PHYLLOSILICATE TRANSITIONS IN FERROMAGNESIAN SOILS: SHORT-RANGE ORDER MATERIALS AND SMECTITES DOMINATE SECONDARY PHASES.

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Introduction: Analyses of X-ray diffraction (XRD) patterns taken by the CheMin instrument on the Curiosity Rover in Gale crater have documented the presence of clay minerals interpreted as smectites and a suite of amorphous to short-range order materials termed X-ray amorphous materials [1-5]. These X-ray amorphous materials are commonly iron-rich and aluminum poor [5] and likely some of them are weathering products rather than primary glasses due to the presence of volatiles [5, 6]. Outstanding questions remain regarding the chemical composition and mineral structure of these X-ray amorphous materials and the smectites present at Gale crater and what they indicate about environmental conditions during their formation. To gain a better understanding of the mineral transitions that occur within ferromagnesian parent materials, we have investigated the development of secondary clay minerals and short-range order materials in two soil chronosequences with varying climates developing on ultramafic bedrock.

Field Sites: We investigated soil weathering within two field locations, the Klamath Mountains of Northern California, and the Tablelands of Newfoundland, Canada. Both sites possess age dated or correlated recently deglaciated soils and undated but substantially older soils. In the Klamath mountains the Trinity Ultramafic Body was deglaciated roughly 15,000 years bp [7] while in the Tablelands a moraine was dated to about 17,600 years bp [8]. The Klamath Mountains feature a seasonally wet and dry climate [9] while the Tablelands are wet year-round [8] with saturated soil conditions observed during sampling and standing water observed within 3 of 4 soil pit sampling locations.

Methods: Four soil pits were excavated at each field location at both the Klamath Mountains and Tablelands. In the Klamaths, two pits (Eunice Bluff: EB, and Deadfall Lake: DfL) were placed in the recently deglaciated Trinity Ultramafic Body and two (String Bean Creek: SBC and Round Mountain: RM) in the unglaciated Rattlesnake Creek Terrain [7]. At the Tablelands, one soil pit was emplaced behind a moraine dated to 17,600 years bp (Devil's Punchbowl: DvP) [8], two soil pits were located in a nearby valley of similar age (Winterhouse Gulch Mouth and Canyon: WHGM and WHGC) [8], and one was located in a valley estimated to have been deglaciated prior to the Quaternary glacial maximum (Trout River Gulch: TRG) [8]. Soil pits were excavated to point of refusal or contact with the water table. Whole rock samples were also collected from within soil pits, float, and nearby bedrock outcrops to provide constraints on parent composition.

Klamath soil samples were stored on dry-ice immediately after collection and all soil samples were stored at -20ºC in the laboratory. The <2mm bulk soil fraction was acquired by dry sieving followed by mixing with 1M NaCl, vortexing, sonication, and centrifugation to extract the clay size fraction [10]. XRD analysis was conducted using a Proto-AXD Bragg-Bentano type X-ray diffractrometer with a Cu Kα tube (1.541Å wavelength), a Dectris hybrid pixel array detector, and Soller slits. XRD analyses were performed on both randomly oriented mounts and oriented mounts with Mg-saturated clay size material that was air dried then solvated with ethylene glycol. Mineral phase and X-ray amorphous abundances were calculated in the BGMN software using samples spiked with 20 wt. % Al_2O_3 [11].

Results and Discussion: XRD analyses indicate parent material mineralogy in the Klamath Mountains includes serpentine minerals, chlorite, talc, amphiboles, and residual non-serpentinized minerals including olivine and enstatite. The Tablelands parent material is more uniform, comprising only serpentine minerals, chlorite, talc, and olivine.

The clay size fraction of the youngest Klamath Mountain soils encompasses lizardite, indicated by a prominent peak at ~7.3Å, chlorite, talc, and an amphibole, as well as interstratified chlorite-smectites (Figure 1). The younger Klamath mountain soils also possess iron oxyhydroxides, indicated by the presence of peaks at ~4.2Å, 2.49Å, and 2.44Å. Some of the peaks are diffuse, indicative of possible nanoscale crystallites. Rietveld refinements indicate substantial development of X-ray amorphous content in the clay size fraction of the youngest Klamath mountain soils (Figure 2). The older Klamath soils exhibit a more smectite rich mineralogy indicated by the presence of (001) peaks that shift after solvation with ethylene glycol and heat treatments (Figure 3). The older Klamath soils possess few to no iron oxides and generally lack the original chlorite fraction. Although Rietveld refinements suggest a higher abundance of serpentine minerals in the String Bean Creek soil than in younger Klamath soils, this likely reflects local variations in parent material lithology. Rietveld refinements suggest a decrease or stabilization in amorphous content within older Klamath soils (Figure 2), though this varies with depth in the soil profile. A plagioclase and quartz component within the older Klamath soils also suggests some accumulation of airborne dust.

The crystalline component of the younger Tablelands soils clay size fraction is predominantly serpentine minerals and iron oxyhydroxides, with some chlorite and residual olivine (Figure 3). Rietveld refinement suggests the older Tablelands soils see uniform depletion in the proportions of all crystalline components and a concurrent increase in the presence of X-ray amorphous materials. While a low abundance of mixed chlorite-smectites is inferred from a broad and low peak found at an extremely low 2θ range, there is no observed peak to suggest the presence of purer smectite phases in any Tablelands soil.

Conclusions: In the Klamath Mountains, two primary silicate weathering reactions may be occurring, 1) a chlorite weathering sequence to interstratified chlorite-smectite which may eventually form purer smectites with time, and 2) a dissolution-precipitation reaction where Fe- and Mg-rich silicates (e.g. serpentine, olivine, amphibole, chlorite) dissolve, short range order and amorphous materials precipitate, and these materials transition into more crystalline smectites with time. In the Tablelands, chlorite is similarly inferred to transition to interstratified chlorite-smectites while X-ray amorphous materials form. However, neither formation of smectites from amorphous precursors nor interstratified clay-minerals is observed, possibly as a result of the much more saturated soil conditions and colder temperatures in the Tablelands than in the Klamath Mountains. These results indicate that the smectites within Gale crater could represent an end product of weathering of original olivine and other mafic minerals, with the substantial accumulations of X-ray amorphous materials indicative either of a weathering sequence that has not proceeded completely to its end products, or that cold temperatures and other environmental conditions inhibited the full transformation of the short range order component into more crystalline smectites. Smectites could also represent an original chloritic fraction that has since transitioned through a mixed chlorite-smectite component into pure smectite phases.

References: [1] Achilles, C.N., et al (2017) *GRP* 122, 2344-2361. [2] Morris R.V. et al. (2016) *NASA Working Doc.* [3] Yen, A.S. et al. (2017) *EPSL* 471, 186-198. [4] Rampe, E.B. et al. *EPSL* 471, 172-185 [5] Dehouck E. et al. *JGR: Planets* 119, 2640-2657 [6] Sutter B. et al. (2017). *GRP*. 122. 2574-2609. [7] Sharp R.P. (1960) *Science* 258, 305-340 [8] Osborn G. et al. (2007) *Can. J. Earth Sci.* 44, 819-834 [9] Alexander E. et al. (2009) *Soil Science* [10] Edwards AP and Bremner JM (1967) Eur. J of Soil Sci [11] Döbelin N. and Kleeborg R. (2015) *J. App. Cryst.* 48, 1573-1580

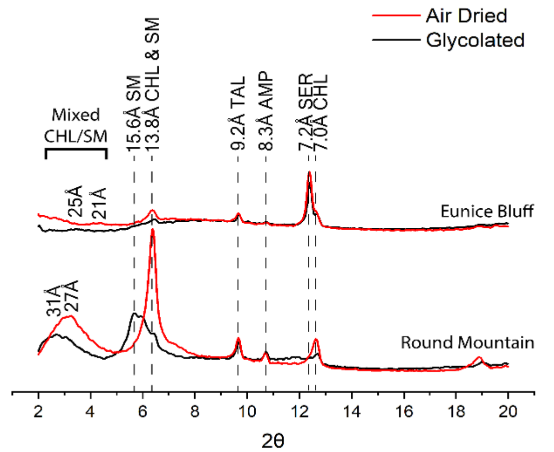

Figure 1: Mg-saturated oriented clay mount from select Klamath Mountain soil C horizons. SER: Serpentine, CHL: Chlorite, TAL: Talc, AMP: Amphibole, SM: Smectite

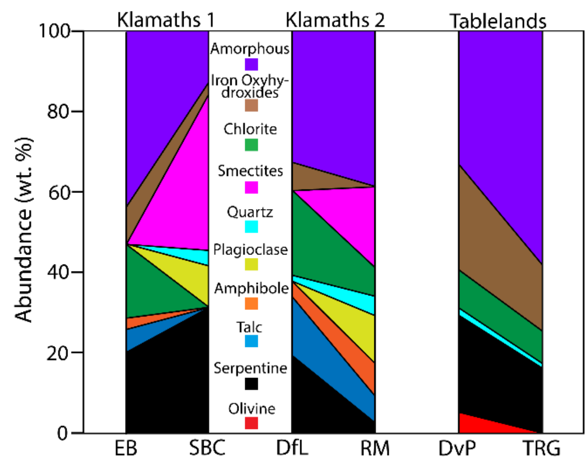

Figure 2: Phase abundances from Rietveld Refinements from the C horizon clay size fraction within each soil pit. Columns show change between younger (left) and older (right) soils. Although interstratified materials are observed in both old and young Klamath soils, they are not included in the Rietveld Refinement.

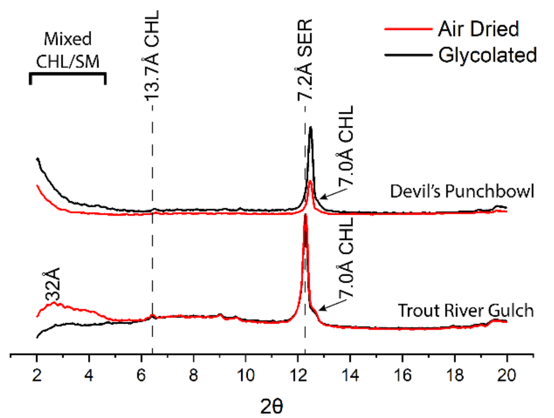

Figure 3: Mg-saturated oriented clay mounts from select Tablelands soil C horizons. SER: Serpentine, CHL: Chlorite, SM: Smectite