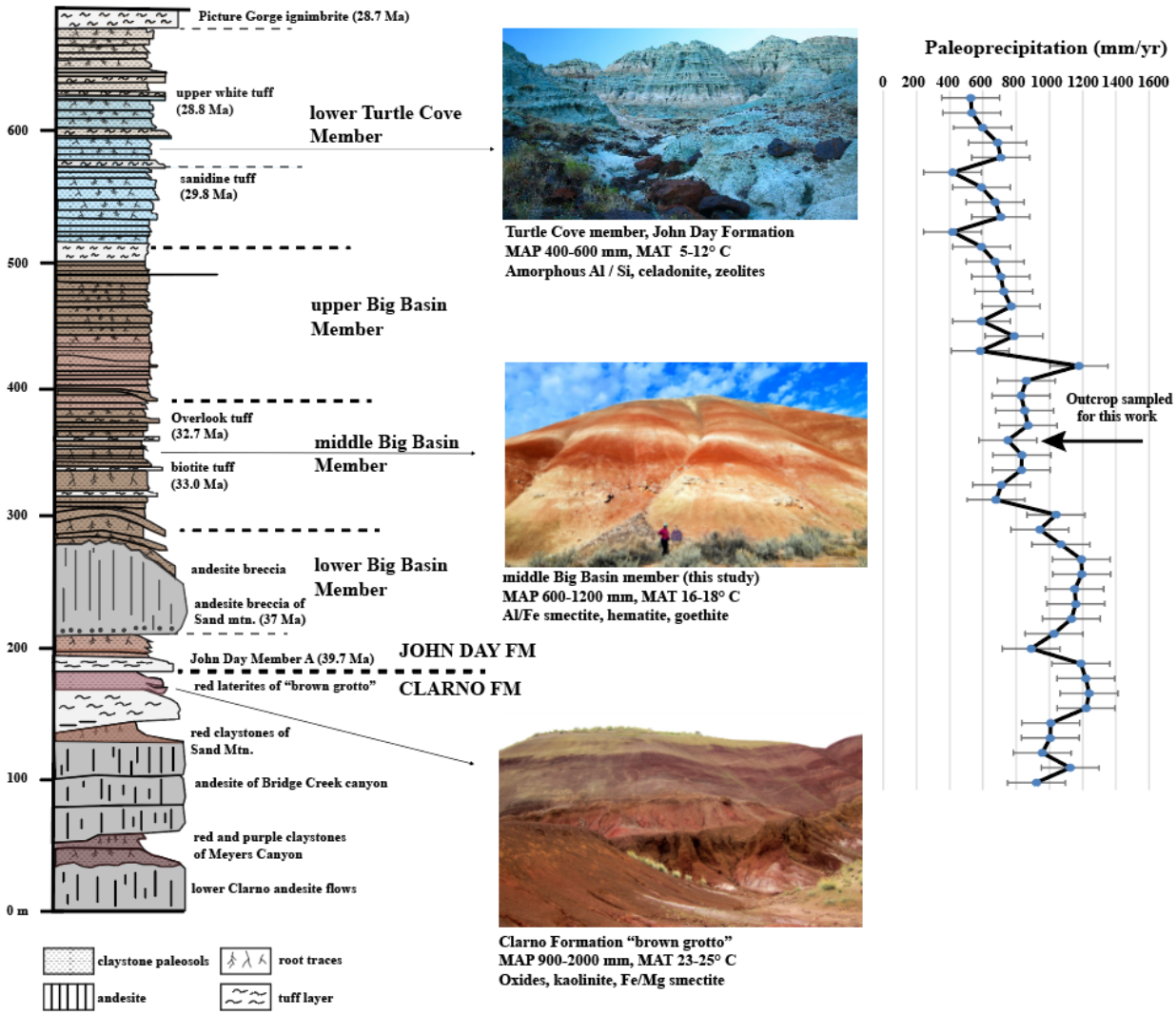

Figure 1. A sequence of Eocene and Oligocene (42-28 Ma) volcaniclastic paleosols in the Clarno and John Day Formations, John Day Fossil Beds National Monument (after [22] and [28]). Declining precipitation through the Eocene/Oligocene boundary is inferred from the mineralogy of paleosols from the Clarno and John Day Formations. Paleoprecipitation estimates are from [28] who used an equation relating molecular weathering ratios (Bases/alumina [$CaO + MgO + Na_2O + K_2O / Al_2O_3$] to mean annual precipitation from a database of modern U.S soils (r=0.79, standard error = 179 mm). The stratigraphic level of paleosols analyzed in this work are indicated (black arrow, far right).

The Eocene (42-39 Ma) Clarno Formation represents the lowest and oldest unit of the Oregon paleosol sequence. The basal Clarno Formation is characterized by andesite flows interspaced with severely weathered paleosols with accumulations of kaolinite, Fe/Mg smectite and oxides (Oxisols and Ultisols in US soil taxonomy) which indicate tropical weathering conditions in the middle to late Eocene [23]. A particularly striking exposure of the late Eocene Clarno Formation at the "Brown Grotto" area of the Painted Hills is characterized by thick (~2-6 meter), repeated profiles of deeply weathered lateritic paleosols (Figure 1, bottom) that are similar to modern soils from Southern Mexico and Central America in climates that are subtropical and humid [23]. Stratigraphically above the Clarno Formation, the early Oligocene (~33 Ma) Big Basin Member of the John Day Formation is characterized by less intensely

weathered paleosols (Alfisols and Inceptisols) that are rich in Al and Fe smectites such as nontronite and montmorillonite (Figure 1, middle). This middle unit represents a dramatic cooling and drying of the climate through the Eocene-Oligocene boundary. Overlying this unit of the paleosol sequence is the mid-late Oligocene (~28 Ma) Turtle Cove Member of the John Day Formation (Figure 1, top). The brown, green and celadon-colored paleosols of this unit are minimally weathered Aridisols (desert soils) and Andisols (amorphous-rich volcanic soils). Paleosols in this unit are characterized by accumulations of amorphous and nanocrystalline materials (e.g., allophane and imogolite), pedogenic calcite, and diagenetic celadonite [24]. There is a dramatic reduction in smectite content and absence of kaolinite which is consistent with weathering under a semi-arid to arid climate regime [27]. Finally, the entire paleosol sequence is capped by approximately 300 vertical meters of flood basalts from the Miocene (~16 Ma) Columbia River Basalt Group. Based on these mineralogical transitions, the Eocene paleosols with accumulations of kaolinite and oxides appear to reflect a subtropical and humid climate, while accumulations of nanophase aluminosilicates and amorphous phases in overlying paleosols indicate stepwise and cooling and drying during the late Oligocene [23].

1.2 Pedogenic weathering on early Mars and comparisons to terrestrial paleosols

From a global perspective, orbital remote sensing from Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (OMEGA) and the Compact Reconnaissance Spectrometer at Mars (CRISM) instrument onboard the Mars Reconnaissance Orbiter provide the most compelling evidence of extensive pedogenic-like alteration across the surface of Mars. Potential weathering sequences have been detected in hundreds of locations across Noachian-age terrains, wherever these ancient rocks are not obscured by dust, sand, or overlying strata [3,4]. OMEGA and CRISM have collectively gathered visible and near-infrared (VNIR) reflectance spectra of sedimentary deposits at Mawrth Vallis, Oxia Planum, Nili Fossae and other altered Noachian terrains. Some of these deposits, such as layered outcrops at Mawrth Vallis, have spectral and stratigraphic similarities to terrestrial paleosol sequences [24,26,29–31]. Spectral refinements for CRISM images (e.g., [32]) are allowing for identification of smaller-scale hydrated mineral deposits at Mawrth Vallis that facilitate a detailed reconstruction of possible geochemical environments on early Mars [33].

Mawrth Vallis

Previous work identified compositional and morphological similarities between the eastern Oregon paleosol sequence and layered outcrops at Mawrth Vallis [24,29,34,35]. The compositional stratigraphy at Mawrth Vallis has been interpreted as a paleosol sequence [24] or a deep weathering profile [6]. Here, a ~200 m stack of layered sedimentary rocks has spectral signatures consistent with pedogenic-like alteration of mafic sediments[36]. The basal Fe/Mg smectite unit at Mawrth Vallis is dominated by spectral signatures of Fe/Mg smectite and is consistent with subaerial alteration under a warm and wet climate [31,37]. This basal unit transitions upward into a thin, ferrous-bearing clay unit that could have resulted from reducing conditions during subaerial weathering. This unit is overlain by layered rocks containing minerals consistent with formation in acidic and evaporitic geochemical settings, inferred from spectral signatures consistent with mixtures of smectite and jarosite (the “doublet’ spectral feature) [33,38,39] . Stratigraphically higher, layered rocks with signatures of Al and Fe smectite are consistent with pedogenic weathering of volcaniclastic sediments under a semi-arid climate. Finally, the uppermost layers are characterized by accumulations of poorly consistent aluminosilicates, suggesting minimal or cool-

climate alteration, which may represent the terminus of warm and wet conditions on early Mars [33]. The entire sequence is then capped by dark-toned sands and/or lava flows. One hypothesis to explain the stratigraphy at Mawrth Vallis is that it may represent the cooling and drying of the Martian climate during the mid to late Noachian [33,40]. Similarly, the Oregon paleosol sequence represents a transition from warm and wet conditions. The intensely weathered basal Clarno Formation paleosols transition upward into less-weathered semi-arid paleosols of the middle Big Basin Member, which contains both oxidized (red, brown) and reduced (yellow, black) paleosols. These are subsequently overlain by minimally weathered paleosols of the Oligocene Turtle Cove Member with accumulations of unweathered volcanic glass, amorphous colloids, calcite and hydrated silica which are thought to represent the terminus of warm and wet climate conditions in eastern Oregon. Terrestrial paleosols at the analog site have therefore been considered analogous to dioctahedral clay sequences on Mars. Layered rocks at Mawrth Vallis currently stand as the best example of a putative paleosol sequence on Mars, but other locations, such as Jezero Crater, also show VNIR spectra consistent with subaerial alteration of mafic sediments.

Jezero Crater

Spectral signatures of Al-bearing clay minerals and/or silica deposits that could have formed in subaerial environments were detected approximately 3 km from the Perseverance rover landing site at Jezero Crater. Across Jezero's western delta and northern fans, there are strong and ubiquitous orbital detections of Al-bearing clay minerals and/or silica that could be either detrital or authigenic in origin [41]. The strongest signatures across the western delta are associated with features that resemble point bar deposits and are consistent with formation in subaerial and/or seasonally waterlogged paleoenvironments [41]. If authigenic in origin, these deposits could be subaerial paleoenvironments and include individual paleosol profiles. If targeted for *in-situ* examination by *Perseverance* rover, these deposits could provide critical information about the climate and duration of delta activity at Jezero Crater [41]. Similarly, terrestrial paleosols examined in this study formed from subaerial weathering of volcaniclastic sediments across alluvial terraces and have accumulated abundant Al clay minerals and amorphous silica [22,23]. The mounting evidence of pedogenic-like processes on Mars emphasizes the need for study of paleosols from Earth to aid in future investigation and interpretation of sedimentary rocks on Mars.

Terrestrial paleosols: Mineralogy and diagenesis

The present study focuses on three paleosol profiles from the early Oligocene (33 Ma) Big Basin Member of the John Day Formation (Figure 1, middle). A detailed analysis of mineralogy and diagenetic alteration of samples taken from paleosol profiles was previously performed **(Broz et al, 2021, in review**). X-ray diffraction evolved gas analysis and visible-near-infrared spectroscopy revealed high abundances (> 80 wt. %) of montmorillonite and nontronite with lesser amounts of hematite, zeolites, gypsum, and hydrated silica. Diagenetic alterations previously observed in these samples included a) "burial gleization" of near-surface horizons, e.g., microbial reduction of Fe^{3+} in near-surface horizons of paleosols, possibly during anaerobic decay of organic matter; b) dehydration of ferrous oxyhydroxides (goethite) to form fine-grained hematite; c) zeolitization to form clinoptilolite, possibly resulting from diagenetic recrystallization of a poorly crystalline smectite; and d) significant mechanical compaction to approximately 70% of the original soil thickness **(Broz et al., 2021, in review).**

Previously, there was no effort to examine the organic component of these paleosols, and the resulting influence of diagenesis on the organic fraction of Mars-analog paleosols is poorly understood. Examination of terrestrial paleosols with Mars flight-analog instruments such as evolved gas analysis

allows for a detailed characterization of the organic fraction (discussed below). This can help ascertain if diagenesis has resulted in severe losses of organic carbon in Mars-analog paleosols, and determine if organic carbon that remains is detectable with analytical techniques relevant to Mars exploration.

1.3 Sample Analysis at Mars (SAM) instrument onboard *Curiosity* Mars Rover

The overall goal of the SAM instrument was to assess the potential for past habitability by characterizing the martian chemical and isotopic composition of the atmosphere and volatile-bearing surface materials [42]. The SAM instrument was integral in providing an understanding of organic materials and phases undetectable by CheMin (e.g., amorphous phases, low abundance phases). SAM heats scooped or drilled rock samples from ~30 – 870° C at 35° C min^{-1}. Evolved gases produced from the thermal decomposition of volatile-bearing phases were analyzed by a quadrupole mass spectrometer (QMS), gas chromatograph columns for GCMS, or a tunable laser spectrometer (TLS) [42]. In evolved gas analysis (SAM-EGA) mode, SAM detected bulk gas evolution, whereas in gas chromatography-mass spectroscopy (SAM-GCMS) mode, SAM performed molecular separation and identification of organic molecules [42,43]. This study focused on SAM-EGA, so SAM-GCMS will not be further discussed. A comprehensive discussion on how organic molecules are detected with SAM- GCMS mode can be found in [42] and [44].

Evolved gases and their release temperatures detected by SAM-EGA provide constraints on the mineralogy and organic content of samples in Gale Crater [43,45–47]. The thermal decomposition of solid samples during SAM-EGA occurs during ramped heating, which releases volatile gases including CO_2, CO, hydrocarbons, and organic fragments (i.e., CH_2, CH_3, C_2H_2 and others) that are detected by the QMS. The intensity (relative abundance) of volatile release is plotted as a function of the release temperature, generating a time and temperature series of data for each volatile gas release. The volatile release peak temperature during sample decomposition depends on the thermodynamics of the reaction and can be used to constrain the composition of minerals and organic carbon in the sample [45], as well as to identify possible associations between minerals and organics [48].

Additional future missions to Mars will also employ EGA-like analysis to search for organic molecules. The Mars Organic Molecule Analyzer (MOMA) onboard European Space Agency's ExoMars 2022 *Rosalind Franklin* rover will use pyrolysis gas chromatography-mass spectrometry (GCMS) and laser desorption spectroscopy to search for biosignatures on Mars. Volatile gases thermally evolved from solid samples in the instrument oven will be separated by the GC and then analyzed individually with the MS [49] as is the case with SAM-GCMS, though MOMA will combine pyrolysis with laser desorption mass spectrometry, a less destructive technique that allows for identification of large intact molecules and polar compounds. The *Rosalind Franklin* rover will land at Noachian –age (3.9 Ga) Oxia Planum which appears to be a westward extension of the lower parts of the stratigraphy observed at Mawrth Vallis [50,51]. Like Mawrth Vallis, strong and ubiquitous spectral signatures of dioctahedral Al-rich clay minerals overlying Fe/ Mg clay minerals suggests Oxia Planum may host remnants of a thick (~200 m) deep weathering profile or paleosol sequence that the rover could encounter during its primary mission.

1.4 Previous detections of organic carbon with SAM-EGA

Organic carbon has been detected in sedimentary rocks at Gale Crater with the SAM instrument using both QMS and GCMS [44,46,47,52]. Abundances of reduced carbon were very low (< 1 wt. %) and restricted to three samples (Cumberland [CB], Confidence Hills [CH], and Mojave [MJ]). Though all CO_2 and CO detected to date is consistent with oxidized organic compounds, it is possible that contamination

by the SAM-GCMS derivatization agent MTBSTFA could have resulted in these peaks. However, high-temperature (> 600° C) CO releases were consistent with endogenous oxidized martian organics. Additionally, chlorinated hydrocarbons (chlorobenzene [m/z 112], ~30 pmol) in the Cumberland drill sample and organo-sulfur compounds including thiophenes and thiols (~90 nmol) in the Mojave and Confidence Hills drill samples were identified in ~3.5 Ga mudstone, but the sources of these organic molecules was not constrained [43,47]. Observation of dichlorobenzene and trichloromethylpropane in the CB sample at Yellowknife Bay could have been produced by chemical reactions between organic molecules and oxychlorines occurring in the SAM ovens. These chlorinated hydrocarbons could have been derived from organic carbon, either from an endogenous martian source and/or from meteoric infall [44,53]. Though organic carbon has been detected by SAM in numerous sedimentary deposits at Gale Crater, the source(s) of the organic molecules are not yet fully understood. Recent work has shown that organic salts such as Ca/ Mg oxalates and/or Ca/Mg acetates may be present in abundances of 1-2 wt. % in modern eolian sediments (Rocknest sample) as well as in ancient sedimentary rocks at Gale Crater (JK and CB samples) [54]. The accumulation of organic salts in eolian deposits suggests they may be a component of regional or global dust on Mars [54].

1.5 Thermal analysis of organic carbon in modern soils and paleosols

Thermal analysis techniques similar to SAM-EGA have been employed for understanding the nature and stability of organic matter in modern terrestrial soils, though at present there are only limited studies of paleosols [30,39]. Past work has shown the thermal decomposition of organic carbon (C) is related to organic carbon composition and particle size in both modern soils [55,56] and paleosols [57]. In modern soils there is an inverse relationship between particle size and proportion of plant biopolymer-derived organic carbon (carbohydrates, lignin) and C from microbial biomass and/or metabolites (protein, aliphatic C) [55]. Larger particle sizes are predominantly associated with labile remains of plant biopolymers, while the clay-size fraction hosts highly recalcitrant (stable) C compounds which include microbial biomarkers of n-C_{14} alkanoic acid [58]. Organic C associated with the clay-size fraction thermally decomposes at higher temperatures (~ 400 - 450° C) compared to C associated with larger size fractions (~150° - 350° C) [57,59]. Thus, the thermal stability of organic carbon associated with clay minerals and/ or persisting as microaggregates reflects increased resistance to oxidation [56] which is one factor among many contributing to stabilization over geological time scales[60].

1.6 Preservation of organic matter in Archean paleosols

Life on Earth has a long history with soil, and some of the oldest biosignatures of life on land are found in paleosols [61–63]. Transmission electron microscopy of the clay size fraction of an Archean (2.6 Ga) paleosol from South Africa showed organic carbon in association with surfaces and interlayer spaces of clay minerals, possibly derived from cyanobacterial mats [17]. An Archean (~2.8 Ga) paleosol from Western Australia contained filamentous, carbon-rich microstructures with regular banding and consistent shape and size [18]. These structures, which contain up to 0.1 wt. % carbon, have been interpreted as putative microfossils of methanogenic microbial mats living on the soil surface[18]. In both Archean paleosol examples, organic carbon was most concentrated in near-surface horizons. Near-surface layers of other Archean paleosols contain additional biosignatures such as isotopically light carbon [64] and sulfur [65]. Early Archean (3.7 Ga) metasedimentary deposits from the Isua supercrustal belt in Greenland which have been considered putative paleosols [64] have $\delta^{13}C_{organic}$ of -24.2 to -27.4 ‰ and show mineralogical

evidence of subaerial acid-sulfate weathering, including abundant crystals of ripidolite interpreted to be pseudomorphs of the sulfate mineral kieserite. These appear to be grouped into a gypsic (By) horizon within a matrix of bertherine schist. Bertherine, a phyllosilicate in the serpentine group, is thought to have formed from metamorphism of a trioctahedral phyllosilicate like saponite [64], thus implying that early Archean Earth surface weathering may have been comparable to late Noachian surface weathering on Mars. The putative Greenland paleosol has been tortured by metamorphism to amphibolite facies and thus any biogenic source for the isotopic fractionation and/or discrimination should be interpreted with caution. In any case, terrestrial paleosols provide compelling evidence of life's ancient relationship with surface environments on Earth, which appears to extend well back into the Archean [17,18,61,66,67].

Though there appear to be similarities between the modes of weathering on the Early Earth and Mars (e.g., anoxic acid sulfate weathering), the use of Archean paleosols as Mars analogs is complicated by severe diagenetic overprinting that often obscures the original mineralogy and organic content of these ancient land surfaces. Younger, less altered paleosols are more suitable candidates for comparisons with putative paleosols on Mars, yet, as discussed below, these are also imperfect Mars analogs.

1.7 Limitations of Cenozoic Mars-analog paleosols

The Eocene-Oligocene (42-28 Ma) eastern Oregon paleosols are an incomplete Mars analog due to several fundamental differences. First, the source of organic carbon within the paleosols is primarily from microbial and/or plant biomass and represents a complex consortium of life above and within the soil profile. Therefore, the organic carbon component of these paleosols and the resulting preservation and degradation mechanisms may not be the same on Mars, but it is possible that putative paleosols at Mawrth Vallis have mineralogy analogous to terrestrial paleosols and thus have a similar mineralogical control on the fate of organic carbon. Nevertheless, the purpose of this study was not to determine the "inputs" of organic carbon in paleosols, but rather to observe the "outcomes" of life on land, e.g., if and how organic carbon is preserved across ancient surface environments.

A principal concern of this work was the assumption that all organic carbon in any lithified paleosol sample was endogenous (e.g., deposited during soil formation) and has subsequently been preserved for ~30 million years. This assumes no contribution from modern plants or microbes or diagenetic alterations which add exogenous organic carbon. For example, modern soils developing atop paleosol outcrops could have delivered exogenous organics to the underlying paleosols.

Another concern is the suite of common diagenetic alterations which alter paleosols, including zeolitization, illitization and burial decomposition of organic carbon which appear to have affected paleosols examined here to some degree (see Results). However, these are all are assumed to remove endogenous organic carbon [1], not deliver it. We tested the hypothesis that organic carbon is endogenous to paleosols by radiocarbon dating bulk samples (see Methods).

Large differences in age (Oligocene, [33 Ma] versus Noachian [4.1-3.7 Ga]) also have implications for diagenesis. John Day paleosols have experienced a range of minor to moderate diagenetic alteration including illitization of smectite, zeolitization and celadonization all resulting from alteration to clinoptilolite facies [9,23], but it is currently unclear if similar diagenetic alteration has affected potential paleosol sequences on Mars. There are also differences in the oxidation state of the atmosphere during subaerial weathering. The Oregon paleosols formed under a thoroughly oxidizing atmosphere but at present the oxidation state of an early Mars atmosphere is not well constrained [68], However, leaching of Fe^{2+} in putative martian paleosols at Mawrth Vallis has been inferred from spectral weathering indices

and is consistent with an anoxic, reducing atmosphere during the Noachian [6]. Lastly, there are most likely differences in the pH of fluids participating in hydrolytic weathering of volcaniclastic sediments. John Day paleosols are thought to have formed by pedogenic weathering with circumneutral-pH fluids, but subaerial alteration on Mars could have preceded with acidic, H_2SO_4 and HCl-rich surface waters as a result of volcanic outgassing of H_2 and SO_2 [2,6]. Despite these significant differences, the paleosol sequence from eastern Oregon offers a natural example to determine if organic carbon can be detected with thermal and evolved gas analysis techniques similar to SAM-EGA.

2. Methods

2.1 Sample collection

The paleosols examined in this study were collected from the Painted Hills Unit of the John Day Fossil Beds National Monument in eastern Oregon, USA. A previous study **(Broz et al., 2021, in review)** determined the mineralogy and diagenetic alteration of the same set of samples examined in the present study. Samples from three individual paleosols in vertical succession were collected approximately 7 km SW of the entrance to the Painted Hills unit of the John Day Formation (44.631105, -120.213107), in the Middle Big Basin Member of the John Day Formation, approximately 6 m above the local Eocene-Oligocene boundary **(Figure 2).** Samples were chosen from this location because they were previously examined for mineralogy and diagenesis, and because $^{40}Ar/^{39}Ar$ dating of volcanic tuffs at this stratigraphic level in the section allow for a constrained age of 33.0 +/- 0.10 to 32.7 +/- 0.03 Ma (Biotite Tuff and Overlook Tuff, respectively) [22].

To minimize contamination from modern organic carbon during sampling, all loose surface soil and saprolite was removed until the lithified, brick-like unweathered paleosol surface was exposed. Below the saprolite of the thin (~30 cm) modern soil, all three paleosols were lithified claystone. Sample collection began by trenching with a rock hammer to a 50 cm depth into (perpendicular to) the lithified paleosol sequence. Next, a set of samples were gathered down a vertical transect at approximately 10 cm intervals, similar to sampling the horizons of a modern soil, but with rock hammer. Large (~1 kg) lithified blocks of claystone were broken out of the outcrop and placed into aluminum foil (ashed at 550° C before use) to ensure subsampling for thermal analysis had sufficient volume to expose fresh sample surface (e.g., no weathered surfaces were selected for analysis). For thermal analysis and radiocarbon dating, small (5-8 g) subsamples were acquired from the inside of bulk lithified samples with steel chisels that were previously ashed at 550° C to remove organic contaminants. These subsamples were then ground to < 0.02 mm using an agate mortar and pestle (ashed at 550° C before use) and stored in glass vials (all ashed at 550° C) prior to thermal analysis and radiocarbon dating.

No vegetation was present within ~30 m of the sampled paleosol sequence **(Figure 2),** likely because the "popcorn" weathering of the smectite-rich modern soil appears to inhibit plant germination and growth**.** The Munsell color and qualitative calcareousness of samples were described during collection **(Figure 3).** The three paleosols sampled were a red Alfisol ("Luca" pedotype from [23]), a tan Entisol ("Kskus" pedotype), and a brown Inceptisol ("Ticam" pedotype (**Figure 3, Table S1**).

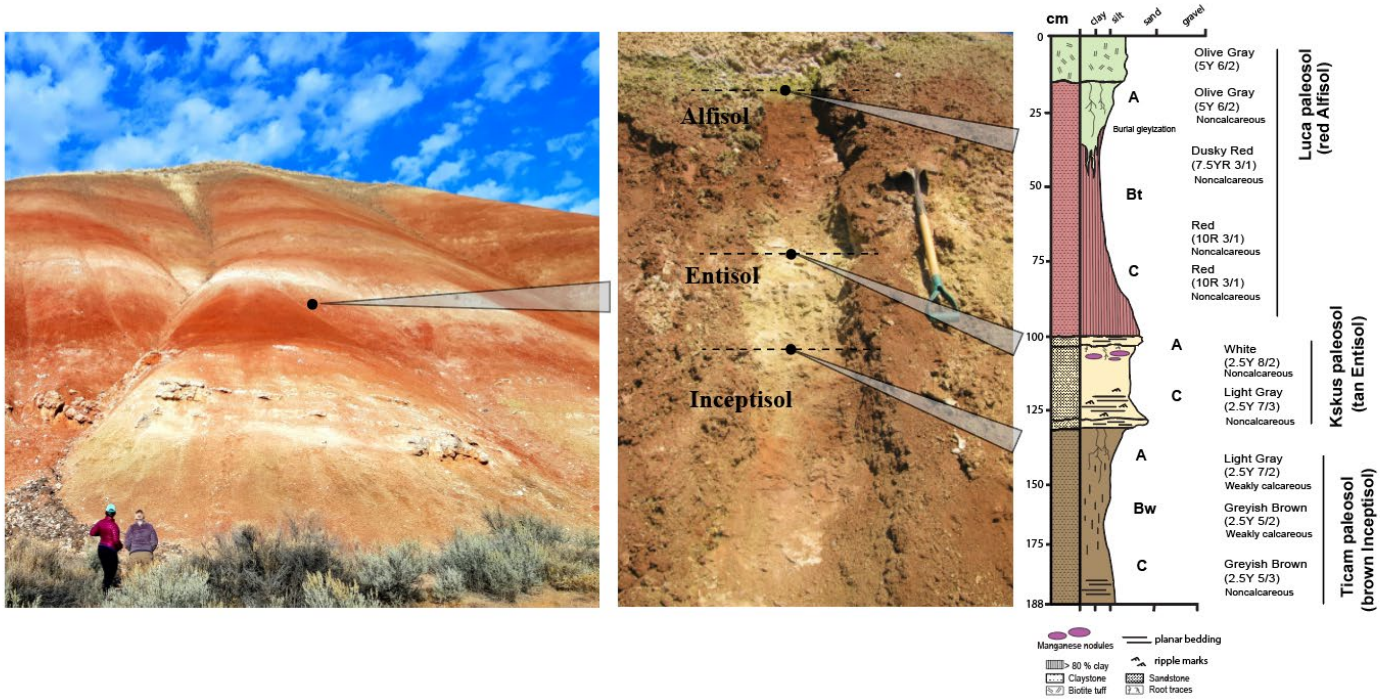

Figure 3. Morphology of three successive paleosols from the early Oligocene (33 Ma) middle Big Basin Member of the John Day Formation in eastern Oregon, USA showing lithology, grain size, horizon designations, and Munsell color. The upper paleosol (red with drab green top) is a moderately weathered red Alfisol (Hapludalf in USDA Taxonomy); stratigraphically below is a minimally weathered and weakly developed Entisol (Fluvent; tan color); the lowest soil (brown color) is an Inceptisol (Andic Eutrochrept, brown color)

2.2 Radiocarbon dating of organic carbon in paleosols

The purpose of radiocarbon (^{14}C) dating was to constrain the age of organic carbon in paleosol samples. Specifically, radiocarbon dating was used to determine if the organic carbon fraction of paleosols was entirely endogenous (deposited during soil formation) and had been preserved for millions of years, or if there had been additions of exogenous organic carbon to paleosols in the last ~45,000 years (the method-level detection limit for radiocarbon dating techniques). A radiocarbon age of organic carbon was obtained from four samples, two from the surface and near-surface horizons (A and Bt horizons) of the stratigraphically highest soil (Alfisol) and two from the surface and near-surface horizons of the stratigraphically lowest profile (Inceptisol). All samples for radiocarbon dating were acid-washed to remove inorganic carbonates before radiocarbon dating. For acid washing, ground paleosol samples (~5 g) were treated with approximately 20 mL of 0.1 M HCl at room temperature, then washed three times with ~30 ml of deionized water and dried at 60° C for 24 hr. Radiocarbon dating of acid-washed paleosol samples was performed at the W.M. Keck Carbon Cycle Accelerator Mass Spectrometer at the University of Irvine. The accuracy and precision (1 σ) of this analysis on modern carbon ($\Delta^{14}C$ >0%) was better than 9‰. Laboratory blanks yielded a $\Delta^{14}C$ value of -996.2 ‰.

2.6 Thermal and evolved gas analysis of paleosol samples

The purpose of this work was to use SAM-EGA-like conditions to characterize bulk gas evolution and to measure abundance of organic and inorganic carbon in Mars-analog paleosol samples. A Setaram Labsys Evo differential scanning calorimeter (DSC) / thermal gravimeter (TG) connected to a Pfeiffer Omnistar QMS was configured to operate similarly to the SAM evolved gas analyzer. The SAM instrument does not have TG/DSC capabilities, but these components permit a better understanding of phase transitions and chemical reactions in laboratory experiments. Approximately 50 mg ± 3 mg of ground paleosol sample (previously stored in glass vials ashed at 500° C to minimize organic contamination) were placed in an Al_2O_3 sample crucible which was ashed at 500° C to remove organic contaminants before use. The sample crucible and an identical empty reference crucible were placed in the furnace and then the system was purged twice with helium gas and then set to a pressure of 30 mbar. Helium was chosen as a carrier gas because it is inert and because it used as a carrier gas in the SAM instrument. The crucibles were heated from approximately 35 °C to 1000 °C at a heating rate of 35°C/min and at a flow rate of 10 sccm. Volatiles ranging from mass/charge (m/z) 1 - 100 were measured. All analyses were performed in duplicate.

Total organic carbon (TOC) content was determined using a Netzsch TG/DSC coupled to a Pfeiffer QMS. Typical TOC determinations via elemental analysis involve an acid pretreatment step to remove carbonates, but acid pretreatments have been shown to alter the original organic carbon content of samples[69]. Paleosol samples were not acid-pretreated for thermal and evolved gas analyses because some organic carbon can be oxidized during acid-washing [69]. An Al_2O_3 sample crucible and an identical reference crucible were placed in the furnace. The instrument was purged twice with ultra-high purity O_2 and set to a pressure of 1000 mbar prior to sample analyses to remove any contamination in the system. Oxygen was chosen as a carrier gas because it encourages complete combustion of all organic and inorganic carbon in samples. The crucibles containing samples were heated from approximately 35 °C to 1000 °C at a heating rate of 35°C/min and at a flow rate of 19 ml O_2/min. A series of three blanks were analyzed before and after each group (n=10) of samples. A calibration curve for CO_2 was created by analyzing a calcite standard (Iceland sparry calcite 40 ụM) at eight sample masses ranging from 0.01 – 4 mg (Table S1). This calibration curve was used to calculate the amount of CO_2 evolved from each sample, and these values were used to calculate total organic carbon. In the present study, carbon was considered organic between 150-550° C and inorganic from ~700-900° C. Organic C was quantified by deconvolving CO_2 peaks if a carbonate-C peak was present. This was done by determining the relative percentage of peak area from inorganic carbon-evolved CO_2 (~700-900° C) then subtracting this value from total carbon-evolved CO_2 peak area to solve for total organic carbon. All evolved gas plots were background-corrected to account for possible atmospheric contamination.

Thermal techniques including TG-DSC-EGA allow for quantitative estimates of organic and inorganic carbon. Inorganic carbon decomposition or combustion evolves CO_2 at high temperatures (~700-900° C) and thus can be distinguished from low temperature (~150-550° C) CO_2 evolutions from the decomposition of organic carbon [46,59]. Iron carbonates such as siderite can decompose in the 450° C range, but previous mineralogical investigation of these samples found no evidence of iron carbonates **(Broz et al 2021, in review).** Thus, the large temperature gap and differences in the thermodynamics of organic and inorganic C decomposition make this method ideal for examining soil and paleosol organic matter without the need for acid pretreatment (e.g., acid fumigation) for carbonate removal.

3. Results/Discussion

3.1 Radiocarbon dating of paleosol organic carbon

Radiocarbon dating of four samples from two different paleosol profiles showed ages between 6265 ± 25 years BP and 14560 ±170 years BP (Table 1). These samples all showed a distinct signature of exogenous organic carbon because the samples were not radiocarbon dead (^{14}C-free).

Table 1. Total organic carbon (TOC), total inorganic carbon (TIC) and radiocarbon dating of paleosols exam

Paleosol	Pedotype ‡	Horizon φ	Depth in profile (cm)	Total C (wt. %)	TOC (wt. %)†	±σ TOC §	TIC (wt. %)	Expected Age	$\Delta^{14}C$‡	±Δ^{14}C
Alfisol	Luca	A	4	0.073	0.031	0.0062	0.042	~33 Ma	-543.07	3.85
Alfisol	Luca	A	14	0.094	0.026	0.0097	0.068			
Alfisol	Luca	Bt_1	46	0.021	0.018	0.0016	0.003	~33 Ma	-838.12	3.37
Alfisol	Luca	Bt_2	63	0.067	ND ʊ	-	0.067			
Alfisol	Luca	C	88	0.033	0.002	0.007	0.031			
Entisol	Kskus	A	100	0.046	0.021	0.0068	0.024			
Entisol	Kskus	C	120	0.036	0.013	0.0037	0.024			
Inceptisol	Ticam	A	125	0.024	0.018	0.007	0.006	~33 Ma	-567.1	1.83
Inceptisol	Ticam	Bw_1	131	0.027	0.008	0.0013	0.019			
Inceptisol	Ticam	Bw_2	160	0.020	0.011	0.0023	0.010	~33 Ma	-545.4	1.33
Inceptisol	Ticam	C	175	0.026	0.001	0.0013	0.026			

† Determined by thermal analysis (TG-DSC-EGA) without acid pre-treatment of samples; average of two duplicates. To encourage complete combustion of organic phases in samples, oxygen was used as a carrier gas for determination of total C, TIC and TOC.
‡ Pedotypes (soil orders) are from Retallack et al. 2000
φ Horizons follow USDA Soil Survey Staff (2014) major horizon designations
ʊ ND = No detection; below limit of quantification
§ Standard error for TOC determination from duplicate analysis
‡ Radiocarbon concentrations are given as fractions of the modern standard (fM), Δ^{14}C, and conventional radiocarbon age.

The occurrence of Holocene-age organic matter in paleosol samples was consistent with diagenetic inputs of organic C. There are several possibilities to explain the accumulation of ^{14}C in the organic fraction of samples. First, a diagenetic event that occurred between ~6 and ~14 Ka BP could have delivered exogenous organics into the underlying paleosols, perhaps during exhumation to the surface and /or leaching of organic acids from surface biota during that time. Cosmogenic exposure dating such as ^{10}Be surface exposure dating would provide important evidence to constrain the exhumation history of the paleosols examined here [70,71]. However, there was no sedimentological evidence of exhumation and re-burial of any of the three paleosols at the field site, so other possibilities to explain the radiocarbon dates were explored.

Another possible source of exogenous organic carbon was from precipitation-driven leaching of dissolved organic carbon from modern biota living in the current weathering zone above the paleosol outcrop. The fraction of modern carbon (fM) across four samples ranged from 0.469 ± 0.039 to 0.1633 ± 0.034 (Table 1) and was highest in the surface (A horizon, 14 cm) of the Alfisol and lowest in the subsurface (Bt horizon, 46 cm), suggesting this paleosol contained a mixture of ancient and modern organic carbon, the latter possibly delivered via precipitation-driven leaching. As such, it is possible that small amounts of exogenous modern organic carbon from the weathered zone above paleosol outcrops

have mixed with larger amounts of ^{14}C-free organic carbon endogenous to paleosols. In this way, a radiocarbon date of ~6-14 Ka BP could represent a mixing of recent/modern organic carbon and ~33 Ma organic carbon. This hypothesis is supported by the erosion rate for the site, which was previously determined to be 4.94 ± 0.05 mm/yr [72]. Using this erosion rate, the 20 cm-thick soils that formed on top of the paleosols are only about 40 years old and could have leached modern organics into the underlying paleosols during this time.

There was also a weak relationship between the radiocarbon age and the depth into the outcrop where the sample was collected (Table 1). Younger radiocarbon dates were observed in shallower samples taken closer to the modern weathering zone. However, a decrease in ^{14}C content with depth is commonly observed in modern soils because subsurface horizons preferentially accumulate older, refractory organic carbon primarily via sorption to surfaces of minerals and amorphous phases [73]. Across four paleosol samples in this work, the radiocarbon age generally increases with depth, suggesting there may be age-depth relationship for samples (Table 1), but this result should be interpreted with caution because only four samples were dated in this work, and because age-depth trends are routinely observed in modern soils [74]. In any case, there may be a sampling depth (i.e., > 1 meter) that significantly reduces or eliminates exogenous carbon additions to paleosols. These results highlight challenges for studying the organic fraction of paleosols while also demonstrating that radiocarbon dating can be a useful technique for constraining organic matter preservation in ancient terrestrial surface environments.

3.2 Thermal and Evolved Gas Analysis

3.2.1 CO_2 and CO evolutions

When subject to thermal and evolved gas analysis, all samples evolved CO_2 at temperatures ranging from ~150 – 800° C and had two distinctive CO_2 peaks (Figure 6). A broad low temperature ~200-500° C peak was followed by a sharp high-temperature peak at ~650-750° C which was observed in all samples. CO_2 evolved at 150-500° C is primarily from organic carbon decomposition [69,75] but also possible are contributions are from CO_2 inclusions in minerals or amorphous phases, or from adsorbed atmospheric CO_2 [46]. The organic C contributing to evolved CO_2 is most likely from simple organic compounds (<350° C) or refractory macromolecular organic compounds (300-600° C) [43].

The endothermic thermal decomposition of Ca carbonate was a probable source of CO_2 release from approximately 550 – 800° C [76,77]. High temperature (> 650° C) CO_2 evolutions generally exceeded the low temperature (150-550° C) CO_2 evolutions in peak area across all samples, though both high temperature and low temperature CO_2 evolutions were on the same order of magnitude. Total inorganic carbon (TIC) values varied from 0.006 to 0.068 wt. % (Table 1) and the ratio of inorganic carbon to total carbon ranged from 0.14 to 1, consistent with variable mixtures of Ca carbonate and organic carbon in each sample. There are well-defined Ca carbonate endotherms in the heat flow data from the Entisol and Inceptisol, but this trend was not so well-defined in the Alfisol (Figure 6) and there also appears to be "doublet" high-temperature CO_2 peaks for the Entisol, suggesting a combination of Ca-carbonate and perhaps dolomite or ankerite, though these phases were not previously observed in XRD diffractograms (**Broz et al., 2021**, in review). DSC-EGA analysis of modern soils containing various amounts of calcite have a similar sharp endothermic CO_2 peak release temperature at ~700° C which was attributed to the thermal decomposition of Ca carbonate [69]. An additional ~900° C endotherm observed in all samples was unrelated to carbonate decomposition and instead was attributed to thermal decomposition of sulfate minerals such as jarosite, which was previously detected in trace amounts with x-ray diffraction (**Broz et al., 2021**, in review). Interestingly, Ca-carbonate was not previously identified from x-ray diffraction

patterns, and thus it is likely that these samples contain inorganic carbonate below detection limit of XRD (~1 wt. %), but not SAM-EGA (0.01 wt. %). This agrees with estimated abundances of TIC which were below 1 wt. % (Table 1) and demonstrates the ability of SAM-EGA-like analyses to detect trace amounts of inorganic carbon in complex pedogenic mineral matrices.

Other sources of high temperature CO_2 release could have result from the decarboxylation of organic compounds in refractory or thermally mature organic matter which occur over a broad range of temperatures (150 - 800° C). Previous investigation showed no coalification of organic matter or development of secondary porosity in any paleosols from the Painted Hills, which were buried by an estimated 1.5 - 2 km of overburden [9,23], suggesting paleosol samples here contain refractory but not thermally mature organic compounds.

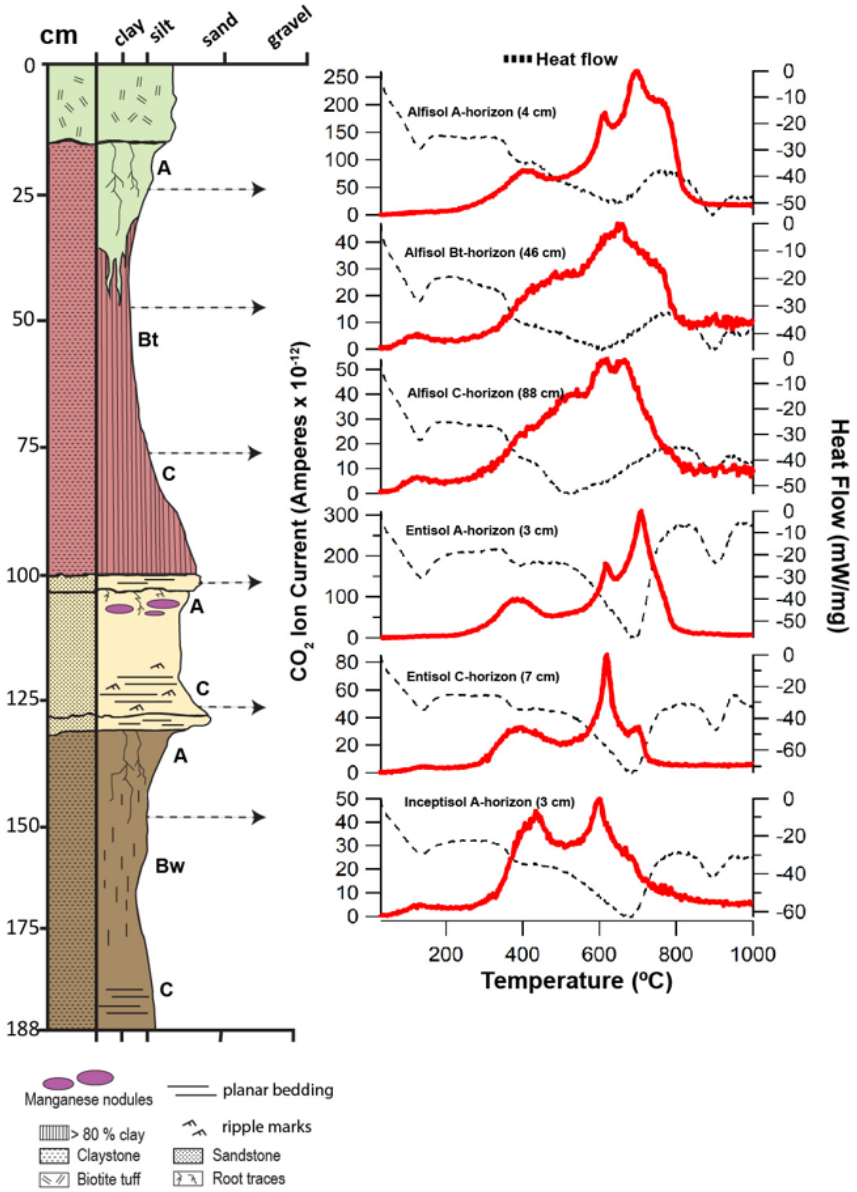

Figure 6. Evolutions of CO_2 (red traces) and heat flow (dashed traces) from early Oligocene (33 Ma) smectite-rich paleosols from the John Day Fossil Beds National Monument, Oregon. Red trace is CO_2 (m/z 44) and

dashed trace is heat flow from differential scanning calorimetry (DSC). Helium was used as a carrier gas for all analyses.

All samples evolved CO with a peak release temperature of ~400° C (Figure 7). The sample with the highest total organic carbon detected (~0.03 wt. %, surface horizon of Alfisol) evolved a CO_2 release peak at ~400 °C that co-occurred with the release of CO. This trend of coevolved CO and CO_2 at ~400° C was observed across all paleosol samples. Evolution of CO was consistent with incomplete combustion of organics and/ or the presence of oxygen-bearing organics [75]. The co-occurrence of CO and CO_2 was not observed at high (~700 °C) temperatures (Figure 7) because the thermal decomposition of Ca carbonate does not produce CO. Thus, evolved CO detections near 400° C were consistent with the decomposition of organic compounds.

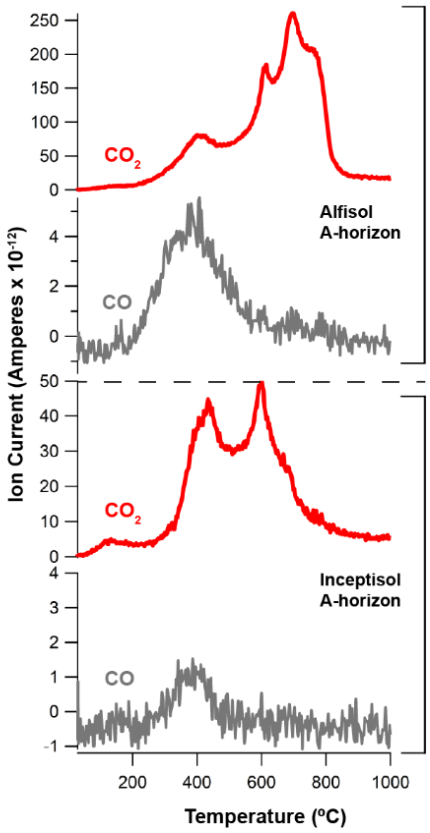

Figure 7. CO_2 (red trace) and CO (m/z 28) (grey trace) evolutions from the surface horizons of smectite-rich paleosols at the John Day Fossil Beds National Monument, Oregon. Top panel is surface (4 cm) horizon of an Alfisol; bottom panel is surface (3 cm) horizon of an Inceptisol

3.2.2 NO evolutions

Nitric oxide (NO; m/z 30) was detected in all paleosol samples (Figure 8) and was consistent with the oxidation of nitrogen-bearing organics. In the sample with the greatest amount of organic carbon (Alfisol A-horizon), evolutions of NO start at ~300° C and show peak release temperature of ~ 400° C and a shoulder at ~ 600° C (Figure 8). Additionally, organic fragments observed in this sample included

CH_2 (m/z 14), CH_3 (m/z 15), and C_2H_2 (m/z 26) (Figure 9). Evolutions of NO were simultaneous with evolutions of these organic fragments at ~400° C, suggesting the oxidation of a nitrogen-bearing organic compound was a significant contributor to evolved NO [78].

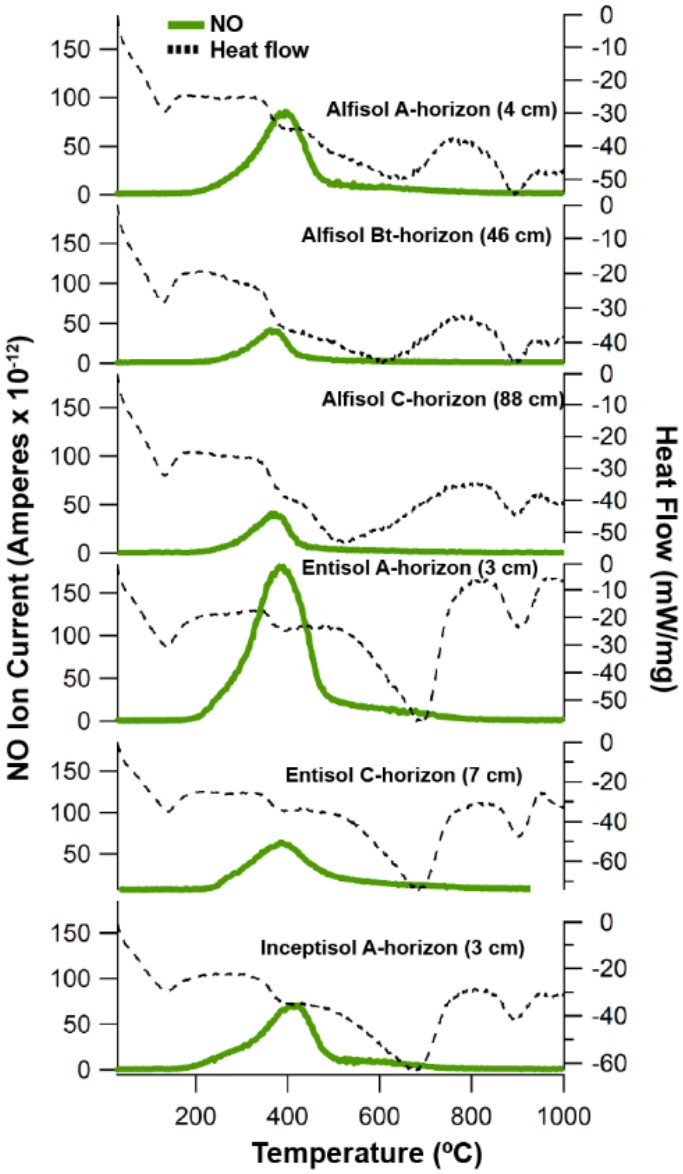

Figure 8. Evolutions of nitric oxide (NO) from smectite-rich paleosols at the John Day Fossil Beds National Monument, Oregon. Green trace is NO (m/z 30) and dashed trace is heat flow from differential scanning calorimetry (DSC).

The thermal decomposition of nitrates can also release NO, though at elevated temperatures (> 500° C) relative to nitrogenated organics [78], and therefore the release peak temperate of NO release can constrain the source of NO. For example Alkali (Na, K) and alkaline earth (Mg, Ca) metal nitrates decompose to NO at temperatures > 560° C [78]. In laboratory experiments under SAM-like conditions, $Fe(NO_3)_3$ begins to decompose to NO at < 200° C and exhibits two distinct releases of NO at ~300 and

~450° C, which has been attributed to dehydration and hydrolysis of $Fe(NO_3)_3$, respectively [78]. Instead, NO release in paleosol samples began at ~250° C and exhibited a single peak at ~400° C across all samples **(Figure 8)**, unlike the dual high-temperature NO peaks from decomposition of $Fe(NO_3)_3$. The simultaneous evolution of NO, CO_2, and organic fragments in paleosol samples analyzed here (Figure 9) are an additional line of evidence suggesting NO releases could have resulted from oxidation and/or decarboxylation of nitrogen-bearing organic compounds.

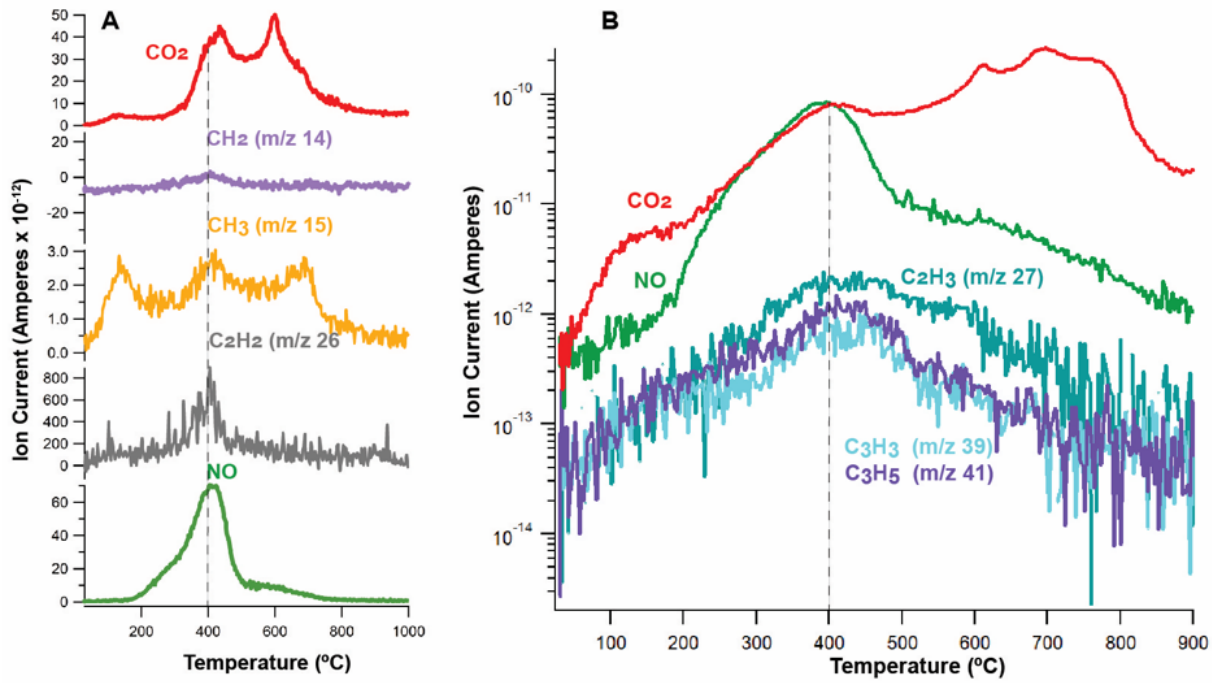

Figure 9. Simultaneous evolutions of CO_2, NO (m/z 30) and organic fragments in paleosol surface horizons. (A) Evolutions of CO_2, NO (m/z 30), and organic fragments (m/z 14, 15, 26) from the surface horizon of the Inceptisol (3 cm). **(B)** Semi-log scale plot of CO_2, NO and additional organic fragments (m/z 27, 39, 41) from the surface horizon (4 cm) of the Alfisol.

One possible source of nitrogen-bearing organic carbon compounds is pyrogenic carbon (char) in paleosol samples that formed as a result of wildfires across the original soil landscape [79]. Nitrogen-bearing organic compounds such as nitriles, pyridine and pyrrole-derive compounds have been observed with pyrolysis GC/MS in modern fire-affected soils [80]. These modern soils were also observed to have a broad ~400° C peak release temperature of NO (m/z 30) during TG-DSC-EGA, suggesting that pyrogenic carbon may be the source of low-temperature NO release in soils. However, the fire history of paleosols in the present study has not yet been investigated. Although it is impossible to determine the original inputs of nitrogen-bearing organics in paleosols, nitrogen may have been incorporated into increasingly stable organic matter as a consequence of forest fires, and may persist in paleosols today as char. Previous authors have reported the occurrence of preserved char in paleosols of late Permian[81] and late Jurassic age[14] paleosols, respectively, so it is plausible that nitrogen-bearing char may be responsible for the overlapping ~400° C NO and CO_2 peaks observed here.

3.3 Possible mechanisms of organic carbon preservation in paleosols

We observed evolutions of volatile gases from clay-rich paleosols that may have resulted from the preservation of organic carbon over geological time scales. The fragmentation of organic molecules during pyrolysis EGA provides limited constraints on the types of molecules present, but it can help determine if there are any associations between minerals and organic molecules. These associations can include physical occlusion, chemisorption and/or adsorption to mineral surfaces, or intercalation in clay minerals [82–85]. A strong correlation between the peak release temperature of organic fragments and the release of H_2O or other volatiles would suggest that organic matter could have been associated with minerals.

One line of evidence that organic molecules may have persisted in association with clay minerals is co-occurring evolutions of organic fragments, CO_2, and water releases from clay dehydroxylation. Al-smectite in the surface horizon of the Alfisol began dehydroxylating at ~400° C (broad H_2O peak) which co-occurred with evolutions of CO_2 and organic fragments (Figure 10). This sample had the highest TOC (~0.03 wt. %, Table 1), a radiocarbon date of ~6300 years BP and a phyllosilicate content of ~85 wt. **%** (Table S1**) (Broz et al., 2021).** The high clay mineral content could be related to the abundance of organic carbon in this sample. However, additional investigations such as microscale imaging (e.g., transmission electron microscopy) and methods to characterize the bonding environments between minerals and organics in paleosols are needed to support this interpretation.

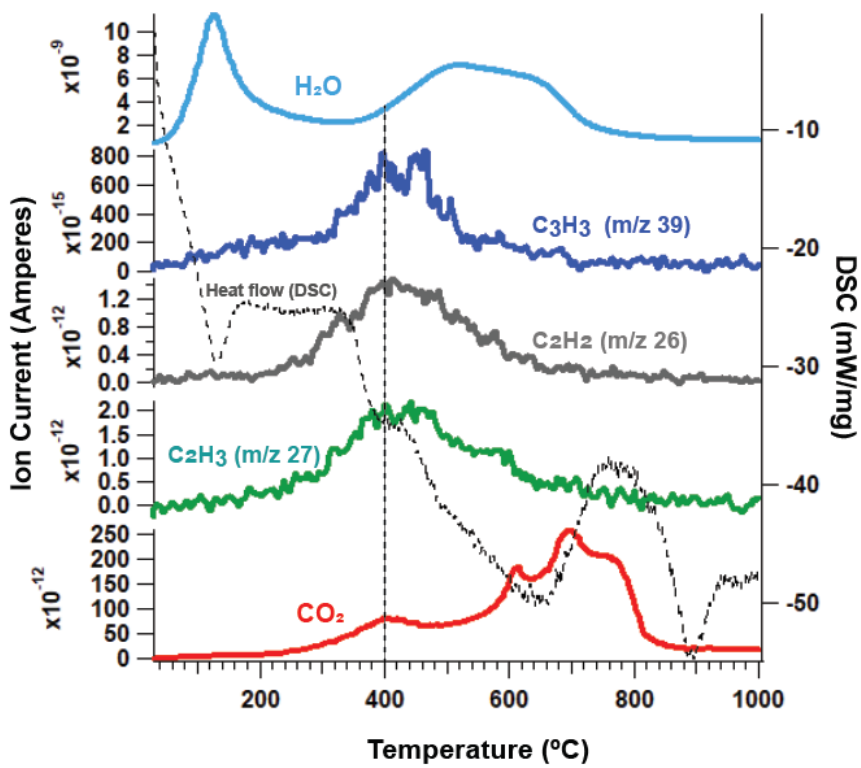

Figure 10. Evolutions of CO_2, organic fragments, and H_2O from the surface horizon of the Alfisol (4 cm). Co-occurring releases of CO_2 and organic fragments at the onset of Al-smectite dehydroxylation (H_2O release at ~400° C, vertical dotted line) suggest organic molecules may have been associated with clay minerals. Dashed trace is heat flow from differential scanning calorimetry (DSC).

It is important to note that there are many competing factors that control the preservation and degradation of organic carbon in terrestrial environments. Minerals themselves may facilitate oxidation of organic carbon compounds [84], as is the case with certain Mn-bearing minerals [86]. Possible mechanisms of

organic carbon preservation in paleosols examined here include the formation of organo-mineral complexes and/or the formation of microaggregates that may increase the biochemical stability of organic molecules, as observed in modern soils [59] and Quaternary paleosols [57]. Paleosols examined here contained between ~70-90 wt. % smectite, primarily as mixtures of montmorillonite and nontronite (Table S2). Smectite clay minerals in particular preserve organic molecules due to their high specific surface area, negatively charged interlayers, and cations which inhibit water flow, thus making them favorable locations for the preservation of organic carbon over millions or possibly billions of years [39,44,60].

Interactions with sulfur can also aid in the preservation of organic molecules in soils and sediments over geological time scales [14,43,85,87]. The incorporation of organic C into the crystal lattice of sulfate minerals can increase thermodynamic stability and therefore increase the temperature of organic carbon decomposition during EGA[85]. Minor detections of jarosite and gypsum in XRD patterns (< 5 wt. %) observed in all paleosol samples, and these minerals could have also contributed to the preservation of organics. Minor SO_2 evolutions at 800° C across all samples (Figure S2) were consistent with the decomposition of sulfate minerals and a single sample (Entisol 7 cm) had a low-temperature SO_2 peak that co-occurred with the CO_2 release at ~400° C. Trace amounts of Mg sulfates in the Alfisol could account for minor SO_2 releases > 700° C including the ~790° C SO_2 peaks [85,88]. At higher temperatures, all soils showed a major release of SO_2 beginning at 900° C which co-occurred with an endotherm, both of which are consistent with the thermal decomposition of crystalline sulfates [46,85]. Since the samples were only heated to ~1000° C for this work, the maximum peak height of this release cannot be ascertained. However, peak SO_2 release temperatures generally did not co-occur with low-temperature CO_2 evolutions across the rest of the samples (Figure S2), so it is unlikely that sulfate minerals played a significant role in organic preservation in samples examined here.

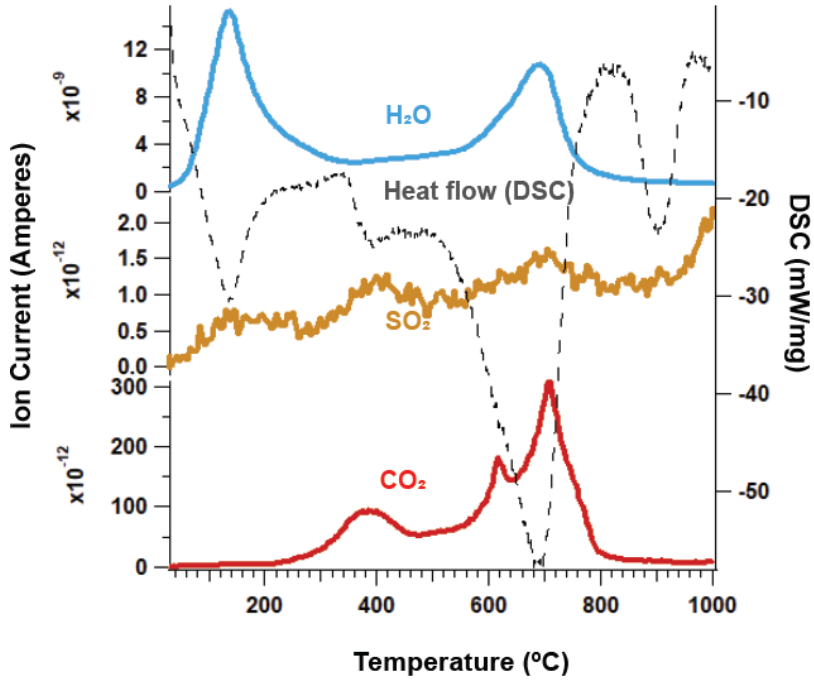

Figure 11. Evolutions of H_2O (blue trace), SO_2 (yellow trace), CO_2 (red trace), and heat flow (dashed trace) from the surface horizon of the Entisol (3 cm). DSC – differential scanning calorimetry (heat flow), H_2O – m/z 18, SO_2 – m/z 64, CO_2 – m/z 44.

3.4 Enrichment of organic carbon in surface layers of paleosols

The near-surface horizons of all paleosols examined here had greater amounts of total organic carbon (TOC) relative to deeper horizons (Figure 12, Table 1). The highest amounts of CO_2 released from decomposition of organic carbon (150-500° C) were in the near surface (A) horizons of all three paleosol types while subsurface layers of paleosols generally had lower quantities of evolved CO_2 from organic carbon (Figure 6, Table 1). The A horizon of the Alfisol had TOC of 0.031 ± 0.006 wt. % and progressively decreased to 0.002 ± 0.007 wt. % in the C horizon.

Samples from the A-horizon of the Alfisol had been affected by burial gleization. Burial gleization is an early diagenetic process in paleosols which involves the reduction of Fe^{3+} to Fe^{2+} by anaerobic microbes as a result of rapid burial [1,89]. This is also thought to promote anaerobic decay of organic matter [1], even in soils that originally formed under oxidizing conditions before burial. Typical burial gleization is closed system alteration, without depletion of total iron, and is usually limited to the surface horizons where organic matter is most concentrated. The surface horizon of the Alfisol examined in this work showed classic evidence of burial gleization with drab-colored mottles and tubular features predominantly in the A-horizon with minor radiation downward into the subsurface (Bt) horizon (Figure 12). Rapid emplacement of a biotite-bearing tuff on the paleosurface of the Alfisol may have led to gleization. Similar trends of near-surface TOC enrichment were noted in the Entisol and Alfisol (Table 1), but these samples lacked chemical and morphological evidence of burial gleization **(Broz et al., 2021, in review).** Previous work on terrestrial paleosols has shown positive and significant correlations between Fe^{2+} and TOC [13]. This supports the interpretation that burial gleization, which increases Fe^{2+} in bulk samples, may have been associated with the preservation of organic carbon in the surface horizon of the Alfisol.

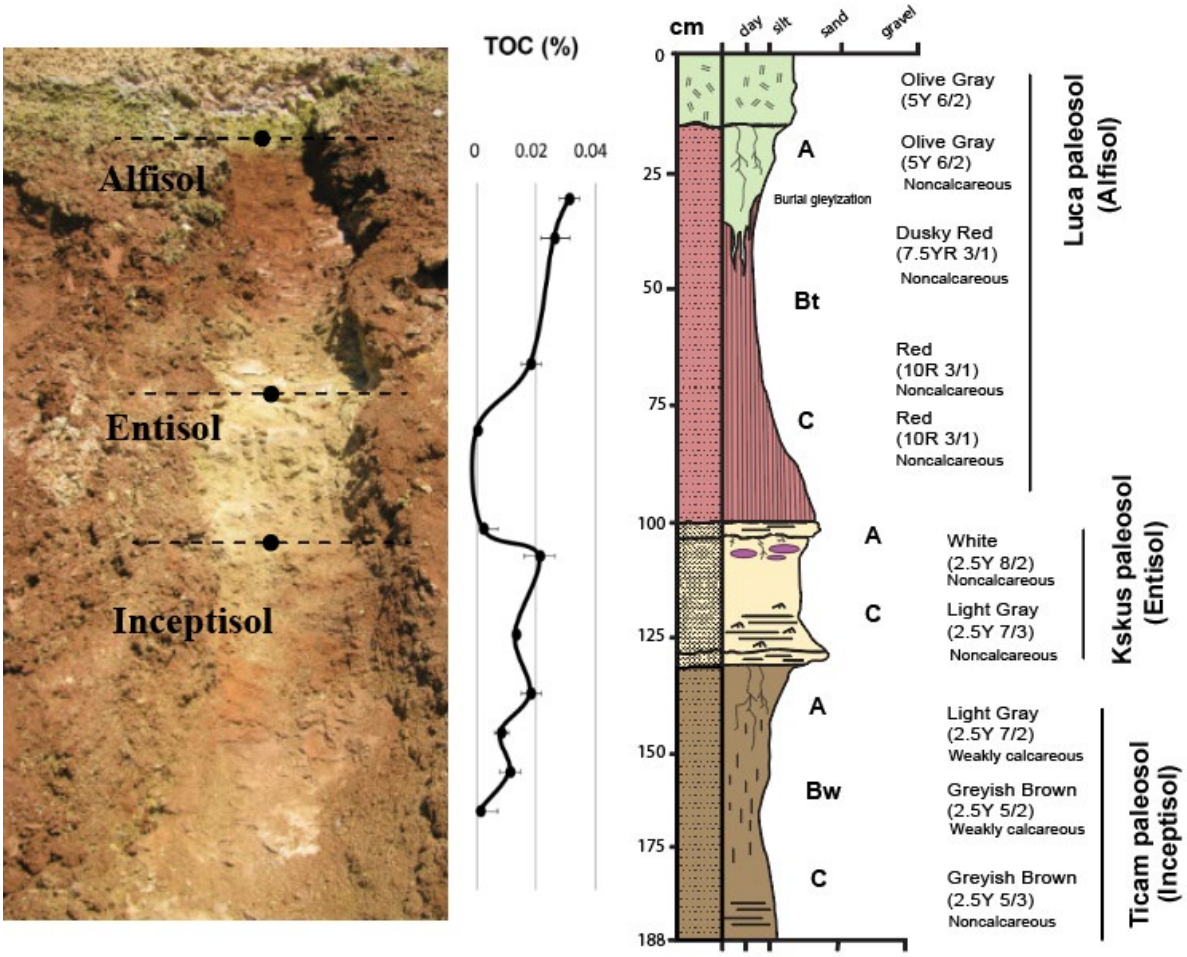

Figure 12. Trends of organic carbon enrichment in the near-surface horizons of three paleosols from the early Oligocene (33 Ma) middle Big Basin Member of the John Day Formation in eastern Oregon, USA**.** The surface (A) horizons of all three profiles had significantly ($P > 0.05$) higher total organic carbon (TOC) content relative to subsurface horizons (Bt, Bw and C horizons, respectively). Average TOC content of samples (n=2) was determined by thermal and evolved gas analysis (oxygen as a carrier gas).

Organic carbon from organisms living in surface horizons of soils may have been preserved upon rapid burial of the paleosurface, and therefore the trend of surface enrichment may represent the preservation of endogenous organic carbon. Alternatively, diagenetic additions of carbon may have accumulated in near-surface layers of each profile. Major losses of endogenous organic carbon from early diagenetic burial decomposition of organic matter are common in paleosols that originally formed under oxidizing conditions such as those examined here [1]. Despite diagenetic additions and losses of organic carbon, the trend of surface enrichment of organic carbon remains apparent, even in soils that formed under strongly oxidizing conditions prior to burial. These results are consistent with other studies of paleosols where surface enrichment of organic carbon was observed [15,18,67,90]. However, it is possible that late diagenetic inputs of organics caused this enrichment, for example, by preferential flow and

accumulation in the paleosurface of each profile. Considering the Holocene radiocarbon dates for these ~33 Ma paleosols (Table 1), results from this work cannot definitively rule out diagenesis as a mechanism for surface enrichment, though it is unlikely that early and/or late diagenetic additions of organic carbon could have preferentially accumulated in the near-surface horizons of these buried soils.

3.5 Implications for Mars

Recent work has considered putative paleosols on Mars as potential high priority environments for *in-situ* analysis [29] and biosignature preservation [7]. This is because the composition and properties of paleosols preserve evidence of paleoclimate, aqueous conditions, and life [7]. A major finding of this study is that near-surface horizons of terrestrial paleosols appear to be a favorable location for SAM-EGA detection of organic carbon. Like modern soils, the surface layers of Mars-analog paleosols examined here show evidence of surface enrichment of organic carbon. Although the early diagenetic process of burial decomposition of organic matter has likely reduced the organic carbon content of these ancient soils by at least two orders of magnitude relative to modern soils [13], the enrichment of organic carbon in surface horizons (~0.03 wt. %) and subsequent depletion in deeper layers (<0.01 wt. %) was readily observable with SAM-EGA analog analysis.

Results from this study also have implications for interpreting the chemical and isotopic biosignature preservation potential of Al and Fe smectite-bearing weathering profiles on Mars. However, as discussed earlier, there are critical limitations to using terrestrial paleosols as analogs to interpret the organic preservation potential of paleosols on Mars, such as major differences in the types and properties of organic molecules deposited during soil formation. Irrevocable differences between Earth and Mars, including climate and a complex terrestrial biosphere, preclude direct comparisons. In any case, observations of refractory organic compounds that persist in terrestrial paleosols with Mars-like mineralogy provides a reference frame for interpreting future observations of putative weathering profiles on Mars. It is possible that clay minerals and/or amorphous phases in martian weathering profiles impart a similar control on the fate of organic carbon.

Results from this work also provide an initial framework for investigation and sampling of martian weathering profiles should they be encountered by current or future landed missions. Future *in-situ* analysis of putative weathering profiles should begin at the surface and sample down the into the unaltered protolith. However, if the entire profile is not accessible for investigation (e.g., outcrop is at a topographic position inaccessible to the rover), the near-surface horizons of the profile, just below the uppermost burial layer, should be considered the highest priority target for remote sensing, contact science, and collection of a drilled sample for sample return to Earth.

Conclusions

The objectives of this study were a) to determine whether the organic carbon content of ~30-million-year-old paleosols can be detected with a thermal and evolved gas analyzer configured to operate like the SAM-EGA instrument onboard *Curiosity* Mars rover, and b) use radiocarbon (^{14}C) dating to constrain the age of organic carbon in bulk paleosol samples. Radiocarbon dating of organic carbon in four paleosol samples revealed the presence of recent and/or modern exogenous organic carbon. Samples from 0 - 20 cm were dated to ~6,200 years BP and had a fraction modern (fM) value of ~0.4, while a single deeper sample collected from 43 cm had a radiocarbon age of ~14,600 years BP and ~0.16 fM. The presence of radiocarbon in paleosols could have resulted from the diagenetic addition of small amounts of

modern (< 1 Ka) organic carbon which mixed with ^{14}C-free endogenous organic carbon. Alternatively, a diagenetic event between 6-14 Ka could have introduced exogenous organics, possibly through groundwater alteration and/or precipitation-driven leaching of dissolved organic carbon. There may be a sampling depth (e.g., > 1 meter into the outcrop) which decreases or eliminates organic additions from exogenous sources. It is possible, however, that diagenesis has pervasively introduced exogenous organic carbon to deeper samples. Holocene-age radiocarbon dates supported the hypothesis that paleosols from the site contain exogenous organic carbon. These results highlight major challenges for determining the source(s) and age of organic matter in terrestrial paleosols. Radiocarbon dating should be used in future analog studies to help distinguish diagenetic organic inputs from original endogenous inputs.

SAM-EGA-like characterization of paleosols showed evolutions of CO, NO, CO_2, and organic fragments. Coevolutions of CO_2 and organic fragments at ~400° C suggested the presence of refractory organic carbon. However, like other oxidized terrestrial paleosols of Cenozoic age and older, only trace amounts (<0.1 wt. %) of organic carbon was detected, which most likely was a result of diagenetic decomposition of organic matter over geological time scales. Many samples examined in this work typically contained very low amounts (~0.01 wt. %) of organic carbon, but these low values were nevertheless detectable by SAM-like evolved gas analysis of bulk samples. These results suggest the organic fraction of potential martian weathering profiles may be detectable with evolved gas analysis, even if organic concentrations are low.

A major result of this work was that organic carbon was concentrated in near-surface horizons of paleosols while deeper horizons were depleted in organic carbon. Like modern soils, these ancient soils were enriched in organic carbon in near-surface horizons, and it appears that this trend persisted in these samples despite burial decomposition of organic carbon over geological time scales. Alternatively, diagenesis could have pervasively introduced exogenous organic carbon, but it is unlikely such organic contamination would preferentially accumulate in the surface layers of each successive buried soil profile. Surface enrichment of organic carbon in possible weathering profiles on Mars may therefore constitute a putative chemical biosignature. This work demonstrates that analytical techniques similar to SAM-EGA can detect trace amounts of organic carbon in complex pedogenic mineral matrices. The search for past life on ancient land surfaces of Mars should include targeting Martian weathering profiles for *in-situ* biosignature investigation and Mars Sample Return.

Additional Information

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Author Contribution Statement

A.P.B and J.V.C designed the study, performed all laboratory analyses and drafted the manuscript. J.V.C, D.W.M, P.D.A, and B.S contributed to data analysis and interpretation. B.H.H identified similarities between Mars and John Day paleosols and assisted with fieldwork and data interpretation. L.C.R.S provided radiocarbon analyses and interpreted the data. J.V.C, P.D.A, B.S, D.W.M, and L.C.R.S supervised the project. A.P.B drafted all figures. All authors contributed to the manuscript.

Author Disclosure Statement

No competing financial interests exist.

Supplementary data is available online at:

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