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Soil weathering and accumulation rates of oxalate-extractable phases derived from alpine chronosequences of up to 1Ma in age

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Abstract: In this study we compare newly-developed chemical weathering data with previously published data from soils developed along two chronosequences of glacial deposits in the European Alps and the Rocky Mountains (Wind River Range, USA). By combining these chronosequences, we are able to present a comprehensive dataset that represents a time period of >1 Ma. We describe weathering trends of important elements using a number of weathering indices (e.g., K + Ca/Ti ratio, the weathering 'index B' of Kronberg and Nesbitt (1981) and the open mass transport function). Further, we describe the accumulation of Al, Fe, Si and Mn oxyhydroxides (including partially organic phases) as a function of time, and derive the corresponding accumulation rates. We calculated pedogenetically formed oxyhydroxides using an approach based on immobile elements. Our study represents one of only a few studies that describe rates of soil chemical weathering over a period as long as 1 Ma. Results show that rates of chemical weathering clearly decrease along the chronosequences with increasing age of the soils. We find weathering rates are nearly four orders of magnitude lower in the 1 Ma-old soils than in the young soils. Our results suggest that the older soils may be reaching a steady state for these chemical properties in their present environments. A power function best explains the measured time-trends of the 'index B' and (K+Ca)/Ti ratios in the soils. The best time-trend model for pedogenic weakly- to poorly crystalline phases and the relative losses/gains (based on the open-system mass transport function) were obtained with an exponential decay model function. In terms of the soil system, the decreases in the accumulation rate of the oxyhydroxides appears to be influenced not only by the factor of time but by climate as well (increased precipitation at higher altitudes slows the decrease in weathering rate over time). Thus, our 1 Ma chronosequences also become pedogenic gradients since we describe variations in soil properties along biogenic gradients.

DOI: <https://doi.org/10.1016/j.geomorph.2012.01.021>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-67106>

Journal Article

Accepted Version

Originally published at:

Dahms, Dennis; Favilli, Filippo; Krebs, Rolf; Egli, Markus (2012). Soil weathering and accumulation rates of oxalate-extractable phases derived from alpine chronosequences of up to 1Ma in age. *Geomorphology*, 151-152:99-113.

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1 **Soil weathering and accumulation rates of oxalate-extractable phases derived**
2 **from alpine chronosequences of up to 1 Ma in age**

3
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14

15 **Abstract**

16 In this study we compare newly-developed chemical weathering data with previously published
17 data from soils developed along two chronosequences of glacial deposits in the European Alps and
18 the Rocky Mountains (Wind River Range, USA). By combining these chronosequences, we are
19 able to present a comprehensive dataset that represents a time period of ≥ 1 Ma. We describe weath-
20 ering trends of important elements using a number of weathering indices (e.g. K+Ca/Ti ratio, the
21 weathering ‘index B’ of Kronberg and Nesbitt (1981) and the open mass transport function). Fur-
22 ther, we describe the accumulation of Al, Fe, Si and Mn oxyhydroxides (including partially organic
23 phases) as a function of time, and derive the corresponding accumulation rates. We calculated pe-
24 dogenetically formed oxyhydroxides using an approach based on immobile elements. Our study
25 represents one of only a few studies that describe rates of soil chemical weathering over a period as

26 long as ~1 Ma. Results show that rates of chemical weathering clearly decrease along the chronose-
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30 function best explains the measured time-trends of the 'index B' and (K+Ca)/Ti ratios in the soils.
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32 losses/gains (based on the open-system mass transport function) was obtained with an exponential
33 decay model function. In terms of the soil system, the decreases in the accumulation rate of the
34 oxyhydroxides appears to be influenced not only by the factor of time but by climate as well (in-
35 creased precipitation at higher altitudes slows the decrease in weathering rate over time). Thus, our
36 ~1 Ma chronosequences also become pedogenic gradients since we describe variations in soil prop-
37 erties along biogenic gradients.

38

39 Keywords: Chronosequence, pedogenic gradient, soils, weathering, steady state, Alps, Wind River
40 Range

41

42 **1. Introduction**

43 Weathering rates or rates of element depletion or accumulation on the catchment or profile scale are
44 often obtained by mass balance studies (input-output budgets) and give important indications about
45 the reactivity of a corresponding soil or catchment (e.g. April et al, 1986; Johnson and Lindberg,
46 1992; Wright et al., 1992; Bain et al., 1994; Drever, 1997; Olsson and Melkerud, 2000; Bernasconi
47 et al., 2011 etc.). Three techniques have commonly been applied to measure rates of chemical wea-
48 thering (Porder et al., 2007): a) quantification of mass loss from minimally eroded soils of known
49 age using chronosequences (Jenny, 1941; Taylor and Blum, 1995), b) catchment-scale river sam-
50 pling (e.g. White and Blum, 1995; Riebe et al., 2004), and laboratory experiments (e.g. White and

51 Brantley, 2003). All three approaches are subject to some uncertainties.

52 The time over which natural chemical weathering occurs (White and Hochella, 1992) can usually
53 not be reproduced by experimental studies (see White and Brantley, 2003). Chronosequences are
54 useful for estimating field weathering rates (element depletion rates, mineral transformation rates
55 etc.; e.g. Föllmi et al., 2009a,b; Mavris et al., 2011 etc.) and also permit the differentiation of sur-
56 faces of differing age (e.g. Fitze, 1982; Dahms, 2002, 2004).

57 Soil development, in the chemical sense, can be considered as roughly synonymous with weather-
58 ing (Bohn et al., 1985). Thus, studying characteristics of soil weathering over time may give in-
59 sight into the influence of time on the rates of chemical weathering. According to Jenny (1941),
60 soils are understood to develop under the influence of the following state factors: parent material,
61 climate, topography, biological activity and time. In order to be quantitatively useful, Jenny (1941)
62 suggested treating the state factors as independent variables, in the sense that field locales exist
63 where the factors can be considered to vary independently. The ways in which a factor is considered
64 to be independent are: (1) if the range of variability of the factor is quite small, and (2) if variation
65 in the factor is large, it has only a negligible effect on the property studied. Thus, a sequence of
66 soils formed on progressively older landscapes is considered a chronosequence, and the quantitative
67 variability of a characteristic along these landscapes is a chronofunction (Birkeland, 1999; Mahaney
68 et al., 2011).

69 Pedogenic gradients are defined as the variations in soil properties along bioclimatic gradients
70 (Tedrow 1968, 1977; Birkeland et al., 1989) and often are determined by analysing soil chronose-
71 quences (Bockheim, 1980; Jenny 1980; Birkeland 1984; Birkeland et al., 1989). Soil chronose-
72 quences can provide information about the weathering regimes, soil morphogenesis (see Mahaney
73 et al., 2011) and have greatly advanced our understanding of short- to long-term landscape proc-
74 esses (Milner et al., 2007; Walker et al., 2010). Soil development has been successfully correlated
75 to land surface age in several regions, although in some case such studies were complicated by ero-

76 sion and sedimentation as well as possible tectonic activity (Scarciglia et al., 2006; Sauer et al.,
77 2010). Thus, the study of chronosequences has a long tradition, and both ecologists and soil scien-
78 tists have used the concept of substituting space for time to understand ecosystem and soil evolution
79 (see Ruhe and Walker, 1968; Gile et al., 1981; Walker and del Moral, 2003; Walker et al., 2010;
80 Bernasconi et al., 2011).

81 Soils sampled on moraines and other glacial and periglacial deposits such as rock glaciers can either
82 be helpful indicators to estimate the (relative) age of the landform or, provided that independent
83 dating is available, to derive rates of different time-dependent processes (Egli et al., 2001, 2003;
84 Munroe, 2008; Schaller et al., 2009). Weathering indexes or clay mineral assemblages may provide
85 a differentiation of soils even within a relatively narrow time range and give insight into processes
86 that have occurred at the specific sites. When used as an age indicator, soil development data, how-
87 ever, should be combined with other relative or numerical age data (Birkeland, 1973; Dahms, 2004;
88 Böhlert et al., 2011a) because soil development is, in many respects, not a linear process and
89 chronosequences may be perturbed by the other state factors.

90 Chemical and mineralogical analyses of soil chronosequences offer several methods of distinguish-
91 ing landforms of different ages based on their weathering state (Alexander and Burt, 1996; Evans,
92 1999; Egli et al., 2001, 2003). Well-known soil age indicators are for instance soil pH, rubification,
93 transformation of pedogenic Fe and Al (Birkeland, 1999) and the presence of clay minerals such as
94 smectite (Righi et al., 1999). However, several of them are not applicable to soils in alpine areas as
95 the greatest changes in soil properties occur within approximately 3000 – 4000 years, asymptoti-
96 cally reaching a kind of limiting value after about 15 ky (cf. Fitze, 1982; Egli et al., 2001) and no
97 real changes are observable thereafter.

98 The effects of time on weathering rates can be seen in systematic decreases in natural rates in pro-
99 gressively older weathering environments (e.g. Egli et al, 2001; White and Brantley, 2003). Over
100 centuries to millennia, the rates of primary mineral depletion and secondary clay and metal oxide

101 formation progressively decrease with soil (surface) age (Taylor and Blum, 1995; Hodson et al.,
102 1999; Stewart et al., 2001, Egli et al., 2001).

103 Chronosequences often have only a very limited number of data points (and sites) because the plot
104 of only 1 single point (e.g. elemental leaching rates over a whole soil profile) requires intensive
105 laboratory analyses. Here we compare the trends with time of published weathering data obtained
106 from the European Alps with newly-developed data from the Rocky Mountains (Wind River Range,
107 USA; Fig. 1). This technique enables us to present a set of comprehensive data over a time range of
108 c. 1 Ma. This also allows us to reduce the influence of spatial variability on weathering trends for a
109 robust view of soil weathering over an extended timescale.

110 Datasets reporting the weathering rates of elements over millennia up to 1 Ma are, furthermore,
111 rare. As weathering occurs, secondary mineral phases form that initially have poorly or weakly
112 crystalline characteristics. Only few datasets exist for long-term trends in production or accumula-
113 tion rates of oxyhydroxides (Fe, Al) (e.g. Birkeland et al., 1989).

114

115

116 **2. Study sites**

117

118 We compared new and previously-published datasets on soil chronosequences in order to differen-
119 tiate trends within several alpine regions and to complete trends with additional data. The sites from
120 Stough Creek Basin in the Wind River Range (WRR) are comparable with sites from the European
121 Alps; soils from Sinks Canyon (WRR), however, have no Alpine correlates in this study. All Alpine
122 and WRR soils developed in glacial deposits whose ages have been previously correlated to known
123 glacial stages of the Rocky Mountains and the European Alps. Parent material is granitic glacial till
124 at all the Wyoming sites, while soils at the Alpine sites were mostly developed in till (different
125 types of moraines) but in some cases relict rock glaciers.

126 The mean annual precipitation and temperature of the individual investigation sites are given in Ta-
127 bles 1 and 2. In general, the European sites have a moister climate (1100 – 2000 mm/y) than the
128 Wind River Range (up to 1000 mm/yr in Stough Creek Basin, but only 340 mm/yr in Sinks Can-
129 yon). Depending on the age and climatic zone of the deposits, pioneer plant communities, shrubs or
130 grassland and forest vegetation is present.

131 Pedogenesis through the observed time frame has not been continuous and completely similar. Cli-
132 mate variability over the past ~1 Ma has been considerable. During the Holocene and Late Pleisto-
133 cene (last 20 ky), however, the climatic variability at the Wind River Range and Alpine sites can be
134 considered as more or less similar (see also Böhlert et al., 2011a). Because of the extreme age of
135 some of the soils in the Wind River Range (>500 ka) some sites have experienced several warm and
136 cold phases. These soils consequently integrate the effect of such climatic variations. For example,
137 soils developed on Bull Lake-age piedmont moraines (~130 ka, OIS-6) of the WRR show thinner,
138 coarser A-horizons than those on adjacent soils developed in Pinedale-age moraines (LGM, OIS-2).
139 This anomaly was created when Foehn winds off the active Pinedale glaciers stripped the finer par-
140 ticles out of the Bull Lake soils. This process also caused A-horizon processes to affect the upper B-
141 horizons of these soils (Hall, 1999; Applegarth and Dahms, 2001). We assume similar processes
142 also were active on older deposits/soils.

143 Age control of the sites is provided by geomorphologic mapping and relative age-relationships
144 (Maisch, 1981, 1992; Dahms, 2002, 2004), surface exposure dating (^{10}Be , ^{26}Al) and radiocarbon
145 dating (Tables 1 and 2; for the WRR: Dahms, 2004; Fabel et al., 2004; and for the Alps: Hantke,
146 1983; Keller and Krayss, 1993; Wipf, 2001; Keller and Krayss, 2005; Maisch et al., 2005; Ivy-Ochs
147 et al., 2007; Favilli et al., 2009; Egli et al., 2010; Böhlert et al., 2011b).

148 The moraines in the Alps could usually be clearly attributed to glacial stages: e.g. Late Glacial
149 Maximum (or soon thereafter), Daun (Oldest Dryas), Egesen (Younger Dryas; 1 to 3 phases), Holo-
150 cene and recent. In the Wind River Range relative and numeric age-dating enable the discrimination

151 of the following: glacial landforms of Little Ice Age, Black Joe, Alice Lake, Temple Lake, Pine-
152 dale, Bull Lake and Sacajawea Ridge stages, and two pre-Sacajawea Ridge deposits that could be
153 attributed to much older glacial events of the mid-late Pleistocene (Dahms, 2004). Thus, in the
154 European Alps, soil chronosequences were available with ages covering a time span of 20 ky and in
155 the Wind River Range with ages extending back to possibly as old as 1.2 Ma.

156

157

158 **3. Materials and methods**

159 *3.1. Sampling strategy and soil chemistry/physics*

160 Soil material was collected from excavated profile pits on undisturbed locations where no influence
161 of creep processes was visible (all on broad moraine crests at Wyoming sites). Although some sites
162 in the Alps were on rather steep slopes, they were fully covered with vegetation and no obvious
163 signs of soil erosion or accumulation were detectable. As soon as a vegetation cover is established
164 in Alpine areas, soil erosion is almost negligible (see also Norton et al., 2010). Profiles were dug to
165 the C horizon when possible. 2-3 kg of soil material per horizon were taken for the analyses (Hitz
166 et al., 2002). The bulk density (fine earth and soil skeleton) was measured using a specific soil core
167 sampler in the Alps and from paraffin-coated peds in the WRR (Dahms, 2002, 2004).

168 Oven-dried (70°C) samples were sieved to < 2 mm. Fe, Al and Si concentrations were determined
169 after treatment with NH₄-oxalate (buffered at pH 3, labelled 'o') (McKeague et al., 1971). The ex-
170 tracts were centrifuged for 8 minutes at 4000 rpm and filtered (mesh size 0.45 µm, S&S, filter type
171 030/20). Element concentrations were measured using atomic absorption spectroscopy (AAAnalyst
172 700, Perkin Elmer). The oxalate treatment extracts both the weakly- and poorly crystalline phases
173 and some of the organic phases, but normally does not dissolve the strong humus-metal complexes
174 (Mizota and van Reeuwijk, 1989).

175 Measurement of the total element content of fine earth and skeleton was done by means of X-ray
 176 fluorescence (XRF). Approximately 10 g of soil material were milled to < 50 µm in a tungsten car-
 177 bide disc swing mill (Retsch® RS1, Germany). 4 g of soil powder was mixed with 0.9 g of Li-
 178 cowax® C Micro-Powder PM (Clariant, Switzerland), pressed into a 32 mm-pellet and analysed
 179 using an energy dispersive X-ray fluorescence spectrometer (SPECTRO X-LAB 2000, SPECTRO
 180 Analytical Instruments, Germany). Additional soil chemical and physical characteristics are pre-
 181 sented in previous publications (Egli et al., 2001, 2002, 2003, 2010; Dahms, 2002, 2004; Favilli et
 182 al., 2009, Böhlert et al., 2011a; Mavris et al., 2010).

183

184 3.2. Stocks, accumulation and weathering rates

185 The oxalate-extractable Fe_o, Al_o, Si_o and Mn_o stocks were calculated according to the following
 186 equation:

$$187 \quad Me_{stock} = \sum_{a=1}^n Me_i \Delta z_i \rho_i (1 - RM) \quad (1)$$

188 where Me_{stock} denotes the metal abundance (kg/m²), Me the metal concentration (kg/t), Δz_i the
 189 thickness of layer i (m), ρ = soil density (t/m³) and RM the mass proportion of rock fragments.

190 Differences in chemical composition of the parent and soil material can be used to derive weather-
 191 ing properties. In most cases, chemical and biophysical weathering is not isovolumetric and the soil
 192 volume may dilate or collapse during soil evolution. Using enrichment/depletion amounts deter-
 193 mined from concentration profiles of immobile elements such as Ti or Zr, element specific gains
 194 and losses are determined and, in the case of known-age landforms, long-term weathering rates are
 195 calculated (for theoretical and mathematical background, see Chadwick et al., 1990 and Egli and
 196 Fitze, 2000). Volumetric changes assumed to occur during pedogenesis are determined by adopting
 197 the classical definition of strain, $\varepsilon_{i,w}$ (Brimhall and Dietrich, 1987):

$$198 \quad \varepsilon_{i,w} = \frac{\Delta z_w}{\Delta z} - 1 \quad \text{or} \quad \varepsilon_{i,w} = \left(\frac{\rho_p C_{j,p}}{\rho_w C_{j,w}} \right) - 1 \quad (2)$$

199 with Δz as the columnar height (m) of a representative initial volume of unweathered parent mate-
 200 rial p and Δz_w is the weathered equivalent height (m) w , $C_{i,p}$ is the concentration of the immobile
 201 element i in the parent material (kg/t) and $C_{i,w}$ as the concentration of the immobile element i in
 202 weathered product. The calculation of the open-system mass transport function $\tau_{j,w}$ is defined by
 203 (Chadwick et al., 1990):

$$204 \quad \tau_{j,w} = \left(\frac{\rho_w C_{j,w}}{\rho_p C_{j,p}} (\varepsilon_{i,w} + 1) \right) - 1 \quad \text{or using equation (2)} \quad \tau_{j,w} = \left(\frac{C_{j,w} \cdot C_{i,p}}{C_{i,w} \cdot C_{j,p}} \right) - 1 \quad (3)$$

205 where $C_{j,p}$ (kg/t) is the concentration of element j in the unweathered parent material, $C_{j,w}$ is the
 206 concentration of element j in the weathered product (kg/t), and ρ_p and ρ_w are the bulk density (t/m^3)
 207 of the parent material and the weathered soil, respectively.

208 This approach is used to calculate the relative element losses of each soil horizon.

209 To estimate the amount of pedogenetically formed Fe_o , Al_o , Si_o and Mn_o in soils, concentrations of
 210 these compounds in the soil column must be compared with the parent material. Using the concept
 211 of immobile elements, gains and losses of Fe_o , Al_o , Si_o and Mn_o can be derived.

$$212 \quad M_{j,w} = Me_{j,w} \left(\frac{\tau_{j,w}}{1 + \tau_{j,w}} \right) \Delta z_w \rho_w (1 - RM) \quad (4)$$

213 With n soil layers, the mass accumulation of the element j is given by:

$$214 \quad M_{j,w}(\Delta z_w) = \sum_{a=1}^n Me_{j,w} \left(\frac{\tau_{j,w}}{1 + \tau_{j,w}} \right) \rho_w (1 - RM) \Delta z_w \quad (5)$$

215 where $\tau_{j,w}$ corresponds to the mass transport function and Δz to the weathered equivalent of the
 216 columnar height.

217 Accumulation rates of Fe_o , Al_o , Si_o and Mn_o are expressed as the amount of pedogenetically formed
 218 phases divided by the soil (surface) age (t). This gives a production rate $R_{j,w}$ per unit area (equation
 219 6).

$$220 \quad R_{j,w} = \frac{M_{j,w}(\Delta z_w)}{t} \quad (6)$$

221 For soils developed on bedrock the potential errors are confined to local heterogeneities in bedrock
222 composition. The estimate of the initial composition becomes more difficult when soils are devel-
223 oped on sedimentary parent materials such as loess deposits, debris, or till. For such deposits, the
224 least weathered horizon in the soil profile is assumed to be the parent material. We recognize that
225 soils in glacial deposits often have a certain loess input (e.g., Shroba and Birkeland, 1983; Muhs et
226 al., 1992; Dahms, 1993); however, our present methods cannot quantify loess input to these soils
227 and there is, consequently, some minor error for the quantification of the purely pedogenetically-
228 derived phases.

229

230 3.3. *Weathering indexes*

231 Several indexes have been defined to characterise chemical weathering in soils. The general princi-
232 ple of all these indexes is similar and based on the ratio of the base cations (Ca, Mg, K, Na) to Al
233 and/or Si. We used the ‘index B’ of Kronberg and Nesbitt (1981) that is defined by the molar ratio:

$$234 \quad B = \frac{CaO + K_2O + Na_2O}{Al_2O_3 + CaO + K_2O + Na_2O} \quad (7)$$

235 The molar ratio of (K+Ca)/Ti is used as a ‘dating’ method for rock varnish in semi-arid to arid re-
236 gions (Harrington and Whitney, 1987). As Ti is considered to be an immobile element, the ratio can
237 be used as a weathering index: the lower the ratio, the higher the degree of weathering.

238

239 3.4. *Statistics*

240 The individual datasets were checked for normal distribution using a Shapiro-Wilk test (SigmaPlot
241 11.0 (Systat Software Inc.); Jann, 2005). This procedure was checked using a two-tailed test for
242 significance. The age usually showed a non-normal distribution (even after log-transformation).
243 Consequently, the Spearman rank correlation coefficient was used.

244

245

246 **4. Results**

247 *4.1. General characteristics of the soils*

248 The total elemental content of the fine fraction of the Wind River Range soils is given in Table 3.

249 The analyses confirm the granitic character of all sites. This is expressed by the high SiO₂, Al₂O₃,
250 Fe₂O₃ and low base cation contents.

251 The average total elemental content of the parent material is given in Table 4. The average compo-
252 sition of the parent material in the Wind River Range does not substantially differ from the parent
253 material composition of the European Alps; although, from a statistical point of view, slight differ-
254 ences are discernible for Mg, K, Fe, Si, P and Mn. From this point of view, similar geochemical
255 conditions exist for all sites.

256 The oxalate-extractable contents for the Wind River Range soils are given in Table 5. With increas-
257 ing age, higher concentrations at greater soil depths could usually be measured (although this was
258 not the case for the topsoil). The oxalate-extractable contents for the European Alps were reported
259 previously by Egli et al. (2001, 2002, 2003, 2010), Favilli et al. (2009), Böhlert et al. (2011a) and
260 Mavris et al. (2010). Concentration – depth functions are given in Fig. 2. The concentrations of the
261 oxalate-extractable forms are usually considerably higher in the soils of the Alps than in the WRR.
262 The initial content of Fe_o in the parent material, and to a lesser extent for Si_o and Al_o, is higher in
263 the Alps. In contrast to the Wind River Range, there is a pronounced podzolisation effect in the
264 Alps with very low concentrations in the eluvial horizon (where the concentrations dropped almost
265 to zero; Fig. 2).

266

267 *4.2. Mass balance calculations, weathering indexes*

268 Assuming an increasing element loss with increasing age (a more ‘mature’ weathering state of the
269 soil), the open-system mass transport function $\tau_{j,w}$ should decrease with increasing soil age. Gener-
270 ally, this is the case. The scatter, however, is relatively high. In Fig. 3, the mean $\tau_{j,w}$ values of Fe

271 and Al and of the base cations (BC) are plotted as a function of time and area (Wind River Range
272 vs. European Alps). Trends with decreasing $\tau_{j,w}$ values in the topsoil as a function of time can be
273 observed. In the European Alps, this decrease is more pronounced pointing to more intense elemen-
274 tal losses (and consequently a higher weathering intensity) over time.

275 As Ti is considered to be an immobile element (White, 1995; Stiles et al., 2003), the (K+Ca)/Ti ra-
276 tio can be used as a weathering index: the lower the ratio, the higher the degree of weathering. The
277 (K+Ca)/Ti ratio in the topsoil (OE, E, A) and subsoil horizons of the Wind River Range showed a
278 slightly significant temporal trend (Fig. 4). A more significant amount of K and Ca is leached with
279 time leading to a passive enrichment of Ti.

280 If not plotted in a logarithmic form (Figs. 3, 4), the open-system mass transport function and the
281 (K+Ca)/Ti ratio both tend to an asymptotic value. The trend for the (K+Ca)/Ti ratio is best ex-
282 pressed using a power law function and the one for $\tau_{j,w}$ using an exponential decay model (see sec-
283 tion 5).

284 The ‘index B’ (Kronberg and Nesbitt, 1981) is shown (Fig. 5) as a function of time and soil horizon
285 (topsoil and B horizon). For both the Wind River Range and the European Alps, a distinct time
286 trend is present. The slope of the curve for A horizons in the European Alps is slightly steeper than
287 for those in the WRR. The change per unit of time (and thus the reaction rate) also seems to be
288 higher in the Alps. In the B horizon, however, the decreasing tendency of the ‘index B’ is similar
289 for both regions.

290

291 *4.3. Stocks and accumulation rates of Fe_o , Al_o , Si_o and Mn_o*

292 The pedogenetically formed stocks of Fe_o , Al_o , Si_o and Mn_o increase considerably with time. This
293 increase seems to be, again, more distinct in the European Alps. In Fig. 6, the total stocks are plot-
294 ted as a function of time together with recently published results of the Damma proglacial area
295 (Dümig et al., 2011). The Damma proglacial area is located in the central Swiss Alps (and conse-

296 quently close to our sites presented in section 2; Fig. 1). As few data are available for very young
297 soils in Alpine areas, the datasets of the Damma proglacial were included.

298 The pedogenic stocks of Fe_o , Al_o , Si_o and Mn_o are lower than their overall abundance in the profile.
299 No data are available that would have allowed for a calculation of the pedogenic Fe_o , Al_o , Si_o and
300 Mn_o forms for the Damma proglacial area (as no data about the total elemental content, including
301 immobile elements, were published). The time trend of the pedogenic stocks is similar to the total
302 stock. Using these time trends of pedogenic weakly- and poorly crystalline forms, corresponding
303 formation rates can be derived (Fig. 7). At the beginning of soil formation, these rates are similar in
304 the Wind River Range and European Alps study areas. With time however, the rates seem to de-
305 crease more distinctly at the Wind River Range sites (although the scatter is high for the European
306 Alps).

307

308

309 **5. Discussion**

310 An important requirement for the use of soil chronosequences, including those in glacial forelands,
311 is that the influence of soil-forming factors other than time should be negligible (Jenny, 1941).
312 However, this requirement is often not met (Bardgett et al., 2005) as glacial forelands and, later, the
313 developed soils represent complex and dynamic environments (Anderson, 2007).

314 Despite such shortcomings, distinct trends along the sequences and even some differences between
315 the Wind River Range and the European Alps are seen. As the soil pits were opened at (topographi-
316 cally) stable sites having a similar geochemical composition (parent material) and because the vege-
317 tation cannot be considered as a fully independent state factor, differences between the sites could
318 be attributed predominantly to the factors time and climate.

319 Mass balance calculations, weathering index ('index B') and the $(K+Ca)/Ti$ ratio all indicate that
320 significant leaching losses of major base cations have occurred (Fig. 4). These losses led to a corre-

321 sponding passive enrichment of Al or Fe (Martínez Cortizas et al., 2003). The (K+Ca)/Ti ratio re-
322 flects the situation in the topsoils (O, OE and E horizons). Although with a partially high scatter, we
323 can recognize a trend as a function of time. The weathering ‘index B’ shows a clearer time-trend
324 and thus seems to be a more robust indicator (that does not react too sensitively to local variables).
325 This type of trend is also known from other study areas (Egli et al., 2008). Our results demonstrate
326 that base cation leaching has been the dominant process over the whole observation period. If al-
327 most no disturbances — such as erosion, deposition (or ‘upbuilding’ according to Johnson et al.
328 (1990)), or pedoturbation — occurred during the life-time of a soil, chronosequences may indicate
329 rates of pedogenic processes (Costantini et al., 2009).

330 Our measured decreases in weathering rates are also supported by laboratory data. White and
331 Brantley (2003) state that the reaction rates of silicate minerals decreases with the duration of
332 chemical weathering. The average silicate weathering rate R ($\text{mol m}^{-2} \text{s}^{-1}$) was described by a power
333 function $R = 3.1 \times 10^{-13} t^{-0.61}$. Our findings fit this function well, as a power function was found both
334 for our ‘index B’ and the (K+Ca)/Ti ratio data. Intrinsic surface area, which increases with the dura-
335 tion of weathering, is shown to account for a third of the exponential decrease in the weathering
336 rate. Other factors, including progressive depletion of energetically reactive surfaces and accumula-
337 tion of leached layers and secondary precipitates, contribute to the decrease in weathering rates.

338 Weathering in the topsoil seems to proceed faster in the European Alps. This can be explained by
339 higher precipitation here leading to subsequently higher leaching rates of elements from the soil
340 (see also Egli et al., 2003). The apparent lower weathering rates in moraine soils of the Wind River
341 Range, however, seemed to be slightly influenced by aeolian influx (Dahms, 1993; Dahms and
342 Rawlins, 1996). The influence of loess deposits can be partially inferred by the quantity of silt and
343 clay in A horizons and the mineralogical composition (Dahms, 1993). The dominant minerals in
344 loess are usually quartz (Ollier, 1969; Bronger and Heinkele, 1989), mica and kaolinite giving rise
345 to elemental inputs such as Si, Al and K. The aeolian input is estimated to be in the range of 0.23 to

346 $31.0 \times 10^{-7} \text{g cm}^{-2} \text{d}^{-1}$ for parts of the Wind River Range (Dahms and Rawlins, 1996). This input of
 347 elements slightly affects the trend of the considered weathering indexes and the open-system mass
 348 transport function. Furthermore, the loess input also affected the acidity of some soils (Table 5).
 349 Despite some differences in the chemistry of the bedrock, distinct trends of Al(o), Fe(o), Si(o) and
 350 Mn(o) can be obtained and formation rates of pedogenetically-formed phases can be derived (Fig.
 351 6).

352 The chronofunctions of the abundance of weakly- and poorly crystallised phases (pedogenically
 353 formed) and of the open mass transport function $\tau_{j,w}$ were best-fitted to data using the exponential
 354 decay model. The exponential decay model (cf. Lichter, 1998) is given by:

$$355 \quad f(t) = a + (b - a)e^{-kt} \quad (8)$$

356 where a represents an asymptote, b the initial quantity, and k the decay constant. This function ex-
 357 presses $\frac{dM_s}{dt}$ according to equation 9. We emphasise that any regression model merely approxi-
 358 mates reality, and that several models might be equally effective (cf. also Bockheim, 1980; Schaetzl
 359 et al., 1994).

360 The abundance and change in abundance per unit area and unit time (formation rates) of the
 361 weakly- and poorly crystalline metals (M_s) are a function of: the rate at which metals are released
 362 from primary minerals (R_w), aeolian input (R_{ae}), leaching rates in the soil (L_s), erosion (E_s) and
 363 transformation rate of the weakly and poorly crystalline into crystalline forms (T_s).

364 This can be described by the following equation:

$$365 \quad \frac{dM_s}{dt} = R_w + R_{ae} - E_s - L_s - T_s \quad (9)$$

366 For Mn, a complete dataset was only available for the Wind River Range. Similar to Fe, Al and Si,
 367 however, the rates decrease distinctly (and significantly) as a function of time (Fig. 7). The decrease
 368 of the rates fits best with a power law.

369 With the exponential decay model, a steady state of metal abundances seems to be reached some-
370 where between 10 and 100 ky. This means that with time $\frac{dM_s}{dt} \approx 0$ and consequently
371 $R_w + R_{ae} \approx E_s + L_s + T_s$. As the increase of metal contents and corresponding abundances can hardly
372 occur endlessly, the decay model is in good agreement with theoretical expectations. For the Euro-
373 pean Alpine sites, however, no data were available for soils having an age > 30 ky. Consequently,
374 the curve beyond that age is somewhat speculative for these sites and should be verified with addi-
375 tional Alpine sites (having an age of 100 ky and more).

376 Dorji et al. (2009) found that the detailed picture of a chronosequence can be complicated by minor
377 localised reversals of these trends. It may be that local back-filling and post-incision additions of
378 soil parent material facilitates the persistence of minor peculiarities and apparent inconsistencies.
379 Pedogenesis through the observed time frame has not been continuous and completely similar at all
380 sites. The study of long-term soil and weathering mechanism signals must, necessarily, cope with
381 such inconveniences (as only natural archives – which includes soils – can give an insight into
382 long-term processes). Although the conditions for soil evolution were not perfectly continuous and
383 identical at all sites, the established sequences are meaningful and give a useful insight into forma-
384 tion rates and soil functions.

385

386

387 **6. Conclusions**

388 As noted by Böhlert et al. (2011a), the selected parameters (mass balance, weathering indexes) are
389 good parameters that enable an insight into evolutionary processes of the investigated soils. Similar
390 to findings of laboratory experiments (e.g. White and Brantley, 2003), weathering rates in soils de-
391 crease with time. Depending on the parameter investigated, a power function ('index B',
392 (K+Ca)/Ti) or an 'exponential decay model function' (accumulation of pedogenically formed
393 weakly- and poorly crystalline phases, τ) best explains the measured trends.

394 In this study, a data compilation, stock and rate calculation of weakly- and poorly crystallised
395 phases (Fe, Al, Si, Mn) was performed for alpine sites of the Rockies and European Alps. The pe-
396 dogenically formed, weakly- and poorly crystallised phases were calculated using an approach
397 based on immobile elements. As one of few attempts to date, overall formation rates of these phases
398 are plotted as a function of soil age (and up to ~1 Ma). The formation rates distinctly decrease with
399 increasing age of the soil. This rate of decrease is not only influenced by the factor of time but also
400 by climate (higher precipitation rates lead to a slower rate decrease). These results also suggest that
401 the older soils may be reaching a steady state for these chemical properties in their present envi-
402 ronments.

403

404

405 **7. Acknowledgements**

406 We would like to thank B. Kägi and M. Hilf for the help in the laboratory. We are, furthermore, in-
407 debted to two unknown reviewers for their helpful comments on an earlier version of the manu-
408 script.

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Table 1

Table 1. Characteristics of the Wind River Range sites.

Site / soil profile	Longitude °E	Latitude °N	Elevation m asl	Aspect °N	Slope %	Slope form*	Parent material	Location	Vegetation	Soils (Soil Taxonomy; Soil Survey Staff, 2010)	Soil age** y	MAP mm/y	MAT °C	Source
Bigfoot Lake														
9	109° 1'7"	42°38'12"	3414	-	0	planar	Granitic till	end moraine	Lichen-covered boulders	Typic Cryorthent	150	800-900	-3.3	Dahms, 2002;
6	109° 1'4"	42°38'22"	3365	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Haplocryoll	9930	800-900	-3.0	
5	109° 0'57"	42°38'22"	3353	-	0	planar	Granitic till	lateral/end moraine	Alpine grassland	Typic Haplocryoll	12930	800-900	-2.9	
1	109° 0'39"	42°38'31"	3347	-	0	planar	Granitic till	lateral moraine	Alpine grassland	Typic Haplocryoll	14500	800-900	-2.9	
Stough Creek Basin														
12	109° 0'27"	42°37'40"	3475	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Cryorthent	1500	800-900	-3.7	Dahms, 2002
10	108°59'59"	42°37'58"	3414	-	0	planar	Granitic till	kame terrace/lat eral moraine	Alpine grassland	Typic Haplocryoll	22000	800-900	-3.3	
Roaring Fork Pass														
2	108°59'58"	42°39'19"	3347	-	0	planar	Granitic till	lateral moraine	Alpine grassland	Typic Haplocryoll	22000	800-900	-2.9	Dahms, 2002
Pete's Lake Road														
1	108°53'15"	42°43'40"	2640	-	0	planar	Granitic till	lateral moraine	Limber pine - common juniper	Ustic Argicryoll	130000	600	1.2	Dahms, 2004;
2	108°53'8"	42°43'36"	2579	-	0	planar	Granitic till	lateral moraine	Limber pine - common juniper	Ustic Haplocryoll	22000	550	1.4	Fabel et al., 2004
Fairfield Creek														
5	108°51'13"	42°44'8"	2329	-	0	planar	Granitic till	lateral moraine	Limber pine, juniper,	Ustic Argicryoll	65000	500	2.6	Dahms, 2004;

2	108°51'29"	42°44'10"	2426	-	0	planar	Granitic till	lateral moraine	Limber pine, juniper, sagebrush	Ustic Argicryoll/Palecryoll	630000	500	2.0	Fabel et al., 2004
Deer Spring 1	108°48'48"	42°44'7"	2304	-	0	planar	Granitic till	lateral moraine	Sagebrush, fescue, wheatgrass	Ustic Argicryoll/Palecryoll	850000	500	3.2	Dahms, 2004; Fabel et al., 2004
Table Mountain 1	108°45'36"	42°45'20"	2225	-	0	planar	Granitic till	unidentified till feature	Sagebrush, fescue, wheatgrass	Ustic Argicryoll/Palecryoll	1200000	450	3.4	Dahms, 2004

* perpendicular to slope

** surface age

Table 2

Table 2. Characteristics of the Alpine sites.

Site / soil profile	Longitude °E	Latitude °N	Elevation m asl	Aspect °N	Slope %	Slope form*	Parent material	Location	Vegetation	Soils (Soil taxonomy; Soil Survey Staff, 2010)	Soil age** y	MAP mm/y	MAT °C	Source
Val di Rabbi														
S1	10° 27'36"	46° 13'42"	2100	60	32	planar	Paragneiss till	Lateral moraine	European larch, common Juniper	Typic Haplocryod	17311	1300	1.5	Favilli et al., 2009
S2	10° 27'29"	46° 13'39"	2230	70	55	planar	Paragneiss till	Lateral moraine	Rhododendron, dwarf shrubs, alpine grassland	Typic Haplocryod	11106	1300	0.7	
S3	10° 28'34"	46° 13'30"	2380	320	5	planar	Paragneiss till	Lateral moraine	Alpine grassland	Typic Cryorthent	10754	1300	0	
S4	10° 28'33"	46° 13'29"	2370	300	10	planar	Paragneiss till	Solifluction, ground moraine	Alpine grassland	Typic Cryorthent	8860	1300	0	
S5	10° 27'36"	46° 13'42"	2083	240	32	concave	Paragneiss till	Lateral moraine	European larch, common Juniper	Typic Haplocryod	10837	1300	1.5	
S6	10° 27'36"	46° 13'44"	2076	5	38	planar	Paragneiss till	Lateral moraine	European larch, common Juniper	Typic Haplocryod	4729	1300	1.6	
S7	10° 27'29"	46° 13'44"	2100	3	43	planar	Paragneiss till	Lateral moraine	European larch, common Juniper	Typic Haplocryod	5452	1300	1.5	
S8	10° 26'18"	46° 13'54"	2552	200	33	concave	Paragneiss till	Inactive rockglacier	Alpine grassland	Humic Dystrocryept	9203	1300	-1.1	
S9	10° 26'20"	46° 13'48"	2449	90	0	planar	Paragneiss till	Recessional moraine	Alpine grassland	Typic Haplocryod	11197	1300	-0.4	
Morteratsch														
S1	9° 56'39"	46° 26'49"	1930	330	10	planar	Granitic till	ground moraine	Green alder scrub	Typic Cryorthent	138	1100	0.7	Mavris et al., 2010 Egli et al.,
S2	9° 56'41"	46° 26'52"	1930		15	planar	Granitic till	ground moraine	Green alder scrub	Typic Cryorthent	128	1100	0.7	

S3	9° 56'36"	46° 26'44"	1930	280	<5	planar	Granitic till	ground moraine	Epilobietum fleischeri with single willow shrubs and Alpenrose	Typic Cryorthent	108	1100	0.7	2003; Maisch et al., 2005
S4	9° 56'36"	46° 26'42"	1935	320	<5	planar	Granitic till	ground moraine	Epilobietum fleischeri with single willow shrubs and Alpenrose	Typic Cryorthent	98	1100	0.7	
S5	9° 56'28"	46° 26'33'	1950	30	<5	planar	Granitic till	ground moraine	Pioneer grass communities	Typic Cryorthent	68	1100	0.7	
S6	9° 56'25"	46° 26'16'	2015	330	<5	planar	Granitic till	ground moraine	Epilobietum fleischeri with single willow shrubs and Alpenrose	Typic Cryorthent	48	1100	0.3	
S7	9° 56'06"	46° 26'13"	2015	260	<5	planar	Granitic till	ground moraine	Pioneer grass communities	Typic Cryorthent	48	1100	0.3	
S8	9° 56'07"	46° 26'20"	1990	150	<5	planar	Granitic till	ground moraine	Pioneer grass communities	Typic Cryorthent	58	1100	0.5	
S9	9° 56'08"	46° 26'25"	2000	30	<5	planar	Granitic till	ground moraine	Pioneer grass communities	Typic Cryorthent	73	1100	0.4	
S10	9° 56'13"	46° 26'33"	1980	60	<5	planar	Granitic till	ground moraine	Epilobietum fleischeri with single willow shrubs and Alpenrose	Typic Cryorthent	78	1100	0.5	
A	9°56'38"	46°26'50"	1930	330	10	planar	Granitic till	Lateral moraine	Green alder scrub	Typic Cryorthent	150	1100	0.7	
AC	9°56'27"	46°26'55"	1920	320	10	convex	Granitic till	Lateral moraine	Larch, Scots pine	Typic Dystrocryept	1300	1100	0.8	
AP	9°57'03"	46°27'02"	2030	350	10	planar	Granitic till	Lateral moraine	Larch, Scots pine	Typic Haplocryod	12500	1100	0.5	
Schmadri	7°52'36"	46°30'17"	2030	350	<5	planar	Granitic till	Lateral moraine	Alpine grassland	Typic Haplocryod	3500	2000	0.5	Egli et al., 2001;

	7°52'46"	46°30'26"	2020	10	<5	planar	Granitic till	Lateral moraine	Alpine grassland	Typic Haplocryod	11500	2000	0.5	Wipf, 2001
Val Mulix														
S1	9° 44'50"	46° 34'56"	2100	35	11	planar	Granitic till	Lateral moraine	Larch, Swiss pine, heath	Typic Haplocryod	14900	1250	-1.1	Böhlert et al., 2011b; Maisch, 1981
S2	9° 45'07"	46° 34'35"	2060	0	16	planar	Granite	lower rock glacier lobe	Alpine grassland	Typic Haplocryod	10000	1250	-0.8	
S3	9° 45'13"	46° 34'41"	2150	315	9	planar	Granitic till	Lateral moraine	Alpine grassland	Typic Haplocryod	10700	1250	-1.3	
S4	9° 45'11"	46° 34'30"	2130	300	8	planar	Granite	middle rock glacier lobe	Alpine grassland	Typic Haplocryod	9600	1250	-1.2	
S5	9° 45'16"	46° 34'29"	2280	300	6	planar	Granite	upper rock glacier lobe	Alpine grassland	Typic Haplocryod	8600	1250	-2	
Meggerwald														
	8°22'17"	47°03'39"	620	325	< 10	planar	Granitic till	ground moraine	White fir, blueberry, European beech	Typic Haplorthod	19200	1300	7.5	Hantke, 1983; Keller and Krayss, 2005; Maisch, 2000; Egli et al., 2002; Egli et al., 2010
	8°22'29"	47°03'31"	614	325	< 10	planar	Granitic till	ground moraine	White fir, blueberry, European beech	Spodic Dystrudept	19200	1300	7.5	
Gletsch														
	8° 21'52"	46° 33'53"	1760	-	0	planar	Granitic till	end moraine	Pioneer grass communities	Typic Udorthent	150	2000	1.2	Egli et al., 2001; Zumbühl and Holzhauser, 1988
	8° 21'50"	46° 33'54"	1760	-	0	planar	Granitic till	end moraine	Pioneer grass communities	Typic Udorthent	260	2000	1.2	
	8° 21'46"	46° 33'52"	1760	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Udorthent	300	2000	1.2	

8° 21'45"	46° 33'51"	1760	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Dystrudept	450	2000	1.2
8° 21'42"	46° 33'49"	1760	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Dystrudept	700	2000	1.2
8° 21'41"	46° 33'48"	1760	-	0	planar	Granitic till	end moraine	Alpine grassland	Typic Dystrudept	3000	2000	1.2
8° 21'23"	46° 33'40"	1790	-	0	planar	Granitic till	Lateral moraine	Alpine grassland	Typic Haplorthod	10500	2000	1.2

* perpendicular to slope

** surface age

Table 3

Table 3. Total content (major components; fine earth fraction) of the Wind River Ranges soils.

Soil	Horizon	Surface age y	Depth cm	Na ₂ O %	MgO %	K ₂ O %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ %	P ₂ O ₅ %	MnO %	TiO ₂ %
BFL 9	Cox	150	0-5	3.24	2.06	2.85	3.23	13.95	4.28	62.96	0.483	0.049	0.620
	Cu1		5-15	3.31	1.79	3.03	2.95	13.82	3.94	66.06	0.476	0.041	0.581
	Cu2		15-25	3.36	1.68	3.02	2.94	13.75	3.93	66.90	0.428	0.038	0.518
SCB 12	A	1500	0-2	3.01	2.09	3.18	3.51	13.73	4.44	63.87	0.479	0.054	0.716
	Cox		2-10	3.15	2.02	3.40	3.49	14.14	4.17	64.51	0.436	0.053	0.677
	2Cv		10-30	3.35	1.87	3.36	3.56	14.10	4.10	66.11	0.446	0.049	0.692
BFL 6	A	9930	0-10	1.80	2.15	2.43	3.06	11.69	3.75	51.38	0.518	0.076	0.615
	2Bt		10-20	2.44	2.15	2.63	2.79	13.93	3.92	58.37	0.347	0.046	0.539
	2Cox1		20-28	2.49	1.79	2.67	2.48	12.91	3.31	58.39	0.216	0.037	0.534
	2Cox2		28-45	2.82	2.39	2.32	3.25	14.17	4.44	61.87	0.257	0.051	0.590
BFL 5	A 0-9	12930	0-9	2.17	1.81	2.76	2.29	12.35	3.46	55.41	0.448	0.053	0.560
	2Bt		9-22	2.32	2.41	2.82	2.27	13.42	4.20	56.92	0.536	0.049	0.683
	2Cox1		22-55	1.85	2.85	2.68	2.40	15.52	4.76	65.25	0.296	0.045	0.752
	2Cox2		55-75	3.75	1.81	3.37	1.73	13.79	3.23	67.14	0.305	0.028	0.555
BFL 1	A	14500	0-8	1.63	1.94	2.58	2.36	12.08	3.49	51.82	0.599	0.073	0.639
	Bt		8-18	2.29	1.84	2.53	2.35	13.88	3.71	58.81	0.468	0.049	0.585
	2BC		18-28	3.34	1.51	3.09	2.80	13.93	3.28	66.48	0.373	0.038	0.525
	2Cox1		27-65	2.89	2.20	3.04	2.72	14.60	4.22	62.27	0.304	0.047	0.671
	2Cox2		65-90	3.18	2.23	3.12	3.09	13.98	4.44	64.04	0.436	0.050	0.711
SCB 10	A	16000	0-6	1.05	2.00	1.65	2.35	9.09	4.08	35.92	0.471	0.059	0.672
	Ej		6-7	1.31	2.39	1.88	2.24	11.13	5.14	42.31	0.492	0.041	0.907
	Bw		7-11	1.37	1.69	1.74	2.05	10.50	3.99	43.32	0.612	0.029	0.646
	2ABb		11-23	2.09	1.73	2.01	2.14	12.40	4.02	52.80	0.585	0.035	0.633
	2Btb		23-29	3.31	1.73	2.08	2.72	14.33	4.18	60.87	0.311	0.036	0.687
	3Cox1b		29-75	3.96	1.44	2.27	3.17	14.62	4.20	65.45	0.388	0.032	0.545

	3Cox2b		75-85	3.70	1.62	2.43	3.00	14.75	4.77	63.91	0.334	0.036	0.629
RFP 2	A	16000	0-13	1.31	1.76	2.06	1.83	11.63	3.60	50.41	0.485	0.082	0.610
	2Bt1		13-23	2.37	2.56	2.11	2.14	14.14	4.75	59.83	0.225	0.046	0.645
	2Bt2		23-50	2.70	2.53	2.15	2.44	13.79	4.96	59.64	0.210	0.055	0.642
	2BC		50-60	3.20	2.15	2.43	2.47	14.65	4.41	62.95	0.260	0.054	0.564
	2Cox		60-75	3.28	2.24	2.32	2.59	14.77	4.61	62.15	0.265	0.055	0.602
PLR 2	A	22000	0-10	2.56	1.29	2.77	2.51	13.57	3.91	62.95	0.344	0.063	0.536
	AB		10-20	2.90	1.21	2.80	2.54	13.96	3.84	64.46	0.326	0.051	0.582
	BW		20-30	3.20	1.12	2.81	2.75	13.95	4.67	67.36	0.311	0.036	0.616
	Cox		30-50	2.60	1.27	2.57	2.89	13.77	3.74	62.72	0.322	0.027	0.550
	2C		> 50	2.14	1.27	2.49	2.78	12.13	3.89	56.60	0.259	0.030	0.567
FC5	A	65000	0-7	1.43	1.27	2.16	3.28	9.90	3.30	47.58	0.356	0.052	0.571
	Bt1		7-25	2.52	1.32	2.62	2.76	13.00	3.73	62.14	0.305	0.035	0.612
	2Bt2		25-50	3.07	1.24	2.82	2.84	13.38	3.75	64.51	0.274	0.027	0.502
	2Coxx		50-85	3.17	1.16	2.66	2.88	13.14	3.57	66.87	0.248	0.028	0.514
	2C		> 85	3.49	0.97	2.74	2.88	13.21	3.33	69.21	0.213	0.024	0.444
PLR1	A	130000	0-8	1.31	1.58	2.58	1.71	12.57	3.70	65.29	0.325	0.086	0.649
	Bt1b		8-30	1.30	1.63	2.45	1.53	12.63	4.08	66.49	0.272	0.068	0.702
	Bt2b		30-50	1.27	1.66	2.43	1.46	12.74	4.01	69.16	0.242	0.064	0.700
	Bt3b		50-85	0.87	1.98	2.10	1.27	12.89	4.06	67.82	0.180	0.059	0.678
	2Coxb		85-100	2.07	1.90	2.46	2.32	13.12	4.57	63.30	0.272	0.048	0.713
FC2	A	630000	3-5	1.09	1.58	2.93	2.07	12.32	3.08	54.42	0.356	0.057	0.530
	Bt1		5-23	1.30	1.71	2.83	1.57	14.05	3.08	55.10	0.224	0.032	0.472
	2Bt2b		23-45	1.24	1.78	3.36	1.44	14.67	2.67	61.54	0.110	0.019	0.376
	2Coxb		130-210	1.25	1.88	2.65	1.59	13.54	2.67	60.82	0.083	0.015	0.346
	2Cb		> 210	1.24	2.02	2.68	1.75	13.77	3.98	60.19	0.142	0.025	0.436
DS1	A	850000	0-11	1.02	1.83	3.11	1.67	14.71	3.92	57.57	0.265	0.069	0.731
	Btb1		11-30	1.12	2.15	2.76	1.74	15.48	3.94	58.03	0.184	0.041	0.593
	2Bt2b		30-150	0.74	2.50	2.53	1.98	15.41	2.67	55.43	0.106	0.021	0.411
TM-1	A	1200000	0-12	1.60	1.68	2.45	2.23	16.77	5.67	53.82	0.318	0.045	0.834

B	12-20	1.60	1.38	2.72	2.09	15.71	5.00	55.18	0.238	0.039	0.743
Bt1b1	20-45	1.51	1.53	2.38	2.16	16.57	5.42	54.32	0.245	0.042	0.807
Bt2b1	45-60	1.58	1.54	2.44	2.21	16.56	5.47	53.80	0.268	0.044	0.792
Coxb1	65-85	1.67	1.41	2.66	2.07	16.18	5.09	55.12	0.237	0.044	0.785
ABb2	85-115	1.38	1.59	2.51	2.16	15.12	4.99	52.70	0.298	0.048	0.703
Bt1b2	115-150	1.18	1.69	2.79	1.67	14.33	4.50	57.21	0.179	0.034	0.655
Bt2b2	150-200	1.45	1.54	2.91	1.87	15.45	5.08	54.90	0.152	0.026	0.641
Bt3b2	200-300	1.24	1.62	2.82	1.77	15.22	5.23	55.49	0.140	0.027	0.731
Cox1b2	300-400	1.65	1.54	1.95	2.79	16.22	3.92	55.23	0.153	0.017	0.678
Cox2b2	400-500	1.38	1.51	2.77	1.69	16.29	4.78	55.36	0.108	0.026	0.644

Table 4. Average composition (major inorganic compounds) of the parent material (fine earth) of both investigation regions.

	Na ₂ O (%)	MgO (%)	K ₂ O (%)	CaO (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	P ₂ O ₅ (%)	MnO (%)	TiO ₂ (%)
Alps (n=30)										
Average	3.01	1.07	3.58	0.98	13.80	3.17	66.92	0.128	0.055	0.762
SD	0.98	0.67	0.74	0.61	2.81	1.90	6.59	0.030	0.027	0.450
Median	3.11	0.99	3.51	0.93	14.48	2.77	67.18	0.13	0.053	0.805
Wind River Range (n = 22)										
Average	2.73	1.79	2.73	2.68	14.09	4.03	62.92	0.290	0.037	0.589
SD	0.85	0.44	0.38	0.57	1.01	0.56	3.88	0.113	0.012	0.102
Median	3.02	1.80*	2.68*	2.83	13.90	4.04*	63.60*	0.28*	0.036*	0.586

*Differences between the Alps and the Wind River Range are significant based on the Mann-Whitney test

Table 5

Table 5. Concentrations of oxalate-extractable Fe, Al, Si and Mn (fine earth), pH and some physical properties of the Wind River Range soils

Surface age (y)	Soil	Horizon	Depth (cm)	Layer (cm)	Gravel-w%	Bulk density (g/cm ³)	pH (CaCl ₂)	Fe (mg/kg)	Mn (mg/kg)	Si (mg/kg)	Al (mg/kg)
150	BFL 9	Cox	0-5	5	42	1.35	4.6	1055	47	259	476
		Cu1	5-15	10	56	1.77	4.5	1014	39	110	304
		Cu2	15-25	10	56	1.77	4.5	784	27	49	195
1500	SCB 12	A	0-2	2	31	1.35	4.9	1978	72	379	739
		Cox	2-10	8	47	1.77	4.9	856	49	366	444
		2Cu	10-30	20	51	1.77	4.9	885	34	272	379
9930	BFL 6	A	0-10	10	7	0.98	5.3	1598	246	112	1298
		2Bt	10-20	10	29	1.20	5.1	663	13	9	845
		2Cox1	20-28	8	34	1.54		259	4	18	183
		2Cox2	28-45	17	33	1.77	4.7	259	4	18	183
12930	BFL 5	A 0-9	0-9	9	22	0.94	5.2	1100	77	128	1320
		2Bt	9-22	13	31	1.26	4.7	498	32	139	1728
		2Cox1	22-55	33	32	1.62	4.4	338	6	42	385
		2Cox2	55-75	20	46	1.77	4.5	143	2	14	68
14500	BFL 1	A	0-8	8	8	1.21	5.2	809	106	190	2025
		Bt	8-18	10	20	1.27	4.9	795	43	193	2403
		2BC	18-28	10	40	1.32	5.0	431	11	83	508
		2Cox1	27-65	38	43	1.45	4.6	598	9	68	505
		2Cox2	65-90	25	53	1.77	4.7	576	10	62	188
16000	SCB 10	A	0-6	6	3	0.96	4.4	2275	161	81	1784
		Ej	6-7	1	3	1.10		2871	19	108	2153
		Bw	7-11	4	4	0.97	4.0	2437	13	90	2211
		2ABb	11-23	12	17	1.01	4.0	1969	27	75	2334

		2Btb	23-29	6	22	1.20	4.2	949	19	35	1116
		3Cox1b	29-75	46	37	1.54	4.5	220	4	5	314
		3Cox2b	75-85	10	46	1.77	4.3	210	13	25	746
16000	RFP 2	A	0-13	13	6	1.03	4.4	3327	448	168	2787
		2Bt1	13-23	10	17	1.17	4.2	1804	9	83	1732
		2Bt2	23-50	27	35	1.34	4.2	1856	13	98	1716
		2BC	50-60	10	33	1.54	4.2	523	25	34	2701
		2Cox	60-75	15	42	1.77	4.2	633	28	454	3141
22000	PLR 2	A	0-10	10	20.5	1.26	5.1	2383	331	67	1582
		AB	10-20	10	23.1	1.35	5.2	1205	179	84	972
		BW	20-30	10	40.7	1.45	5.1	2253	70	84	646
		Cox	30-50	20	41.6	1.77	5.3	267	15	16	360
		2C	> 50	10	52.8	1.83	5.4	746	12	21	290
65000	FC5	A	0-7	7	16.2	1.26	5.3	1366	131	67	691
		Bt1	7-25	18	27.3	1.54	5.4	1831	67	105	606
		2Bt2	25-50	25	26.3	1.59	5.6	1810	18	79	375
		2Coxx	50-85	35	32.5	1.77	5.6	235	27	23	262
		2C	> 85	10	39.6	1.83	5.8	1041	20	44	165
130000	PLR1	A	0-8	8	18.4	1.26	5.3	2240	415	175	1145
		Bt1b	8-30	22	16.5	1.54	5.3	1795	287	137	1039
		Bt2b	30-50	20	12.4	1.59	5.3	1530	241	123	999
		Bt3b	50-85	35	7.5	1.59	5.5	1326	256	145	1164
		2Coxb	85-100	15	53.1	1.77	5.5	666	89	56	477
630000	FC2	A	3-5	5	20.8	1.07	5.6	1636	202	139	1386
		Bt1	5-23	18	18.1	1.41	5.3	507	59	58	695
		2Bt2b	23-45	107	16.8	1.58	5.5	320	26	60	664
		2Coxb	130-210	80	14.1	1.77	6.0	82	1	49	294
		2Cb	> 210	10	7.7	1.83	6.0	123	1	70	447

850000	DS1	A	0-11	11	14.5	1.31	5.5	1415	219	126	1144
		Btb1	11-30	19	20.1	1.47	5.4	732	99	99	1329
		2Bt2b	30-150	120	36.2	1.53	5.5	136	12	55	738
1200000	TM-1	A	0-12	12	0.0	1.26	6.4	554	97	105	368
		B	12-20	8	0.7	1.83	6.5	519	75	92	282
		Bt1b1	20-45	15	0.0	1.54	6.2	488	86	91	312
		Bt2b1	45-60	15	2.0	1.59	6.0	563	106	102	347
		Coxb1	65-85	20	1.2	1.77	5.9	737	105	104	432
		ABb2	85-115	30	5.2	1.26	6.2	1028	131	118	700
		Bt1b2	115-150	35	17.9	1.54	6.0	581	73	75	756
		Bt2b2	150-200	50	18.4	1.54	5.7	188	20	61	450
		Bt3b2	200-300	100	11.6	1.59	5.8	265	43	80	457
		Cox1b2	300-400	100	18.5	1.77	6.1	174	35	64	367
		Cox2b2	400-500	100	16.1	1.77	6.0	228	39	65	241

Figure captions

Fig. 1. Location of the study sites (data source and imagery: Harris Corp, Earthstar Geographic LLC; sci Lands – scientific landscapes, Göttingen). European Alps: VdR = Val di Rabbi, M = Morteratsch, Sc = Schmadri, VM = Val Mulix, MW = Meggerwald, Gl = Gletsch; Wind River Range: BFL = Bigfoot Lake, SCB = Stough Creek Basin, RFP = Roaring Fork Pass, PLR = Pete's Lake Road, FC = Fairfield Creek, DS = Deer Spring, TM = Table Mountain.

Fig. 2. Concentration – depth function for the oxalate-extractable Fe (Wind River Range and European Alps) and Mn (only Wind River Range). The soil profiles are classified according to their surface age.

Fig. 3. Time trend of the open mass transfer function $\tau_{j,w}$ (mean value) in the topsoil for the base cations (BC: Ca, Mg, K, Na) and Fe and Al. The trend is modelled using an exponential decay model (see equation 8). The fitting parameters are for BC: Wind River Range ($a = -0.22$; $b = 0$; $k = 0.000091$), Alps ($a = -0.62$; $b = 0$; $k = 0.000094$) and for Al + Fe: Wind River Range ($a = -0.22$; $b = 0$; $k = 0.000092$), Alps ($a = -0.61$; $b = 0$; $k = 0.000102$).

Fig. 4. (K+Ca)/Ti ratio in the topsoil and in the B horizon of the Wind River Range as a function of time.

Fig. 5. Weathering index B (according to Kronberg and Nesbitt, 1981) in the topsoil and in the B horizon for the Wind River Range and the Alps as a function of time.

Fig. 6. A) Total stocks of oxalate-extractable Fe, Al and Si (including the sites of the proglacial area Damma; Dümig et al., 2011) and B) pedogenetically formed abundances of Fe, Al, Si and Mn as a function of time (without the proglacial area Damma due to missing data). The Pedogenetic stocks of Fe, Al, Si and Mn were calculated according to the equations 4-6. The trend for the pedogenetically forms is modelled using an exponential decay model (see equation 9). WRR = Wind River Range.

Fig. 7. Accumulation rates of pedogenetically formed Fe, Al, Si and Mn forms (for Mn: data is only available for the Wind River Range).

Figure 1
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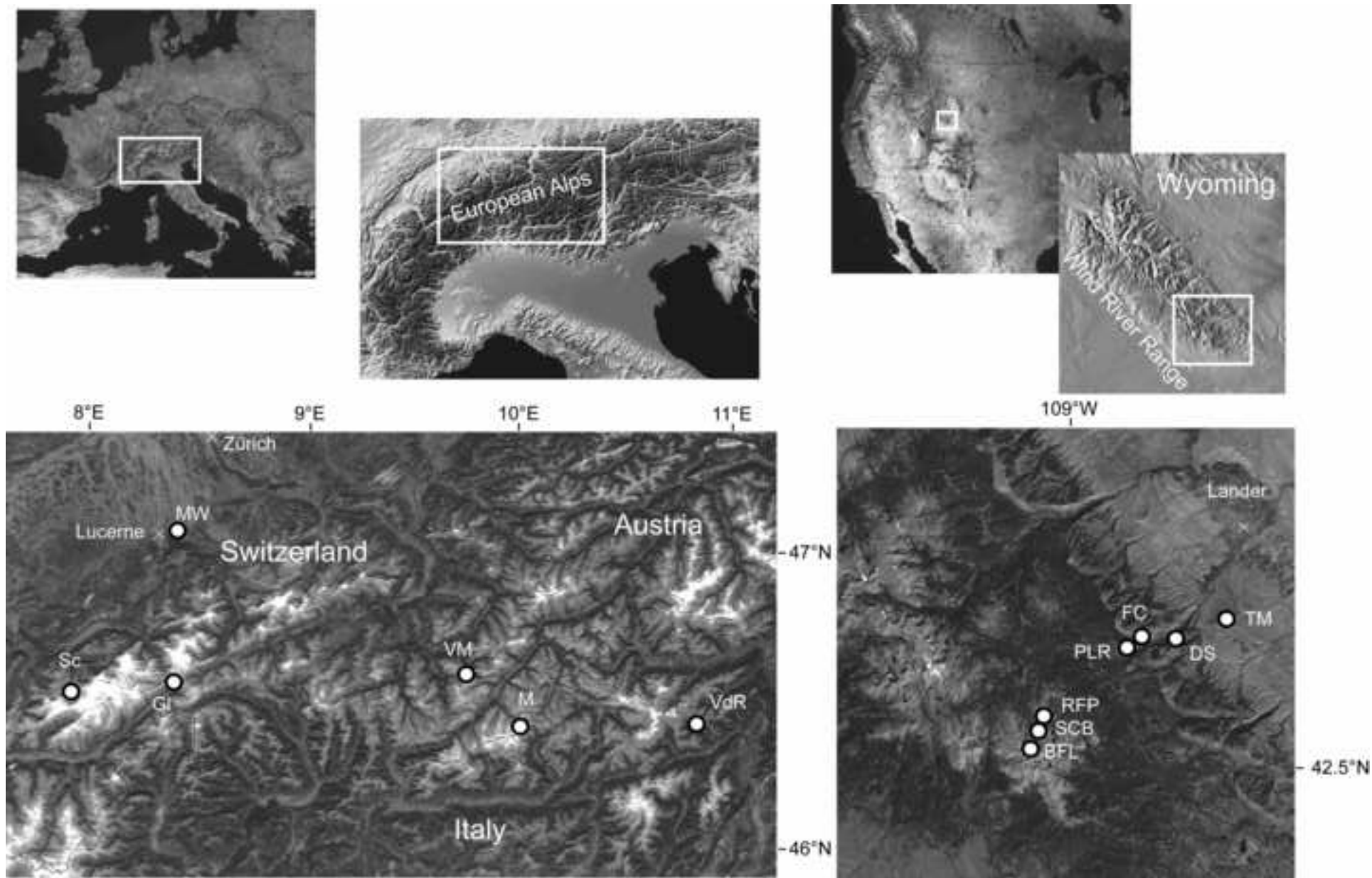


Figure 2
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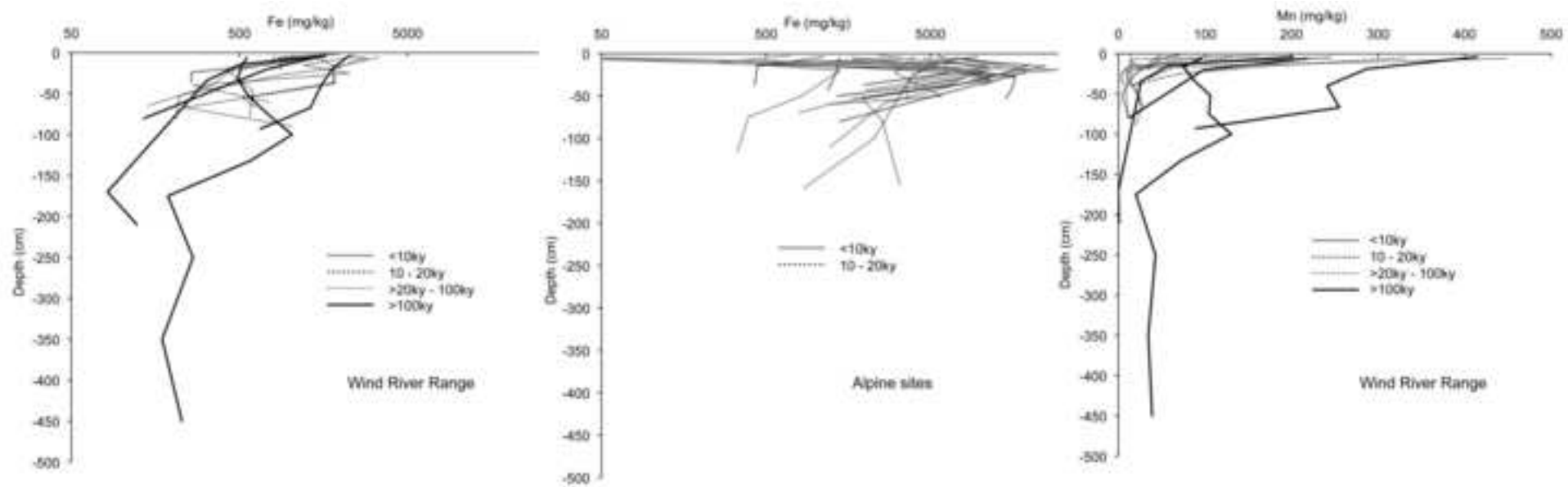


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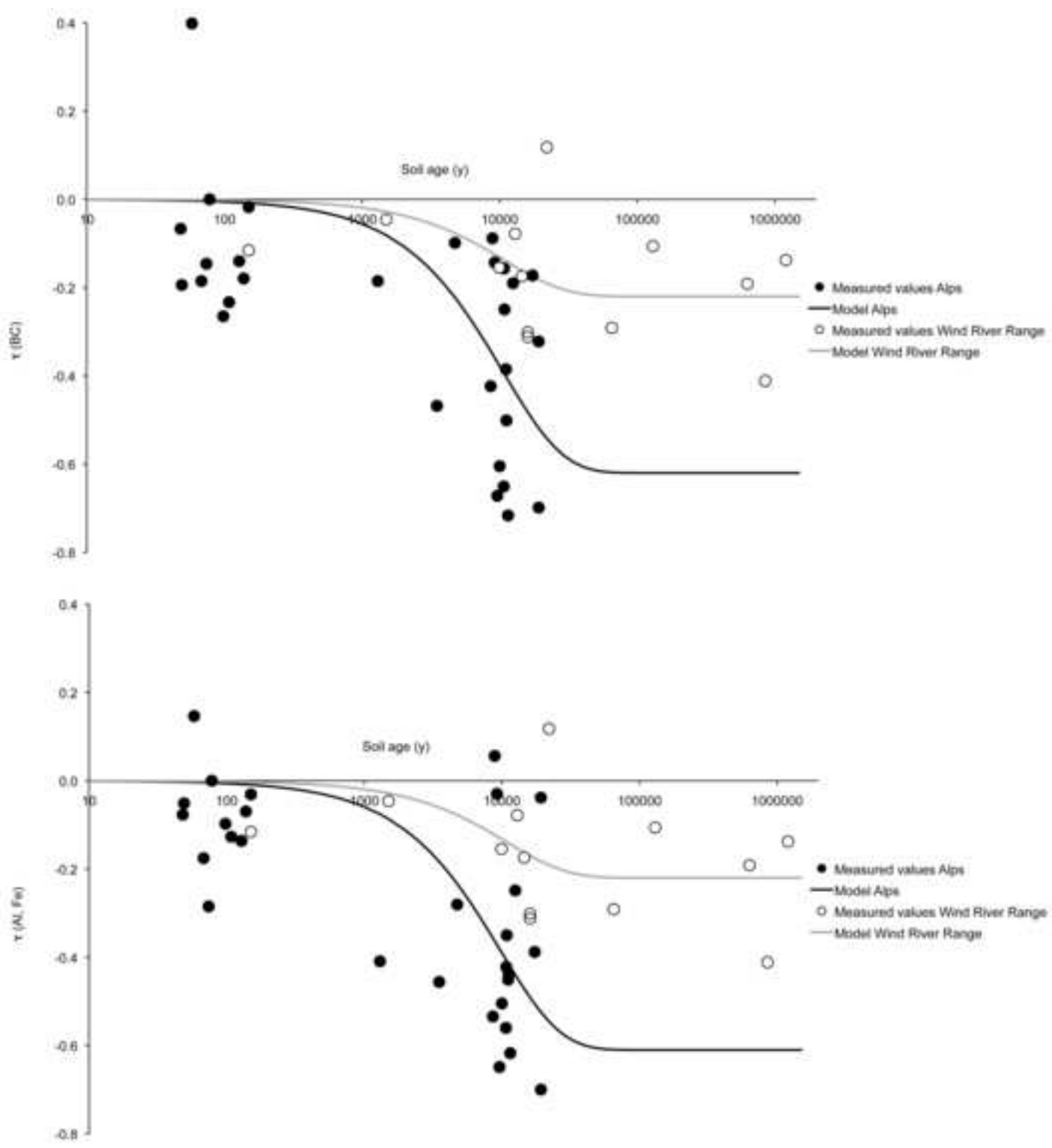


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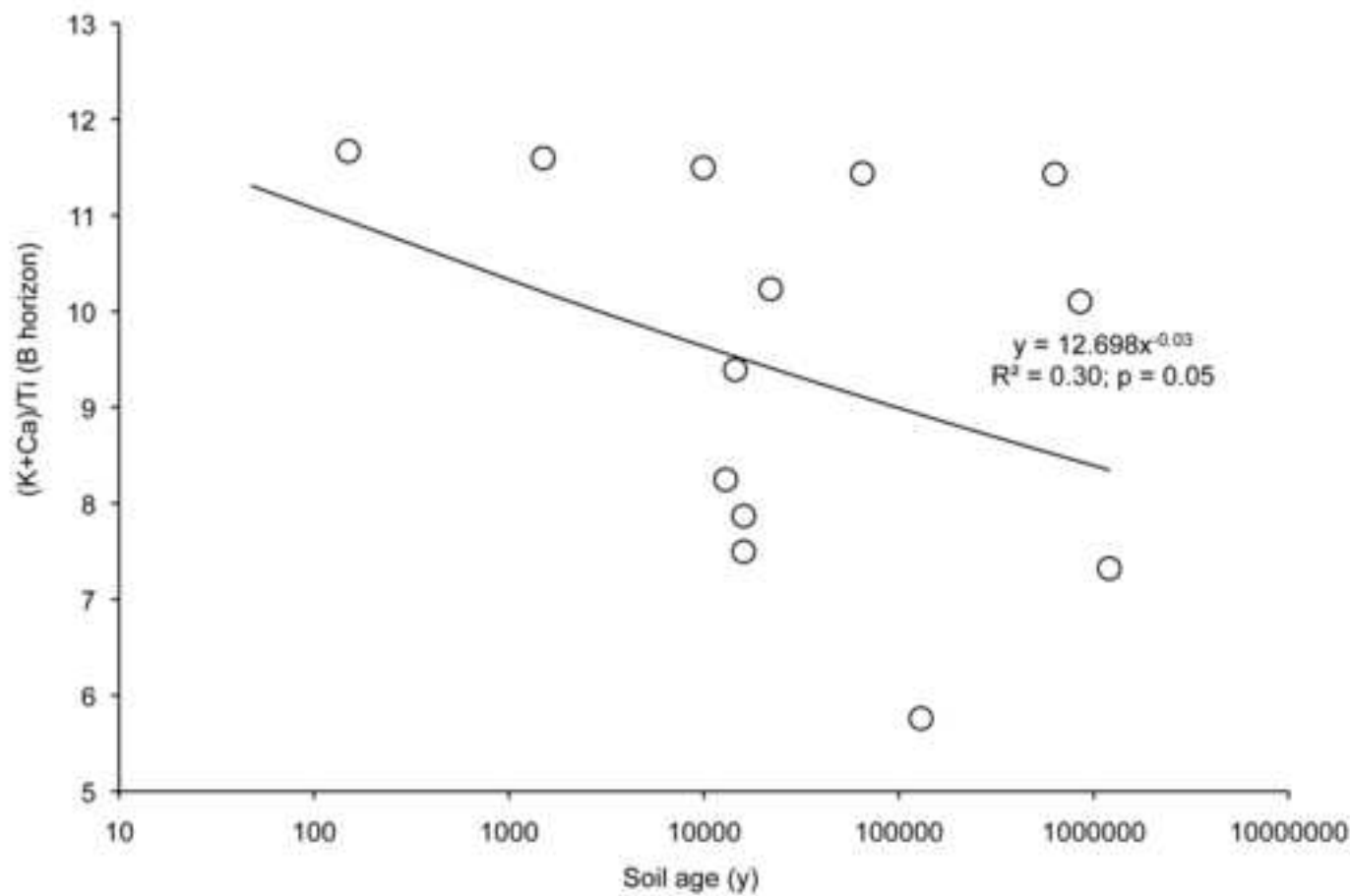
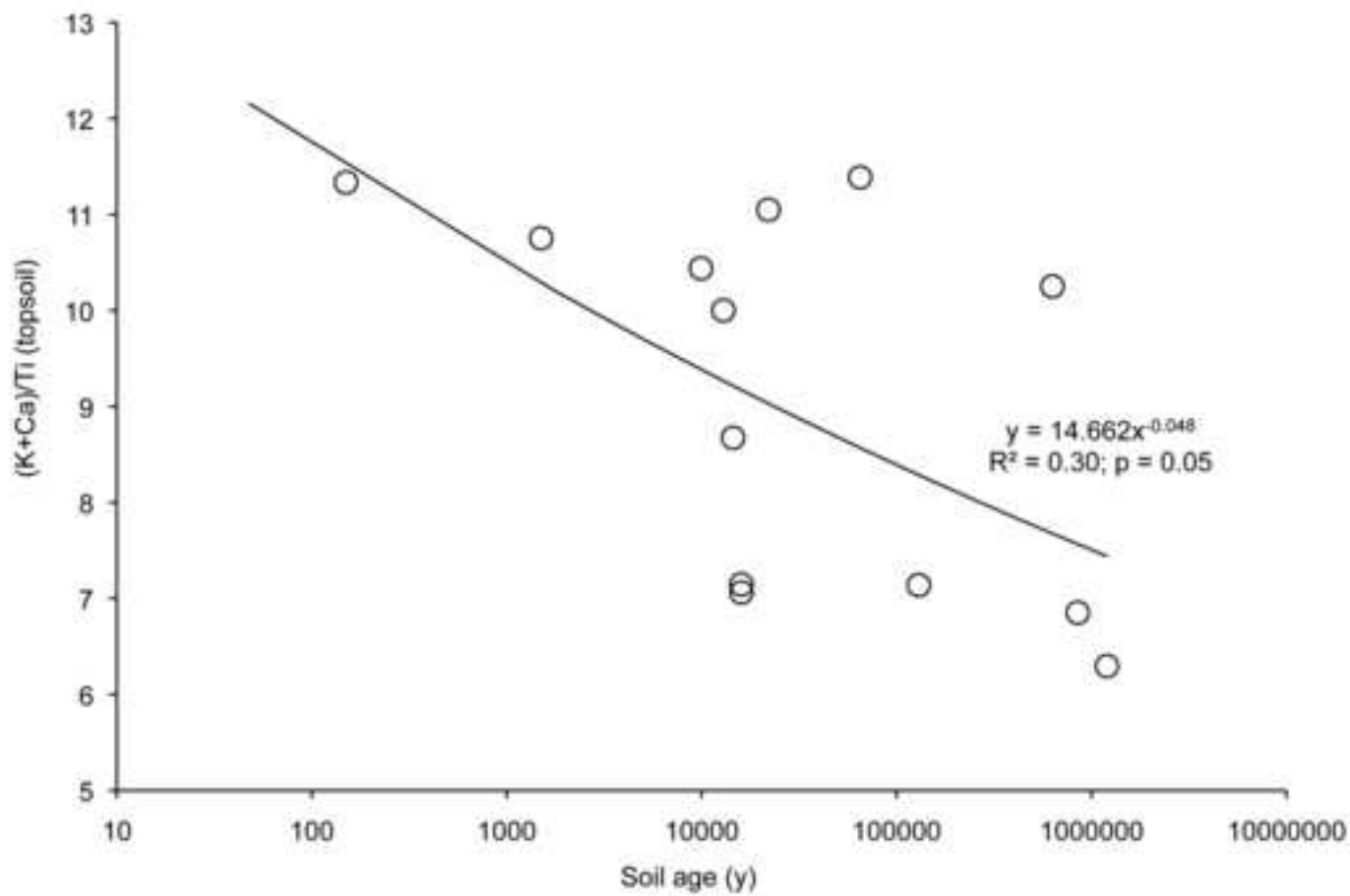


Figure 5

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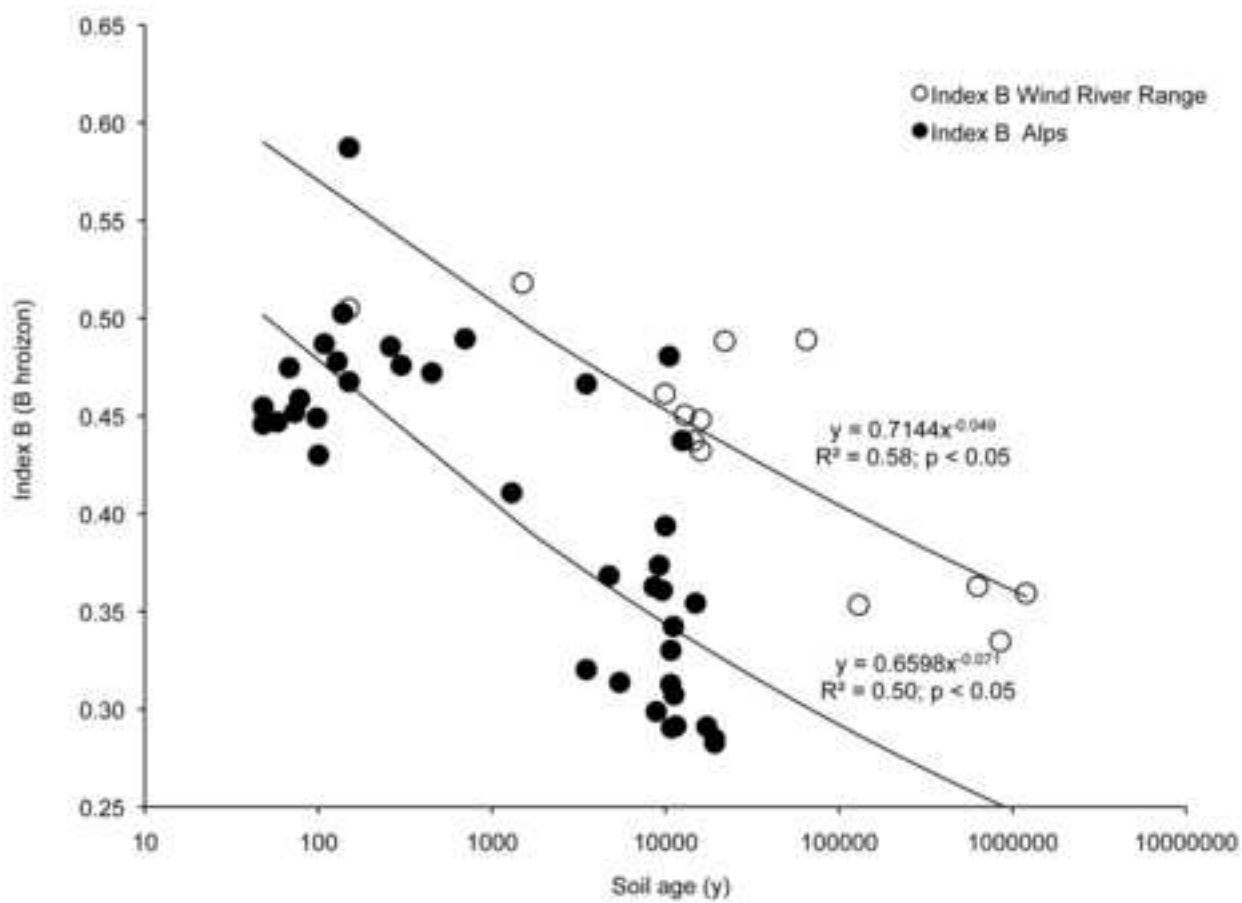
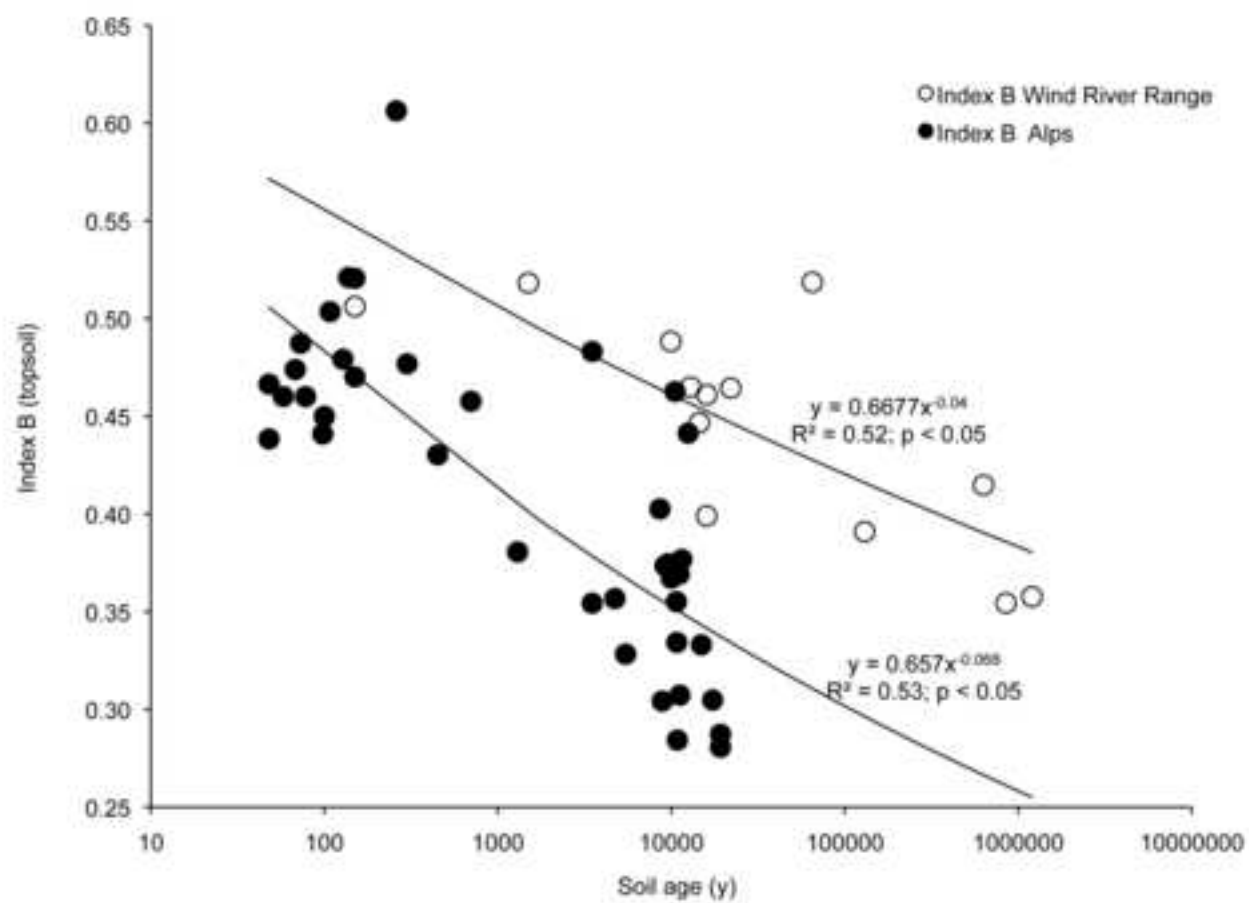


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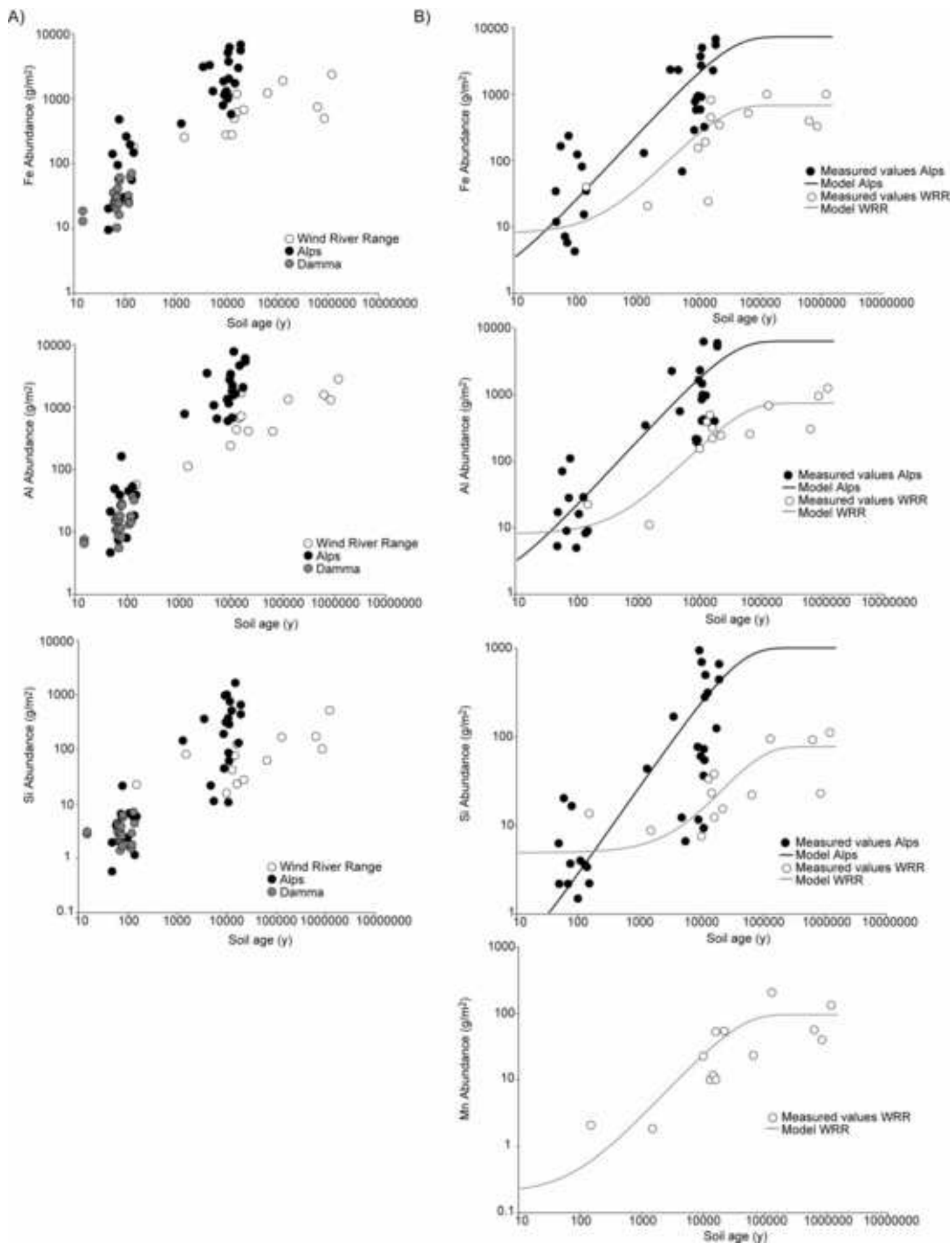


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