Dear Antonio Jordán (Topical Editor),

Thank you for the thoughtful comments. We have addressed all the recommended changes. Please find attached a revised version of the manuscript with marked changes.

Sincerely,

Samuel Araya (on behalf of all authors)

1 **Thermal alteration of soil organic matter properties: a systematic study to**

2 **infer response of Sierra Nevada climosequence soils to forest fires**

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# Abstract

Fire is a major driver of soil organic matter (SOM) dynamics, and contemporary global climate change is changing global fire regimes. We conducted laboratory heating experiment of soils from five locations across the western Sierra Nevada climosequence to investigate thermal alteration of SOM properties and determine temperature thresholds for major shifts in SOM properties.  Topsoils (0 to 5 cm depth) were exposed to a range of temperatures that are expected during prescribed and wild fires (150, 250, 350, 450, 550 and 650 °C). With increase in temperature, we found that the concentrations of C and N decreased in a similar pattern among all five soils that varied considerably in their original SOM concentrations and mineralogies. Soils were separated into discrete size classes by dry sieving. The C and N concentrations in the larger aggregate size fractions (2-0.25mm) decreased with increase in temperature that at 450 °C temperature, the remaining C and N were almost entirely associated with the smaller aggregate size fractions (<0.25mm). We observed a general trend of $^{13}$C enrichment with temperature increase. There was also $^{15}$N enrichment with temperature increase followed by $^{15}$N depletion when temperature increased beyond 350 °C. For all the measured variables, the largest physical, chemical, elemental, and isotopic changes occurred at the mid-intensity fire temperatures, i.e. 350 and 450 °C. The magnitude of the observed changes in SOM composition and distribution in three aggregate size classes, as well as the temperature thresholds for critical changes in physical and chemical properties of soils (such as specific surface area, pH, cation exchange capacity) suggest that transformation and loss of SOM are the principal responses in heated soils. Findings of this systematic investigation of soil and SOM response to heating are critical for predicting how soils are likely to be affected by future climate and fire regimes.

**Keywords:** Thermal alterations, Soil Organic Matter, Fire, Climosequence.

# 1. Introduction

Fire is a common, widespread phenomenon globally (Bowman et al., 2009) that conditions the dynamics of soil and soil organic matter (SOM). Vegetation fires burn an estimated 300 to 400 million hectares of land globally every year (FAO, 2005). In the US alone, over 80,000 fires were reported in 2014–including about 63,000 wildland fires, and 17,000 prescribed burns that burned over 1.5 million and 970,000 ha of land, respectively (National Interagency Fire Center, 2015). In the Sierra Nevada, vegetation fires have a major influence on the landscapes. Ecological functions such as plant regeneration, habitat revitalization, biomass accumulation and nutrient cycling, are influenced by fires (McKelvey et al., 1996). Historically most fires were caused by lightning fires and vegetation fires play important role in maintaining the health of many ecosystems around the world (Harrison et al., 2010). In recent decades, anthropogenic activities have become major causes of vegetation fires (Caldararo, 2002). Moreover, climate and climatic variations exert a strong control on the distribution, frequency, and severity of fires (Harrison et al., 2010). Significant changes in global fire regimes are anticipated because of climate change including increased frequency of fires in the coming decades (Pechony and Shindell, 2010; Westerling et al., 2006). However, our understanding of how climate change and changes in fire regimes will interact to influence topsoils in fire affected ecosystems is limited.

In addition to combustion of aboveground biomass and alteration of vegetation dynamics, fires also affect the physical, chemical and biological properties of soils (Certini, 2005; González-Pérez et al., 2004; Mataix-Solera et al., 2011). The degree of alteration caused by fires depends on the fire intensity and duration, which in turn depend on factors such as the amount and type of fuels, properties of above ground biomass, air temperature and humidity, wind, topography, and soil properties such as moisture content, texture and soil organic matter (SOM) content (DeBano et al., 1998). The first-order effects of fire on soil are caused

1  by the input of heat causing extreme soil temperatures in topsoil (Badía and Martí, 2003b;

2  Neary et al., 1999) resulting in loss and transformation of SOM, changes in soil

3  hydrophobicity, changes in soil aggregation, loss of soil mass, and addition of charred

4  material and other combustion products (Albalasmeh et al., 2013; Araya et al., 2016; Mataix-

5  Solera et al., 2011; Rein et al., 2008; Santos et al., In press).

6  The duration of burning regulates the amount of energy transferred through the soil. Fires

7  with longer residence time and lower temperature typically impact the soil and SOM more

8  than fires with shorter residence time that burn at a higher temperature (Frandsen and Ryan,

9  1986; González-Pérez et al., 2004). Penetration of heat down a soil profile depends on

10  intensity and duration of fire as well as the thermal conductivity of the soil (Steward et al.,

11  1990). Soil has a low thermal conductivity that in fires only the top few centimeters of soil

12  experiences extreme temperature. For example, in short duration or low severity fires

13  temperatures typically reach only 100 – 150 °C at 5 cm depth with no significant change of

14  temperature at 30 cm depth (DeBano, 2000; Janzen and Tobin-Janzen, 2008).

15  Fire has multiple, complex effects on carbon (C) dynamics in soil. Wildfires alone lead to the

16  release of up to 4.1 Pg C $yr^{-1}$ to the atmosphere in the form of carbon dioxide, with an

17  additional 0.05 to 0.2 Pg C $yr^{-1}$ added to the soil as black or pyrogenic carbon ash (Singh et

18  al., 2012). The changes in SOM characteristics due to combustion include reduced solubility

19  of OM due to loss of external oxygen containing functional groups; reduced chain length of

20  fatty acids, alcohols and other alkyl compounds; higher aromaticity due to transformation of

21  carbohydrates and lipids; production of pyrogenic carbon; formation of heterocyclic nitrogen

22  (N) compounds; and macromolecular condensation of humic substances (González-Pérez et

23  al., 2004). In the long term, fires can affect soils by altering and removing vegetation and

24  topsoil biomass, and increasing soil erodibility (Carroll et al., 2007; DeBano, 1991),

1  subsequently leading to a shift in plant and microbial populations (Janzen and Tobin-Janzen,

2  2008).

3  The aim of this study is to determine the effects of heating temperatures on important SOM

4  properties. We used a laboratory heating experiment on five soils from a well-characterized

5  climosequence in the western Sierra Nevada mountain range (Dahlgren et al., 1997). We

6  analyzed changes in SOM quantity and quality following heating treatment with the aim to:

7  (1) determine magnitudes of change in SOM properties associated with different fire heating

8  temperatures; (2) identify critical thresholds for these changes; and (3) infer the implications

9  of changing climate on topsoil SOM properties that might experience changing fire regime.

10  This study aims to contribute to the systematic evaluation and development of ability to

11  predict the effect of different intensity fires on soil properties under changing climate and fire

12  regimes.

13  **2. Materials and methods**

14  Following laboratory heating of five soils from western Sierra Nevada to temperatures

15  ranging from 150 to 650 °C, we analyzed changes in SOM quality and quantity. We

16  measured the changes in C and N concentration in the soil and changes in the distribution of

17  C and N to different aggregate size classes. We also measured changes in isotopic

18  composition of $^{13}C$ and $^{15}N$ in the soils and in the different aggregate size classes. Changes in

19  SOM quality was analyzed using Fourier-transform infrared (FTIR) spectroscopy of soils.

20  Description of the study site is given in Section 2.1 and details of the methods used are given

21  in Sections 2.2 to 2.4.

22  **2.1. Study site and soil description**

23  For this study, we collected soils from five sites across an elevation transect along the

24  western slope of the central Sierra Nevada, California (Figure 1); the sites were previously

1 characterized by Dahlgren et al. (1997). We selected four forested sites that are likely to

2 experience forest fires and a fifth lower elevation grassland site. The thermal alterations of

3 bulk soil physical and chemical properties from the same study soils was previously reported

4 in Araya et al. (2016).

5 All the sites have a Mediterranean climate characterized by warm to hot dry summers and

6 cool to cold wet winters. Mean annual air temperature ranges from 16.7 °C at the lowest site

7 located at 210 m to 3.9 °C at the highest elevation site which is at an elevation of 2865 m.

8 Annual precipitation ranges from 33 cm at the lowest site to 127 cm at the highest site

9 (Dahlgren et al., 1997; Rasmussen et al., 2007) (Table 1).

10 The lower elevation woodlands of Sierra Nevada experience less frequent fires than further

11 upslope and the fires are often fast moving and lower severity (Skinner and Chang, 1996). At

12 the middle-elevation zone of Sierran forest, the mixed conifer zones, frequent fires are low to

13 moderate severity at lower altitudes but fire frequency generally increases with altitude

14 towards the upper elevation of the mixed conifer forest (Caprio and Swetnam, 1993). Fires

15 are infrequent and low severity within the high altitude, Subalpine, zone of Sierra (Skinner

16 and Chang, 1996).

17 Soils from the lowest elevation site, Vista Series soils (210 masl), fall within the oak

18 woodland zone (elevations < 1008 masl). This is the only soil in our study that does not have

19 an O-horizon. The soil has dense annual grass cover and its A-horizon SOM originates

20 mainly from root turnover. The Musick Series soils (1384 masl) lie within oak/mixed-conifer

21 forest (1008—1580 masl) and mixed-conifer forest (1580—2626 masl). These soils receive

22 the highest litter fall biomass. The Shaver and Sirretta Series soils (1737 and 2317 masl,

23 respectively) fall within the mixed-conifer forest range zone while the Chiquito Series soils

24 (2865 masl) lies within the subalpine mixed-conifer forest range (2626—3200 masl). These

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1 soils have lower litter fall compared to the lower elevation soils (van Wagtendonk and Fites-

2 Kaufman, 2006).

3 The western slope of central Sierra Nevada presents a remarkable climosequence of soils that

4 developed under similar granitic parent material and are located in landscapes of similar age,

5 relief, slope and aspect (Trumbore et al., 1996) with significant developmental differences

6 attributed to climate. The soils at mid-elevation range (1000 to 2000 masl) tend to be highly

7 weathered while soils at high and low elevations are relatively less developed (Dahlgren et

8 al., 1997; Harradine and Jenny, 1958; Huntington, 1954; Jenny et al., 1949). Among the most

9 important changes in soil properties along the climosequence include changes in soil organic

10 carbon (SOC) concentration, base saturation, and mineral desilication and hydroxyl-Al

11 interlayering of 2:1 layer silicates. Soil pH generally decreases with elevation and the

12 concentrations of clay and secondary iron oxides show a step change at the elevation of

13 present-day average effective winter snowline, i.e. 1600 m elevation (Tables 1 and 2)

14 (California Department of Water Resources, 1952-1962; Dahlgren et al., 1997).

15 **2.2. Experimental design and sample collection**

16 Triplicate samples (0 to 5 cm depth) were collected at the five sites, approximately 10 m

17 apart from each other. Any overlaying organic layer was removed prior to sampling so that

18 only mineral soil was collected. The soils were air-dried at room temperature and passed

19 through 2 mm sieve. Prior to furnace heating, the soils were oven dried at 60 °C overnight.

20 Soil bulk density and field soil moisture were determined from separate undisturbed core

21 samples collected from each site (Table 2).

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22 Sub-samples from each soil were heated in muffle furnace to one of six selected maximum

23 temperatures (150, 250, 350, 450, 550 and 650 °C). To ensure uniform soil heating and

24 reduce formation of heating gradient inside, the soils were packed 1 cm high in a 7 cm

1  diameter porcelain flat capsule crucibles. Oxygen supply was not limited during the

2  heating—the volume of soil sample to volume air in furnace was approximately 1:50.

3  Furnace temperature was ramped a rate of 3 °C min$^{-1}$ and soils were exposed to the maximum

4  temperature for 30 minutes. Once cooled to touch, soils were stored in in air-tight

5  polyethylene bags prior to analysis.

6  The six heating temperatures were selected to correspond with fire intensity categories that

7  are based on maximum surface temperature (DeBano et al., 1977; Janzen and Tobin-Janzen,

8  2008; Neary et al., 1999), that is, low intensity (150 and 250 °C), medium intensity (350 and

9  450 °C), and high intensity (550 and 650 °C). These fire intensity classes generally

10 correspond with thresholds for important thermal reactions in soils observed by differential

11 thermal analyses (Giovannini et al., 1988; Soto et al., 1991; Varela et al., 2010). Heating rate

12 of 3 °C min$^{-1}$ is preferred in laboratory fire simulation experiments (Giovannini et al., 1988;

13 Terefe et al., 2008; Varela et al., 2010), the slow heating rate prevents sudden combustion

14 when soil's ignition temperature is reached at about 220 °C (Fernández et al., 1997, 2001;

15 Varela et al., 2010). The samples were exposed to the maximum set temperature for a period

16 of 30 minutes. This length of time ensures that the entire sample is uniformly heated at the set

17 temperature and is in keeping with wide majority of similar laboratory soil heating

18 experiments (for example Badía and Martí, 2003a; Fernández et al., 2001; Giovannini, 1994;

19 Varela et al., 2010; Zavala et al., 2010). The duration of soil heating under vegetation fires is

20 highly varied and not uniform across landscape (Parsons et al., 2010). The same heating

21 procedure was used for all the soils so that it would be possible to compare how the soils

22 from different climate regimes are likely to respond to the fires.

**2.3. Laboratory analysis**

Dry-aggregate size distribution was measured by sieving. Samples were dry sieved into three aggregate size classes: 2–0.25 mm (macro-aggregates), 0.25–0.053 mm (micro-aggregates) and <0.053 mm (silt and clay sized particles or composites). These aggregate size classes were selected to enable comparison with other studies that investigated the effect of different natural and anthropogenic properties on soil aggregate dynamics and aggregate protected organic matter (Six et al 2000).

C and N concentrations and stable isotope ratios were measured using an elemental combustion system (Costech ECS 4010 CHNSO Analyzer, Costech Analytical Technologies, Valencia, CA, USA) that is interfaced with a mass spectrometer (DELTA V Plus Isotope Ratio Mass Spectrometer, Thermo Fisher Scientific, Inc., Waltham, MA, USA). For the analyses, air-dried soil samples were ground to powder consistency on a ball-mill (8000M MiXer/Mill, with a 55 ml tungsten Carbide Vial, SPEX SamplePrep, LLC, Metuchen, NJ, USA) and oven dried at 60 °C for over 36 hours. This lower temperature and longer duration oven-drying was used to avoid possible heating related C or N changes that might occur if drying was done 105 °C (Kaiser et al., 2015). The C and N concentration results were corrected for moisture by oven-drying subsamples at 105 °C overnight. The C and N concentration results were corrected by adjusting for moisture as: $W_{adj} = W \times (100 - W_m)$. Where $W_{adj}$ is the adjusted percent concentration, $W$ is the concentration before moisture adjustment and $W_m$ is the percent moisture content. All concentration changes resulting from moisture adjustment were a decrease of less than 1% of the value. The stable isotope ratios are presented using the δ notation (per mill, ‰) as δ $^{13}$C and δ $^{15}$N calculated as: $\delta = [(R_{sample} - R_{standard})/R_{standard}] \times 1000‰$; where $R$ is ratio of $^{13}C/^{12}C$ for δ $^{13}$C, and $^{15}N/^{14}N$ for δ $^{15}$N. The standards used for analyses are atmospheric N$_2$ δ $^{15}$N and Vienna Pee Dee Belemnite (VPDB) δ $^{13}$C.

1 Bulk soil organic matter composition was analyzed using Fourier-transform infrared (FTIR)

2 spectroscopy on a Bruker IFS 66v/S vacuum FT-IR spectrometer (Bruker Biosciences

3 Corporation, Billerica, MA, USA). We used diffuse reflectance infrared Fourier-transform

4 (DRIFT) technique (Ellerbrock and Gerke, 2013; Parikh et al., 2014). Powder samples were

5 dried overnight at 60 °C and scanned in mid-IR from 4000 to 400 $cm^{-1}$. We used Non-KBr

6 diluted samples after preliminary analyses showed that dilution was not necessary. KBr

7 dilution is not required for soils with low (<10%) organic matter concentrations (Ellerbrock

8 and Gerke, 2013; Reeves III, 2003). The FTIR spectrum was collected using KBr background

9 and was baseline corrected using to the Rubberband correction method with the default 64

10 baseline points that is part of the OPUS software (Bruker Corporation, 2009).

11 **2.4. Statistical Analysis**

12 All quantitative results are expressed as means of three replicates ± standard error, unless

13 otherwise indicated. Differences of means were tested by Analysis of Variance (ANOVA)

14 and pairwise comparison of treatments done using Tukey's HSD test at $p<0.05$ significance

15 level. The normality of the data and the homogeneity of variances was checked using

16 Shapiro-Wilk's and Levene's tests respectively. All statistical analysis were performed using

17 R statistical software (R Core Team, 2014). The Pearson correlation coefficient was used to

18 examine relationships between C concentration and changes in soil properties.

19 **3. Results**

20 **3.1. Carbon and nitrogen concentration**

21 The initial concentration of C ranged from 1.5% (Vista soil, 210 m) to 7.7 % (Musick soils,

22 1384 m). Soil C concentration continuously decreased with increasing temperature. The

23 largest decrease occurred between temperatures of 250 and 450 °C. At 450 °C, all soils lost

24 more than 95% of their original C. C concentration changes with heating above 450 °C were

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1     small and not statistically significant at p<0.05. The C:N ratio ranged from 10 (Vista soils,

2     210 m) to 29 (Musick soils, 1384 m). Following a similar pattern to C concentration changes,

3     the C:N ratio decreased with an increase in heating temperature (Figure 2).

4     The loss of C and N from soils due to heating showed a similar response among all five soils

5     (Figure 2). After 250 °C, all the soils lost more than 25% of their initial C (except Shaver

6     soils that lost only about 10%). At 350 °C all soils lost 50 to 70% of C. Heating at 450 °C led

7     to the loss of more than 95% of their initial C for all soils in this study. However, the rate of

8     loss of N was lower than that of C. At temperatures greater than 550 °C there was 5 to 15%

9     of soil N still remaining. Consequently, we observed a decrease of C:N ratio with increased

10     heating temperature. All soils continued to lose about 15% soil N for every 100 °C increase

11     and maintained more than 60% of their N at heating temperatures up to 350 °C. After heating

12     at 450 °C, all soils lost more than 60% of their original soil N and 85% by 550 °C.

13     **3.2. Carbon and nitrogen stable isotopes**

14     The $\delta^{13}C$ composition of all soils was indicative of C-3 vegetation. Soil $\delta^{13}C$ composition

15     was most negative at about -28‰ for the lowest elevation Vista site (210 m) and the value

16     got consistently less negative with an increase in elevation reaching -24‰ for the highest two

17     sites (i.e. >2317 m elevation). For all soils, there was a general trend of $\delta^{13}C$ enrichment with

18     temperature increase (Figure 2). The largest change (2.5 to 3.0‰) occurred at heating

19     temperature between 250 and 450 °C for the lower elevation soils and between 150 and

20     450 °C for the two highest elevation soils. For the two highest elevation soils, there was a

21     significant (p <0.05) depletion above that temperature. For all soils, except Musick (1384 m)

22     and Shaver (1737 m), the maximum enrichment occurred at 450 °C. All soils showed a

23     similar pattern $\delta^{15}N$ composition change with temperature. The soils were increasingly $\delta^{15}N$

1  enriched with temperature increase up to 350 °C. At temperatures above 350 °C, the soils got

2  more $\delta^{15}N$ depleted with the most negative $\delta^{15}N$ occurring at 650 °C (Figure 2).

3  **3.3. Carbon and nitrogen distribution in aggregate size fractions**

4  C and N concentrations, as well as $^{13}C$ and $^{15}N$ stable isotope ratios were measured for

5  individual soil aggregate size class. The analysis was done on samples heated up to a

6  temperature of 450°C. The concentration of C and N in samples heated above 450 °C was too

7  low to measure significant changes in C distribution in the different aggregate size classes.

8  The distribution of C in the three aggregate sizes fractions followed the same general pattern

9  with increase in the heating temperatures. The macro aggregate size fraction (2-0.25 mm) had

10  the least C concentration and silt-clay size particles (<0.053 mm) had the largest

11  concentration of C (Figure 3). N concentration for the macro size aggregates was below the

12  detection limit at 450°C for Chiquito and Sirretta. The change in C and N concentration

13  across heating temperature was similar for all soils

14  The distribution of C and N in different size aggregates did not change noticeably except at

15  450 °C where concentration in all three fractions converged to zero. The distribution of N in

16  the three aggregate sizes fractions was similar to that of C and followed a similar pattern

17  across all the heating temperatures. Similarly, the macro aggregate size fraction (2-0.25 mm)

18  had the least amount of N concentration and silt-clay size particles (<0.053 mm) had the

19  largest concentration of N. For Shaver (1737 m), Sirretta (2317 m) and Chiquito (2865 m)

20  soils, the macro size aggregate N concentration was too low and could not be detected

21  (Figure 3). The atomic C:N ratio generally stayed the same for all soils through the

22  temperatures. C:N ratio was highest in macro size aggregates, which had lowest C and N

23  concentrations, followed by micro and by silt-clay sizes for all soils.

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1  The stable isotope composition of $^{13}C$ was very similar between aggregate sizes with silt-clay

2  size aggregates being slightly more enriched except for Shaver (1737 m), which had slightly

3  more enriched macro aggregates. On the other hand, the $\delta^{15}N$ values showed clear differences

4  among aggregate fractions even though the measured values of $\delta^{15}N$ did not change notably

5  with combustion temperatures. $\delta^{15}N$ was highest in silt-clay size particles and lowest in

6  macro size aggregates with the micro size aggregates showing intermediate values. The

7  pattern of change in $\delta^{15}N$ across combustion temperatures did not affect this order of $\delta^{15}N$

8  values among aggregate fractions. Most of the C and N in the soils was associated with the

9  larger, macro and micro, aggregate size fractions. With the exception of Vista (210 m) soils,

10  the concentrations in macro aggregates continued to decrease with an increase in temperature,

11  and the remaining C and N concentrations were distributed between the smaller aggregate

12  fractions (Figure 4). At 450 C, most of the C and N of the higher altitude soils (Shaver,

13  Sirretta and Chiquito) was now associated with the silt-clay sized fractions.

14  **3.4. FTIR spectroscopy**

15  Changes in chemical composition of SOM due to heating were analyzed by infrared

16  spectroscopy using Diffuse reflectance infrared Fourier transform (DRIFT) technique. The

17  spectra and peaks after contrasting levels of thermal treatments exhibited qualitative

18  similarities among the different soils. FTIR spectra for the soils are shown in Figure 5. One

19  notable change that occurred in the functional group composition of SOM with heating is the

20  lowered absorbance intensity of aliphatic methylene groups (as represented by the aliphatic

21  C–H stretching peak that appear at bands between 2950 – 2850 cm$^{-1}$) at >250 °C in all soils.

22  When comparing intensity of peaks at 2910 – 2930 and 2853 cm$^{-1}$ wave numbers (from

23  aliphatic methyl and methylene groups, band A) with those at 1653 and 1400 cm$^{-1}$ (oxygen

24  containing carboxyl and carbonyl groups, band B), the decrease in prominence in the

25  aliphatic C-H peak occurs early in the heating sequence while the C=O band shows little

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1  relative change. In addition, after heating at a temperature of 550 °C all soils lost the O–H

2  stretching peaks (between 3700 – 3200 cm$^{-1}$). In a pattern that is more prominent for the

3  Musick soil that had the highest concentration of OM, the aromatic C=C stretch around 1600

4  cm$^{-1}$ gets more resolved with increase in heating temperature. This pattern in the C=C is

5  visible, but less well resolved in the rest of the soils, especially the Vista soil that showed the

6  least resolved aromatic C=C stretch peak at this region.

7  **4. Discussion**

8  **4.1. Changes in SOM concentration, distribution and composition**

9  Our results show significant effects of combustion temperature on concentration, distribution,

10 and composition of SOM on topsoils that experience the most intense heating during

11 vegetation fires. Topsoils have relatively high OM and low clay content that render them

12 more sensitive to heating as the SOM experiences significant changes during heating. In our

13 study system, the effect of fire heating on SOM ranged from slight distillation (volatilization

14 of minor constituents) typically at temperatures below 150°C, to charring which typically

15 starts at temperatures above 350°C and complete combustion, consistent with findings of

16 previous studies (Badía and Martí, 2003b; Certini, 2005). Our findings also confirmed that

17 regardless of the differences our soils had in mineralogy and other soil physical and chemical

18 properties, the heating treatments (as proxy for wild fires) led to consistent decrease in

19 concentration of soil C. This was in agreement with previous studies that showed decrease in

20 soil C concentration in topsoil after fires (for example Badía et al. (2014); Certini (2005)).

21 However, this loss of C is expected to be restricted to topsoil while it is expected that the C

22 concentration in subsoil is likely to remain unchanged or may even increase (for example

23 Dennis et al. (2013); Kavdır et al. (2005)) due to incorporation of necromass from surface

24 biomass (Almendros et al., 1990; Knicker et al., 2005).

1    We observed significant changes in concentration, distribution, and composition of SOM

2    with increasing heating temperature. The steep decline in concentration of C in soil that we

3    observed between this study is consistent with decrease of about 25% C at 250°C and an

4    almost 99% loss at 450°C (Figure 6). The magnitude of C loss with heating we observed is

5    similar to the findings of Terefe et al. (2008); and Ulery and Graham (1993) that investigated

6    changes in soil C using artificial heating experiment. Similarly, Giovannini et al. (1988) also

7    found OM decrease started at 220 °C with about 15% loss of OM and about 90% OM loss at

8    460 °C; while Fernández et al. (1997) reported 37% of SOM loss at 220 °C and 90% at

9    350 °C. Furthermore, along with the change in C concentration, between 150 °C and before

10   almost total loss of C above 450 °C, the SOM went through significant qualitative changes

11   that included decrease in C:N ratio, enrichment in $\delta^{13}C$ isotope, changes in $\delta^{15}N$ isotope, and

12   changes in FTIR spectra. Loss in N after fire heating is the result of combustion and

13   volatilization (Fisher and Binkley, 2000). In this study, we observed that N is not as

14   significantly reduced until 350°C with about 75% N remaining as opposed to greater than

15   50% loss of C concentration at the same temperature (Figure 6). Previously studies had

16   showed that moderate to high intensity fires convert most organic-N into inorganic forms of

17   N, such as Ammonium (Certini, 2005; Huber et al., 2013). Ammonium is the immediate

18   combustion product that contributes to formation of nitrate ($NO_3^-$) by nitrification reactions in

19   weeks or months after fire. Other studies have showed that a considerable amount of N is

20   transferred into pyrogenic OM products, to black N (de la Rosa and Knicker, 2011; Knicker,

21   2010), which would also explain the decrease of the C:N. Decrease in C:N ratio with fire

22   heating has previously been observed in both laboratory and field fire studies (Badía and

23   Martí, 2003a; Certini, 2005; Fernández et al., 1997; González-Pérez et al., 2004) .

24   SOM has a C isotopic composition that reflects the $\delta^{13}C$ signature of native vegetation. Plants

25   are depleted in $\delta^{13}C$ relative to atmosphere. The $\delta^{13}C$ composition for our soils indicated that

1    the dominant source of OM in all soils is C3 plant biomass that had average $\delta^{13}C$ of -27%,

2    with the higher elevation soils having more positive $\delta^{13}C$ than the low elevation. Enrichment

3    of $^{13}C$ with heating is consistent with the loss of plant derived C. In addition, the fact that

4    lipids (that have relatively more $\delta^{13}C$ depleted than the woody materials) are combusted at

5    lower temperatures than woody materials (such as cellulose and lignin), might contribute to

6    the enrichment of $\delta^{13}C$ with heating (Czimczik et al., 2002). The stable C and N isotope

7    composition of our soils showed significant fractionation with temperature. $\delta^{13}C$ values

8    became more positive (enriched in $\delta^{13}C$) up to 450 °C where up to 99% of C was lost (Figure

9    6). At higher temperature there was a less uniform pattern among the soils. For the last <1%

10   C, Sirretta and Chiquito soils continued to be more negative (depleted in $\delta^{13}C$) at higher

11   temperature while for the rest of the soils there was a slight depletion at 550°C followed by a

12   slight enrichment at 650 °C (Figure 2). The depletion of $\delta^{13}C$ at 550 and 650 °C we found in

13   this study is likely a result of SOM charring as there was little or no decrease in C

14   concentration between these temperatures. In a wood charring experiment (non-oxygen

15   atmosphere) at 150, 340 and 480 °C, Czimczik et al. (2002), observed an enrichment of $\delta^{13}C$

16   at 150 °C where there was no C concentration change but a depletion of $\delta^{13}C$ at 340 and

17   480 °C with charring where the C concentration increased over 50% due to charring.

18   Fires tend to lead to enrichment of $^{15}N$, this is particularly observed in soils immediately in

19   the  aftermath of fires (Boeckx et al., 2005; Grogan et al., 2000; Herman and Rundel, 1989;

20   Huber et al., 2013), but there is limited information available on the exact temperature ranges

21   that cause specific levels of $^{15}N$ enrichment. In this study, we observed enrichment of $^{15}N$ up

22   to 350 °C and depletion after 350 °C for all soils (Figure 2). It is likely that the continued $^{15}N$

23   enrichment with heating is the result of fractionation due to combustion and volatilization of

24   organic matter which discriminate against $^{15}N$. However, the exact mechanism behind

25   continued depletion of $^{15}N$ when heated above 350 °C remains unclear. One potential

1    explanation for the $^{15}$N depletion at higher temperatures could be indiscriminate removal of N

2    as higher temperatures cause the combustion and volatilization process to happen instantly,

3    compared to charring of OM at lower temperatures. In a post fire-analysis of $\delta^{15}$N on a sub-

4    alpine ecosystem in Australia, Huber et al. (2013), found that the $^{15}$N enrichment of bulk

5    surface soil (from unburnt leaves) was higher than that of the charred OM, which was again

6    higher than that of the ash. They attributed this difference in enrichment level to be the result

7    of the lower heating intensity experienced by the bulk soil which provided slower processes

8    for greater fractionation, while higher heat intensity experienced in by the ash result in full

9    combustion of plant material providing little opportunity for isotopic discrimination. The

10   temperature range where we observed the depletion of $^{15}$N in our experiment corresponds

11   with the range where steep decline in N concentration happened (Figure 6), which would be

12   consistent with the explanation.

13   *4.1.1. Implication of SOM changes with heating*

14   The alterations and loss of SOM is likely more important cause of soil property changes

15   rather than alterations to soil minerals. SOM is vulnerable to temperatures while soil minerals

16   are only affected at much higher temperatures (Araya et al., 2016). In addition, all of the soils

17   in our study are characterized by low clay content and low concentration of reactive minerals,

18   but high concentration of SOM especially in topsoil leading to strong relationships between

19   SOM concentrations and soils' physical properties.

20   Degradation of lignin and hemicellulose begins between 130 and 190 °C (Chandler et al.,

21   1983); and  carbohydrate signal is completely removed from $^{13}$C NMR spectra by 350 °C.

22   Furthermore, Knicker observed loss of stable alkyl C and carboxyl C at 350 °C leading to

23   enrichment of aromatic functional groups in the remaining residue, consistent with what

24   would be expected from incomplete combustion of OM during fires, leading to

1  transformation and production of charred products (Almendros et al., 2003; Knicker et al.,

2  1996). FTIR analyses from our work showed that the aliphatic O−H stretch peak (bands 3700

3  – 3200 cm$^{-1}$) disappeared at temperatures above 550 °C for all soils accompanied by nitriles

4  or methanenitrile C≡N stretch (2300 – 2200 cm$^{-1}$) at temperature above 450 suggesting

5  condensation of aromatic functional groups.

6  Loss of OM from soil due to combustion has multiple implications on soil physical and

7  chemical properties. Simple linear correlation between C concentration changes and other

8  soil physical and chemical changes that we observed with heating (reported here and in Araya

9  et al. (2016)) show that more than 80% of the variability in mass loss, aggregate strength,

10  SSA, pH, CEC and N concentrations is associated with changes in C concentration at the

11  different heating temperatures. Table3 summarizes the correlation coefficients of soil

12  property changes with change in C concentration. Analyses of associations between C

13  concentration and several soil properties showed linear association between: C and N

14  ($R^2$ >0.8), mass loss ($R^2$ >0.8, except for Vista and Sirretta soils), pH ($R^2$ >0.8, except for

15  Shaver and Sirretta), CEC ($R^2$ >0.7, except for Chiquito). Linear association between C

16  concentration and aggregate strength ($R^2$ >0.7, except for Musick and Chiquito which had

17  $R^2$ ~0.7). Specific surface area showed relation with C ($R^2$ >0.7 except for Vista and Musick).

18  In this study, the greatest changes in SOM occurred between temperatures 250 and 450 °C

19  and we found that temperatures below 250 °C had little effect on the quality and quantity of

20  SOM. This implies that lower intensity fires, such as typical prescribed fires, where soil

21  surface temperatures do not exceed 250 °C (Janzen and Tobin-Janzen, 2008) have minimum

22  impact on SOM.

**4.2. Climate Change Implications**

Investigation of the response of climosequence soils to different heating temperature in this study enables us to infer how, in the long-term, changes in climate are likely to alter the effect of fires on topsoil physical and chemical properties. Along our study climosequence, we observed critical differences in response of topsoils based mostly on concentration OM in soil and soil development stages of each soil. Soil OM concentration and composition in particular has been shown to respond to changes in precipitation amount and distribution, as is expected in the Sierra Nevada (Berhe et al., 2012b). Consequently, changes in soil C storage associated with climate change are expected to lead to different amounts of C loss due to fires. This is evidenced by the observed highest total mass of C loss from the mid-elevation Musick soil that had the highest carbon stock, compared to soils in either side of that elevation range. Anticipated changes in climate in the Sierra Nevada mountain ranges are expected to include upward movement of the rain-snow transition line exposing areas that now receive most of their precipitation as snow to rainfall and associated runoff (Arnold et al., 2015, 2014; Stacy et al., 2015). Upward moving of the rain-snow transition zone under anticipated climate change scenarios and associated more intense weathering at higher elevation zones can render more C to loss during fires. More than 80% of the variability in mass loss, aggregate strength, SSA, pH, CEC and N concentrations is associated with changes in C concentration (Table 3). Hence, as the vulnerability of these ecosystems to increased fire frequency increases, due to climate change (Westerling et al., 2006), we can expect more soil C loss with fires, along with associated changes in soil chemical and physical properties. In particular, our findings of important changes in soil physical and chemical properties occurring between 250-450 ºC are important for recognizing that critical transformations of topsoil SOM are likely to occur when, as a result of climate change, systems that are adapted to low severity fires experience medium to high severity fires.

1 The different responses of soil aggregation in our climosequence to the treatment

2 temperatures also suggest potential loss and transformation of the physically protected C pool

3 in topsoil. Degradation of aggregates during fire (Albalasmeh et al., 2013) is likely to render

4 aggregate-protected C to potential loses through oxidative decomposition, leaching and

5 erosion. Moreover, in systems such as the Sierra Nevada which are dominated by steep

6 slopes, movement of the rain-snow transition zone upward is likely to increase proportion of

7 precipitation that occurs as rain. The kinetic energy of raindrops and the observed increase in

8 hydrophobicity of soils  after fires (Johnson et al., 2007; Johnson et al., 2004) can lead to

9 higher rates of erosional redistribution of especially the free light fraction or particulate C that

10 is not associated with soil minerals (Berhe et al., 2012a; Berhe and Kleber, 2013; McCorkle

11 et al., 2016; Stacy et al., 2015).

## 5. Conclusion

13 Previously, considerable amount of work had been published to demonstrate how fires affect

14 OM concentration and composition in biomass. This study fills critical gaps by determining

15 how and to what extent OM in soil experiences changes due to heating. The findings of this

16 study also showed that changes in soil properties during heating are closely related to changes

17 in C concentrations in soil. The temperatures most critical to C loss and alteration were found

18 to be 250 °C, where charring of organic matter starts and 450 °C where most of the SOM is

19 combusted. Most soil properties exhibited a steep change in this temperature range. SOM

20 exhibited largest change, i.e. soils became enriched in $^{13}$C and $^{15}$N isotopic composition until

21 approximately 90% of C and N was lost, at higher temperatures slight depletion of $^{13}$C and

22 steep depletion of $^{15}$N is observed. FTIR spectroscopy showed the reduction and

23 disappearance of aliphatic OH functional groups with temperature increase and accumulation

24 of aromatic carbon groups.

1 This study presented the effects of heat input on topsoil properties. The study is necessary to

2 understand thermally induced changes on soil properties in isolation from other variables that

3 accompany vegetation fires such as the addition of pyrolysis products from plants and ash,

4 and the fire induced soil moisture dynamics. Findings from this study will contribute towards

5 estimating the amount and rate of change in carbon and nitrogen loss, and other essential soil

6 properties that can be expected from topsoil exposure to different intensity fires under

7 anticipated climate change scenarios.

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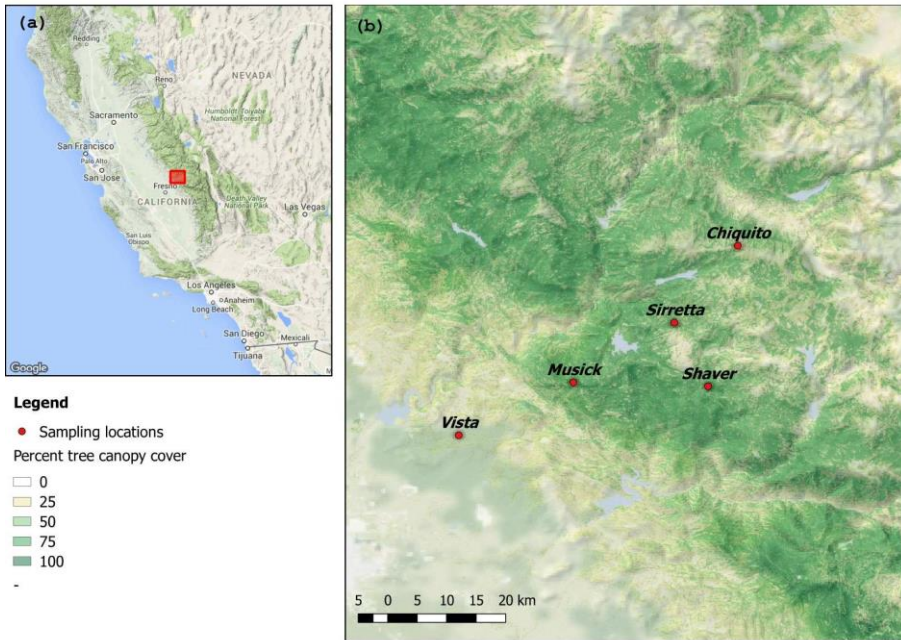
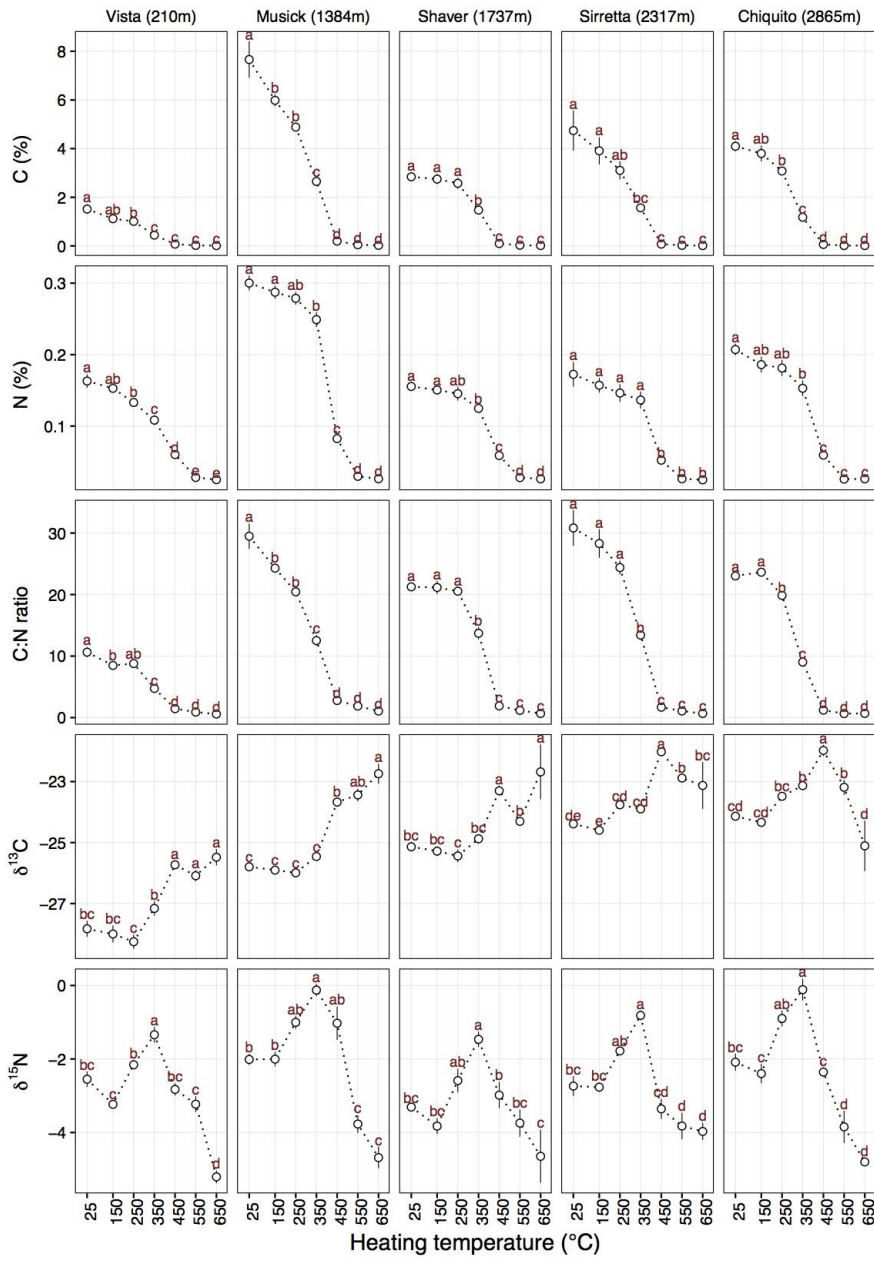

1 **Figures**

3 Figure 1: (a) Location of the sampling site on the western slopes of the Sierra Nevada,

4 California, and (b) map of the five sampling locations and percent tree canopy cover (U.S.

5 Geological Survey, 2014).

1   Figure 2: Bulk soil Carbon and Nitrogen concentrations, C:N atomic ratio, and $\delta^{13}C$ and $\delta^{15}N$

2   isotope (‰) changes with increase in heating temperature. Error bars represent standard error

3   where n=3. Different letters represent significantly different means ($p<0.05$) at each

4   temperature after Tukey's HSD testing.

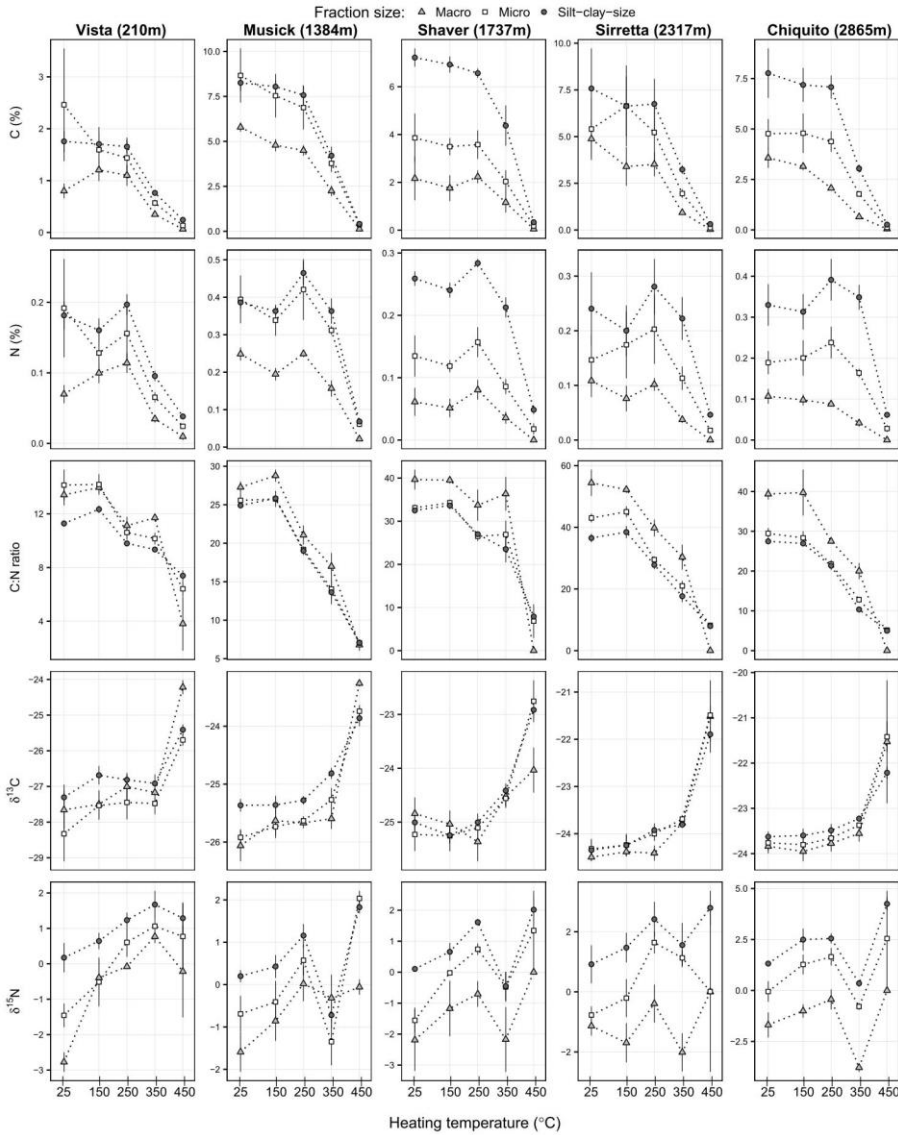
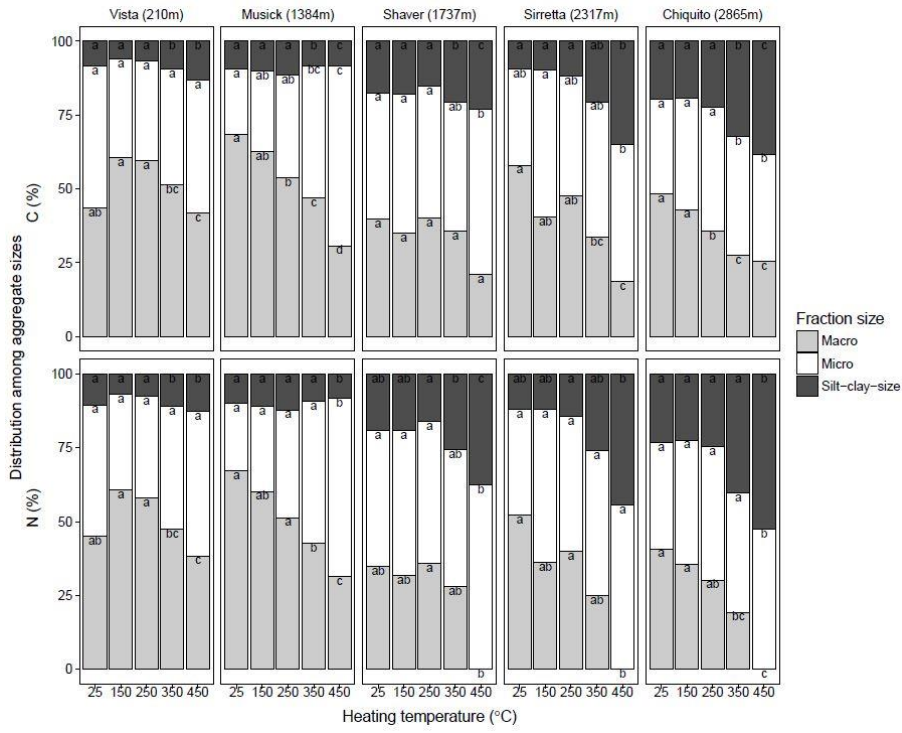



Figure 3. C and N concentrations, C:N atomic ratio, and $\delta^{13}C$ and $\delta^{15}N$ isotope (‰) changes

in macro (2-0.25 mm), micro (0.25-0.053 mm) and silt-clay sized (<0.053 mm) aggregates

with increase in heating temperature. Error bars represent standard error where n=3.

2  Figure 4: C and N distributions in macro (2-0.25 mm), micro (0.25-0.053 mm) and silt-clay

3  sized (<0.053 mm) aggregates.

**Vista (210 m)**

(a)

**Musick (1384 m)**

(b)

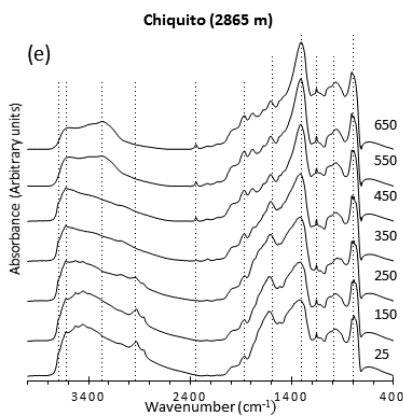
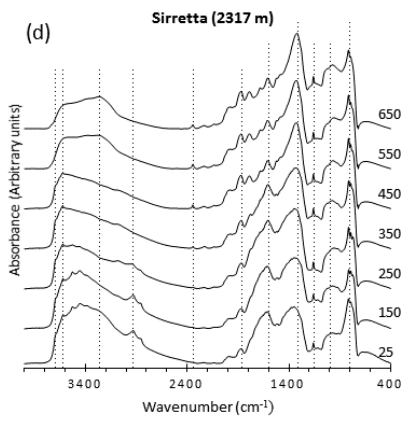
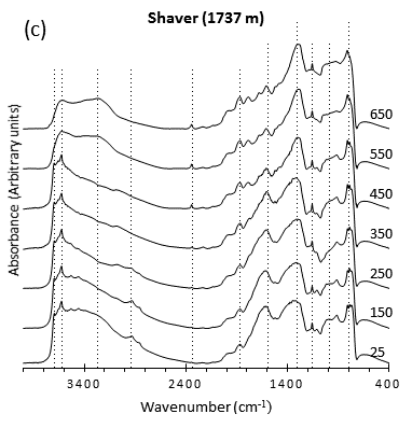
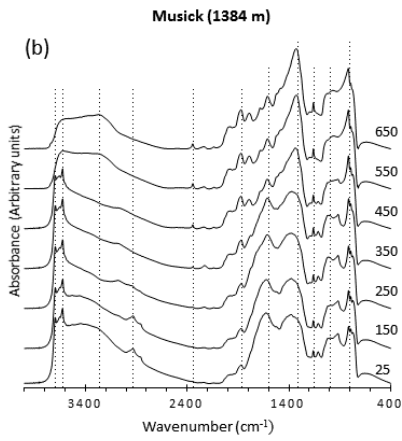
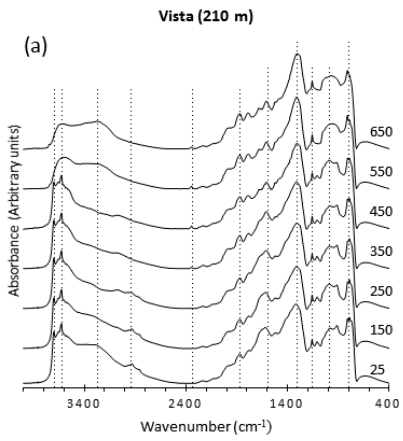
**Shaver (1737 m)**

(c)

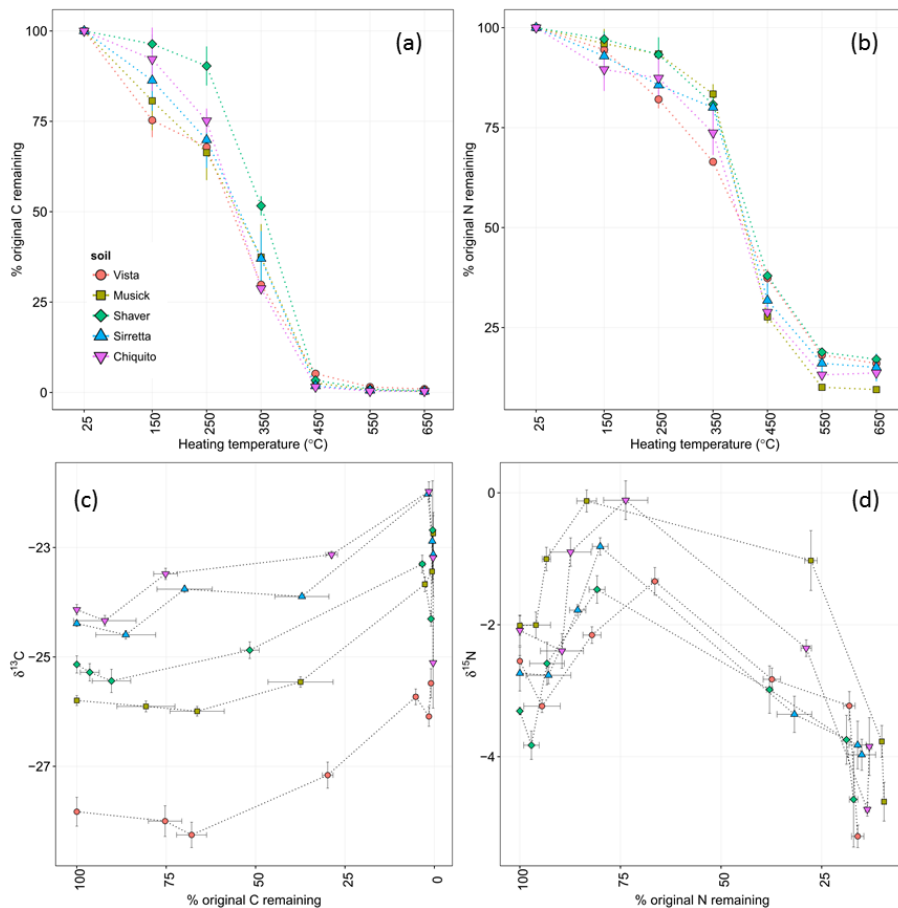
**Sirretta (2317 m)**

(d)

**Chiquito (2865 m)**

(e)

| Absorption peaks (cm⁻¹) | Peak assignment |
|---|---|
| 3700, 3625 | O-H |
| 3270 | O-H, N-H (H bonded) |
| 2940 | C-H (Aliphatic) |
| 2345 | C≡N |
| 1870 | C=O |
| 1600 | C=C, C-O, C=O |
| 1310 | C-H |
| 1159, 995 | Ester, Phenol, C-O-C, C-OH |
| 800 | C-H (Aromatic) |

1    Figure 5: FTIR spectra of the five soils at the different heating temperatures. Heating

2    temperatures, in Celsius, are shown to the right of each spectrum.

4    Figure 6: (a) Percentage of C and (b) N loss with heating; and (c) change in $\delta^{13}C$ and (d) $\delta^{15}N$

5    versus percent of total C and N lost from soils (error bars represent standard error where

6    n=3).

## **Tables**

Table 1 Soil classification and site description for the five sites along elevational transect in the western slopes of the Sierra Nevada (adapted from Dahlgren et al., 1997)

| Soil Series | Elevation (m) | Ecosystem | MAT[a] (°C) | MAP[b] (cm) | Precip[c] | Dominant vegetation (listed in order of dominance) | Soil taxonomy (family) |
|---|---|---|---|---|---|---|---|
| Vista | 210 | Oak woodland | 16.7 | 33 | Rain | Annual grasses; *Quercus douglasii*; *Quercus wislizeni* | Coarse-loamy, mixed, superactive, thermic; Typic Haploxerepts |
| Musick | 1384 | Oak/mixed-conifer forest | 11.1 | 91 | Rain | *Pinus ponderosa*; *Calocedrus decurrens*; *Quercus kelloggii*; *Chamaebatia foliolosa* | Fine-loamy, mixed, semiactive, mesic; Ultic Haploxeralf |
| Shaver | 1737 | Mixed-conifer forest | 9.1 | 101 | Snow | *Abies concolor*; *Pinus lambertiana*; *Pinus ponderosa*; *Calocedrus decurrens* | Coarse-loamy, mixed, superactive, mesic; Humic Dystroxerepts |
| Sirretta | 2317 | Mixed-conifer forest | 7.2 | 108 | Snow | *Pinus jeffreyi*; *Abies magnifica*; *Abies concolor* | Sandy-skeletal, mixed, frigid; Dystric Xerorthent |
| Chiquito[d] | 2865 | Subalpine mixed-conifer forest | 3.9 | 127 | Snow | *Pinus contorta murrayana*; *Pinus monticola*; *Lupinus* species | Sandy-skeletal, mixed; Entic Cryumbrept |

[a] Mean annual air temperature, calculated from regression equation of Harradine and Jenny (1958); [b] Mean annual precipitation; [c] Dominant form of precipitation; [d] Tentative soil series

Table 2 Bulk density, water content, pH, C concentration, cation exchange capacity (CEC),
specific surface area (SSA) and particle size distribution for the five soils (mean ±standard
error, n=3)

| Soil series and elevation (m) | Bulk density (g/cm³) | Gravimetric water content (%) | pH (CaCl₂) | Carbon (%) | CEC (cmolc/kg) | SSA (m²/g) | Particle size distributionᵃ (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Sand | Silt | Clay |
| Vista (210) | 1.26 ±0.07 | 0.7 ±0.0 | 5.53 ±0.0 | 1.51 ±0.2 | 8.40 ±1.1 | 1.75 ±0.2 | 79 | 11 | 10 |
| Musick (1384) | 0.90 ±0.06 | 9.3 ±1.6 | 4.67 ±0.1 | 7.66 ±0.8 | 25.20 ±2.0 | 4.98 ±0.3 | 60 | 27 | 15 |
| Shaver (1737) | 0.98 ±0.06 | 8.3 ±1.1 | 4.85 ±0.3 | 2.84 ±0.2 | 10.67 ±2.1 | 3.08 ±0.3 | 80 | 15 | 5 |
| Sirretta (2317) | 0.61 ±0.09 | 9.9 ±2.2 | 4.54 ±0.1 | 4.74 ±0.8 | 12.23 ±2.6 | 6.63 ±0.8 | 80 | 15 | 5 |
| Chiquito (2865) | 1.17 ±0.03 | 6.1 ±1.9 | 3.96 ±0.1 | 4.10 ±0.2 | 6.03 ±1.8 | 1.00 ±0.04 | 80 | 16 | 4 |

ᵃ Particle size distribution of top soil profile from Dahlgren et al. (1997): Vista (0 – 14 cm),
Musick (0 – 29 cm), Shaver (0 – 4 cm), Sirretta (0 – 6 cm) and Chiquito (0 – 6 cm)

Table 3 Linear correlation coefficients of changes in soil properties with changes in C
concentration. All correlation coefficients have p-values < 0.01 unless otherwise indicated.

| Soil | | | Correlation coefficient ($r^2$) values | | | |
|---|---|---|---|---|---|---|
| | Mass loss | SSA | Aggregate Stability | pH ($CaCl_2$) | CEC | N concentration |
| Vista | 0.74 | 0.73 | 0.21[a] | 0.77 | 0.78 | 0.89 |
| Musick | 0.89 | 0.58 | 0.77 | 0.89 | 0.96 | 0.83 |
| Shaver | 0.82 | 0.58 | 0.68 | 0.74 | 0.78 | 0.93 |
| Sirretta | 0.60 | 0.34[b] | 0.47 | 0.67 | 0.87 | 0.86 |
| Chiquito | 0.82 | 0.62 | 0.78 | 0.88 | 0.44 | 0.87 |

[a] p = 0.078; [b] p = 0.035