

PERSISTENCE OF FE-CONTAINING X-RAY AMORPHOUS MATERIAL FAVORED IN COOLER CLIMATES. A. D. Feldman¹, E. M. Hausrath², O. Tschauer², E. B. Rampe³, ¹University of Nevada, Las Vegas (feldma2@unlv.nevada.edu), ²University of Nevada, Las Vegas, ³NASA Johnson Space Center

Introduction: X-ray diffraction (XRD) measurements have demonstrated that X-ray amorphous material makes up between 15 to 73 wt.% of Gale crater sediments, with a large fraction of this X-ray amorphous material being Fe-rich and siliceous [1,2]. The identity of this X-ray amorphous material (hereafter referred to as amorphous) and its relationship with crystalline phases remains elusive [1], hampering our ability to understand the environmental conditions that result in the formation and persistence of this material over geologic time. Though [3] postulated that ‘gel-like’ material might form an intermediate step during smectite formation in Fe/Mg-rich soils derived from ultramafic material, to the best of our knowledge little work has examined the persistence of Fe-containing poorly crystalline material as a function of time and climate. To gain a better understanding of the persistence of amorphous material in Fe-rich soils under different climatic conditions, we have investigated mineral and chemical transitions in terrestrial soils derived from ultramafic parent material of different ages within mediterranean and subarctic climates.

Methods: Bulk samples of soil and gravel were collected from 6 soil pits in the Klamath Mountains of California and 4 soil pits in the Tablelands of Newfoundland, Canada. The Klamaths possess mean annual temperatures of ~9 to 12°C [4]. The Tablelands possess a mean annual temperature of <4°C [5]. In the Klamaths, samples were collected from soils dating to 12.1 kya, ~20-30 kya, and ~30-60 kya, and from unglaciated soils [6,7]. In the Tablelands, samples were collected from 17.6 kya and ~25-30+ kya soils, as well as two undated soils estimated to be intermediate in age between the prior soils [8]. Bulk soil (<2mm diameter) was sieved from the soil+gravel samples, followed by extraction of the clay size fraction (<2 μm diameter) by sonication, suspension, and settling [9] for further analyses, as weathering products are likely concentrated in this size fraction [10]. The clay size fraction was analyzed using XRD to determine the crystalline and amorphous material abundances. The bulk soil was analyzed through the application of selective dissolution techniques to determine the reservoirs of Fe within secondary materials.

XRD Analyses. XRD analyses utilized a Proto-AXD Bragg-Bentano type X-ray diffractometer with a Cu Kα source (1.541 Å wavelength). XRD analyses of the clay size fraction were conducted on oriented mounts following Mg-saturation, air drying, and solvation with

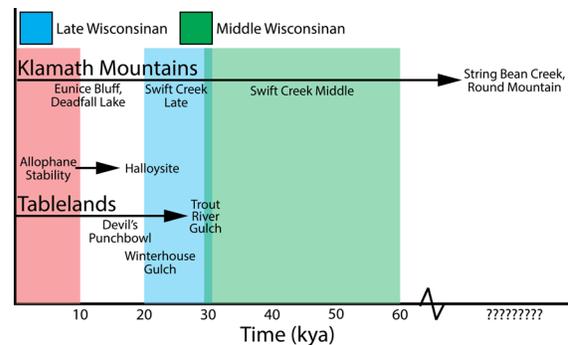


Figure 1: Soil ages for all sampling sites. Klamaths ages from [6,7], Tablelands from [8]. The stability window for allophane, an Al-rich amorphous silicate, is from [9].

ethylene glycol vapor, and after K-saturation and heating to 550°C, and on randomly oriented mounts spiked with 20 wt.% α -Al₂O₃. Crystalline and amorphous abundances were calculated from the spiked patterns using the Rietveld method in the Profex software [12].

Selective Dissolutions. Selective dissolution methods were applied to examine Fe within secondary products. A hydroxylamine hydrochloride method (25 mL of 0.25 M NH₂OH-HCl + 0.25 M HCl to 100 mg sample) was applied to bulk soil material to determine Fe within amorphous and poorly crystalline materials, both (oxyhydr)oxides and silicates (FeH) [14]. A citrate dithionite method (25 mL of 0.57 M Na₃C₆H₅O₇·2H₂O to 400 mg Na₂S₂O₄ and 750 mg sample) was used to examine Fe within amorphous and crystalline (oxyhydr)oxides (FeD) [15]. We calculated the FeH/FeD ratio as an estimate of the crystallinity of Fe within secondary material in each soil, with the caveat that the ratio does not account for Fe incorporated within crystalline clays.

Results and Discussion:

XRD Analyses. Amorphous material is the most abundant weathering product within the youngest Klamath and Tablelands soils, with some goethite present (Fig. 2, A, B, E). Smectites first appear in the clay size fraction of the ~30-60 kya Klamath soil, concurrent with a decrease in the amorphous material abundance (Fig. 2, C). Smectite abundance increases in the oldest Klamath soils (Fig. 2, D). Amorphous material dominates the clay size fraction in all Tablelands soils regardless of age (Fig. 2: E→H), and is consistently greater in abundance in the Tablelands soils than within the Klamath soils. Smectites are absent from the entirety of the Tablelands soils (Fig. 2, E→H).

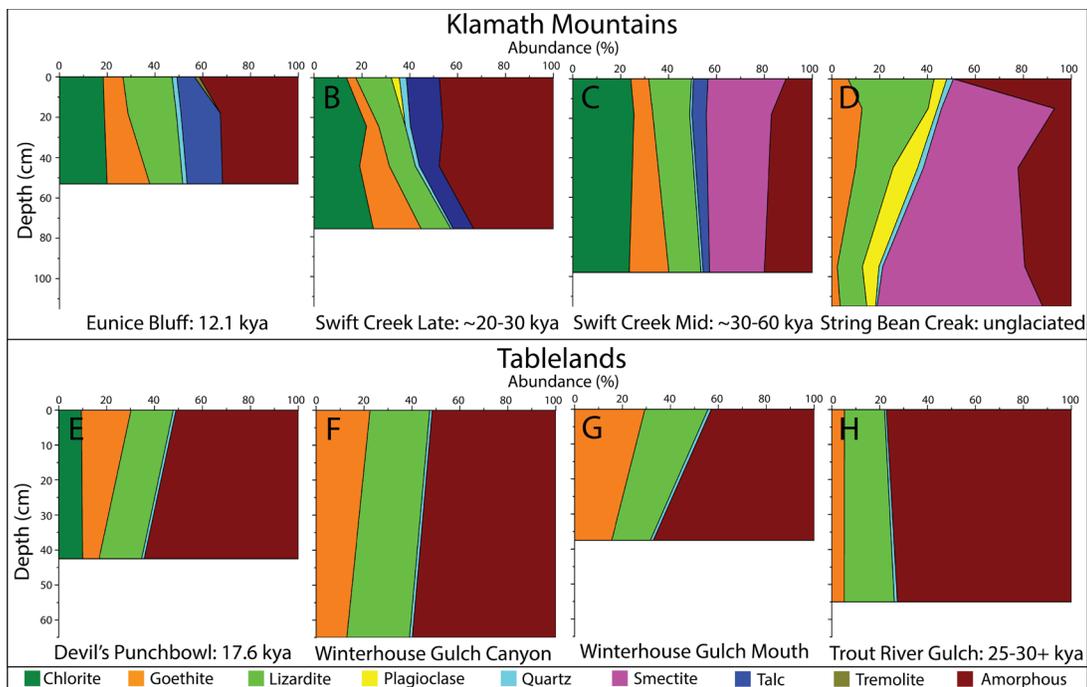


Figure 2: Abundances of mineral and amorphous constituents within Klamath Mountains and Tablelands soils clay size material.

Selective Dissolutions. Fe in the bulk Klamath soils is primarily found within crystalline oxyhydroxides as defined by the FeH/FeD ratio (Fig. 3). Fe crystallinity initially increases between the ~12.1 kya to ~20-30 kya Klamath soils. However, Fe-containing secondary material is less crystalline in the oldest Klamath soils (Fig. 3). This decrease in the crystallinity of Fe-containing secondary material within the Klamath soils corresponds to a decrease in amorphous material abundance measured by XRD and the formation of smectites, possibly indicating the incorporation of Fe into proto-smectites in the oldest soils. In the Tablelands soils, with one exception in the youngest soil, >50% of Fe in secondary products is found within

amorphous and poorly crystalline materials and does not appear to exhibit correlation with age (Fig. 3).

Conclusions: Fe-rich amorphous material longevity appears correlated with mean annual temperature. Colder conditions favor the preservation of amorphous material over conversion to crystalline phases, and warmer conditions favor conversion to more crystalline phases, potentially including smectites. These results are thus consistent with previous work suggesting widespread occurrences of amorphous material on Mars indicate a predominantly cold Martian climate since the formation of the observed amorphous material [15,16].

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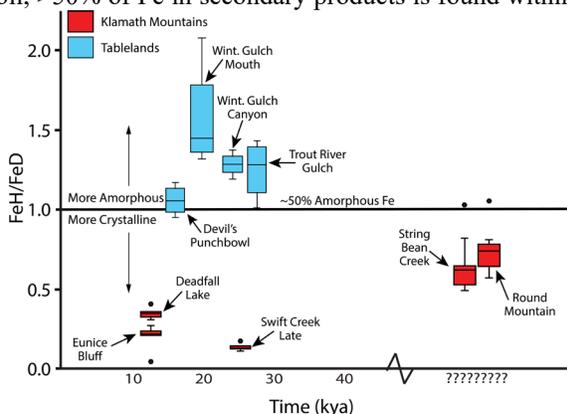


Figure 3: FeH/FeD ratios within the bulk soil from the Klamath Mountains and Tablelands. 0:1 ratio indicates 100% Fe within crystalline (oxyhydr)oxides, 1:1 ratio indicates ~50% of Fe is within amorphous materials, >1:1 indicates more Fe within amorphous materials.