

Soil Evolution and Mass Flux of Basaltic Cinder Cones in a Cool, Semi-Arid Climate

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Soil developmental processes on young volcanic cinders in cool, semiarid climates are not well understood and previously under-studied, but present a unique setting within which to study neoformation of soils under well-dated time constraints. This study investigates the development of physical, chemical, and mineralogical soil properties on a chronosequence of basaltic cinder cones, aged approximately 2.1, 6.9, and 13.9 ka, at Craters of the Moon National Monument and Preserve in southern Idaho. Representative parent material, coarse fragments, and soil samples were analyzed using selective dissolutions and total elemental digests. Elemental mass balance data were used together with the soil physicochemical data to investigate weathering and secondary mineral formation within each soil profile. The highest degree of weathering was identified on the 13.9 ka profile, followed by the 6.9 and 2.1 ka soils. Short-range ordered minerals, including allophane and ferrihydrite, dominate the colloidal fraction of all soils, with greatest proportions in the oldest soil. Dominant soil-forming processes documented along the chronosequence of basalt-derived soils are the accumulation of organic carbon, weathering of rock fragments, loss of base cations, redistribution of Fe, Al, and Ti, and the accumulation of secondary short-range order and crystalline minerals. This study provides critical information to elucidate rates and processes of early stage weathering, dust influence, and soil evolution on cinders in cool and dry climates.

Abbreviations: 2.1 CG, 2.1 ka site; 6.9 BCB, 6.9 ka site; 13.9 SC, 13.9 ka site; Al_d , dithionite-citrate-bicarbonate extractable Al; Al_o , ammonium-oxalate extractable Al; Al_p , sodium-pyrophosphate extractable Al; AOD, ammonium-oxalate; CIA, compound index of alteration; CROM, Craters of the Moon National Monument and Preserve; DCB, dithionite-citrate-bicarbonate; Fe_d , dithionite-citrate-bicarbonate extractable Fe; Fe_o , ammonium-oxalate extractable Fe; Fe_p , sodium-pyrophosphate extractable Fe; Fe_t , total Fe; OC, organic C; ka, thousands of years before present; Si_o , ammonium-oxalate extractable Si; SRO, short-range order; XRD, x-ray diffraction.

Numerous studies have investigated soil evolution as a function of time in drylands that include assessment of Holocene soils (e.g., McFadden and Weldon, 1987; Chadwick et al., 1990; Merriitts et al., 1992; Langley-Turnbaugh and Bockheim, 1998; Zhang et al., 2007), but very few detail studies of well dated soils with volcanic cindery parent material in colder drier settings. In the current study, we have identified a chronosequence that ranges from 2000 to 14,000 yr, a relatively short development time. Investigating soil development on such a relatively young chronosequence will provide insight into the neoformation of minerals and transformations of clay, organic matter, and elements within a condensed time frame.

Mass-balance models are used to elucidate soil processes and provide a method of quantifying additions, losses, transfers, and transformations of elements within the solum (Brimhall and Dietrich, 1987; Brimhall et al., 1991; Brimhall et al.,

Core Ideas

- Soil development across a chronosequence of basaltic cinder cones.
- Elemental mass balance data were used to investigate secondary mineral formation.
- Elucidate rates and processes of early stage weathering.

Soil Sci. Soc. Am. J. 82:1177–1190

doi:10.2136/sssaj2018.02.0071

Received 1 Mar. 2018.

Accepted 1 June 2018.

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1992; Chadwick et al., 1990). A mass-balance approach coupled with traditional soil analyses provides for greater quantification of soil processes, including physical and chemical alteration of soil material and secondary mineral synthesis.

In southern Idaho, United States, volcanic eruptions at Craters of the Moon National Monument and Preserve (CROM) (Fig. 1) provide an ideal setting to examine soil evolution over thousands of years in basaltic parent materials (Kuntz et al., 1985). Volcanic soils forming in similar parent material and located in close proximity to one another can be used to study millennial-scale weathering processes. Weathering rates of volcanic glass within these soils are influenced by the characteristics of the glass, as well as the nature of the weathering environment. Basaltic tephra, with higher concentrations of cations such as Al, Fe, Mg, and Ca, tend to weather more rapidly into short-range ordered (SRO) minerals, including allophane, imogolite, ferrihydrite, and metal-humus complexes than those of more siliceous tephra (Wada, 1989; Shoji et al., 1993b). Allophane minerals are a group of naturally occurring, noncrystalline hydrous aluminosilicates (van Olphen, 1971) that have a range in Al/Si ratios, with end-members of aluminum-rich (2:1) and silicon-rich (1:1) allophanes. Allophane and imogolite are most abundant in soils formed in tephra composed of colored glass (Shoji et al., 1993b). The rapid weathering of colored glass causes the release of elements more quickly than occur in crystalline minerals, leading to supersaturation of soil solutions with respect to metastable materials, that is, allophane and imogolite. Mafic parent materials also favor the formation of allophane and imogolite by releasing bases that maintain a favorable pH for their synthesis (Shoji et al., 1993b).

Studies examining soil formation on cinder cones composed of basaltic tephra in a cool, arid climate have not previously been reported. The relatively rapid weathering rates of minerals associated with basaltic ejecta coupled with the cool, arid climatic conditions at CROM provide a unique context in which to characterize pedogenesis over a period of time ranging from approximately 2 to 14 ka.

The purpose of this paper is to determine weathering processes and products in soil forming on young basaltic cinder cones. The specific objectives of this research are to (i) examine the physical, chemical, and mineralogical properties of soils forming along a chronosequence and (ii) identify the dominant weathering processes involved in soil evolution in mafic-volcanic material in the cool, dry climate at CROM.

METHODS

Study Area

Craters of the Moon National Monument and Preserve is located in the eastern Snake River Plain in south-eastern Idaho (43°42' N lat., 113°50' W long.) and encompasses 1500 km² of lava fields, rangelands, and a variety of volcanic features (Fig. 1). Late-Pleistocene and Holocene volcanic activity produced a series of basaltic cinder cones within the northern portion of CROM (Kuntz et al., 1985; 1986). Three sites dominated by cindery material were selected on tephra deposits aged 2.1, 6.9, and 13.9 ka (Kuntz et al., 1986; Stuiver and Reimer, 1993) (Fig. 1). Cindery material is defined as more than 60% by weight volcanic ash, cinders, lapilli, pumice, and pumice-like fragments with less than two-thirds by volume of the coarse fragments occupied by pumice and pumice-like fragments (Soil Survey Staff, 2014). Sampling locations were selected to minimize variation in the soil-forming

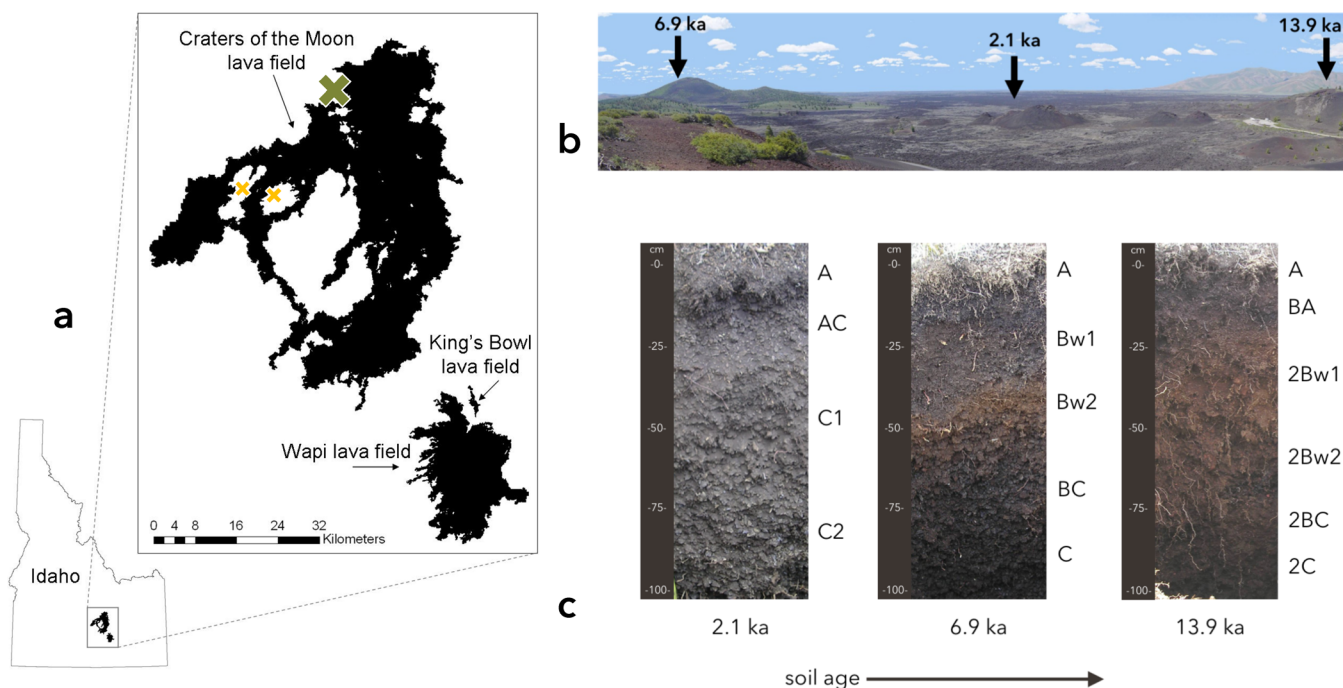


Fig. 1. Study location in southern Idaho (a) with the green X marking the location of the cinder cone chronosequence studied and yellow Xs marking the locations of dust sample collection. Cinder cones are labeled as 6.9 ka (6.9 ka Big Cinder Butte), 2.1 ka (2.1 ka Cinder Garden), and 13.9 ka (13.9 ka Sunset Cone) (b). Soil profiles and horizonation are shown in c.

factors (excluding time) with (i) representative soil development for the specific-aged cone, (ii) a north or northeast aspect, (iii) similar slope (20 to 25%) and (iv) minimal human disturbance or evidence of erosion. All sites are located within 5 km of one another, and are at an elevation of approximately 1800 m. The mean annual air temperature is 6 °C with a frigid soil temperature regime and the mean annual precipitation is 380 mm with a xeric soil moisture regime (Western Regional Climate Center, 2014; Soil Survey Staff, 2017).

Site locations will be referred to by their estimated age in kiloannus and abbreviated cinder cone name. Soil profiles on a young-, intermediate-, and older-aged cinder cone were selected on the 2.1 ka Cinder Garden (2.1CG), 6.9 ka Big Cinder Butte (6.9 BCB), and 13.9 ka Sunset Cone (13.9 SC). The sites (2.1 CG, 6.9 BCB, 13.9 SC) are dominated by antelope bitterbrush [*Purshia tridentata* (Pursh) DC.], rubber rabbitbrush (*Ericameria nauseosa* [Pall. ex Pursh] G.L. Nesom & G.I. Baird), wax currant (*Ribes cereum* Douglas), mountain big sagebrush (*Artemisia tridentata* Nutt. ssp. *vaseyana* Rydb.), mountain snowberry (*Symphoricarpos oreophilus* A. Gray), dwarf monkeyflower [*Mimulus nanus* (Hook. & Arn.) G.L. Nesom], deceptive groundsmoke (*Gayophytum decipiens* F.H. Lewis & Szwejkowski), dwarf buckwheat (*Eriogonum* Michx.), Thurber's needlegrass [*Achnatherum thurberianum* (Piper) Barkworth], and squirreltail [*Elymus elymoides* (Raf.) Swezey].

Soil Characterization

Soil profiles were excavated to a 1-m depth, described using standard techniques, and sampled by morphological horizon (Schoeneberger et al., 2012; Soil Survey Staff, 2014). Samples of cinders were collected from a depth of approximately 1 m from all profiles and assumed to represent unaltered parent material. The selected cinders were glassy, iridescent, and unweathered. Soil samples were air dried and passed through a 2-mm sieve. Percentages of coarse fragments were calculated on an oven-dry weight and volume basis. Particle-size analysis was performed on the < 2-mm fraction. Samples were pretreated to remove organic matter using 6% NaOCl adjusted to pH 9.5 (Soil Survey Laboratory Staff, 2004). Sand, silt, and clay contents were determined via wet sieving, centrifugation, and pipette methods (Soil Survey Laboratory Staff, 2004), and presented on an oven-dry basis.

Due to the high coarse fragment content, bulk density measurements of cores were not possible. Density of coarse fragments and fine-earth fractions were calculated separately and combined to estimate overall soil bulk density (ρ_b):

$$\rho_b = (\text{Co}F_v \times \rho_{\text{Co}F}) + (F_v \times \rho_F) \quad [1]$$

where $\text{Co}F_v$ is volume of coarse fragments, F_v is the volume of the fine-earth fraction, $\rho_{\text{Co}F}$ is density (g cm^{-3}) of coarse fragments, ρ_F is density of the fine-earth fraction (< 2 mm), and ρ_b is density of weathered soil plus voids. Ratio of coarse fragments ($\text{Co}F_v$) and fine-earth fraction (F_v) were determined on a volume basis as a fraction of total soil volume by measuring volumes of $\text{Co}F$ and

< 2 mm fractions separately in the laboratory. The weathering of cindery coarse fragments affects overall soil characteristics, therefore, bulk density calculations also include the density of coarse fragments as well as the < 2-mm soil in each horizon.

Chemical and Mineralogical Analyses

Grain counts were performed on the very fine sand fraction of the surface horizons in triplicate. Very fine sand grains were mounted on glass slides with a refractive index oil of 1.54 and examined using a polarizing light microscope. At least 300 grains per sample were counted and identified, and percentages were calculated based on type of glass or other minerals. Three general categories of volcanic glass were identified from very fine sand and silt fractions. The first is brown- and red-colored smooth glass that originated from local basaltic eruptions at CROM and has undergone relatively little weathering. The second is brown- and red-colored, pitted glass that is more-weathered glass from local CROM eruptions. The presence of pitted glass is indicative of weathering. The final type is clear siliceous glass present in minor amounts in the 13.9SC surface horizon corresponding to material that has been transported to CROM from a more Si-rich, Fe-poor volcanic eruption located at a considerable (> 50 km) distance from these sites.

A combination of selective dissolution techniques was used to determine the amount and distribution of secondary minerals. Dithionite-citrate-bicarbonate (DCB) (Al_d, Fe_d) extractions were performed according to the procedures of Jackson et al. (1986) and Aguilera and Jackson (1953), and provide a measure of secondary oxyhydroxides that have weathered from primary minerals and volcanic glass. Acid-ammonium oxalate (AOD) ($\text{Al}_o, \text{Fe}_o, \text{Si}_o, \text{Ti}_o$) extractions were performed according to McKeague and Day (1966) and Jackson et al. (1986), and provide a measure of poorly crystalline oxides. Acid-ammonium oxalate-extractable aluminum (Al_o) also provides a good estimation of short-range ordered aluminosilicates, in particular allophane and imogolite. The Al/Si ratio of these minerals is calculated by subtracting sodium-pyrophosphate Al (Al_p) from Al_o and dividing by Si_o (Si is not extracted to any significant extent by pyrophosphate). Sodium-pyrophosphate (Al_p, Fe_p) extractions were performed according to Higashi and Wada (1977) and Bascomb (1968) and provide a measure of humus complexes. Subtracting Fe_o and Fe_p from Fe_d provides an estimate of crystalline Fe oxides. Extracted Fe, Al, Si, and Ti were analyzed by inductively coupled plasma spectroscopy. Soil pH was measured on a 1:1 soil/ H_2O mixture (Soil Survey Laboratory Staff, 2004).

Allophane content can be estimated using Al_o , Al_p , and Si_o contents in the following calculation (Parfitt and Wilson, 1985):

$$\% \text{ allophane} = \frac{\text{Si}_o}{\left(-0.067 \frac{\text{Al}_o - \text{Al}_p}{\text{Si}_o} + 0.27 \right)} \quad [2]$$

Total elemental analyses of the < 2-mm fraction and coarse fragment samples were performed. To characterize and account

for the influence of eolian inputs, five surface soil samples from non-cinderland surfaces throughout CROM were also analyzed for total elemental composition. Non-cinderland surfaces are characterized as forming in parent material other than volcanic cinders, and in this case, silicon-rich eolian materials accumulated between lobes of basalt flows aged 2 to 18 ka (Kuntz et al., 1985; 1986). A description of the sources of eolian inputs through time is summarized in Vaughan et al. (2011). All samples were ashed at 500 °C to remove organic matter, fused with lithium-metaborate, dissolved in dilute HNO₃, and analyzed by inductively coupled plasma spectroscopy at ACME Analytical Laboratories, Ltd. (Bartenfelder and Karathanasis, 1988; Vancouver, BC). Total C and S were measured by dry combustion (Nelson and Sommers, 1996). Internal standards, blind standards, and duplicates were analyzed for quality control.

Mass Balance and Other Calculations

Mass-balance analyses of a chronosequence requires acquisition of well-dated, unweathered parent material, selection of soil profiles that have not been subjected to physical erosion, and the assumption of the immobility of particular elements to account for soil dilation or collapse. Comparisons of bulk density, volume, and chemical composition between soil horizons and parent material are required to investigate the transformations that occur over time. On cinder cone surfaces at CROM, coarse fragments dominate soil volume and weight, therefore total elemental concentrations of the whole soil were calculated. The mass percentage of < 2 mm and coarse fragments and the elemental compositions of each fraction were incorporated to calculate a whole soil concentration.

$$C_{j,ws} = (CoF_m \times C_{j,CoF_w}) + (F_m \times C_{j,F_{ws}}) \quad [3]$$

where $C_{j,ws}$ is the concentration (g 100 g⁻¹) of element j in the weathered soil (ws), C_{j,CoF_w} is the concentration (g 100 g⁻¹) of element j in the weathered coarse fragments (CoF_w), $C_{j,F_{ws}}$ is the concentration (g 100 g⁻¹) of element j in the < 2-mm fraction of weathered soil, CoF_m is the percent of coarse fragments by mass, and F_m is the percent of < 2-mm fraction by mass. Since coarse fragments are also weathering in these soils, reported concentrations of the weathered soil include concentrations of both coarse fragments and < 2-mm soil in each horizon.

Strain, or volume change, was determined using the following equation (Chadwick et al., 1990):

$$\epsilon_{i,ws} = \frac{\rho_{pm} C_{i,pm}}{\rho_{ws} C_{i,ws}} - 1 \quad [4]$$

where $\epsilon_{i,ws}$ represents strain of an immobile element (i) in weathered soil (ws), ρ is bulk density (g cm⁻³) of parent material (pm) and weathered soil (ws), $C_{i,pm}$ is the concentration of an immobile element (i) in the parent material (pm), and $C_{i,ws}$ is the concentration of an immobile element (i) in the weathered soil (ws).

The open-system mass transport function ($\tau_{j,w}$) is defined by (Chadwick et al., 1990):

$$\tau_{j,ws} = \left(\frac{\rho_{ws} C_{j,ws}}{\rho_{pm} C_{j,pm}} (\epsilon_{i,ws} + 1) \right) - 1 \quad [5]$$

where mass transport of element j in weathered soil is calculated using density (ρ) and elemental composition (C) data in conjunction with volume change derived from the calculation of strain (ϵ) (Eq. [6]) (White, 1995). The mass transport function is the mass fraction of an element added or removed from the system during weathering relative to the mass of the element originally present in the parent material (Eq. [7]).

Calculation of elemental losses with respect to specific horizons or a group of horizons incorporates the strain function as explained by Egli and Fitze (2000):

$$\bar{m}_{j,flux}(z_w) = \sum_{a=1}^n C_{j,pm} \rho_{pm} \left(\frac{1}{\epsilon_{i,ws} + 1} \right) \tau_{j,w} \Delta z_{ws} \quad [6]$$

Units of mass flux ($\bar{m}_{j,flux}$) are g cm⁻² with n horizons. Delta z_{ws} represents the horizon thickness (cm).

An enrichment factor, $C_{j,ws}/C_{j,pm}$, was used to compare the concentration of a particular element in weathered soil to the concentration of the same element (j) in the parent material. The equation is derived from Eq. [7] (Chadwick et al., 1990):

$$\frac{C_{j,ws}}{C_{j,pm}} = \frac{\rho_{pm}}{\rho_{ws}} \times \frac{1}{(\epsilon_{i,ws} + 1)} \times (1 + \tau_{j,ws}) \quad [7]$$

The enrichment factor of each sample is determined by residual enrichment (ρ_{pm}/ρ_{ws}), strain ($\epsilon_{i,ws}$), and mass transport ($\tau_{j,ws}$). The enrichment factor is the ratio of chemical concentration of an element in the weathered soil to the concentration in the parent material (Eq. [7]). Open-system enrichment results from the translocation of elements across the sample volume boundaries (Chadwick et al., 1990). Closed-system enrichment occurs with redistribution of the element within the soil horizon but not outside. If analyses of depth vs. weight percentage and enrichment factor indicate an elemental decrease, but mass flux is negligible, the apparent elemental increase is due to closed system enrichment.

Carbon accumulation rates were calculated by taking the weighted average to 1-m depth of OC and dividing it by the age of the soil.

$$\text{accumulation rate} = \frac{\overline{C_{j,ws}}}{t} \quad [8]$$

where $\overline{C_{j,ws}}$ is the weighted average of the concentration of element j in g m⁻² in weathered soil (ws) and t is time in years.

A weathering index was calculated according to the following formula:

$$CIA = \frac{Al_2O_3}{Al_2O_3 + CaO + K_2O + Na_2O} \times 100 \quad [9]$$

(Nesbitt and Young, 1982) where CIA is compound index of alteration, and elemental compositions were determined on an oxide basis from total elemental dissolutions.

Consideration of the Influence of Eolian Dust

Loess is pervasive in the eastern Snake River Plain with the main source being outwash deposits along the Snake River (Scott, 1982). Between 16 and 25 ka, loess accumulated at a rate of 0.6 m ka⁻¹ (Phillips et al., 2009; Pierce et al., 1982). Between 12.6 and 14.4 ka, the Snake River became incised due to reduced discharge from glacial times, and this incision greatly reduced the vegetation-free outwash deposits formerly acting as loess sources. Although loess covers all Pleistocene-aged lava flows, it is thin on 17.4-ka Bonneville Flood deposits and near absent on a 6 ka lava flow (Phillips et al., 2009).

The addition of eolian material presents challenges related to the application of the mass balance approach, discussed above. To quantify eolian inputs to the chronosequence profiles, five surface loess samples (0–15 cm) from cracks in lava and on plains adjacent to lava flows were collected as potential sources of dust. These samples were collected approximately 25 km to the south-east of the chronosequence profiles along the path of prevailing winds (Fig. 1). The total elemental composition of these samples were determined as discussed above.

Disparate geologic materials can vary in concentration and ratio of relatively immobile elements (Zr, Ti, Y, Nb). These differences allow for a quantitative estimate of dust contribution to soil. We employed the contrasting immobile element ratios between basaltic cinders and dust samples to estimate the contribution of dust to cinderland soils using a simple mixing model:

$$f_{\text{dust}} = \left[\frac{(Zr/Nb)_{\text{ws}} - (Zr/Nb)_{\text{pm}}}{(Zr/Nb)_{\text{pm}} - (Zr/Nb)_{\text{dust}}} \right] \times 100 \quad [10]$$

where f_{dust} is the percent by weight of the soil in a particular horizon derived from eolian sources, and ws, pm, and dust subscripts refer to the soil, cinder parent material, and dust (adapted from Heckman and Rasmussen, 2011).

RESULTS AND DISCUSSION

Pedon Characterization

Soil color, texture, and bulk density (Table 1) are strongly influenced by the SRO minerals weathered from the parent material, along with soil organic matter. Changes in soil color are indicative of mineral formation and translocation within the soil profile, as well as surface horizon inputs of organic matter, which are especially apparent in the oldest soil. Dark colors inherited from the parent material were described throughout the 2.1 CG profile (Table 1). Increased reddening is evident as soil age increases and reflects the process of rubification where Fe is weathered from primary minerals and coats soil particles (Buol et al., 2011). Across the chronosequence soil hues progress from 10YR to 7.5YR (comparing the C horizons of the youngest soils to the B horizons of the 6.9 BCB profile) and to 5 YR for the B horizons of the oldest soil (13.9 SC).

The degree of redness in soils is a function of the type and amount of pedogenic Fe-minerals forming and the result of colloidal material coating soil particles, including iron-humus complexes and iron oxides. Horizons with hues of 7.5YR indicate the presence of ferrihydrite while 5YR suggests ferrihydrite and or hematite (Schwertmann, 1993). In a different soil chronosequence study at CROM with sites of similar ages Baker et al. (2010) showed that most of the Fe-bearing portion of the clay fraction was comprised of ferrihydrite.

Table 1. Characterization data for soils derived from basaltic tephra along a chronosequence at Craters of the Moon National Monument and Preserve.

Horizon	Depth	Texture†		Color	Structure‡	CoF§	sand	silt	clay	ρ _b ¶	pH
	cm	mod#		(moist)		%	g kg ⁻¹			g cm ⁻³	
Cinder Garden soil (2.1CG)											
A	0–20	ci	s	10YR 2/2	0, sg	16	894	93	14	0.87	6.46
AC	20–30	–	s	10YR 2/1	0, sg	11	889	97	14	0.91	6.44
C1	30–60	xc	s	10YR 2/1	0, sg	56	936	31	33	0.41	6.45
C2	60–90	–	ci	10YR 2/1	0, sg	86	896	57	47	0.32	nd ††
Big Cinder Butte soil (6.9BCB)											
A	0–16	ci	sl	10YR 2/2	1, sbk	19	600	322	78	0.87	5.88
Bw1	16–29	xc	sl	7.5YR 3/3	1, sbk	71	754	188	58	0.40	6.02
Bw2	29–47	–	ci	7.5YR 3/4	1, sbk	89	779	158	62	0.32	6.03
BC	47–76	xc	ls	10YR 2/1	0, sg	60	822	124	54	0.42	6.00
C	76–100	xc	ls	10YR 2/1	0, sg	60	819	117	64	0.42	6.00
Sunset Cone soil (13.9SC)											
A	0–7	ci	sl	7.5YR 2.5/1	1, sbk	16	640	246	115	0.69	6.16
BA	7–25	vci	sl	7.5YR 3/2	1, sbk	29	578	264	157	0.59	6.18
2Bw1	25–43	vci	sl	5YR 3/4	2, sbk	40	677	226	97	0.75	5.94
2Bw2	43–69	xc	sl	5YR 3/4	2, sbk	74	710	195	95	0.48	6.39
2BC	69–83	xc	sl	10YR 2/1	0, sg	79	778	147	74	0.45	6.37
2C	83–100	xc	ls	10YR 2/1	0, sg	81	875	76	49	0.45	6.55

† s, sand; ci, cinders (>90% cinders); sl, sandy loam; ls, loamy sand.

‡ 0 = structureless; 1 = weak; 2 = moderate; sg, single grain; sbk, sub-angular blocky.

§ CoF, coarse fragments.

¶ calculated ρ_b , bulk density (see text).

mod, coarse fragment modifier; ci, cindery; vci, very cindery; xc, extremely cindery.

†† no data (nd) collected due to high volume of coarse fragments.

Table 2. Distribution of very fine sand grains in the surface horizons along the chronosequence at Craters of the Moon National Monument and Preserve. Three samples were analyzed from each site. Values are means with standard error in parentheses.

Site†	colored/pitted glass	colored/smooth glass	clear glass	other
	%			
2.1CG	12.8 (1.3)	82.2 (4.3)	0.0 (0.0)	5.0 (2.3)
6.9BCB	18.8 (3.3)	67.9 (8.3)	0.0 (0.0)	13.3 (5.6)
13.9SC	25.4 (5.0)	55.0 (4.6)	2.9 (2.1)	16.7 (5.3)

† Cinder Garden soil (2.1 CG), Big Cinder Butte soil (6.9 BCB), and Sunset Cone soil (13.9 SC).

At the 2.1 CG site, soil development is minimal with textures of cindery sand, extremely cindery sand, and cinders. This soil has an organic-enriched A horizon, an AC horizon, and a C horizon (Fig. 1 and Table 1). Dark soil colors were inherited from the Fe-rich, mafic parent material rather than the accumulation of organic materials. The 6.9 BCB soil is moderately well developed compared to other soils along the chronosequence, with an A, Bw1, Bw2, BC, and C horizon sequence. Cindery to extremely cindery sandy loams and loamy sands dominate this profile. Weak subangular blocky structure has developed in the A and B horizons. The 13.9 SC soil is the most highly developed, with an A, AB, 2Bw, 2Bw2, 2BC, and 2C horizon sequence. Soil textures range from cindery sandy loam to extremely cindery loamy sand with weak to moderate subangular blocky structure. Evidence of a two basaltic parent materials with different elemental composition was identified on the 13.9-ka cinder cone. The time of deposition is assumed to be similar with one layer being deposited on top of the other in close succession (Kuntz et al., 1985).

Changes in particle-size distribution and bulk density also provide evidence of physical and chemical weathering as a function of time. The percentage of coarse fragments increases considerably with depth in all three soil profiles. Coarse cinder fragments weather into smaller sand- and silt-sized particles as well as neoformed minerals. The bulk densities of the parent cinders at CROM range from 0.28 to 0.31 g cm⁻³. As soils at CROM weather from coarse cindery material into finer-textured materials, the bulk density increases (Table 1). Along with the increase in sand, silt, and clay comes an increase in bulk density reaching a maximum of 0.91 g cm⁻³ near the surface of the 6.9 BCB soil. The surface horizons across the chronosequence have substantially higher bulk density values than the subsurface horizons below 50 cm ($p < 0.05$). This is contrary to what occurs in Si-rich, rhyolitic or dacitic ashes, which decrease in bulk density as they weather (Shoji et al., 1993a). The abundant vesicles in basaltic cinders lead to extremely low bulk densities in fresh deposits. Most soils developed on volcanic materials have low bulk densities, ranging from 0.4 to 0.8 g cm⁻³ (Shoji et al., 1993a). The particle densities of volcanic materials are similar to that of other mineral soils; therefore, the vesicular nature of the cinders is the main reason for the low bulk density values observed at CROM.

Chemical and Mineralogical Properties

Quantification of Eolian Inputs. The distribution of very fine sand in the surface horizons of all profiles is presented in Table 2. The increase in colored and/or pitted glass from the 2.1 to the 13.9-ka soils, shows the influence of time on mineral weathering. The incorporation of approximately two to four times more very fine sand grains other than glass in the surface horizons of the 6.9- and 13.9-ka soils is indicative of comminution of minerals and eolian material being incorporated into the surface horizons. Further quantification of eolian inputs will be presented in the section discussing mass balance calculations below.

Selective Dissolution

Iron Oxide, Oxyhydroxides, and Iron-Humus Complexes.

The DCB extractable Fe (Fe_d), a measure of secondary Fe oxyhydroxides, increases dramatically as cinder cone age increases (Table 3). The 2.1 CG soil Fe_d values are elevated (9.6–8.2 g kg⁻¹) in the upper 60 cm compared to Fe_d below 60 cm (6.1 g kg⁻¹). The 6.9 BCB soil has considerably greater amounts of secondary Fe than the younger soils, and the values also decrease with depth (Table 3). The oldest, 13.9 SC soil, has high Fe_d values to 83 cm below the soil surface, indicating the deepest weathering profile along the chronosequence. Baker et al. (2010) studied a soil chronosequence at CROM (with soils ranging from 2 to 15 ka) and noted a dominance of ferrihydrite in the clay fraction of the soil that increased in crystallinity with soil age. Small amounts of iron-substituted smectite were also detected in that study (Baker et al., 2010).

Sodium pyrophosphate-extractable Fe (Fe_p), an indicator of Fe-humus complexes in the soil, ranges from 0.2 to 0.5 g kg⁻¹ in the lower horizons and 0.4 to 2.0 g kg⁻¹ in the surface horizons across the chronosequence (Table 3). Higher Fe_p values were measured in the older profiles with organic-rich surface horizons. The values are two to three times greater near the soil surface and steadily decrease with depth. The CROM soil Fe_p values are substantially lower than Fe_p measured in volcanic-rich soils of warmer, more humid climates (Zehetner et al., 2003; Shoji et al., 1982; Shoji and Fujiwara, 1984; Parfitt et al., 1984; Shoji et al., 1985), where greater vegetative production and lower soil pH result in conditions more conducive to the formation of metal-humus complexes compared to the CROM soils. The soil pH along the chronosequence ranges from 6.4 to 7.2 (Table 1), with a mean of 6.7, indicating a relatively unsuitable environment for the formation of humus complexes (Shoji et al., 1993b).

Ammonium oxalate extractable Fe (Fe_o), a measure of poorly crystalline oxides, ranges from 13.9 g kg⁻¹ in the subsurface of 2.1CG to a high of 46.0 g kg⁻¹ in the 2Bw1 horizon of 13.9 SC (Table 3). The weighted mean Fe_o/Fe_d ratio to a 1-m depth decreases from roughly 2.3 to 1.3 as age increases along the chronosequence (Table 3), indicating a potential increase in the less active Fe fractions over time (Schwertmann and Taylor, 1989). Estimation of amorphous secondary Fe on the basis of Fe_o may not be accurate at CROM because ammonium oxalate is likely also extracting magnetite, which is inherited from the parent

Table 3. Selective dissolution data from soil profiles along a chronosequence at Craters of the Moon National Monument and Preserve.

Horizon	depth cm	Al _o †	Si _o †	Fe _o †	Fe _d ‡	Al _d ‡	Al _p §	Fe _p §	Fe _t ¶	allophane#	Fe _o :Fe _d †‡	Al:Si††
g kg ⁻¹												
Cinder Garden soil (2.1 kcal BP, 2.1 CG)												
A	0–20	8.1	6.9	22.2	9.6	1.5	0.9	1.4	117.4	34.5	2.3	1.04
AC	20–30	7.6	7.2	19.9	9.2	1.6	0.7	1.2	118.6	35.0	2.2	0.96
C1	30–60	6.2	5.8	18.9	8.2	1.4	0.3	0.6	118.8	28.7	2.3	1.02
C2	60–90	10.0	6.2	13.9	6.1	1.0	0.2	0.2	116.9	37.8	2.3	1.58
Big Cinder Butte soil (6.9 kcal BP, 6.9 BCB)												
A	0–16	13.5	15.2	30.4	18.8	9.0	1.6	1.5	114.7	69.8	1.6	0.79
Bw1	16–29	12.3	15.2	27.8	18.1	6.0	0.9	1.0	112.3	69.2	1.5	0.75
Bw2	29–47	6.8	9.4	17.1	15.9	4.0	1.1	1.5	119.3	40.9	1.1	0.61
BC	47–76	8.4	11.9	20.3	15.5	3.1	0.7	1.2	117.3	52.5	1.3	0.65
C	76–100	5.4	6.8	16.2	10.0	1.7	0.2	0.4	116.9	31.0	1.6	0.76
Sunset Cone soil (13.9 kcal BP, 13.9 SC)												
A	0–7	8.2	5.3	18.5	16.8	6.7	1.8	2.0	93.4	120.0	1.1	1.22
BA	7–25	7.4	4.8	16.1	24.8	8.3	1.2	1.8	98.3	100.0	0.6	1.30
2Bw1	25–43	20.2	17.9	46.0	22.7	8.1	0.8	1.3	105.7	90.7	2.0	1.08
2Bw2	43–69	15.2	14.6	33.3	23.2	6.6	0.6	0.9	123.0	72.0	1.4	1.00
2BC	69–83	11.4	12.4	26.3	22.8	6.0	0.4	0.7	123.0	59.1	1.2	0.89
2C	83–100	9.3	10.9	22.6	16.7	3.0	0.2	0.3	120.2	51.0	1.4	0.83

† Ammonium-oxalate extractable Al (Al_o), Si (Si_o), and Fe (Fe_o).‡ Dithionite-citrate-bicarbonate extractable Fe (Fe_d) and Al (Al_d).§ Na-pyrophosphate extractable Al (Al_p) and Fe (Fe_p).¶ Total Fe (Fe_t).

theoretical calculation (Parfitt and Wilson, 1985), see Eqn. (2) in Methods.

†† Ammonium-oxalate extractable Al (Al_o) minus Na-pyrophosphate extractable Al (Al_p) divided by ammonium-oxalate extractable Si (Si_o).

material (Walker, 1983). Ammonium-oxalate-extractable Fe remains an indication of the amount of SRO Fe containing minerals present; however, they are not necessarily *secondary* SRO minerals and may be inherited from the parent material.

Short-Range Ordered Aluminosilicates and Aluminum-Humus Complexes. Soil Al:Si ratios throughout CROM are near 1:1 (Table 3), suggesting that the SRO aluminosilicate mineral allophane likely predominates in these soils rather than imogolite, which has an Al/Si ratio of 2:1 (Parfitt and Henmi, 1980). Additionally, Baker et al. (2010) demonstrated the likely presence of allophane in the clay fraction of other CROM soils through FTIR analysis. Allophane content increases with soil age (Table 3). For the older soils, the surface horizons of the 13.9 SC soil have roughly two times greater allophane content compared to the 6.9 BCB soil. Allophane contents decrease with depth for both of these soils. These age and depth relations with allophane content reflect the control of time on mineral weathering.

Sodium pyrophosphate-extractable Al (Al_p) ranges from 0.2 to 1.8 g kg⁻¹ throughout all soil profiles (Table 3). The highest values occurred in the surface horizons of the older profiles, reflecting the greater organic matter content. Compared with volcanic soils forming in more humid climates, the Al-humus complexes (as with the Fe-humus complexes) in the CROM soils are not as abundant (Shoji et al., 1982; Shoji and Fujiwara, 1984; Parfitt et al., 1984).

Taxonomic Implications

The three soil profiles examined possess andic soil properties

that are the result of tephra weathering into SRO minerals including allophane, imogolite, ferrihydrite, and metal-humus complexes. As stated in the *Keys to Soil Taxonomy*, andic soil properties in coarse-textured soils where 30% or more of the fine-earth fraction is 0.02 to 2.0 mm must contain the following in the fine-earth fraction: i) phosphate retention of 25% or more; ii) % Al_o + 1/2 Fe_o equal to 0.4% or more; iii) volcanic glass content of 5% or more; and iv) % Al_o + 1/2 Fe_o times (15.625 + volcanic glass content [%]) = 36.25 or more (Soil Survey Staff, 2014). Phosphate retention is > 40% in all soils studied and volcanic glass comprises 83 to 96% of the sand fractions. The % Al_o + 1/2 Fe_o in all horizons is 1.6 to 4.3 in all horizons across the chronosequence, likely due to the inadvertent dissolution of the primary mineral, magnetite. The use of this criterion in soils formed in basaltic tephra requires further consideration as the potential exists for Al_o + 1/2 Fe_o to indicate greater weathering than has actually occurred as the result of pedogenesis in these young volcanic soils. A potential alternative to avoid the inclusion of young soils formed in tephra as possessing andic soil properties, and likely classified as Andisols rather than Entisols, could be to calculate the ratio of these values relative to the parent material. This relative difference would indicate change in properties via pedogenesis.

Despite the variability in the properties of the soils along the chronosequence, the profiles all classify as ashy-pumiceous, amorphous Xeric Vitricryands based on Soil Taxonomy (Soil Survey Staff, 2014) and Vitric Silandic Andosols (Skeletal, Arenic) based on the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015). The degree of soil development over the time scale of this study (e.g., increased clay content, soil reddening, and

Table 4. Weighted mean of organic C, Mg, Ca, Si, Al, Fe, and Ti flux and rate to a 1-m depth for soil profiles at Craters of the Moon National Monument and Preserve. Geochemical fluxes and rates were calculated using for each horizon with respect to a strain function explained by Egli and Fitze (2000; Eq. [6]).

Site†	organic C		Mg		Ca		Si		Al		Fe		Ti	
	flux	rate	flux	rate	flux	rate	flux	rate	flux	rate	flux	rate	flux	rate
	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹	g cm ⁻²	g m ⁻² yr ⁻¹
2.1 CG	0.1	0.48	-0.08	-0.38	-0.09	-0.43	0.29	1.37	0.10	0.50	0.18	0.86	0.01	0.04
6.9 BCB	0.19	0.28	-0.06	-0.09	-0.18	-0.26	-0.10	-0.14	0.01	0.02	-0.02	-0.03	0.00	0.00
13.9 SC	0.66	0.47	-0.22	-0.16	-0.38	-0.27	0.11	0.08	0.07	0.05	0.01	0.01	-0.01	-0.01

† Cinder Garden soil (2.1 CG), Big Cinder Butte soil (6.9 BCB), Sunset Cone soil (13.9 SC).

quantities of secondary and SRO minerals) although measureable, is not sufficient to result in distinct classifications. These soils are mapped as the Bigcinder soil series with several other competing series mapped in the general vicinity; however, most differences are a function of soil temperature regime rather than management implications or land use potential (United States Department of Agriculture, Natural Resources Conservation Service, and United States Department of the Interior, National Park Service, 2010). The dominant land use is wildlife habitat and limited livestock grazing, although livestock are not permitted in this portion of the National Monument.

Mass Balance Analyses

Mass balance equations provide another means of examining pedologic processes (Brimhall and Dietrich, 1987; Brimhall et al., 1991; Chadwick et al., 1990; Egli and Fitze, 2000). For CROM soils, niobium was selected as the immobile element for calculations of strain. Other commonly used immobile elements, especially Ti, appear to be mobile as evidenced by the strain profile in these soils, while Nb is relatively immobile and inert.

Due to the abundance of coarse fragments, the elemental compositions of the >2-mm fraction were included in the mass

balance calculations (Tables 1 and 4). Both Fe and Ca contents decreased in coarse fragments in the upper horizons, and generally follow the same depth profile as the fines, with one exception being a slight increase in coarse fragment Al concentrations at the surface. Such patterns indicate that the coarse fragments have undergone weathering within the oldest soil. Analyses of soils on a whole-soil basis provide a more complete picture of weathering in this system due to the presence of rapidly-weatherable glassy coarse fragments, and their departure from the parent material concentrations (Tables 2, and 4). Coarse fragments are not typically incorporated into these calculation; however, omitting the coarse fragments from this calculation would inaccurately represent the elemental content of the entire soil horizon volume.

Limitations to using a mass balance approach include selection of representative parent material for analyses, accurate determination of bulk density, and the possibility of elemental additions from sources other than the parent material, such as atmospheric or eolian dust. Quantification of the specific contributions from eolian mineral additions via direct measurement are not available for these sites. The elemental compositions of potential eolian source materials, however, are markedly different with absolute values of 22% greater mean SiO₂ and 13% less

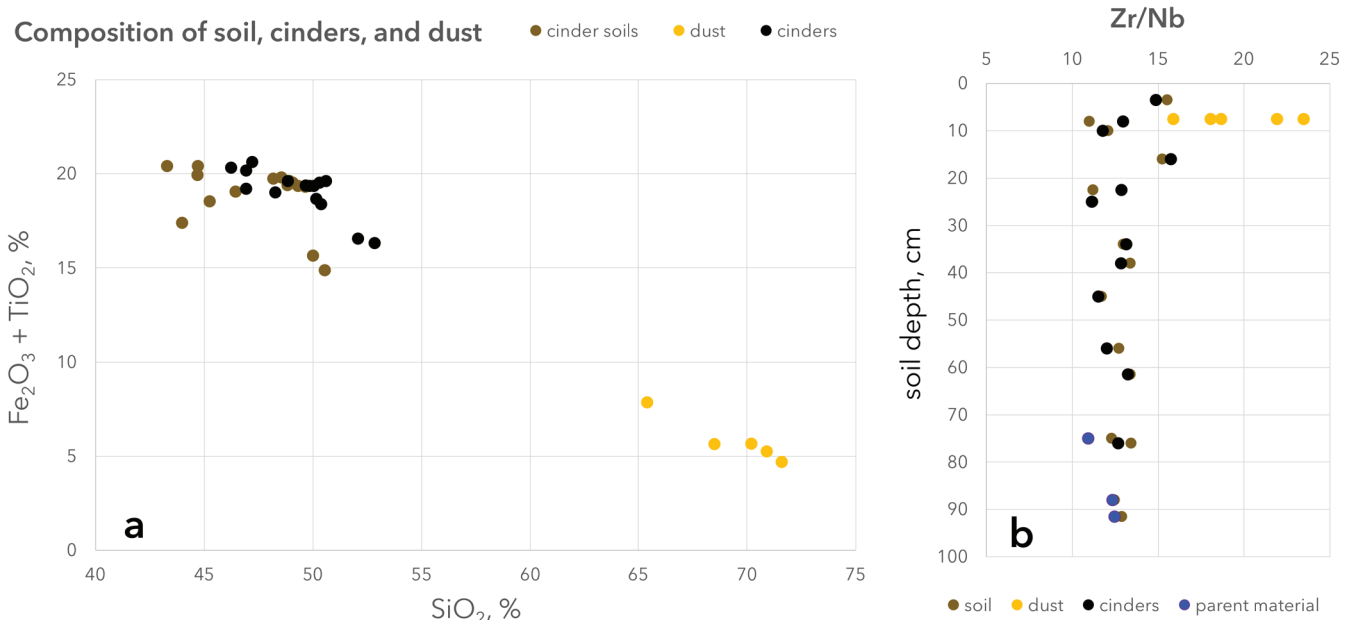


Fig. 2. Select elemental composition of soil, cinders, and dust sampled from soil profiles along the 13.9 ka chronosequence at Craters of the Moon National Monument and Preserve. The comparison between SiO₂ and Fe₂O₃ plus TiO₂ (a) highlights the stark difference in elemental composition between the cinderland soils and dust samples. The ratio between theoretically immobile elements Zr and Nb shows slight difference in ratios that allowed for quantification of dust accumulation in the soils (b).

mean Fe_2O_3 plus TiO_2 contents than the basaltic parent material at CROM (Fig. 2, Fig. 3). The ratio between relatively immobile elements is less distinct however, and with the observed mobility and high concentration in Ti at these sites, Nb and Zr were used. The ratio of Zr to Nb in dust samples ranged from 15.9 to 23.5 (mean 19.6) while the chronosequence soil (< 2 mm) ranged from 10.9 to 13.4 (mean 12.8) and the basaltic cinder parent material ranged from 10.9 to 12.5 (mean 11.9) (Fig. 5b). Although there are only small differences in the ratios between the samples, using them in the mixing model (Eq. [10]) suggests a small amount of dust contributions in the chronosequence profiles (0 to 11.4%) with the greatest potential contribution in the surface horizon of the 13.9-ka profile.

The wide difference in SiO_2 contents between the dust and chronosequence samples supports the hypothesis that these young soils developed after the last glacial period while the rate during a period characterized by low rates of dust accumulation was low and therefore possess minimal eolian input (Fig. 3). These results are also supported by research conducted on loess accumulation rates and loess dating throughout the eastern Snake River Plain, which indicate relatively little eolian accumulation on surfaces younger than ~ 13 ka (Vaughan et al., 2011; Phillips et al., 2009; Pierce et al., 1982). Based on these values, and the fact that profiles collapse with respect to parent material, cinders appear to be the dominant parent material at CROM in the past 13.9 ka.

Enrichment in Carbon

During soil development, substantial amounts of organic carbon (OC) are added to the CROM soils from open-system influxes to the soil profile. Organic C has the second greatest percentage mass change (after Fe) relative to the parent material (Fig. 4). The depth profiles, enrichment factor, and mass transport of the three soils follow the same general trend with greater OC accumulation in the near-surface horizons. Overall, the 13.9 SC profile has the greatest OC accumulation followed by the 6.9 BCB and 2.1 CG profiles. The amount and flux of OC incorporated into the soil profiles increases as profile age increases (Table 4). The positive mass flux of OC in all soils indicates an influx of material leading to dilation of the soil profiles, however, due to other elemental transformations, strain profiles show that in general the soils are collapsing relative to the parent material (bulk density data in Table 1).

The average rate of OC accumulation varies across the chronosequence. The 2.1 CG 1-m profile accumulated $0.48 \text{ g OC m}^{-2} \text{ yr}^{-1}$ (Fig. 4, Table 4) with the rate being a result of overlying vegetation contributing considerable organic debris. The 6.9 BCB 1-m profile accumulated $0.28 \text{ g OC m}^{-2} \text{ yr}^{-1}$ while the 13.9 SC 1-m profile accumulated C at a higher rate, similar to the 2.1 CG profile ($0.47 \text{ g OC m}^{-2} \text{ yr}^{-1}$). Andisols forming in more humid climates dwarf the rates observed at CROM with OC accumulation rates of 21.1 to $22.9 \text{ g OC m}^{-2} \text{ yr}^{-1}$ in Japan (Table 5) (Sakai et al., 2010), and 37.2 to $39.3 \text{ g OC m}^{-2} \text{ yr}^{-1}$ in Hawaii (Vitousek et al., 1983). Whereas OC accumulation rates much more comparable to CROM were shown in ba-

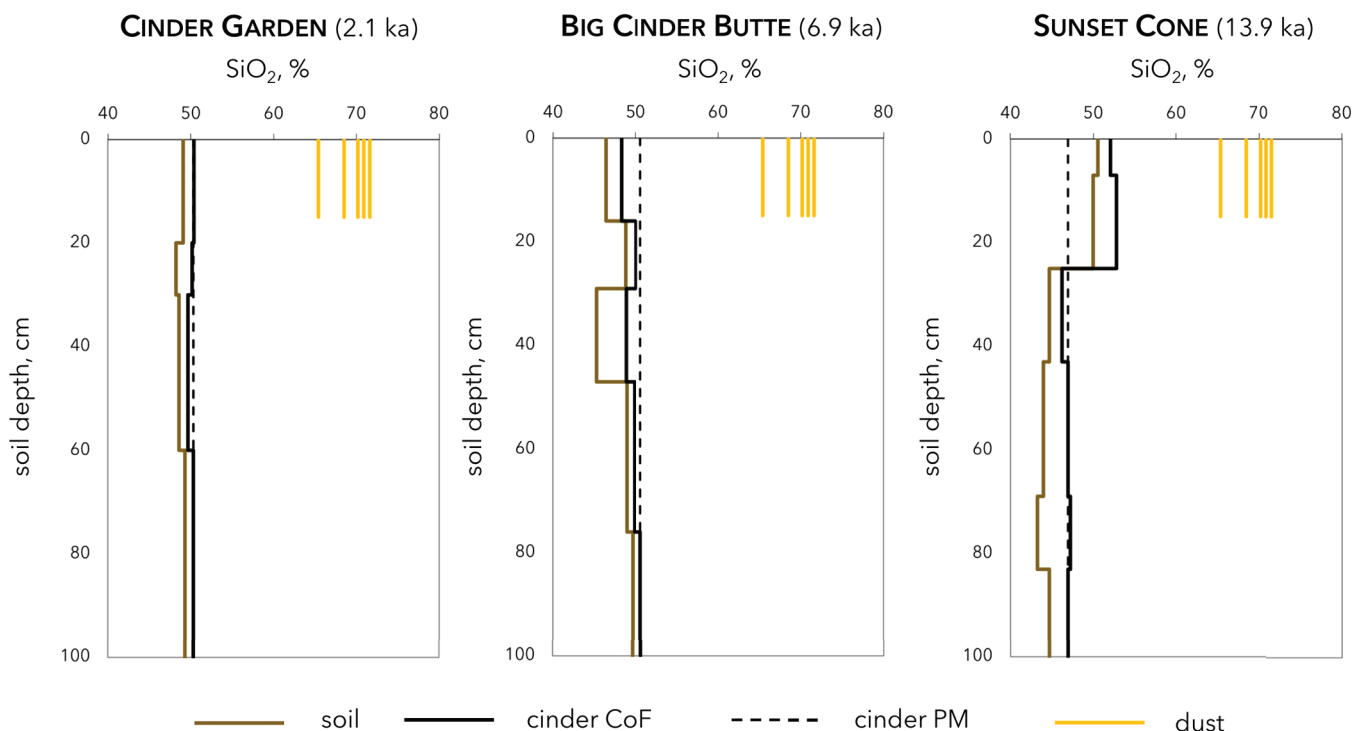


Fig. 3. Depth plots of SiO_2 concentrations at the Cinder Garden (2.1 ka), Big Cinder Butte (6.9 ka), and Sunset Cone (13.9 ka) chronosequence soil profiles. Yellow lines indicate the five dust samples collected from 0–15 cm, while brown, black, and black dashed colors indicate the soil (< 2 mm), cinders (> 2 mm coarse fragments [CoF]), and unweathered cinder parent material (PM). Note the difference between the SiO_2 concentration of the soil and coarse cinders in the upper two horizons and the subsurface of Sunset Cone. These differences can be attributed to a shift in elemental composition during the eruptive event.

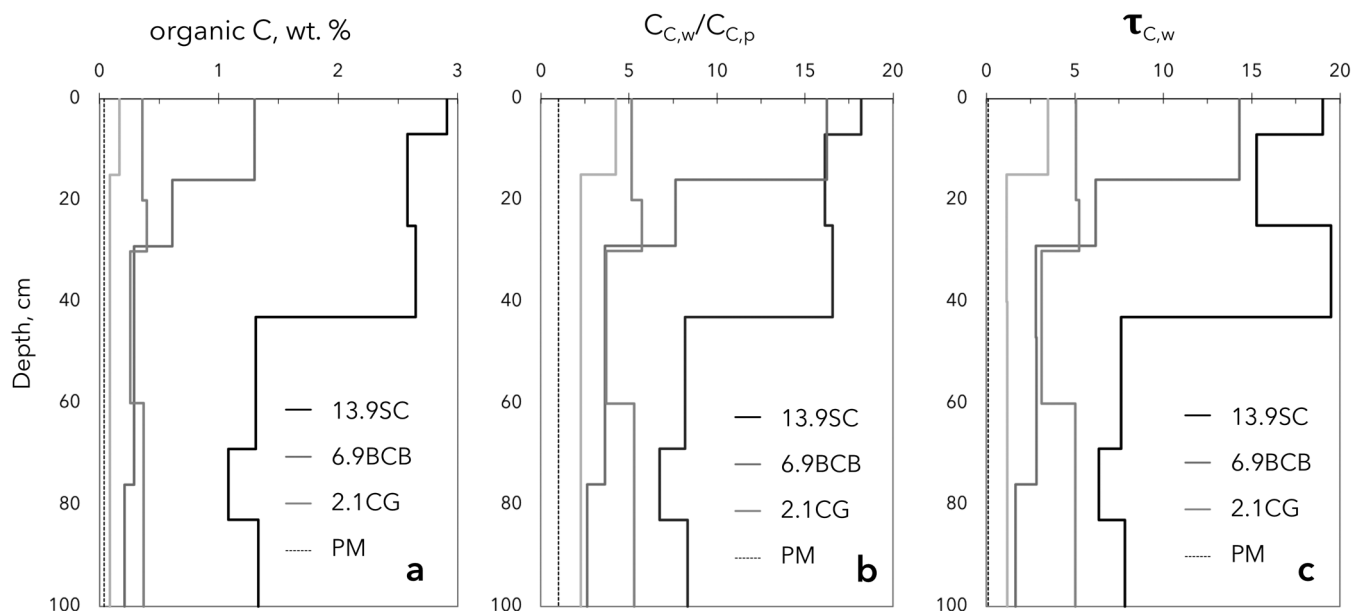


Fig. 4. Depth plots of (a) weight percent organic C, (b) enrichment factor ($C_{C,w}/C_{C,p}$), (c) and the transported mass fraction (τ) of C for the Cinder Garden (2.1 CG), Big Cinder Butte (6.9 BCB), and Sunset Cone (13.9 SC) soil profiles. Vertical dashed lines represent parent material (PM).

saltic lapilli parent material in the semiarid climate of Lazarote, Canary Islands, Spain: 0.6 to $1.2 \text{ g OC m}^{-2} \text{ yr}^{-1}$ (Table 5) (Jahn and Stahr, 1996). Soil OC accumulation rates on cinder cones at CROM contrast deeply with values observed on organic soils (Lithic Torrifolists) formed from vegetation on basaltic lava flows in the same climate within the CROM National Monument and Preserve (Vaughan et al., 2011). Organic soils contained 200 to 4000 kg C m^{-2} and accumulated C at a mean rate of approximately 200 g C yr^{-1} (Vaughan et al., 2011).

Depletion of Silicon and Base Cations

The depth profiles of the weight percentage of Ca and Mg indicate general depletions near the soil surface. A negative mass flux of Mg and Ca is observed in all profiles (Table 4). Calcium and Mg contents in the upper 60 cm of all soils are lower than the contents in the parent material. The oldest profile, 13.9 SC, shows the most substantial loss of bases, followed by 6.9 BCB, and 2.1 CG. Base cations are likely depleted from the upper part through both plant uptake and chemical weathering (Weil and Brady, 2017). All soil profiles have negative mass flux of Ca, Mg, and other bases (Na and K not shown). Weathering rates are strongly influenced by the rate of leaching through the soil profile and subsequent removal of weathering products (Shoji et al., 1993a).

Taylor and Blum (1995) observed that a chronosequence in a mountain front sagebrush setting (MAP 23 cm , MAT 2°C) showed substantial negative flux in bases over 21 to $> 297 \text{ ka}$ (Table 6). The results from this study were similar to those determined in an alpine tundra setting (MAP $50\text{--}70 \text{ cm}$, MAT -4°C) over only 0.4 to 11 ka (Taylor and Blum, 1995). The negative flux of Ca through the profile in the alpine tundra site aged 11 ka was 1.80 g cm^{-2} while in the mountain front region, the negative Ca flux was 2.29 g cm^{-2} after 21 ka . The increase in precipitation in the tundra was likely responsible for the greater leaching from these soils. After 13.9 ka at CROM (MAP 38 cm , MAT 6°C), Ca loss was 0.38 g cm^{-2} (Table 6). This value is considerably less than those observed at the aforementioned sites and is likely a result of timing of precipitation and composition of parent material, and potential eolian inputs.

Greater losses of Si are observed in the surface horizons of the 2.1 CG and 6.9 BCB soils than in the 13.9 SC profile. The influx of Si in the oldest soil is indicative of open-system enrichment from outside sources. Minor amounts of windblown eolian dust on the soil surface may have contributed to this influx (Vaughan et al., 2011). The coarse cinder fragments in the upper part of this soil, however, also have elevated Si contents, suggesting that there was likely an influx of a distinct basaltic volcanic material with slightly higher Si content on the surface of this soil profile. The Si content

Table 5. Mean soil organic carbon accumulation rates in soil formed in tephra from different climates.

Study location	MAP† <i>mm</i>	MAT‡ <i>C</i>	organic C rate $\text{g m}^{-2} \text{ yr}^{-1}$	reference
2.1CG, Idaho, United States	380	6	0.48	this study
6.9 BCB, Idaho, United States			0.28	
13.9 SC, Idaho, United States			0.47	
Canary Islands, Spain	144	16–20	0.6–1.2	Jahn and Stahr, 1996
Japan	1186	13.5	21.1–22.9	Sakai et al., 2010
Hawaii, United States	2200–4500	15–17	37.2–39.3	Vitousek et al., 1983

† MAP, mean annual precipitation.

‡ MAT, mean annual temperature.

Table 6. Mean flux of calcium in three ecosystems as a function of mean annual precipitation (MAP), mean annual temperature (MAT), and age (Taylor and Blum, 1995).

Study ecosystem	MAP†	MAT‡	Age	Ca flux
	mm	C	ka	g cm ⁻²
Cindercone	380	6	13.9	0.38
Mountain sagebrush ecosystem	230	2	21	2.29
Alpine tundra	500–700	–4	11	1.8

† MAP, mean annual precipitation.

‡ MAT, mean annual temperature.

of the parent material of the 13.9 SC soil is 219 g kg⁻¹, while the coarse fragments in the upper 18 cm have a mean of 245 g kg⁻¹ Si. It is likely that an eruption of material with different chemical composition followed the initial eruption 13.9 ka ago, and it is likely this material is from an eruption not analyzed in this study due to the difference in elemental composition and proximity of source material (Kuntz et al., 1985).

Mass balance analyses along the soil chronosequence at CROM indicate changes in base cation concentrations occurring over a relatively short duration. Base cations and Si are removed from the system via weathering. The major elements can be ranked according to their mobility as: Si < Ca < Mg < K < Na, with some depletions approaching 15%. Studies have shown near 100% depletion in Ca on marine terraces up to 240 ka (Merritts et al., 1992). In the cool, dry climate at CROM, losses of that magnitude require substantially more time to occur. The results from this study indicate small magnitude changes in element distribution over short time scales, however, these changes are significant enough to develop strongly contrasting physical and chemical properties in young soil profiles formed over thousands of years (Fig. 1, Table, 1).

Redistribution of Iron, Aluminum, and Titanium

Weight percentages of Fe and Ti decline in surface horizons of the 13.9-ka BP profile (Fig. 5). This decrease relates to the probable influx of more Si-rich eolian dust and basaltic tephra that is slightly more Si-rich and Fe-poor than the parent cinders forming the lower horizons. In addition, the movement of Fe from the surface into the subsurface via leaching and secondary mineral formation cause a decrease in Fe and Ti in the surface horizon (Vaughan et al., 2011). The coarse fragments in the upper two horizons have a mean of 103 g kg⁻¹ Fe and 10.3 g kg⁻¹ Ti while the < 2 mm fraction has a mean of 96 g kg⁻¹ Fe and 9.4 g kg⁻¹ Ti, showing a decrease in Fe and Ti in the surface relative to subsurface horizons. There is a zone of Al accumulation at 25 cm and Fe at 43 cm that corresponds to the depth of the 2Bw1 and 2Bw2 horizons, respectively. The mass transport function that accounts for profile strain shows an increase in Fe, Al, and Ti below 25 cm. This accumulation is the result of open- and closed-system enrichment from overlying eluvial horizons and decrease of other elements (Si and base cations) within the horizons. This results in a residual enrichment in Fe, Al, and Ti.

Decreased Fe, Al, and Ti mobility is observed in the 6.9 BCB soil with respect to profile depth (Fig. 5). There are zones of loss in the near surface horizons coupled with minor zones of accumulation in the underlying Bw2 horizon. The same general trends are observed as in the younger profile with losses of Fe, Al, and Ti in the surface and accumulations in the upper subsurface. The 2.1 CG profile shows slight increases in the mass flux of Fe, Al, and Ti from the surface to a 1-m depth (Fig. 5) showing some indication redistribution of elements from parent cinders into secondary minerals.

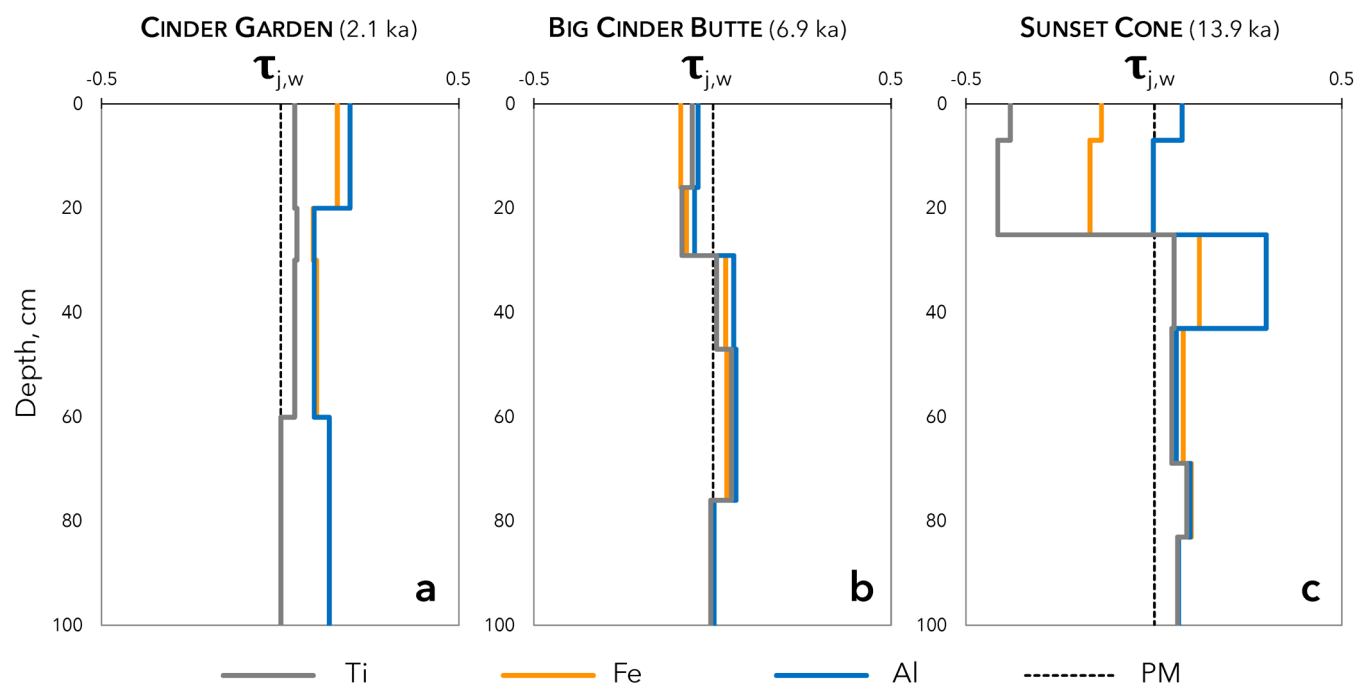


Fig. 5. Depth plots of transported mass fraction (τ) of Fe, Al, and Ti for the (a) Cinder Garden (2.1 CG), (b) Big Cinder Butte (6.9 BCB), and (c) Sunset Cone (13.9 SC) soil profiles. Vertical dashed lines represent values for the parent material (PM).

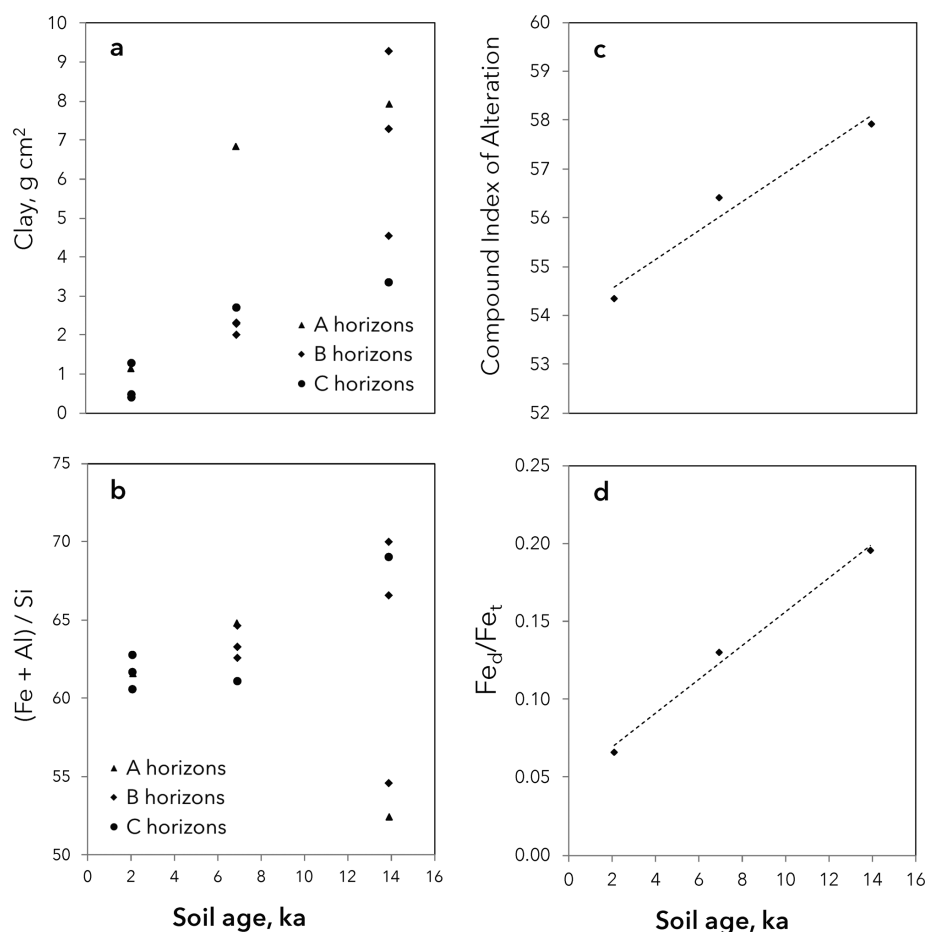


Fig. 6. Relationship between the (a) clay content and (b) Fe plus Al divided by Si versus age in soils along a chronosequence at Craters of the Moon National Monument and Preserve. Points represent the mean of values measured from all soil horizons (triangles are A horizons, diamonds are B horizons, and circles are C horizons) along the chronosequence. Weighted mean to a 1-m depth of (c) compound index of alteration (CIA) ($r^2 = 0.964$ at $p < 0.05$) (Eq. [9]) (Nesbitt and Young, 1982), and (d) weighted mean to a 1-m depth of dithionite-citrate-bicarbonate extractable Fe (Fe_d) divided by total Fe (Fe_t) as a function of soil age ($r^2 = 0.988$ at $p < 0.05$).

Weathering of Parent Material and Soils

Processes of Soil Formation and Weathering

Soil evolution occurs within all soils along the chronosequence; however, evidence of this is expressed more readily as as pedogenesis is better expressed. Even the oldest profile lacks a dominance of crystalline secondary minerals, suggesting that the soil weathering stage is still relatively young on the CROM soils. The relatively slow weathering rates are caused by cool temperatures and low precipitation, which facilitate the formation of only SRO minerals in the time the soils have had to develop.

Key trends over time include an increase in organic matter, SRO minerals, crystalline minerals, bulk density, and < 2-mm soil material coupled with the subsequent decrease in coarse fragments. The 2.1 CG soil shows the least degree of weathering followed 6.9 BCB and 13.9 SC soils. To assess the amount of weathering over time, the relationship between clay content, soil age, and percentage Fe_2O_3 plus percentage Al_2O_3 divided by SiO_2 was determined (Fig. 6). Clay content increases as weathering proceeds (Fig. 6). As time progresses, desilication occurs while Fe and Al contents remain somewhat constant as they are weath-

ered from volcanic glass to form secondary SRO or crystalline minerals. Soils forming in other parent materials under wetter and or warmer climates will likely have a more rapid weathering progression than CROM soils (Eggleton et al., 1987; Zhang et al., 2007).

Weathering Indices and Rates

Weathering indices provide a method of examining the magnitude of weathering as a function of time. The CIA illustrates the relative loss of bases and has been proposed as a measure of the initial stages of weathering (Zhang et al., 2007). The CIA values for intensely weathered materials approaches 100, while lower CIA values indicate lesser amounts of weathering (Nesbitt and Young, 1982). The weighted means to a 1-m depth of CIA are strongly related to soil age (Fig. 6). As soil age and weathering increase, base cations are leached from the soil.

The amount and type of Fe oxides are also often used as an indicator of soil development. Dithionite citrate bicarbonate-extractable Fe is used as a proxy for the amount of total secondary Fe oxides that have formed in soils. As shown in this study, older, more weathered soils contain greater Fe_d . The ratios of weighted mean to a 1-m depth of Fe_d/Fe_t show a strong correlation with soil age (Fig. 3).

Weathering rates increase as temperature and precipitation increases. Volcanic soils forming under warm conditions with xeric soil moisture regimes tend to have higher degrees of humification due to the moist winters and dry summers (Shoji et al., 1993a). The climate at CROM is drier than the sites examined by Shoji et al. (1993a), and therefore the soils have less pronounced humus accumulation. Volcanic soils receiving less than 1000 mm of annual precipitation typically have a clay fraction dominated by allophane and imogolite (Shoji and Fujiwara, 1984). X-ray diffraction (XRD) patterns indicate that ferrihydrite and allophane are the dominant clay-sized SRO minerals in all four profiles (XRD data not shown). Broad peaks indicative of allophane are present in the clay fractions of all soils. Both two-line and six-line ferrihydrite are present; however, when both minerals are present differentiating the two-line from the more crystalline six-line phase is difficult. After dissolution with AOD, minor amounts of smectite and likely ilmenite ($FeTiO_3$) minerals were identified. Due to the short formation time in these soils and the dry, cool climate, fewer crystalline minerals have formed than in more humid, warmer climates.

SUMMARY

Soils forming on cinder cones at CROM present an opportunity to examine elemental mass-balance dynamics over thousands of years of soil evolution in a cool, dry climate. As a result of minimal eolian inputs, elemental dynamics are attributed to soil development. Variations in the type and amount of minerals within soil profiles across the chronosequence are observed. Soil physical, mineralogical, and chemical properties demonstrate that time is an influential factor in soil evolution in this dry, frigid climate. Physical development is revealed through soil color changes, increased bulk density, clay accumulation, and decreased coarse fragment content. Mineralogically, these soils have begun to accumulate SRO minerals including allophane, ferrihydrite, and metal-humus complexes with secondary Fe mineral content increasing with soil age. Crystalline minerals are minor components of the colloidal fraction and may, in part, be inherited from eolian sources.

Soil forming processes along the chronosequence of cinder cones are characterized by: (i) organic matter accumulation in surface horizons; (ii) loss of bases due to plant uptake and weathering of primary minerals; (iii) open-system translocation of Fe, Al, and Ti from surface to subsurface horizons; (iv) physical weathering of coarse fragments; and (v) accumulation of SRO and crystalline minerals. Most notably, this study reveals measurable amounts of weathering and mineralogical transformation over 10,000 yr in an arid climate.

ACKNOWLEDGMENTS

This work was supported in part by the Natural Resources Conservation Service. Special thanks to Anita Falen for her meticulous soil storage system that allowed for analysis of dust source material as well as her general resourcefulness as the University of Idaho Pedology Lab technician.

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