Cooler and Wetter Conditions Favor Fe-Rich Amorphous Material Formation and Persistence in Terrestrial Soils Chemically Similar to Sediments at Gale Crater, Mars

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Overview

▪Sedimentary rocks and aelian sediments at Gale crater, Mars contain between 15-73 wt.% X-ray amorphous material. [1]

▪The Gale crater amorphous material is Fe-rich, siliceous, often Mg-rich, and contains weathering products based on high volatile content [1]

▪Little is currently known about the makeup of the amorphous material, its relationships with the crystalline phases, or what it indicates about past climatic conditions at Gale crater

▪We are studying terrestrial Fe/Mg-rich soils to identify climatic influences on the formation and development of Fe-rich amorphous material

▪Methods: XRD analysis coupled with Rietveld refinement and bulk and selective dissolution techniques

▪Within Fe/Mg-rich soils, Fe preferentially concentrates into clay-size weathering products while Mg appears depleted relative to bedrock concentrations

▪Cooler and wetter conditions favor formation and longevity of Fe-rich amorphous material

▪Warmer climatic conditions favor formation of crystalline oxyhydroxides in young soils with development of smectites over time

Introduction

X-ray amorphous material has been detected in all samples measured within Gale crater, Mars to date, with smectites commonly found in ancient fluviolacustrine mudstones [1]. Chemical data indicate the amorphous material is Fe-rich and at least partly incipient weathering products [1]. Despite its prevalence, little is known about the nature of the Fe-rich amorphous material or its relationship with the crystalline phases present. In this study we are investigating pedogenesis within terrestrial Mars-analog ultramafic soils of different ages within mediterranean, subarctic, and desert climates. Bulk and selective digestion methods and Rietveld refinements of powder XRD patterns are utilized to examine climatic effects upon soil mineralogy and chemistry and the formation and longevity of Fe-containing amorphous material.

Methods

Sample Collection and Processing

•Soil pits excavated by hand to contact with bedrock, a C horizon, or standing water (only in the Tablelands)
•Soil (<2mm) sieved from full gravel + soil material
•Bulk soil subsamples powdered in an agate pulverisette
•Clay size fraction (<2 µm) extracted via suspension and settling [2]

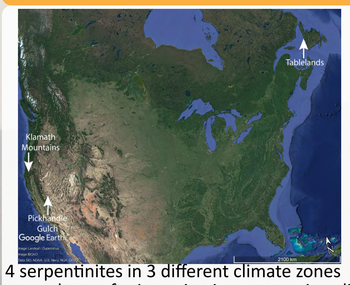
Mineralogy

X-ray Diffraction -- Proto AXRD, Cu kα
▪Bulk Soil - randomly oriented mounts
▪Clay-Size Fraction - randomly oriented and oriented mounts
*Amorphous material concentrates in clay sizez fraction [3]
*Oriented Mounts = Mg-saturated and air dried, Mg-saturated and ethylene glyvol vapor saturated, K-saturated and heated to 550 °C
Rietveld Refinement
▪Amorphous and crystalline abundances in clay-size fraction
▪Crystalline Standard: 20 wt. % α-Al_2O_3
▪BGMN package [4] and Profex GUI [5]

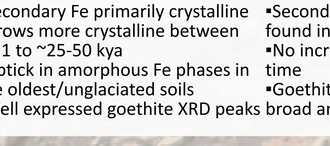
Chemistry

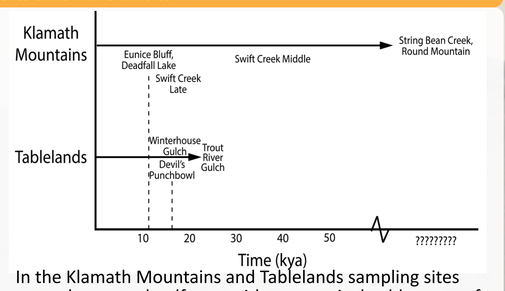
Selective Dissolutions of Bulk Soil
▪Determine secondary Fe content in different soil reservoirs
▪Hydroxylamine Hydrochloride (FeH): Attacks amorphous Fe oxyhydroxides and silicates [6]
▪Citrate Dithionite (FeD): Attacks amorphous and crystalline oxyhydroxides [7]
▪Sodium Pyrophosphate (FeP): Attacks organically complexed Fe [6]
▪Supernatants analyzed by atomic absorption spectroscopy
Bulk Dissolution of Clay Size Fraction
▪1:1 HF:HNO_3 and analyzed via quadrupole ICP-MS

Field Sites

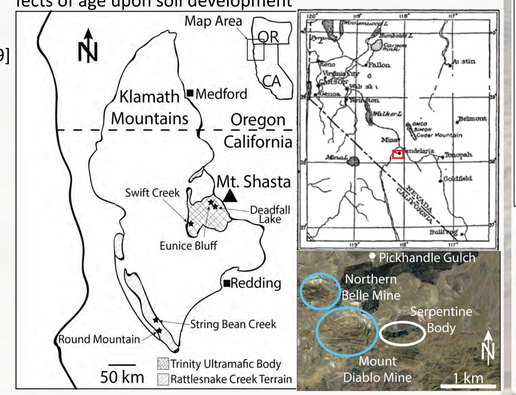


4 serpentinites in 3 different climate zones were chosen for investigation to examine climatic influences on chemical weathering of serpentinite bedrock and serpentine soils
1. Klamath Mountains (right)
Mean Annual Temperature: 12.7-12.8 °C [9]
Mean Annual Precipitation: 98.7-109.1 cm [9]
2. Tablelands (below)
Mean Annual Temperature: 13.0 °C [10]
Mean Annual Precipitation: 6.1 cm [10]
3. Pickhandle Gulch (far right)
Mean Annual Temperature: 3.9 °C [9]
Mean Annual Precipitation: 120.3 cm [9]



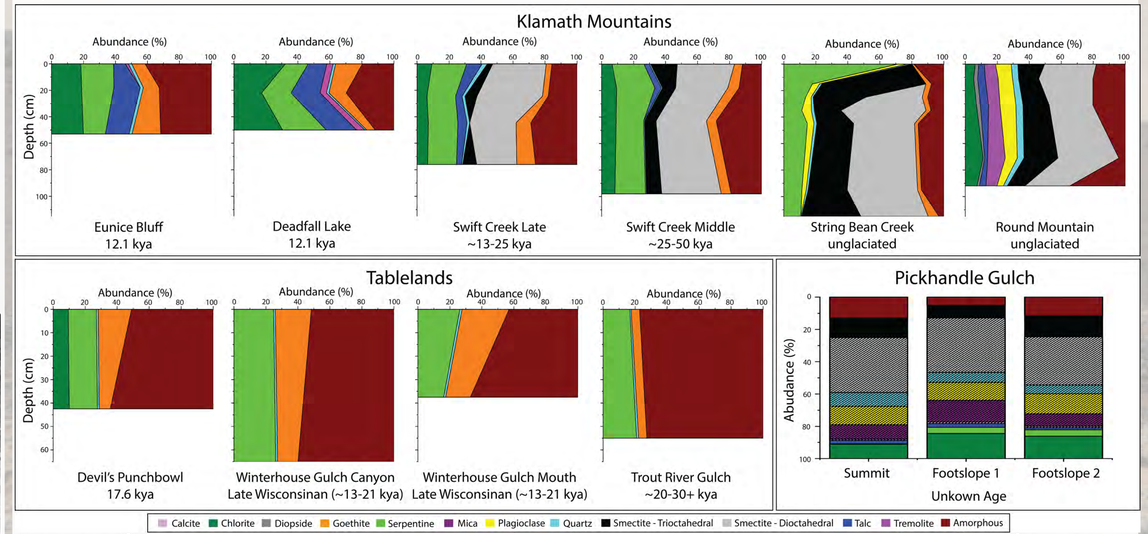


In the Klamath Mountains and Tablelands sampling sites were chosen on landforms with progressively older ages of deglaciation or that were not glaciated to examine the effects of age upon soil development



Clay-Size Fraction Mineralogy

Crystalline Phase and Amorphous Material Abundances Calculated by Rietveld Refinement of Clay Size Samples spiked with 20 wt.% α-Al_2O_3.



Klamath Mountains

▪Young soils contain primariy inhereted phases, older soils contain primarily weathering products
▪Initial formation of amorphous material and Fe-oxyhydroxides in young soils
▪Development of smectites in older soils and decreased amorphous content

Tablelands

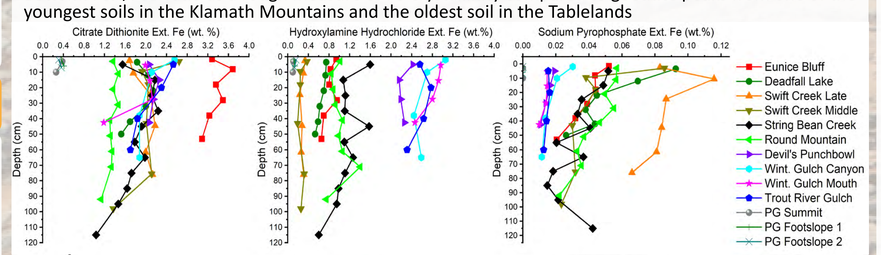
▪Amorphous material dominates the clay-size fraction regardless of soil age
▪No development of smectites in any soil regardless of age
▪Amorphous material abundance increases in the oldest soil

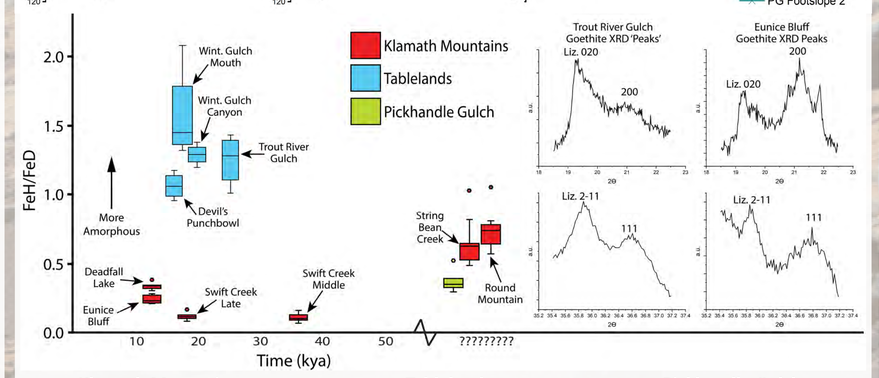
Pickhandle Gulch

▪Clay-size fraction dominated by phases resulting from dust influx (muscovite, plagioclase, quartz, dioctahedral smectites)
see hatch marks for phases in dust
▪Minimal amorphous content
▪Minimal inhereted phases from parent material (Talc, Serpentine, Chlorite)

Fe-Crystallinity

Top: wt. % Fe extracted from powdered bulk soil material by the citrate dithionite (FeD), hydroxylamine hydrochloride (FeH), and sodium pyrophosphate (FeP) selective dissolutions
Bottom: FeH/FeD ratio as a rough measure of Fe-crystallinity compared to goethite peaks from one of the youngest soils in the Klamath Mountains and the oldest soil in the Tablelands





Klamath Mountains

▪Secondary Fe primarily crystalline
▪Grows more crystalline between 12.1 to ~25-50 kya
▪Uptick in amorphous Fe phases in the oldest/unglaciated soils
▪Well expressed goethite XRD peaks

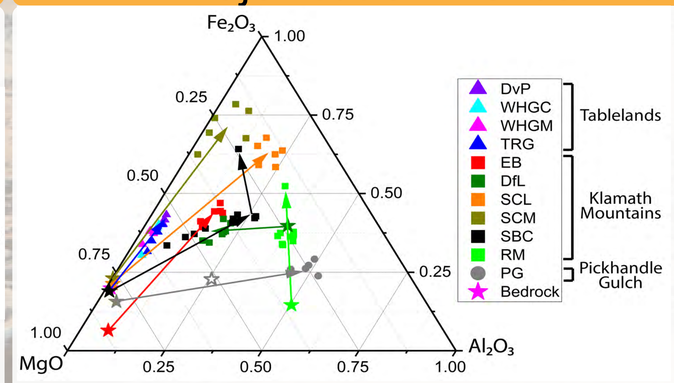
Tablelands

▪Secondary Fe almost if not entirely found in amorphous material
▪No increase in crystallinity over time
▪Goethite XRD 'peaks' exceedingly broad and low amplitude

Pickhandle Gulch

▪Secondary Fe primarily crystalline
▪Much less secondary Fe overall than within the wetter climate zones
▪Minimal amorphous Fe-phases
▪No organic complexation of Fe

Major Cation Trends in Clay-Size Fraction



MgO, Fe_2O_3, and Al_2O_3 values normalized to 1. Stars denote bedrock concentrations, triangles and squares and circles denote oxide concentrations in the clay size fraction. The open star denotes a weathered bedrock sample at Pickhandle Gulch

Klamath Mountains

▪Concentration of Fe into clay size fraction material
▪Mg depleted compared to bedrock
▪Young soil (DfL) = Al-depletion from lack of dissolution of Al-bearing primary silicates

Tablelands

▪Concentration of Fe into clay size fraction material
▪Mg depleted compared to bedrock

Pickhandle Gulch

▪Clay-size fraction highly Al enriched compared to bedrock
▪Al enrichment indicative of aeolian influx of Al-smectites and Muscovite

Abbreviations) DvP: Devil's Punchbowk, WHGC: Winterhouse Gulch Canyon, WHGM: Winterhouse Gulch Mouth, TRG: Trout River Gulch, EB: Eunice Bluff, DfL: Deadfall Lake, SCL: Swift Creek Late, SCM: Swift Creek Middle, SBC: String Bean Creek, RM: Round Mountain, PG: Pickhandle Gulch

Conclusions

▪Fe-crystallinity affected by climatic conditions
•Wetter conditions favor formation of Fe-rich amorphous material while cold conditions (near to sub-freezing) favor persistence of Fe-rich amorphous material
▪In soils where in-situ aqeous weathering is the primary pedogenic process, Fe is concentrated in the clay size fraction and Mg is depleted relative to parent material concentrations
▪In the desert soils where dust influx is the primary pedogenic process aeolian additions lead to Al enrichment in the clay-size fraction
▪Uptick in amorphous Fe within oldest Klamath Mountain soils potentially reflects the development of Fe-containing proto-smectites
▪The presence of large quantities of amorphous Fe-containing material in Gale crater sediments suggests wet and near-freezing conditions during and near to sub-freezing conditions post-formation

References

[1] Rampe et al. (2020) *Geochemistry*, 80, 2, 125605 [2] Edwards and Bremner (1968) *J Soil Science*, 18, 1, 64-72. [3] Yesavage et al. (2015) *Icarus*, 254, 219-232. [4] Bergmann et al. (1998) *CPD Newsletter*, 20, 5. [5] Doebelin and Kleeberg (2015) *J App Cryst.* 48, 5, 1573-1580. [6] Shang and Zelazny (2008) *Meth. Soil. An. Part 5 Min. Meth.* 33-80 [7] Soil Survey Staff (2004) *Soil Survey Lab. Info. Man.* 305 [8] Arguez et al. (2010) NOAA's US climate normals (1981-2010). *NOAA Nat. Cen. Env. Inf.* 10, V5PN93JP [9] Environment Canada Weather Station 8401335

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