Fe-rich Amorphous Material Formation and Persistence in Ultramafic Soils Consistent with Cold and Wet Conditions on Early Mars

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Introduction

-- X-ray amorphous material comprises 15% to 73% of total mass in all samples drilled to date at Gale Crater and examined by the CheMin diffractometer[1].

-- X-ray amorphous material in Gale crater is Fe-rich, typically Si-rich, and Al-poor, consistent with principally mafic sources[1]

-- Little is known about the nature of amorphous material in martian or terrestrial settings, Fe-rich in particular, nor what the presence of this material indicates about past environmental conditions on Mars.

-- We present results from bulk and nanoscale investigations of amorphous material in ultramafic soils to examine climatic effects on the formation and preservation of Fe-rich amorphous material.

Field Sites

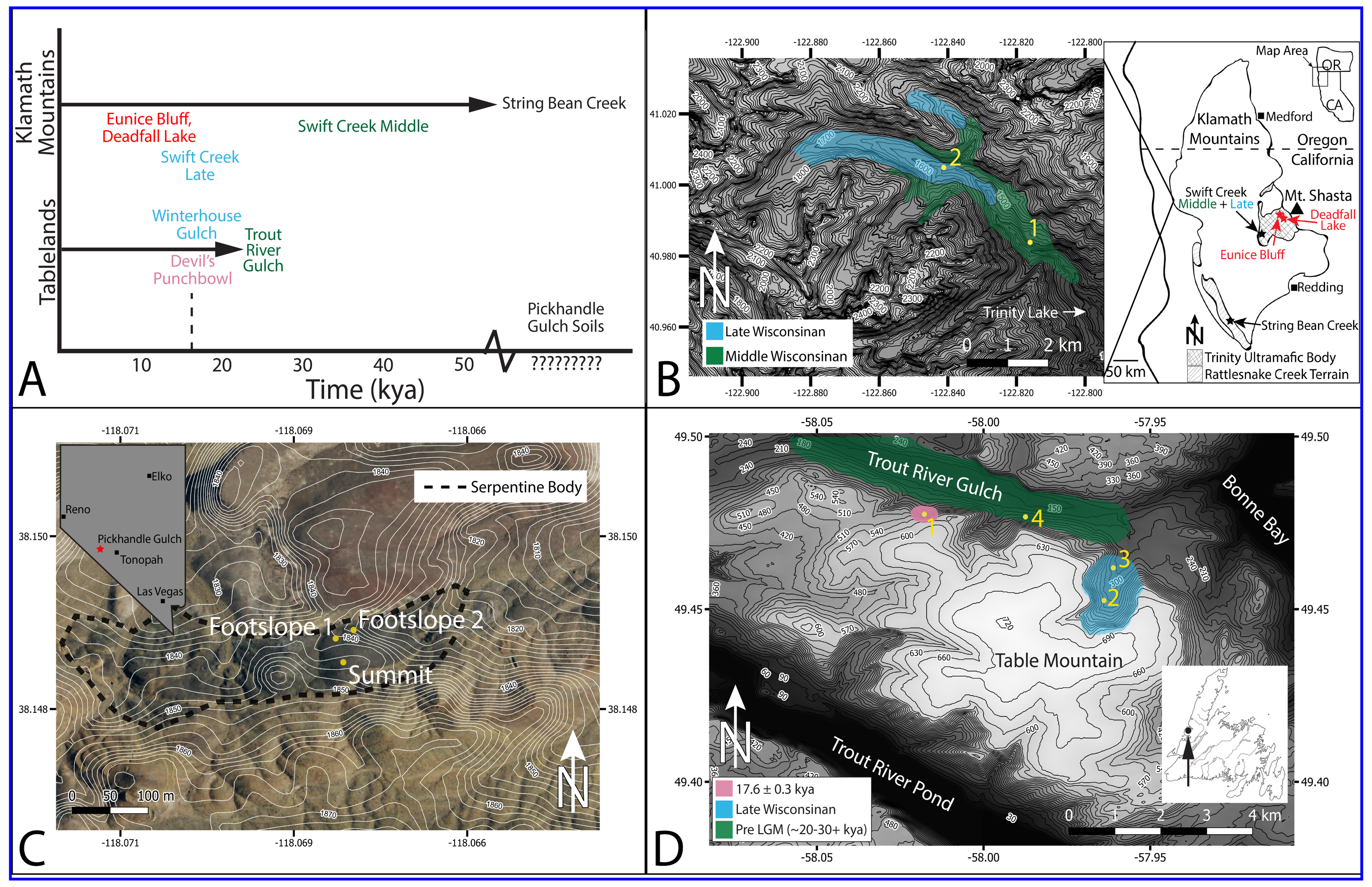
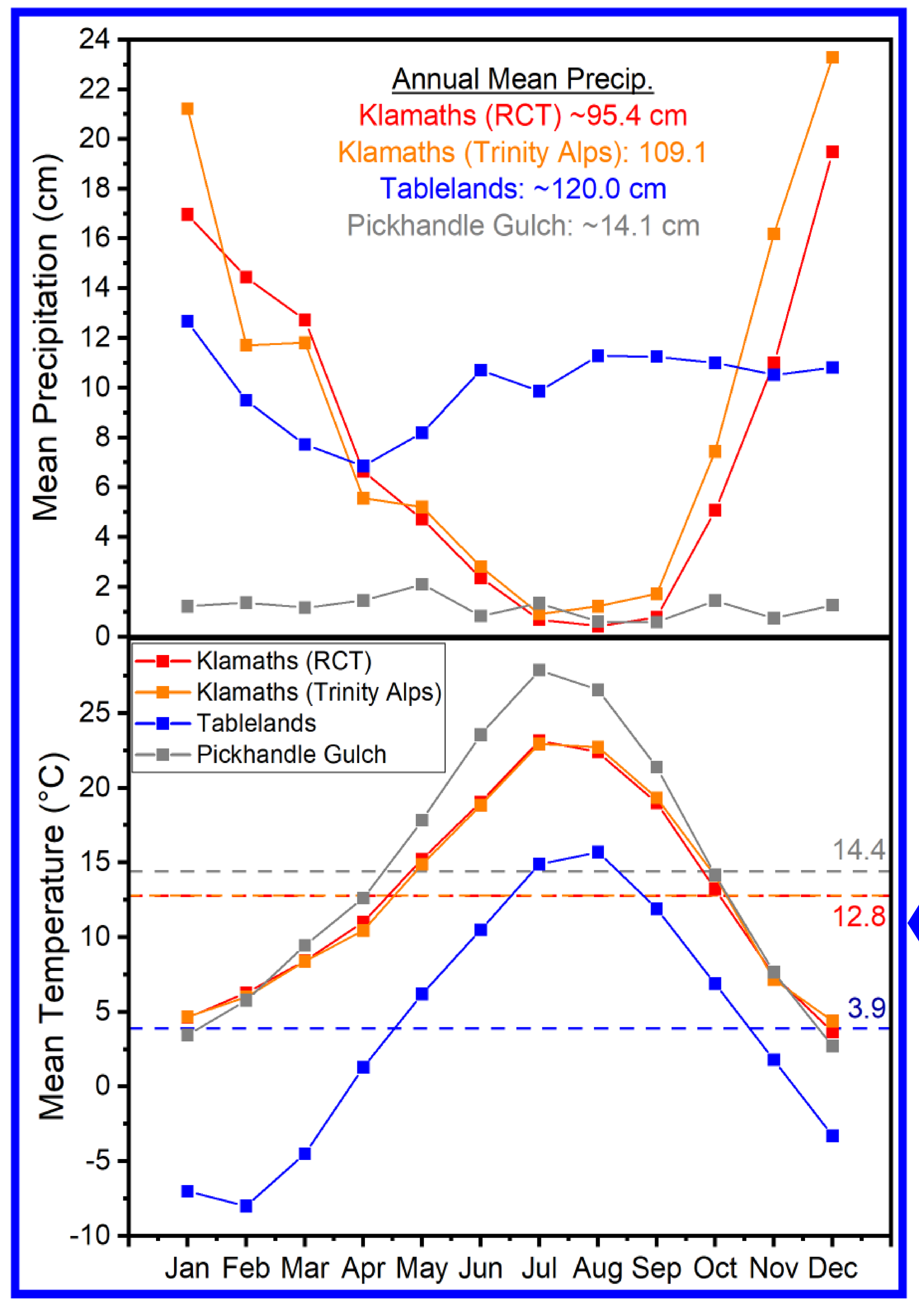


Figure 1: Ages of soils in the Klamath Mountains [2] and Tablelands [3] field sites (A), and sampling locations in the Klamath Mountains in California (B), at Pickhandle Gulch in Nevada (C), and at the Tablelands of Newfoundland, Canada(D)



Ultramafic soils were examined from three varying climatic regions

1. The Klamath Mountains of northern California
   - 2 Sub-locations
     - Trinity Ultramafic Body
     - Rattlesnake Creek Terrane
   - Mediterranean Climate
2. The Tablelands of Newfoundland, Canada
   - Subarctic Climate
3. Pickhandle Gulch, Nevada
   - Desert Climate

The Klamath Mountains and Tablelands were previously glaciated, allowing for an examination of changes in amorphous material over time (Figure 1).

Figure 2: Mean annual precipitation (top) and mean annual temperature (bottom) for field sites in the Klamath Mountains, Pickhandle Gulch, and the Tablelands.
Climate data for US sites from [4]
Climate data for Canadian sites from [5]

Soil Mineralogy and Bulk Chemistry

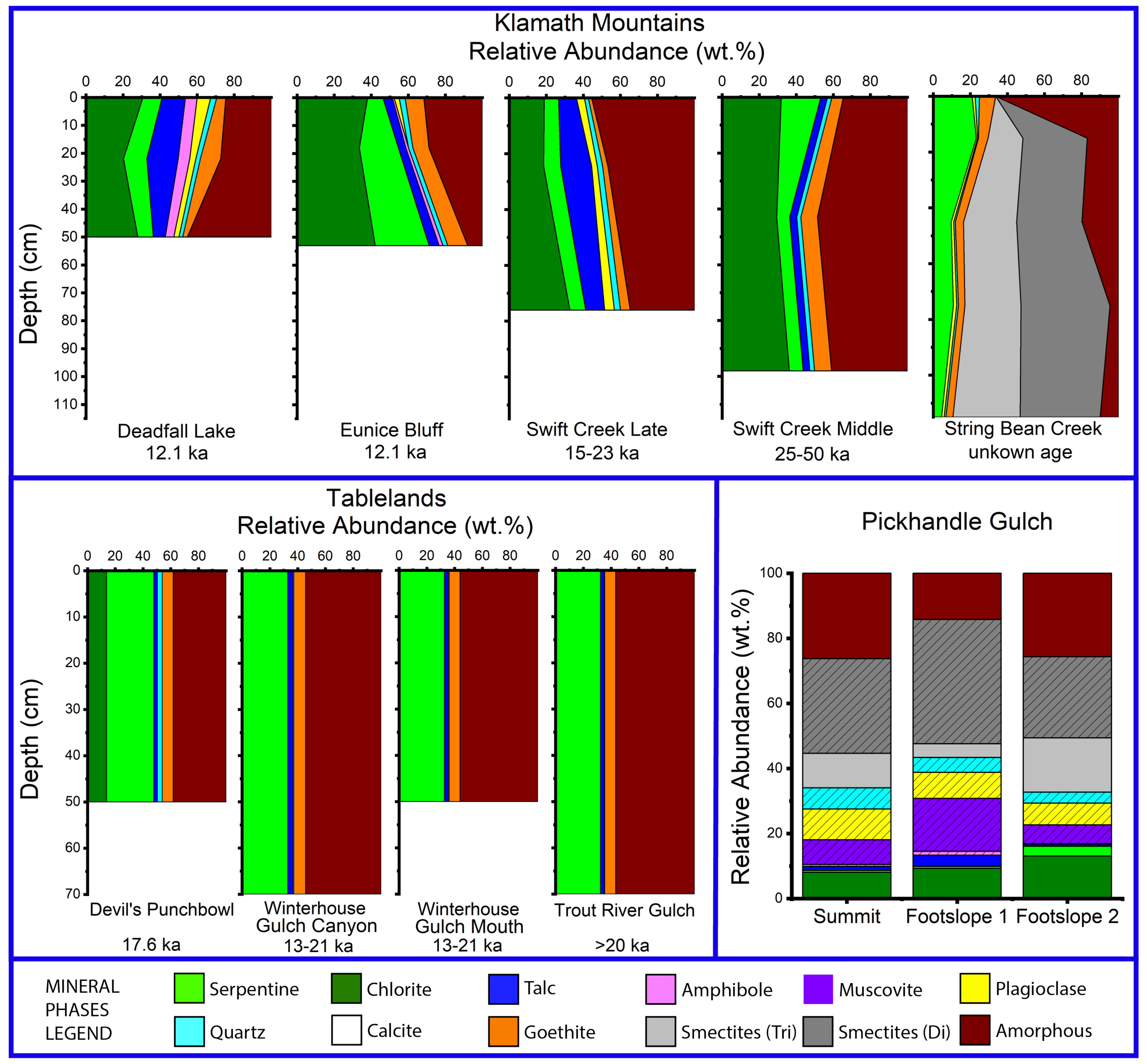


Figure 3: Crystalline phase and X-ray amorphous material abundences within clay-size fraction material from all examined soil pits. Abundances calculated by Rietveld refinement of powder XRD patterns from clay-size fraction samples spiked with 20 wt.% Al_2O_3-α as in [6]. Amorphous material is present in all examined clay-size fraction samples but is most consistently abundent in the clay-size fraction samples of the Tableland samples. Dustborne minerals are minimal in the Klamath Mountains and Tablelands but dominate at Pickhandle Gulch.

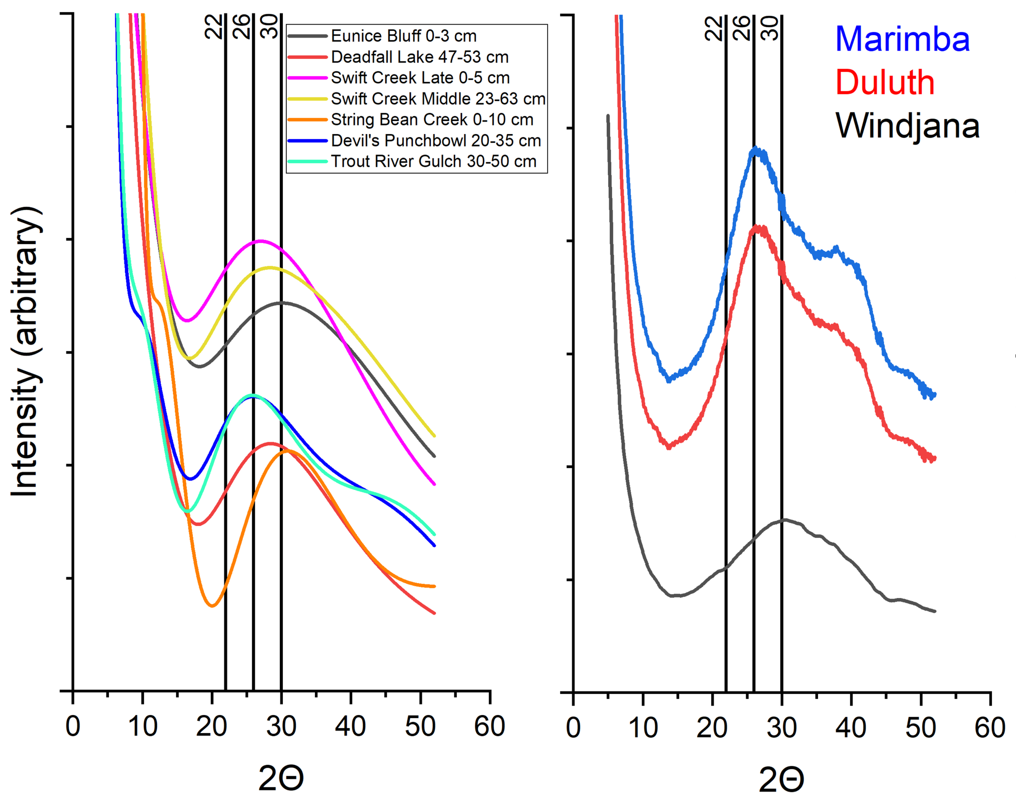


Figure 4: Comparison of the background from Rietveld refinement fits of clay-size fraction material from Klamath Mountain and Tablelands soils (left) with FullPat amorphous fits of CheMin XRD (right) suggest potentially similar Fe-rich amorphous mateiral presence.

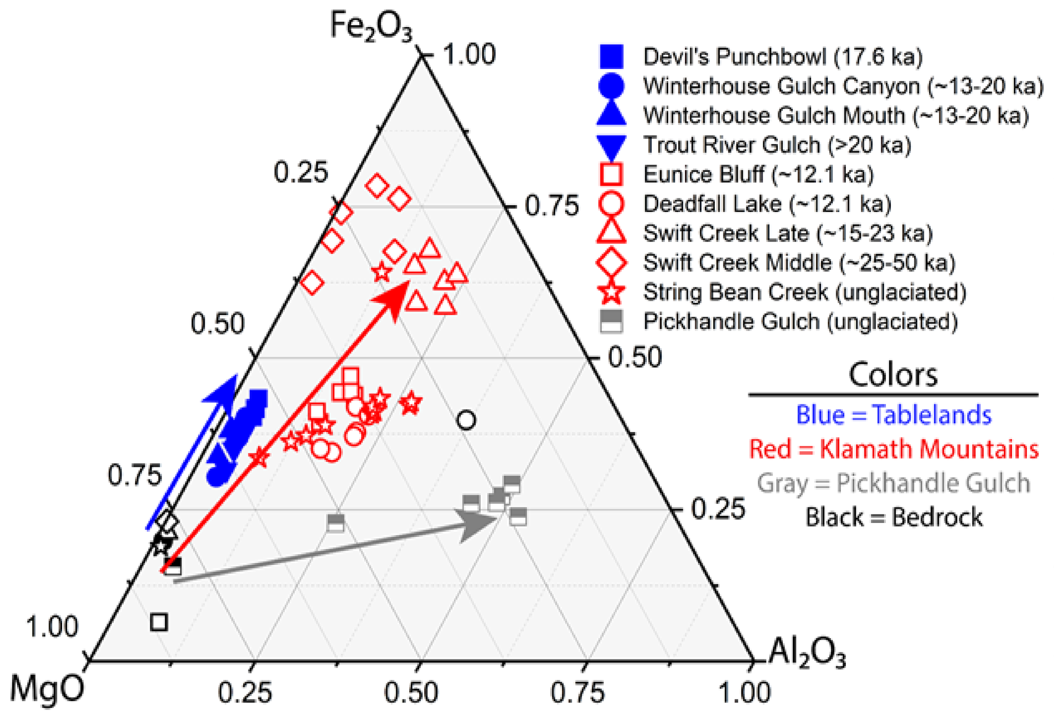


Figure 5: Ternary diagram of MgO, Fe_2O_3, and Al_2O_3 content within bedrock and the soil the clay-size fraction. Chemistry determined by ICP-MS at UNLV following dissolution in HF. Arrows denote overall concentration trends from the bedrock to the clay size fraction material.

Amorphous Material Formation and Persistence

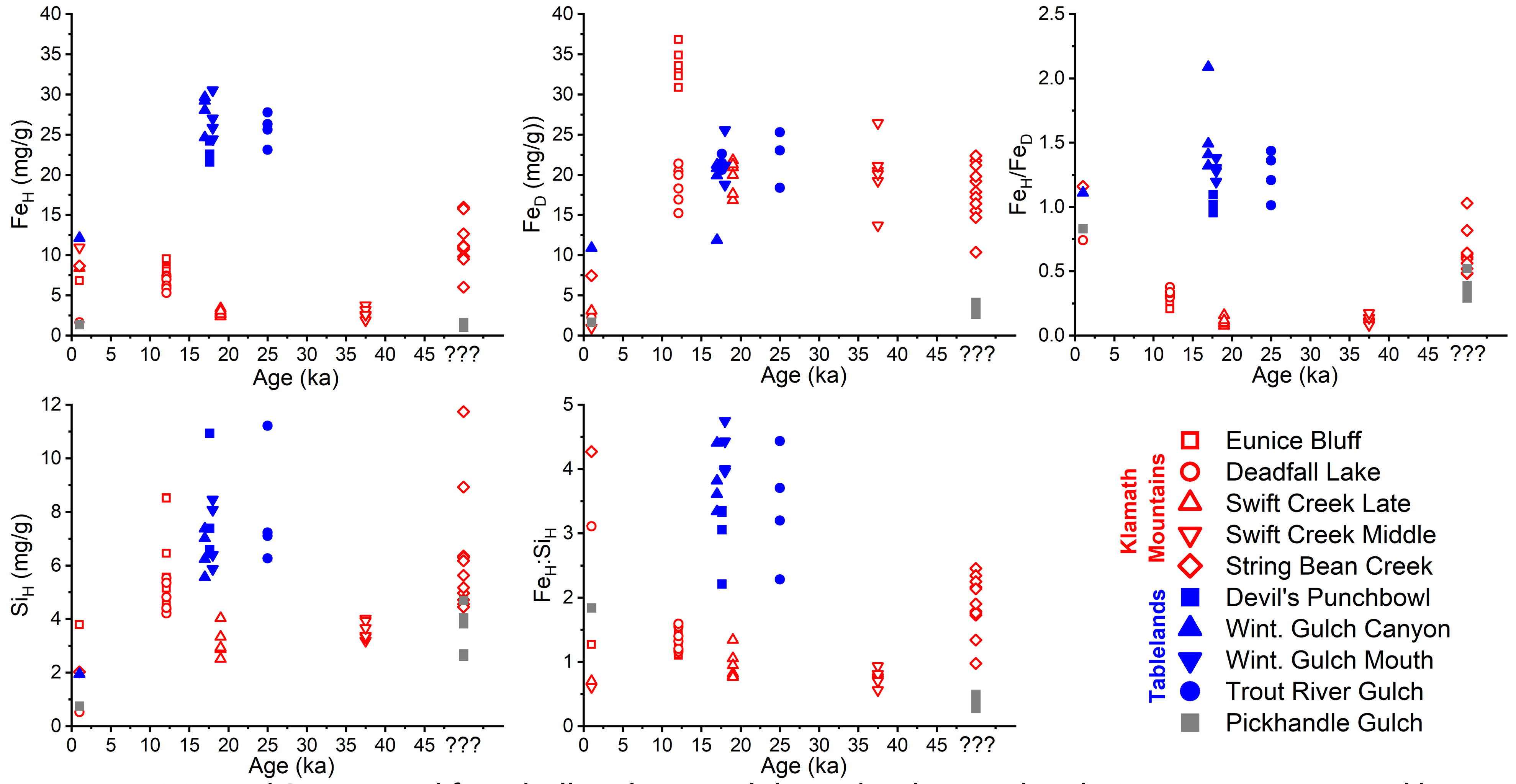
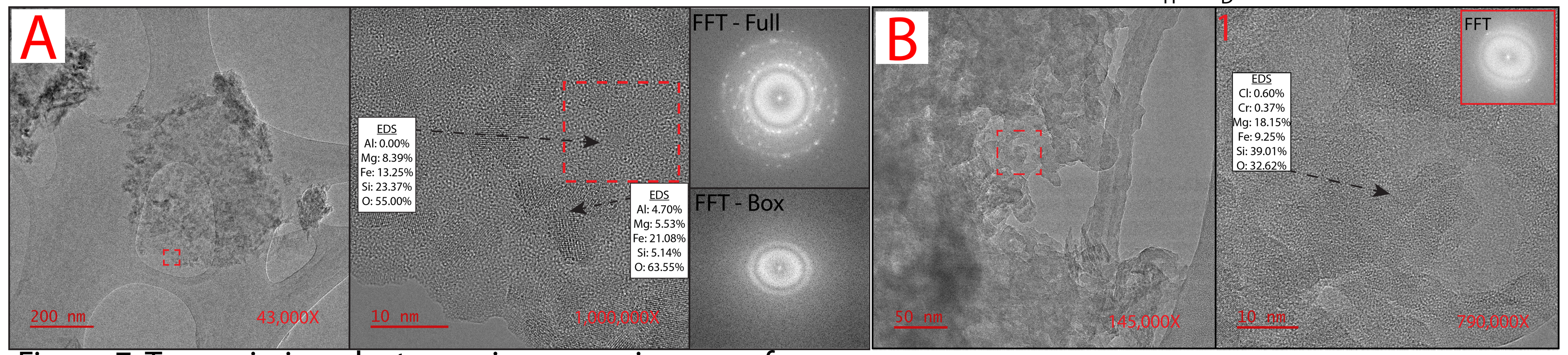


Figure 6: Fe and Si extracted from bulk soil material through selective dissolution agents, measured by atomic absorption spectroscopy, and plotted vs soil age. Hydroxylamine hydrochloride (Fe_H, Si_H) acts as both an acid protonation and reduction agent attacking amorphous to poorly crystalline material [7]. Na-Dithionite (Fe_D) acts as a purely reducing agent at near nuetral pH (~7.3), preferentially attacking Fe-oxyhydroxides as well as some structural Fe within smectites [7]. Fe_H, Fe_D, and Si_H are measured as mg of Fe or Si per g of soil. Data points are from different depth intervals within each soil profile. Bedrock parent material values are given at time = 1 ka. Klamath Mountain sampling sites are geographically disparate (see Figure 1) and one parent material sample was analyzed per soil pit. One parent material sample was analyzed for the Tablelands and Pickhandle Gulch regions respectively as soil pits at these sites were in close proximity geographically (see Figure 1). Amorphous material, and Fe-rich amorphous material in particuarl, is much more abundent in the Tablelands than at other sites. Secondary Fe is also significantly less crystalline (Fe_H/Fe_D) in the Tablelands.



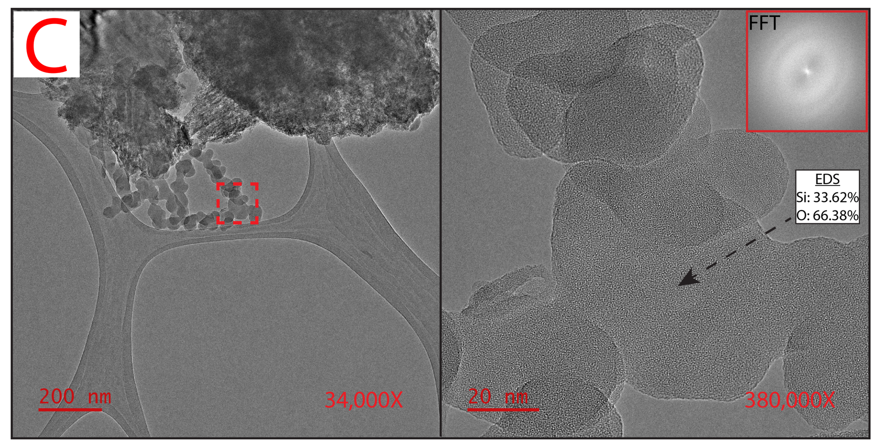


Figure 7: Transmission electron microscopy images of clay-size fraction material taken at the Arizona State University Eyring Materials Center on a FEI Titan ETEM.
A) "Fluffy" mixed Fe/Si/Mg amorphous/nanocrystalline assemblages are present in the Klamath Mountain soil clay-size fraction. Nanocrystalline domains are significantly more Fe-rich and can contain some Al-content.
B) Si/Mg/Fe-rich amorphous material is widespread in the Tablelands soil clays-size fraction and lacks the Klamath's intertwined nanocrystalline component.
C) Pure SiO_2 "globular" amorphous material is present in both the Klamath Mountains and Tablelands soils.

Implications For Mars

--The cool and wet conditions at the Tablelands favor the formation and persistence of Fe-containing amorphous material
--The warm and wet conditions in the Klamath Mountains favor development of crystalline Fe-containing secondary phases
--The dry conditions at Pickhandle Gulch favor accumulation of detrital phases with little in-situ alteration
--Amorphous SiO_2 forms in both the Klamath Mountains and Tablelands soils, suggesting highly siliceous Gale crater amorphous material could form in both warm or cold conditions
--These results indicate that the abundant quantities of Fe-rich amorphous material within Gale Crater bolster arguments for the presence of wet but cold, likely near freezing, conditions during formation, likely followed by long term cold and dry conditions that facilitated the preservation of the Fe-rich amorphous material.

References

[1] Rampe et al. (2020) *Geochemistry* [2] Sharp (1960) *Am. J. of Science* [3] Osborn et al. (2007) Can. J. of Earth Sci. [4] Arguez et al. (2010) NOAA's 1991-2020 US climate normals [5] Environment Canada Weather Station 8401335 [6] Smith et al. (2018) *JGR Planets* [7] Shang and Zelazny (2008) *Methods of Soil Analysis Part 5 Mineralogical Methods: Selective Dissolution Techniques for Mineral Analysis of Soils*

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