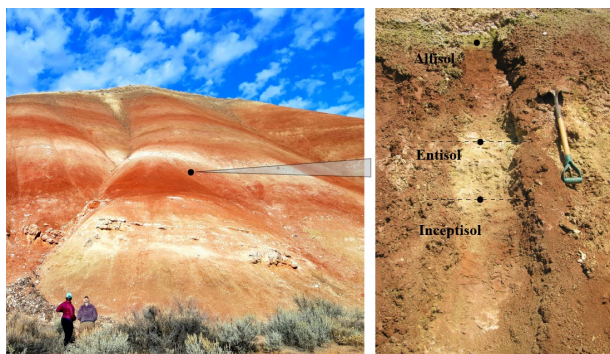


**THERMAL AND EVOLVED GAS ANALYSIS OF MARS ANALOG PALEOSOLS** A. P. Broz<sup>1</sup>, J.V Clark<sup>2</sup>, P.D. Archer<sup>3</sup>, B. Sutter<sup>3</sup>, D.W. Ming<sup>4</sup>, V.M. Tu<sup>3</sup>, L.C.R. Silva<sup>5</sup> and B.H. Horgan<sup>6</sup>, <sup>1</sup>University of Oregon, Eugene, OR, 97403 ([abroz@uoregon.edu](mailto:abroz@uoregon.edu)). <sup>2</sup>Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX, 77058. <sup>3</sup>Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX. <sup>4</sup>NASA Johnson Space Center, Houston, TX. <sup>5</sup>Environmental Studies Program, Department of Geography, University of Oregon, Eugene, OR. <sup>6</sup>Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN.

**Introduction:** Decades of space exploration have shown that three to four billion-year old surface environments on Mars may have been habitable. Ancient surface environments which resemble paleosols (buried sedimentary deposits which formed from subaerial weathering) on Mars have recently been named a high-priority target for biosignature investigation and Mars Sample Return because paleosol mineralogy records valuable information about past climates, and because Archean (~2.6 Ga) paleosols from Earth preserve some of the oldest biosignatures of life on land [1]. However, there has been little effort to characterize terrestrial paleosols with Mars-like mineralogy using instruments analogous to those on current and future missions to Mars, which is imperative for understanding if putative paleosols on Mars should be targeted for future exploration. The objectives of this study were to perform the first comprehensive analysis of Mars-analog paleosols with Mars flight-analog instrumentation and to determine if organic carbon in these paleosols is detectable in the presence of a perchlorate salt.

**Methods:** Early Oligocene (33 Ma) volcanoclastic paleosols rich in dioctahedral phyllosilicates and amorphous materials were collected near the iconic ~400 m thick sequence of paleosols at the Painted Hills in eastern Oregon, USA.



**Figure 1.** Field site and sequence of three paleosols examined in this work

This site was previously considered a Mars analog because of similarities in stratigraphy and mineralogy to Noachian (4.1-3.7) clay deposits at Mawrth Vallis, Oxia Planum and elsewhere on Mars [2-4]. For this

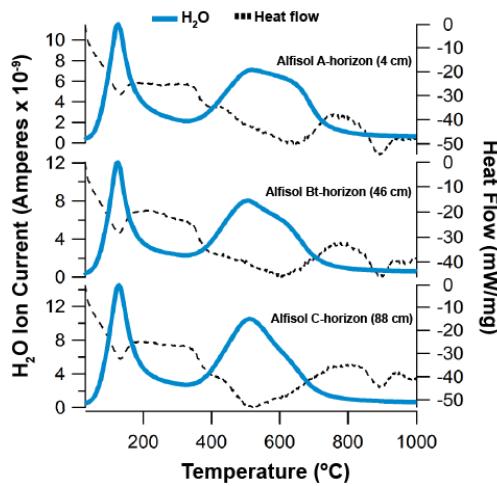
work we collected samples from a vertical transect which spanned three distinct buried soil profiles within the middle Big Basin Member of the John Day Formation, which were individually classified using U.S. soil taxonomy as Alfisols, Entisols, and Inceptisols, respectively (Fig. 1). Geochemical climofunctions previously applied to these paleosols indicate formation over tens to hundreds of thousands of years under warm (>12° C) and wet (>1000 mm MAP) surface conditions [5].

After removing the modern weathered surface, samples were collected by trenching 1 m into the lithified claystone surface below the modern outcrop, selecting ~2 kg lithified blocks, and subsampling the inside of these blocks with a Dremmel tool fitted with an Al<sub>2</sub>O<sub>3</sub> saw, all intended to minimize contamination from modern organics. Radiocarbon dating of four subsamples is being performed to assess whether there were contributions from modern organic carbon. Visible/Near Infrared (VNIR) spectroscopy and x-ray diffraction (XRD) were used to identify crystalline phases in paleosol samples. A thermal and evolved gas analyzer (Labsys EVO) configured to operate similarly to the Sample Analysis at Mars-Evolved Gas Analysis (SAM-EGA) instrument onboard the Mars Science Laboratory *Curiosity* rover was used to constrain mineralogy and organic carbon content. Finally, select paleosol samples were spiked with 1 wt. % Na perchlorate to assess the oxidation of organic carbon in paleosols during SAM-EGA.

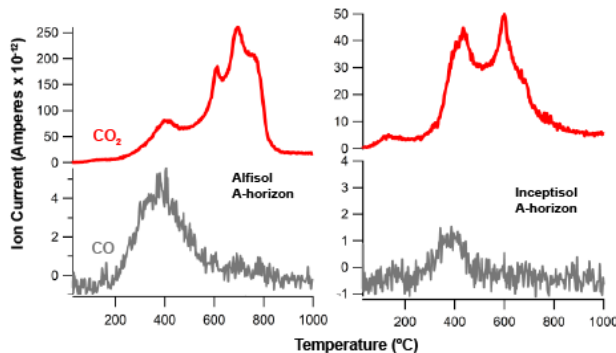
**Results:** Before perchlorate additions, evolved H<sub>2</sub>O was detected in all paleosol samples and was consistent with adsorbed water and the dehydroxylation of a dioctahedral phyllosilicate. Evolutions of H<sub>2</sub>O at 500° C and corresponding endotherms are consistent with the dehydroxylation of a Fe-bearing octahedral layer of a phyllosilicate, e.g., nontronite (Fig. 2). This is consistent with results from VNIR spectroscopy and XRD which showed montmorillonite and nontronite as major phases in all three paleosols (data not shown).

All samples evolved CO<sub>2</sub> with peaks at ~400° C and ~700° C from the thermal decomposition of organic carbon and calcium carbonate (CaCO<sub>3</sub>), respectively (Fig. 3). CO<sub>2</sub> releases between 150-450° C tracked with an exotherm and resulted from the oxidation of organic carbon, while CO<sub>2</sub> releases over 600° C

tracked with an endotherm, suggesting endothermic decomposition of Ca-carbonate. CO (m/z 28) releases co-occurred with evolved CO<sub>2</sub> from the exothermic oxidation of organic C. Organic carbon quantities in all samples ranged from 0.002 - 0.032 ± 0.006 wt. %, and the near-surface horizons of all three paleosols had significantly higher organic carbon content relative to subsurface layers. The organic compounds contributing to evolved CO<sub>2</sub> are most likely from simple organic compounds (<350° C) or refractory macromolecular organic compounds (300-600° C).



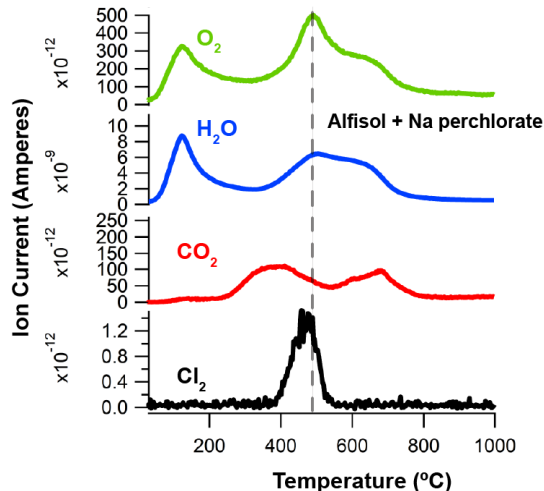
**Figure 2.** Evolutions of H<sub>2</sub>O from an early Oligocene (33 Ma) Alfisol paleosol. Blue trace is H<sub>2</sub>O (m/z 18) and dashed trace is heat flow from differential scanning calorimetry (DSC).



**Figure 3.** Evolutions of CO<sub>2</sub> and CO (m/z 28) from the surface horizons of two paleosols

When Na perchlorate was added to samples, a high temperature (~500° C) sharp O<sub>2</sub> peak resulted from the thermal decomposition of Na perchlorate which was not observed in untreated samples. The peak O<sub>2</sub> release from Na perchlorate decomposition at 500° C (dotted

line, Fig. 5) co-occurred with evolutions of Cl<sub>2</sub> (M/z 70) which is expected when mixtures of water-bearing phases and Na-perchlorates undergo thermal decomposition [6]. Gases produced from thermal decomposition of organic molecules were detectable despite the presence of perchlorate because they evolved at temperatures 100-150° C below the onset of perchlorate decomposition. We did not observe the production of chlorinated hydrocarbons, which are expected to form if oxidation of organics results from thermal decomposition of perchlorate [7].



**Figure 4.** Evolutions of volatiles in the surface horizon of the Alfisol after addition of 1 wt. % Na perchlorate.

This work demonstrates that the near-surface horizons of paleosols should be considered high-priority targets for in-situ biosignature investigation and selection of samples for return to Earth. Future work should use additional oxychlorine compounds with lower temperatures of thermal decomposition because it is possible that other perchlorate salts (e.g., Mg perchlorate) will produce chlorinated hydrocarbons when added to smectite-rich paleosols.

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#### References:

- [1] Watanabe et al. (2000). *Nature*, 408.
- [2] Horgan et al. (2012) *Third Conference on Early Mars*, 1074.
- [3] Hays et al. (2017) *Astrobiology* 17, 4.
- [4] Bishop et al. (2018) *Nature Astronomy*.
- [5] Sheldon et al. (2012) *Journal of Geology* 110.
- [6] Clark et al (2020). *JGR: Planets* [7] Navarro-Gonzalez et al. (2010). *JGR* 115.