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Early stages of soil development on serpentinite: the proglacial area of the Verra Grande Glacier, Western Italian Alps

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15 SOIL FORMATION AND WEATHERING IN TIME AND SPACE

16

17 **Early stages of soil development on serpentinite: the proglacial area of the Verra**
18 **Grande Glacier, Western Italian Alps**

19

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39 **Abstract**

40 Purpose: Climate change is driving strong variations in mountain habitats, such as glacier
41 retreat, which is releasing large surfaces soon colonized by vegetation and attacked by
42 weathering and pedogenesis. Many proglacial soil chronosequences have been studied in
43 different parts of the world, but no study is available on early soil development and
44 pedogenesis on serpentinite.

45 Materials and methods: We analyzed the development of the main chemical (pH, organic
46 matter, nutrients and exchangeable cations) and morphological properties in three soil
47 chronosequences in the Verra Grande Glacier forefield (Italian side of the Monte Rosa Group,
48 Western Alps), characterized by slightly different parent materials (pure serpentinite or
49 serpentinite with small gneiss inclusions) and topography (steep lateral moraines or flat basal
50 till).

51 Results and discussion: Organic matter accumulation, acidification and base and metal
52 leaching are the most important pedogenetic processes active during early stages of soil
53 formation on serpentinite in the upper subalpine altitudinal belt. These processes are
54 associated with minor changes in color and structure showing weak mineral weathering.

55 Biocycling of nutrients is limited on pure serpentinite because of weak primary productivity
56 of the plant community. Pedogenesis is quite slow throughout the forefield, and it is slowest
57 on pure serpentinite. On flat surfaces, where slow erosion permits a fast colonization by
58 Ericaceae, the podzolization process begins after few centuries since moraine deposition,
59 while on steep slopes more time is required.

60 Conclusions: Pedogenesis on serpentinite is extremely slow. The fast colonization by
61 grassland species increases the speed of pedogenetic trends where serpentinitic till is enriched
62 by small quantities of P-rich gneiss. The encroachment of forest-shrub species increases the
63 speed of pedogenetic trends thanks to a strong nutrient biocycling.

64

65 **Keywords** Chronofunctions • Italian Alps • Podzolization • Proglacial soil chronosequence
66 • Soil formation • Subalpine soils

67

69 **1 Introduction**

70 Climate change is driving strong variations in high mountain temperature-limited
71 environments, involving both physical and biological components of the ecosystems. One of
72 the most visible effect is the glacier retreat, which continued with only few interruptions since
73 the end of the Little Ice Age (LIA), around mid 19th century, when glaciers reached their
74 maximum Holocene expansion (Ivy-Ochs et al. 2009).

75 The released surfaces in the proglacial areas (also called "glacier forefields") offer the
76 opportunity of observing the development of soil properties and ecosystem dynamics: habitats
77 characterized by different ages coexist over short distances, reducing the effect of other
78 geographical and climatic factors.

79 The parent material of soils has a prominent importance in the determination of pedogenic
80 trends, especially during the early stages of soil formation. Most of the proglacial
81 chronosequences in the European Alps have been described on silic substrata, a few on
82 calcareous rocks (e.g. Bernasconi et al. 2011; Egli et al. 2001; Mavris et al. 2010; Dümig et
83 al. 2011; Righi et al. 1999); a similar situation is observed in studies performed in other
84 regions (e.g. Ugolini 1966; Burt and Alexander 1996). Extremely scattered data are available
85 about early soil formation and soil chronosequences on serpentinite (examples of revegetation
86 of drastically disturbed serpentine soils are shown by O'Dell and Claassen 2009), and no
87 proglacial chronosequence has ever been studied on ultramafic substrates.

88 This lack of information exists despite the many specific characteristics of serpentine
89 ecosystems. In fact, even if serpentine habitats represent only less than 1% of the world
90 surface, they are common in most orogenic belts, where they create peculiar habitats
91 characterized by three common traits (Whittaker 1954): sparse plant cover and low primary
92 productivity, high levels of endemisms, and different plant communities compared with
93 neighboring areas. These features are caused by the pedogenetic trends on serpentinite, which
94 lead to the formation of soils (commonly called "serpentine soils") typically characterized by
95 unique chemical and physical properties which reduce plant productivity and create stress and
96 toxicity to non-adapted species (the so called "serpentine syndrome", Jenny 1980; Alexander
97 et al. 2007). The "serpentine syndrome" is often associated with several chemical and
98 physical edaphic factors, such as a low Ca:Mg ratio caused by the high amounts of Mg
99 released from the parent material and abundant heavy metals (Ni, Cr, Co). In addition, soils
100 often have low macronutrient (N, P, K) concentrations both because of their paucity in the
101 parent material and of the low plant productivity and are prone to drought and erosion

102 processes (Brooks 1987). Bioaccumulation of Ca and nutrients in the organic matter-rich
103 surface horizons, preventing losses of deficient nutrients, associated with strong Mg leaching
104 in acidic soils, are important processes that reduce the typical infertility of "serpentine soils"
105 in the Alps (D'Amico and Previtali 2012; Bonifacio et al. 2013; D'Amico et al. 2014b).

106 The observation of early development of soil properties and the evaluation of pedogenic
107 processes could give important insights in understanding the factors influencing the specific
108 harsh edaphic properties of serpentine habitats. In particular, the intense weathering processes
109 characterizing freshly ground materials in glacier forefield soils release nutrients (P, Fe, K,
110 Ca) from the parent minerals which may thus be present in relatively high amounts even in
111 soils from nutrient-deficient parent minerals (Roberts et al. 1988). The observation of the
112 different rates and quantities of these elements that are released from the parent till and enter
113 the exchange complex in serpentine soils with different, small amounts of silicic inclusions
114 can give important information on the edaphic limitations for the associated plant colonization
115 and primary succession. On serpentinite, weathering releases also potentially toxic elements
116 (such as Ni and/or excessive Mg), which can deeply impact ecosystem development and
117 surface water quality.

118 In this work we analyzed soils and observed plant colonization along three serpentine
119 chronosequences on the eastern and western lateral moraine systems and on the flat, stable
120 basal till of an Alpine proglacial area, in order to investigate the pedogenic trends and the
121 specific development of the most important edaphic properties in the upper subalpine belt, in
122 the Verra Grande glacier forefield (Italian side of the Monte Rosa Massif). The main aim was
123 to understand the most important processes active during the early stages of pedogenesis on
124 serpentinite in alpine areas. Early pedogenic processes can help in the identification of the
125 edaphic factors involved in the inhibition of plant colonization on raw serpentinitic materials
126 in recently deglaciated areas.

127

128

129 **2 Materials and methods**

130 **2.1 Study area**

131 The Verra Grande glacier forefield is located in the upper Ayas valley (Aosta Valley, North-
132 Western Italian Alps, Italy, Fig. 1). A precise dating of the Little Ice Age (LIA) Verra Grande
133 moraine system is missing, as few pictures or paintings are available before 1945. However,
134 historical reconstructions have been performed according to similarities in glacier responses
135 with the nearby Lys Glacier (located 5.5 km east of the Verra Grande glacier, with similar

136 climatic regimes and neighboring accumulation zones), on which more precise dating is
137 available (Vanni 1945, Cerutti 1985; Carnielli 2005). Some of these reconstructions were
138 performed in the early 20th century, only a few decades after the 1860 LIA secondary glacier
139 maximum, considering the opinions of expert eye witnesses (Monterin 1914). According to
140 these works, the LIA maximum advance (around 1820 in the Lys glacier, Strada 1988) left a
141 terminal moraine near the upper portion of the Pian di Verra Inferiore, at an altitude of about
142 2070 m a.s.l.; a minor advance ended in 1861, when the glacier approached the terminal
143 moraine, leaving a recessional moraine ca. 80 m north of it (Vanni 1945; Cerutti 1985).
144 However, the results of a dendrochronological study performed in five forested 20x20 m
145 quadrates (A to E in Fig. 1b), in order to constrain the dating of the old LIA deposits,
146 indicated a different minimum age of the southernmost terminal moraine. In fact, a tree
147 sampled on the top of this moraine crest, in the vicinities of the A quadrate, germinated
148 around 1550, thus indicating that this morainic arch was deposited before this period. In B
149 (Fig. 1b), on the outer side of the 1860 moraine, the germination year of the oldest specimen
150 was 1887 (determined following the methods described by Leonelli et al. 2011), whereas on
151 the inner side of the crest (C) the germination of the oldest specimen dated 1892. Moving
152 upward, at D and E quadrates, the germination years of the oldest specimens were 1903 and
153 1946 respectively, in agreement with the glacier retreat phases. In particular, the evidence of
154 old trees growing on the top of the small terminal moraine south of the 1860 one (the
155 formerly presumed 1821 frontal moraine), dating back to about 1550, testifies that the largest
156 LIA advance happened well before the maximum advances of 1821 and 1850-60 that
157 occurred in most of the Alpine glaciers (Orombelli and Mason, 1997).

158 Monterin (1914), Sacco (1923), Vanni (1945) showed some other phases of glacial retreat
159 from 1861 until 1945. Therefore it is possible to recognize the materials released during the
160 advance around 1920 and the recessional and lateral moraines abandoned during the 1940s.
161 The small moraines deposited by advances recorded after 1945 (particularly during the 1970-
162 1987 time span) have been destroyed by erosion, and freshly abandoned till is not easily
163 reachable. Since the LIA greatest advance, approximately 3 km were left free of ice, while the
164 altitude of the glacier front increased of more than 600 m, reaching an elevation close to 2700
165 m a.s.l. in year 2012.

166 The altitude range of the sampled area is limited to 2070-2320 m of elevation: above this
167 altitude, excessive steepness and the consequent erosion inhibit ecosystem and soil
168 development. Present-day natural timberline in the area is around 2400 m a.s.l., and the
169 sampled sites lie in the upper subalpine belt.

170 The glacial till is composed of serpentinite of antigoritic type, associated with lenses of
171 chlorite-schists, talc-schists and traces of Ca-bearing minerals derived from rodingite
172 inclusions, belonging to the Zermatt – Saas ophiolite (Mattiolo et al. 1951). The eastern
173 lateral moraines are enriched with small amounts (<10% in volume) of granitic-gneissic
174 clasts, derived from Monte Rosa nappe outcrops.

175 The climate of the Ayas valley is inner-alpine, continental, with low average yearly
176 precipitation. In Champoluc (1450 m a.s.l., 5 km from the study area), the mean precipitation
177 (including snow-water equivalent) is 730 mm y⁻¹, well distributed throughout the year; the
178 average July rainfall is around 60 mm. Higher values are expected in the proglacial area,
179 because of the higher altitude and because the south-north direction of the Ayas valley
180 increases the advection of warm, moist Mediterranean air masses from the south, increasing
181 summer rainfall, while the proximity to the main Alpine divide allows some spillover of
182 precipitation also from the north during strong foehn wind events (Mercalli 2003). Drought
183 stress is possible during some particularly dry summer seasons. The mean annual temperature
184 is between 0 and +2°C (Mercalli 2003).

185 The vegetation growing in the proglacial area consists of pioneer communities dominated by
186 *Salix* ssp, *Dryas octopetala* L., basophilous grasses and serpentine endemic and Ni-
187 hyperaccumulator species (Vergnano Gambi and Gabbrielli 1981; Vergnano Gambi et al.
188 1987), with high bare soil on the western lateral moraines and on the basal till, and with well
189 developed grasslands on the eastern lateral moraines. Scattered portions of the LIA proglacial
190 area and the slopes outside the forefield (climax vegetation) are colonized by forests
191 dominated by European larch (*Larix decidua* Mill.), with sparse stone pine (*Pinus cembra* L.),
192 Norway spruce (*Picea abies* Karst.) and birch (*Betula pendula* Roth) specimens. The
193 understory is dominated by *Rhododendron ferrugineum* L., *Juniperus communis* L. and
194 several Ericaceae.

195

196 **2.2 Soil sampling and analysis**

197 20 sites (soil samples associated with vegetation surveys) were selected along 3 different
198 chronosequences among many other not-sampled observations: 6 sites were on the western
199 lateral morainic crests (W sites), 5 in the eastern ones (E sites), 7 in the flat intramorainic area
200 (C sites, basal till and remnants of frontal/recessional moraines, where soil and ecosystem
201 development could proceed with weaker disturbances) and 2 in pre LIA sites (deposited
202 during the Late Glacial, Younger Dryas, according to Cerutti 1985) (table 1). The E and W
203 sites were characterized by similar steepness. At each site a phytosociological survey was

204 completed in homogeneous areas of 16 m², visually estimating the percent cover of each
205 species. Field description of site and soil profile characteristics was carried out according to
206 FAO guidelines (2006).

207 The following data were collected (in brackets, measure unit and acronyms used from now
208 on): altitude, slope steepness (slope, °), aspect (°), surface rockiness (SR, %), bare soil (NS,
209 %), erosion, the cover of Ericaceae and tree cover (Tcov, calculated as percent area on a 100
210 m² surface). Erosion, SR, NS, herbaceous species and Tcov were determined by visual area
211 estimation. Plant species were identified according to Pignatti (1992).

212 Soil pits were dug in the middle of each plot, down to the C horizon (parent material) and the
213 soil profile was described to assess soil development and main pedogenic processes.
214 Approximately 1 kg of soil was collected from the genetic horizons (where possible). In the
215 field we were not able to obtain samples for the calculation of bulk densities because of
216 excessive stoniness, the abundant presence of medium and/or large roots and/or the extreme
217 thinness of pedogenic horizons.

218 The soil samples were air dried, sieved to 2 mm and analyzed according to the USDA
219 methods (Soil Survey Staff 2004). The pH was determined potentiometrically in water
220 extracts (1:2.5 w/w). Exchangeable Ca, Mg, K and Ni were determined after exchange with
221 NH₄-acetate at pH 7.0. The elements were analyzed by Atomic Absorption
222 Spectrophotometry (AAS, Perkin Elmer, Analyst 400, Waltham, MA, USA). The total C and
223 N concentrations were evaluated by dry combustion with an elemental analyser (CE
224 Instruments NA2100, Rodano, Italy). The carbonate content was measured by volumetric
225 analysis of the carbon dioxide liberated by a 6 M HCl solution. The Organic Carbon (TOC)
226 was then calculated as the difference between total C measured by dry combustion and
227 carbonate-C. Available P (P_{olsen}) was determined by extraction with NaHCO₃. In order to
228 detect the spodic properties of the most developed soils, the oxalate and dithionite-extractable
229 fractions of Fe and Al (Fe_{ox}, Al_{ox}, Fe_d) were measured.

230 In order to obtain a precise mineralogical characterization of the parent material, the coarse
231 sand fraction of C horizons of different terms of the chronosequences was separated by wet
232 sieving, crushed and analyzed by X-ray diffraction as randomly oriented mounts using a
233 Philips PW1710 diffractometer (40kV and 20 mA, graphite monochromator). Scans were
234 made from 5 to 80 °2θ at a speed of 1 °2θ min⁻¹.

235 Some indices were calculated, to detect the pedogenic trends and to compare the chemical and
236 morphological properties in the solum (C horizons were excluded) or in specific pedogenic
237 horizons with the parent material. The data derived from E1 and W1 were considered as

238 parent materials for, respectively, the soils on the eastern lateral moraines, and the ones on the
239 western and central till. TOC contents and pH values were used for building indicators of the
240 two main pedogenic process active on young soils in proglacial areas, which are organic
241 matter accumulation (TOCind) and acidification (pHind). Mineralogical weathering and the
242 formation of pedogenic materials were represented using the Buntley-Westin colour index
243 (BWind, Buntley and Westin 1965). Although it cannot substitute detailed mineralogical or
244 geochemical information, the BW index is a synthetic measure of color changes, it can thus
245 be used to represent all processes that induce a change in Hue and/or in Chroma with respect
246 to the gley-colored ultramafic parent material. We selected this index because it was
247 originally developed for Mollisols, and it is thus not as “hematite-oriented” as others (e.g.
248 redness rating by Torrent et al. (1980) in Mediterranean environments), and because of its
249 simple data requirements. The BWind was calculated from moist Munsell colours: increasing
250 points were attributed to hues with increasing redness (e.g. Gley1: 0; 5Y: 1; 7.5YR: 4) which
251 were multiplied by the chroma.

252 The selected chemical (TOC and pH) and morphological properties (BWind) of each horizon
253 were multiplied by the horizon thickness, and the obtained values were summed to obtain a
254 single index for each solum. The value of pHind for each horizons was calculated as pH
255 difference from the parent material (i.e. E1 and W1). The single profile indices were
256 normalized to a 0-1 scale, by dividing each value by the highest value obtained in the Verra
257 Grande forefield. As we could not measure the soil bulk density, these indicators represent
258 only a qualitative pedogenic trend, as in e.g. Harden et al. (1991).

259 All numerical analysis were carried out using R 2.15.1 software (R Development Core Team
260 2000).

261 The chronofunctions of the pedogenic development indices and of many other edaphic
262 parameters during early stages of pedogenesis were calculated with the *lm* function. Only
263 young sites (0-190 years old) on the eastern and western lateral moraines were used. The best
264 variable transformation was selected according to the significance obtained; usually, the age
265 factor was log-transformed. The chronofunctions should be interpreted in a qualitative way, as
266 the sampling site number was excessively small to obtain statistically significant data.
267 Significant differences in many edaphic parameters between different vegetation types were
268 also checked and displayed as boxplots, using the *multcomp* R package (Hothorn et al. 2008).

269

270 **3 Results**

271 **3.1 Pedogenic trends along the chronosequences**

272 The differences in parent material composition of Eastern and Western moraines were
273 confirmed by mineralogical analyses. The coarse sand fraction of the C horizons was
274 composed almost exclusively of serpentine minerals on the western side, while micas, quartz,
275 amphiboles, alkali feldspars and plagioclases were clearly visible in the soil parent material of
276 the sites on the eastern moraine (Fig. 2). No major mineralogical variations were observed
277 along the LIA chronosequences (not shown).

278 Only A, AC/CA and C horizons were observed on all LIA lateral moraines and on the basal
279 till deposited between present day and 1860 (Table 2). Most LIA soils were classified as
280 Haplic Regosols (Eutric, Skeletic) (IUSS Working Group 2006). The organic matter
281 accumulated in A horizons was mostly composed of living or dead roots; weak signs of
282 humification were noted in some of the oldest LIA soils, particularly on the eastern lateral
283 moraines (darker colors, granular structure). On stable basal till, a fast acceleration of
284 pedogenesis was observed on surfaces deposited between the largest LIA advance and ca.
285 1860, with the development of visibly bleached E horizons, characterized by weak laminar
286 structure and strong weathering of stones. Below this eluvial horizon, an incipient Bs had
287 developed (Entic Podzol). Outside the proglacial area, pre-LIA (late glacial) soils were well
288 developed Podzols (Haplic Podzols, IUSS Working Group 2006) on the eastern side of the
289 valley, Haplic Cambisols (Dystric) on the opposite western slope. A weak mineral weathering
290 in surface horizons of young soils was evidenced by slightly more yellow colors than the
291 bluish substrate (table 2). The chronofunctions of BWind in soils younger than 190 years old
292 (Eq. 1, Fig. 3a) showed a rather slow increase in color development in young soils, which was
293 only slightly faster on the eastern lateral moraines, which was described by the equation:

294

$$295 \text{ BWind} = -0.050 + 0.019 * \log(\text{age}) \quad (p < 0.01, \text{ non significant intercept}) \quad (1)$$

296

297 The BWind calculated in the late glacial Podzol was much higher than the value predicted by
298 the young soils chronofunction.

299 TOCind, indicator of TOC accumulation in all pedogenic horizons, increased faster with time
300 in the eastern lateral moraines soils than in the western ones, but the chronofunction
301 calculated on LIA soils was not significant (Fig. 3b). The rate of TOC accumulation on the
302 flat basal till was often higher. In late glacial soils on the western lateral moraines, the
303 TOCind values slightly positively deviated from the trend found in younger soils, while the
304 difference on the eastern moraines was much larger.

305 Solum acidification (pHind) proceeded faster in LIA soils on the eastern crests (Fig. 3c, Eqs.
306 (2) and (3)):

307

$$308 \text{ pHindW} = -0.249 + 0.098 * \log(\text{age}) \quad (p < 0.05, \text{ non significant intercept}) \quad (2)$$

309

$$310 \text{ pHindE} = -0.455 + 0.187 * \log(\text{age}) \quad (p < 0.05, \text{ non significant intercept}) \quad (3)$$

311

312 The pHind calculated in the late glacial Podzol was much lower than the values predicted by
313 the 0-190 years old soils chronofunction, evidencing a steady state reached between 190 and
314 11500 years ago; a similar trend was found on the western lateral moraines. The faster
315 acidification on the eastern moraines was confirmed also by the three units decrease of pH
316 value in surface horizons from the youngest to pre-LIA sites (Fig. 3d). On the western
317 moraines, the steady state of pH in surface horizons was uncertain, as the chronofunction (Eq.
318 (5)) was not significant.

319

$$320 \text{ pHE} = 8.84 - 0.44 * \log(\text{age}) \quad (p < 0.01) \quad (4)$$

321

$$322 \text{ pHw} = 7.67 - 0.17 * \log(\text{age}) \quad (p < 0.1) \quad (5)$$

323

324 The trend in solum acidification on the flat basal till with high plant cover was similar to that
325 measured on the eastern lateral moraines (Fig. 3c and 3d).

326 Podzolization was identified on the oldest LIA member of the basal till (C8), where Fe_{ox}, Fe_d
327 and TOC were already redistributed to the incipient Bs horizons, and in well developed
328 Podzols on the late-glacial till on the eastern lateral moraines (E6, Table 3).

329

330 **3.2 Soil chemical properties in surface horizons along the chronosequences**

331 Traces of carbonates were found in the young soils in the Verra Grande forefield, probably
332 derived from lenses of oficalcite included in the serpentinite mass (Table 4). They soon
333 disappeared from surface horizons and from the whole profile in the oldest, acidic soils.

334 TOC was normally well correlated with many exchangeable elements and available nutrients
335 (Table 5). In surface horizons in particular, exchangeable Mg, Ca and K, and available
336 macronutrients (N and P) were strongly positively correlated with TOC, particularly on the
337 western lateral moraines and on the basal till. On the eastern moraines, the relationships were
338 more confused and often not significant.

339 N concentrations in surface horizons sharply increased in LIA soils, and were highest on the
340 eastern lateral moraines. In pre-LIA (climax) soils, the N concentrations were slightly lower
341 than in younger soils. N below pioneer communities on the basal till was similar to the
342 western lateral moraines, and lower than below forest-shrub communities (Fig. 4a).

343 The Ca/Mg ratio, important component of the serpentine syndrome, was usually higher than
344 0.5 (Table 4), and had a general decreasing trend with age (Fig. 4b). This was particularly
345 visible on the eastern moraines, where the decrease followed Eq. (6).

346

$$347 \text{Ca/Mg}_E = 1.96 - 0.21 * \log(\text{age}) \quad (p < 0.01) \quad (6)$$

348

349 Available P in surface horizons (Fig. 4c) was at least an order of magnitude lower on the
350 western moraines, composed of pure serpentine, than on the eastern ones, also in initial soils
351 (0.06 vs. 0.72 mg kg⁻¹). On the eastern lateral moraines, available P increased with time
352 according to the chronofunction (Eq. (7)):

353

$$354 P_{\text{olsenE}} = -2.81 + 0.88 * \log(\text{age}) \quad (p < 0.05, \text{ non significant intercept}) \quad (7)$$

355

356 Extremely low P_{olsen} values were measured also on the basal till, except where a forest cover
357 with ericaceous shrub understory had developed. On same-age, stable sites on the basal till,
358 P_{olsen} concentration under larch/Ericaceae showed a 10 fold increase compared to pioneer
359 communities, and it increased much faster in the upper soil horizons.

360 Exchangeable Ni increased in surface layers of LIA soils with time, particularly on the
361 western lateral moraines (Fig. 4d); in older soils, Ni had much smaller values. Exchangeable
362 Ni had a weak correlation with organic carbon (Table 5).

363

364 **3.3 Depth trends in soil chemical parameters and effect of vegetation**

365 The depth trends of many chemical parameters evidenced the rather different speed of
366 pedogenic development in the different morainic environments in the Verra Grande forefield.
367 In particular, the Ca/Mg ratio was usually higher in subsurface than in surface horizons in the
368 western lateral moraines soils (Fig. 5a), in very young soils in general and in weakly
369 podzolised ones. Exchangeable Ni had higher concentration in subsurface horizons than in
370 surface mineral ones under climax and near-climax forest vegetation in stable positions and in
371 the most weathered soils (Table 3, Fig. 5b). The ratio between Ni concentration in subsurface
372 vs. surface horizons under high larch tree cover but low ericaceous shrubs was not higher than

373 under pioneer or grassland communities (not shown). The ratio between TOC concentration
374 in subsurface vs. surface horizons was significantly higher under climax and quasi-climax
375 forest communities (with high ericaceous cover, Fig. 5c) than under other vegetation types;
376 the same significant difference is shown for the TOC concentration normalized by horizon
377 thickness (not shown). Pioneer communities were also characterized by a significantly smaller
378 pH decrease in surface horizons along the chronosequences (Fig. 5d).

379

380 **4 Discussions**

381 **4.1 Slow pedogenesis on serpentinite**

382 Several pedogenetic processes occur in the Verra Grande forefield, under the mutual influence
383 of vegetation and parent material mineralogy (Fig. 6).

384 Soils were weakly developed (Regosols, IUSS Working Group 2006) both from the
385 morphological and chemical points of view, up to 190 years of age. In particular, on the
386 western lateral moraines the soils were the least developed of all. The Buntley-Westin color
387 index suggests a very slow Fe release and crystallization, which can be considered a proxy for
388 a slow mineralogical evolution, particularly in the early stages of pedogenesis. The BW index
389 chronofunction (0-190 years old soils) was slightly steeper on the eastern lateral moraines and
390 on the basal till under larch forest with Ericaceae ("climax" vegetation), thanks to a greater
391 solum thickness associated with more productive and acidifying plant communities. The color
392 development was much greater in the old Podzol on the eastern lateral moraines. The BW
393 index of the old Cambisol in the west was slightly higher than the chronofunction curve,
394 suggesting an increase in the weathering rate in later stages of soil development.

395 If we compare the soil formation rates in the Verra Grande forefield with the ones calculated
396 in other chronosequences (approximating the bulk density at 1.5 g cm^{-3} as in Egli et al. 2014),
397 we observe particularly slow rates in the western lateral moraine system (Fig. 7a): excluding
398 the coarse fragments, the soil formation rate varied between $0 \text{ t km}^{-2} \text{ y}^{-1}$ in the youngest soils
399 and $432 \text{ t km}^{-2} \text{ y}^{-1}$ in 90 years old soils. Higher rates were calculated in LIA soils on the
400 eastern lateral moraines and on the basal till (highest values in 130 years old soils, up to 1000-
401 $1300 \text{ t km}^{-2} \text{ y}^{-1}$), in the range calculated in other Alpine chronosequences on granitoid rocks
402 (Egli et al. 2014, and calculated from the data shown by D'Amico et al. 2014a). However, in
403 Alpine chronosequences on sialic rocks, the rates were highest in the youngest soils (up to
404 $2600 \text{ t km}^{-2} \text{ y}^{-1}$), and then decreased to $300\text{-}1250 \text{ t km}^{-2} \text{ y}^{-1}$ in older LIA ones, following an
405 exponential decline function, thus confirming a delayed start of pedogenesis on serpentinite-
406 dominated parent materials. A humped curve is expected when relating soil production from

407 regolith with soil depth (Humphreys and Wilkinson 2007) and similar trends have been
408 observed in post-mining chronosequences on sandy parent materials under boreal forests (e.g.
409 Celi et al. 2013) or in coastal lake sand dunes (Lichter et al. 1998). A greater specificity of the
410 soil parent material seems to be present in proglacial chronosequences as the humped soil
411 formation curve was visible only in serpentine-dominated soils.

412 The organic matter accumulated in the soil profiles faster in the eastern LIA sites and on the
413 flat basal till, in agreement with the poor primary productivity characterizing the western
414 sites. The accumulation of organic matter in turn influenced the development of all other
415 chemical properties thanks to the increase of the cation exchange capacity that caused a
416 temporary increase in available bases, nutrients and metals.

417 Another effect mainly related to organic matter accumulation was surface acidification, as
418 frequently reported in proglacial areas (e.g. Bernasconi et al. 2011). The higher organic matter
419 accumulation on the eastern lateral moraines induced a faster pH decrease in surface horizons,
420 while the higher initial carbonate content contributed to the higher intercept of the
421 chronofunction. The trends were similar (slightly higher values on flat surfaces) when
422 considering the acidification of the whole profiles (pH_{ind}). In agreement with the humped
423 curve of the soil formation rate, sigmoid curves could generally represent the variations of
424 soil properties with time. The acidification sigmoid in the Verra Grande chronosequences
425 showed different curve parameters on the different morainic environments: a slow pH
426 decrease characterized the first decades, as shown by the negative intercept of the pH_{ind}
427 chronofunction and the intercept in the surface pH chronofunctions higher than the E1 and
428 W1 values. After the encroachment of vegetation (slower and reduced on the western lateral
429 moraines), the acidification rate increased, to reach a steady state in later stages of soil
430 development (evidenced by the late glacial sites, whose pH and pH_{ind} values lie far from the
431 curve based on LIA sites). On the western lateral moraine, the pH values in 190 years old
432 soils were similar to those characterizing old climax soils, but the high micro-scale variability,
433 shown by the non linearity of the pH decrease on LIA materials, makes the steady state
434 difficult to define. A larger number of samples of intermediate ages might show a better pH
435 trend in this environment.

436 A sigmoid curve could also properly represent the TOC accumulation and mineral weathering
437 (BWind) in the western chronosequence, while in the eastern one the speed of soil
438 development increased again in later stages, thanks to the onset of the podzolization process,
439 after some (probably) hundreds or thousands of years.

440 Comparing the acidification trends on serpentinite and on other substrates from different
441 chronosequences in subalpine environments, we observe a slower and shallower pH decrease
442 on serpentinite, thanks to the base-rich parent material. For example, in the nearby Lys
443 forefield (D'Amico et al. 2014a), the initial pH in freshly deposited gneissic till was 6.6 (ca 1
444 unit lower than in the western part of the Verra Grande forefield), and it decreased to 4.6 in
445 130 year old soils. Similar values were obtained in the Damma glacier forefield (Bernasconi
446 et al. 2011). Comparing the TOC concentrations in the most productive chronosequence
447 (eastern lateral moraines), we observe a slower increase, particularly in subsurface horizons,
448 than on gneiss (e.g. D'Amico et al. 2014a; Egli et al. 2001) or in mixed materials (e.g. He and
449 Tang 2008). In order to compare the organic matter accumulation in the Verra Grande
450 chronosequences with other alpine chronosequences, we calculated the TOC_{ind} from
451 available data for the Morteratsch (Egli et al. 2012) and Lys forefield (D'Amico et al. 2014).
452 The TOC accumulation in serpentine soils was usually around the lowest limit of the range
453 measured on granitoid rocks (Fig. 7b).

454 The extremely slow increase in plant cover on pure serpentinite maintained high erosion rates,
455 which reduced the encroachment of new plants and, in turn, slowed down soil development.
456 Erosion was partially reduced by the widespread presence of a thin, black cryptogamic crust,
457 which also increased organic carbon and nutrient concentrations at the surface of these weakly
458 developed soils. Cryptogamic crusts on cold desert soils increase N concentration thanks to
459 N-fixating cyanobacteria and thus ameliorate the physical environment by reducing erosion
460 and increasing water retention; in fact, cryoptobiotic crusts are reported to increase the speed
461 of plant colonization (Breen and Levesque 2008). On the essentially flat intramorainic basal
462 till, plant cover increased slightly faster thanks to reduced erosion. However, the species
463 turnover and the chemical variations with time were extremely slow as well (outside the forest
464 patches).

465 Cryoturbation also limits soil development throughout the Verra Grande forefield, mutually
466 linked with the slow vegetation encroachment and slow pedogenesis. A small active rock
467 glacier, indicator of sporadic permafrost on the Alps (Guglielmin 1997) is present at 2500 m
468 on the western lateral moraine. Evidences of cryoturbation in the soils, such as silt caps on the
469 upper surfaces of stones and a platy vesicular structure, were more visible than in other
470 nearby proglacial areas (D'Amico et al 2014a), possibly thanks to a greater silt content. Frost
471 heave and moving freezing fronts during dry winter months are the main factors involved in
472 silt translocation and the formation of silt caps (Ugolini et al. 2006; Frenot et al. 1995). Frost
473 heave is more effective where vegetation cover is scarce (Ugolini 1966), and its effects

474 include the formation of platy structure with high porosity (vesicular structure). The
475 establishment of vegetation destroys this cryogenic structure, both because of bioturbation
476 and because of reduction in number and amplitude of freeze-thaw cycles (Crocker and Major
477 1955; Ugolini 1966).

478

479 **4.2 The development of serpentine soil properties, and the effect of sialic inclusions**

480 Oficalcite inclusions were probably correlated with the quite high Ca/Mg ratio recorded in
481 young soils of the considered proglacial area, usually higher than 0.5 (Table 3); “normal”
482 values on serpentinite should range between 0.01 and 0.1 (Brooks 1987). Initial soils in the
483 eastern moraine system had the highest Ca/Mg ratio, probably thanks to the presence of
484 plagioclases. The pH decrease may have enhanced carbonate dissolution and Ca leaching,
485 accounting for the decreasing Ca/Mg ratio observed particularly on the eastern lateral
486 moraines. In fact, most acidic soils in Valle d'Aosta have exchangeable Ca/Mg ratios below
487 1.5, also on sialic parent materials (unpublished data). On serpentinite, under forest
488 vegetation, the lowest values were found in the most acidic podzolic soils, while in other less
489 acidified soils Ca biocycling and bioaccumulation tended to increase the Ca/Mg ratio above
490 unity (D'Amico and Previtali 2012; D'Amico et al. 2014b). The ratio between the Ca/Mg ratio
491 in subsurface vs. surface horizons, however, suggests that actually Ca bioaccumulation occurs
492 only on the eastern moraines and on the basal till (higher values in surface horizons). On the
493 western moraines Ca leaching from surface A horizons, likely associated with the dissolution
494 of carbonate traces, was poorly limited by a weak biocycling associated with the low primary
495 production.

496 Exchangeable Ni had an initial increase, followed by a decrease in mature soils, with a
497 sharper trend on the western lateral moraines. In the E soils, the initial increase in Ni was
498 small, probably due to the higher acidification rate. Barren soils often have smaller amounts
499 of exchangeable Ni when compared with vegetated sites (Lazarus et al. 2010; Chiarucci
500 2004); however, in our chronosequences, exchangeable Ni increases faster under low plant
501 cover, while the most developed soils under climax coniferous forest with ericaceous
502 understory have low exchangeable Ni, because of strong leaching (D'Amico and Previtali
503 2012). The depth trend of exchangeable Ni shows metal leaching from surface and
504 accumulation in deeper horizons below larch forest-ericaceous vegetation also in very young
505 soils, where rejuvenating erosive processes are weak, even if no pedogenic Fe or Al
506 production and leaching were detectable (not shown). This depth trend, dependent on the

507 abundance of conifers and Ericaceae, could be related to incipient podzolization, initially
508 active on the most mobile metals (such as Ni).

509 Available phosphorus was probably the single elemental characteristic which differed the
510 most between the two lateral moraine systems. Its concentration rapidly increased on the
511 eastern lateral moraines, after having started at a much higher level on the bare, fresh till, than
512 on the opposite moraine system. In the E sites, the contribution of a sufficient P content,
513 probably derived from the early weathering of sialic rock fragments which contain some P-
514 bearing apatite, permitted a fast, complete colonization by herbaceous species, which reduced
515 erosion despite the slope steepness. It is well known that sialic gneiss and schists (whose
516 presence was verified by XRD analysis) contain 5 or 6 times more P than ultramafic rocks
517 (e.g. Porder and Ramachandran 2013). The more complete plant cover, in turns, is related
518 with the faster increase in TOC concentration in the A horizons on the eastern lateral
519 moraines, accounting for the steeper chronofunction of available P concentration caused by
520 biocycling and bioaccumulation.

521 On the opposite side of the valley, on pure serpentinite, the P concentration was extremely
522 low throughout the chronosequence, and it was probably one of the most important limiting
523 factors for plant colonization in this area (Nagy and Proctor 1997; Vitousek et al. 2010).
524 Thanks to the good correlation with TOC and, thus, with vegetation productivity, the P
525 concentration had two different trends on the flat basal till; it followed more or less the
526 eastern chronofunction under well developed forest vegetation, while it followed the western
527 chronofunction under pioneer vegetation. A weak P bioaccumulation was induced by the
528 cryptogamic crust on the western moraines, but this was limited to few millimeters on the soil
529 surface. Such decoupling indicates a strong effect of vegetation on the bioaccumulation of
530 available P in surface horizons.

531 Available P keeps increasing with time and reaches the highest values in the most acidic and
532 the most developed late glacial Podzol, suggesting a different trend with respect to the usual
533 one of E horizons of podzolic soils (Celi et al. 2013). The general trend towards an
534 amelioration of soil fertility was particularly strong under the most productive subalpine
535 forest vegetation. A strong ameliorating effect of conifers on serpentine soils has been
536 recognized during secondary plant successions in many regions of the world, such as
537 Mediterranean Italy (Chiarucci 2004) or the savannahs of eastern USA (Barton and
538 Wallenstein 1997).

539

540 **4.3 Effect of subalpine vegetation on pedogenesis: incipient podzolization?**

541 Podzols are the climax soils in the subalpine phytoclimatic region, and 600-3000 years are
542 considered necessary for the formation of Podzols on silic materials on the Alps (e.g. Egli et
543 al. 2006; Zech and Wilcke 1977). Much faster rates of Podzol formation have been reported
544 in some proglacial chronosequences in the Aosta Valley, such as in the nearby Lys glacier
545 forefield (D'Amico et al. 2014a): E horizons appeared soon after the establishment of climax
546 subalpine larch forest with a thick ericaceous understory. Also on serpentinite, podzolic soils
547 with thick E horizons overlying weakly developed Bs horizons are commonly found on stable
548 surfaces under subalpine forests with northward aspects in the Aosta Valley (D'Amico et al.
549 2008), in spite of the fact that the high base content and the fast weathering should inhibit
550 podzolization on ultramafic materials (Lundström et al. 2000). Also in our study area, well
551 developed Podzols were characteristic of late glacial materials, particularly on the slightly
552 colder and less steep eastern side of the valley (profile E6), while on the slightly drier western
553 valley side, only Cambisols (Dystric) were found.

554 The onset of podzolization seems to have taken place soon after the substitution of pioneer,
555 basophilous plant communities by acidophilous, "climax" ones, on flat surfaces, during the
556 time lapse between the most extensive LIA advance and 1860. Rather high pH values
557 characterize the bleached E horizon in the older LIA podzolic soils. Similarly high pH values
558 were found in surface A and E horizons of podzolized soils on serpentinite (e.g. Sasaki et al.
559 1968; Lee and Hewitt 1982). We can exclude that this light gray horizon is made of
560 "younger", C-like materials, thanks to the high degree of weathering of the material (the rock
561 fragments were soft and easily crushed by hand pressure), the much lower pH and the
562 widespread presence of this sequence of horizons on the similar-age glacial till.

563 In the nearby Lys glacier forefield, the largest glacier extent was reached in 1821 (Monterin
564 1914), and most glaciers in the Alps reached their largest Holocene extension during the first
565 half of the 19th century (Ivy-Ochs et al. 2009). Similarly, the southernmost LIA moraine of
566 the Verra Grande forefield was attributed to the same glacier advance (e.g. Vanni 1945).
567 However, the development degree of the podzolic soils belonging to the largest LIA glacier
568 extension in the Verra Grande forefield seems incompatible with the moraine's young age
569 (from the extremely weakly developed Regosol on the 1861 material to the podzolic soil on
570 the presumed 1821 till). The presumed 1821 materials (between the 1861 recessional and the
571 terminal LIA moraine) could thus be ascribed to older glacier advances. Indeed some glaciers
572 in the Western and Central Alps approached or reached their maximum LIA extent at the end
573 of the 14th or 17th century instead of the 19th century. For example, the Gorner glacier on the

574 northern flank of the Monte Rosa Massif in Valais (CH) (less than 10 km north of the Verra
575 Grande glacier), reached its maximum LIA extent around 1380 (Holzhauser et al. 2005).
576 Moreover, Mortara et al. (1992), by dating the soil organic fraction in the Ab horizon of two
577 smaller lateral moraines outside the LIA ones (at 2600 m a.s.l. outside the western moraine,
578 and at 2300 m a.s.l. outside the eastern moraine), found that these moraines were deposited at
579 least 950 ± 185 yr B.P. and < 200 yr B.P. respectively. The former date witnesses a period of
580 the Holocene before 1820, when the upper part of the Verra Grande Glacier was more
581 extensive than during the LIA peak, whereas the latter evidences the presence of LIA glacial
582 deposits outside the terminal moraine of the LIA maximum.
583 We can also exclude that this glacial material was deposited in more ancient periods (i.e. late
584 glacial), because of the shallowness of the soil profiles, the much weaker weathering degree
585 and the much higher pH values than those of pre-LIA sites. Moreover, it is well known that
586 Alpine glaciers reached their largest Holocene surface during the LIA (Joerin et al. 2006).
587 Although a more precise dating of the southernmost moraine system is necessary for the
588 development of precise chronofunctions for soil and vegetation development, Entic Podzols,
589 with thin albic and weakly developed spodic horizons (C8), seem to form in 500-1000 years
590 in this serpentinite forefield. The time required for Podzol formation on serpentinitic till
591 apparently is some centuries longer than in nearby gneissic till (D'Amico et al. 2014a), but it
592 is still quite short comparing with the normal range necessary for podzol formation on sialic
593 materials in the Alps (Egli et al. 2006; Zech and Wilcke 1977).

594

595 **5 Conclusions**

596 In this study we evaluated the main pedogenetic processes occurring in recently deglaciated
597 areas on serpentinite in the Western Italian Alps. As usual in proglacial chronosequences,
598 young soils are characterized by acidification, organic matter accumulation and mineral
599 weathering: however, on serpentinite, these processes operate more slowly than on other
600 parent materials. Small quantities of gneiss in the parent till appear to increase the speed of
601 encroachment by grassland species. The higher organic matter input thereby increases the
602 acidification rate and nutrient biocycling. The slopes of the chronofunctions of the main
603 chemical properties and of pedogenetic indicators are often significantly greater and confirm
604 the enhanced rate of pedogenesis where the serpentinitic till is enriched by small quantities of
605 sialic rocks. Strong surface erosion and cryoturbation with very low vegetation cover
606 characterize instead the first few hundreds of years on pure serpentinite. This is associated
607 with soils poor in available nutrients. On flat surfaces (ground moraines), the encroachment

608 by Ericaceae in particularly stable sites seems associated with the onset of podzolization in
609 few hundreds of years. The strong edaphic limitations to plant encroachment and to primary
610 vegetation succession in young serpentine habitats might make these young ecosystems
611 particularly vulnerable to environmental variations caused by global change.

612

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620

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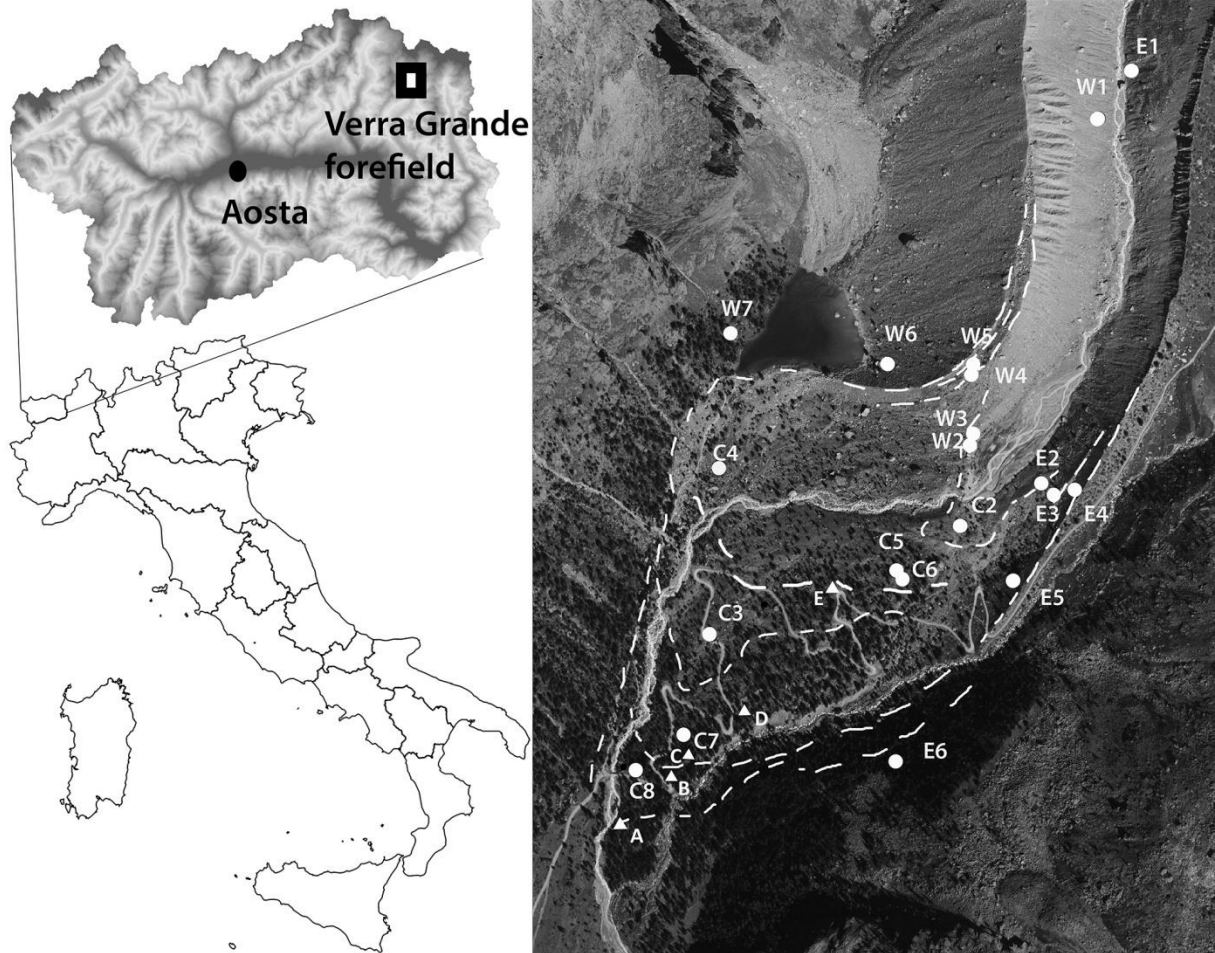
773 **Figure captions**

774

775 Fig. 1: a) The Verra Grande glacier forefield in the North-western Italian Alps. b) Soil

776 sampling sites (full dots) and forest sites where tree maximum age was detected (full triangles

777 from A to E).

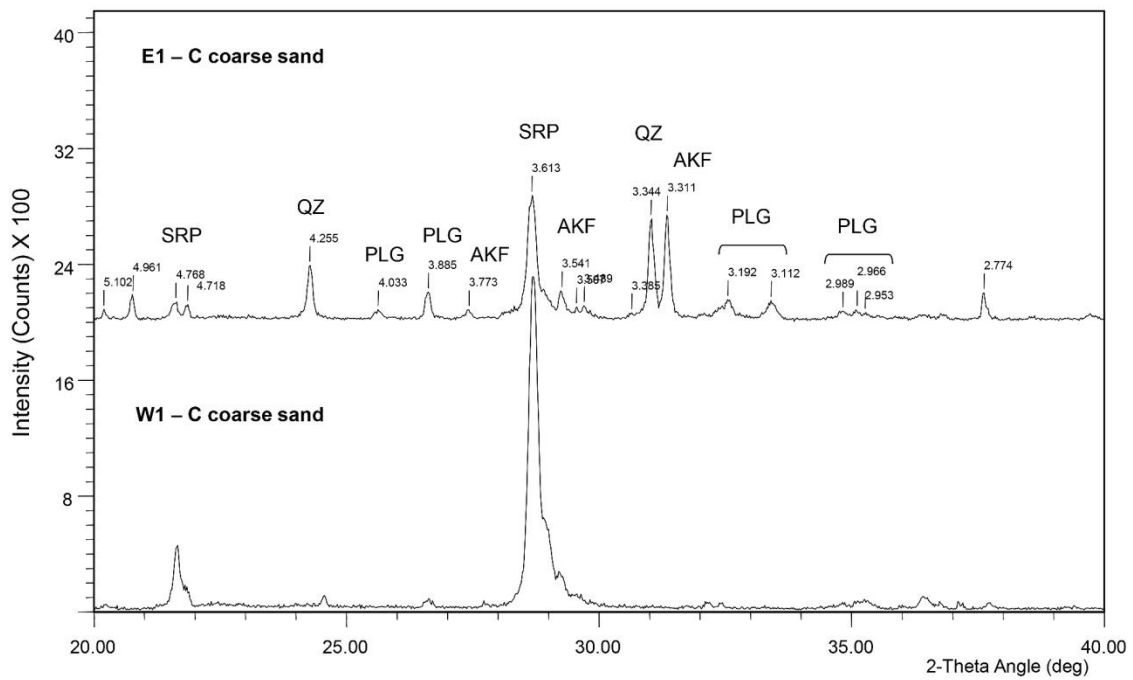


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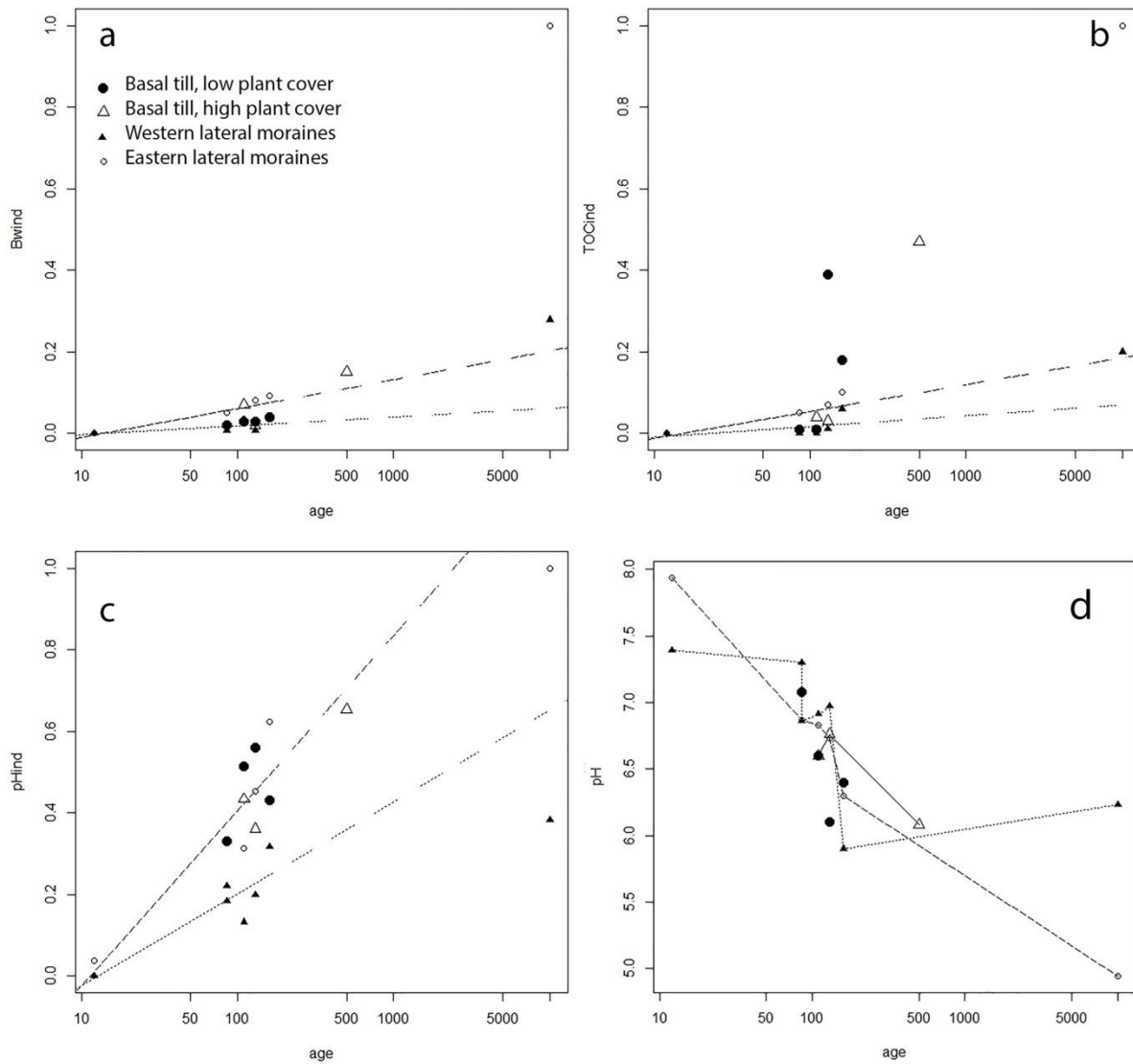
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781 Fig. 2: X-ray diffraction patterns of the coarse sand fraction of C horizons from the eastern
 782 and western initial terms of the chronosequence parent. d-spaces are in Å. Abbreviations are
 783 as follows: SRP: serpentine minerals; QZ: quartz; AKF; alkali-feldspars; PLG: plagioclases.



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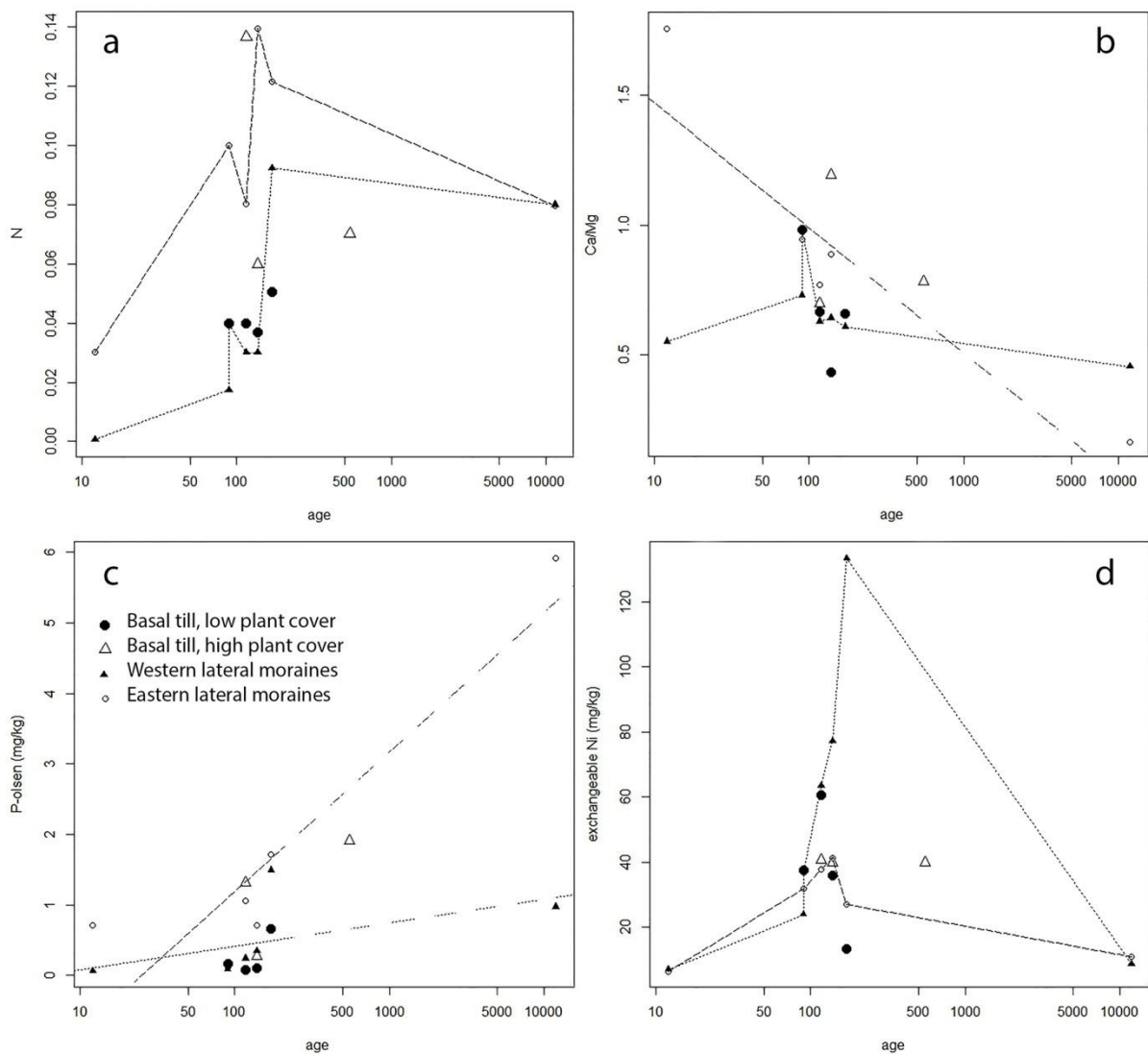
786 Fig. 3: Time trends of pedogenic development indicators: the Buntley and Westin color index
 787 (BWind, a); the TOC normalized by horizon and profile thickness (TOCind, b); the difference
 788 between pH values in soil horizons and the initial soil normalized by profile thickness (pHind,
 789 c); and the pH values. The dashed and the dotted lines in (a), (b) and (c) show the significant
 790 chronofunctions of the indicators respectively in eastern and western lateral moraines,
 791 calculated on LIA soils; the change in the line style denote the end of the validity range of the
 792 chronofunctions. Broken lines in (d) are drawn to better show trends



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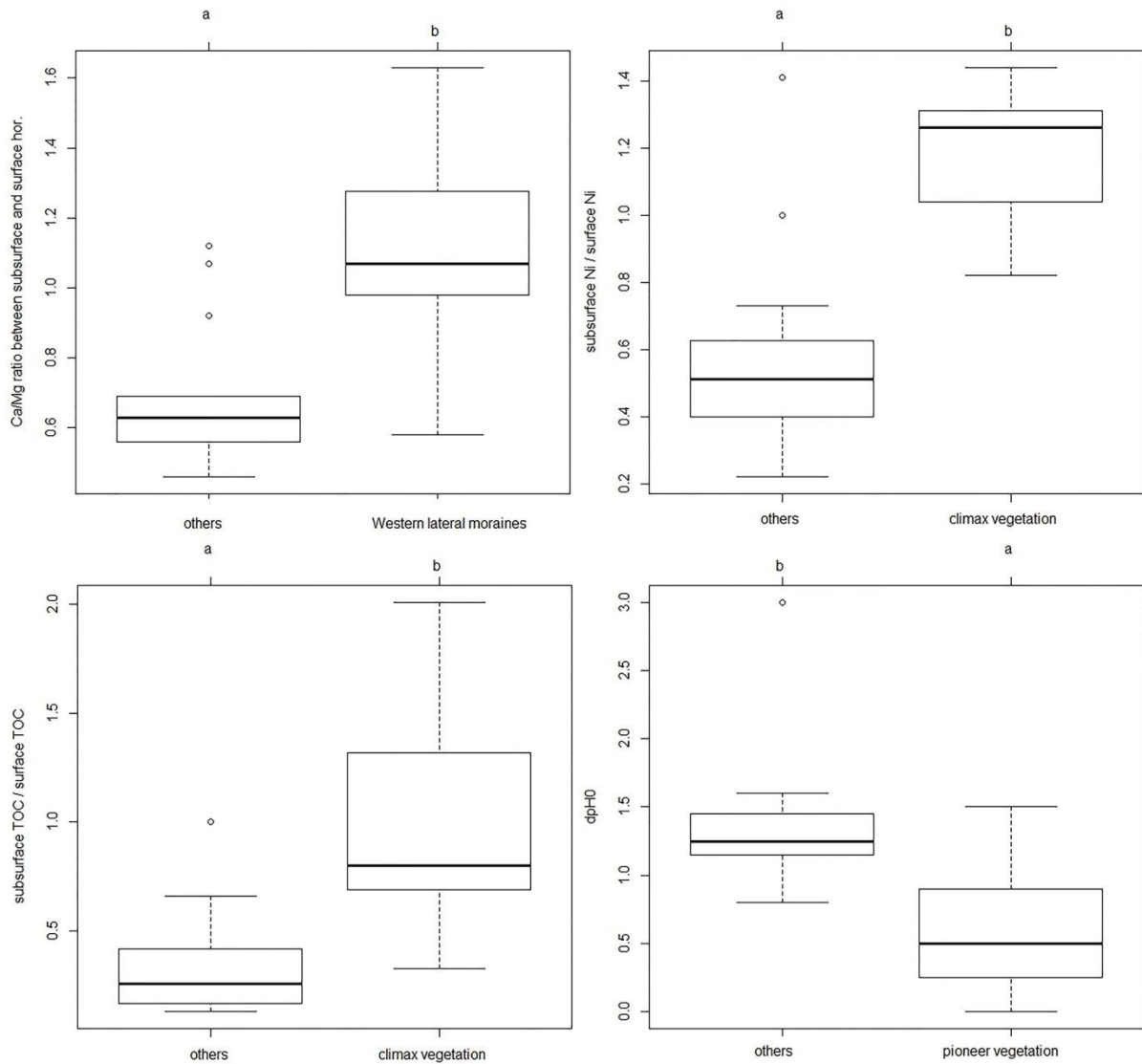
795 Fig. 4: Changes with age of deposition of the moraines of: N (%); Ca/Mg ratio (b); available P
 796 (P_{olsen}) (c); exchangeable Ni (d); on the eastern lateral moraine system (empty circles, dashed
 797 lines), on the western one (filled triangles, dotted lines), in forested flat basal till (large, empty
 798 triangles, large dashed lines) and under pioneer vegetation on flat basal till (large filled
 799 circles, solid lines). All values are derived from surface horizon analysis. The dashed and the
 800 dotted lines in (b) and (c) show the significant chronofunctions of the considered properties
 801 respectively in eastern and western lateral moraines, calculated on LIA soils; the change in the
 802 line style denote the end of the validity range of the chronofunctions. Broken lines are drawn
 803 to better show trends.



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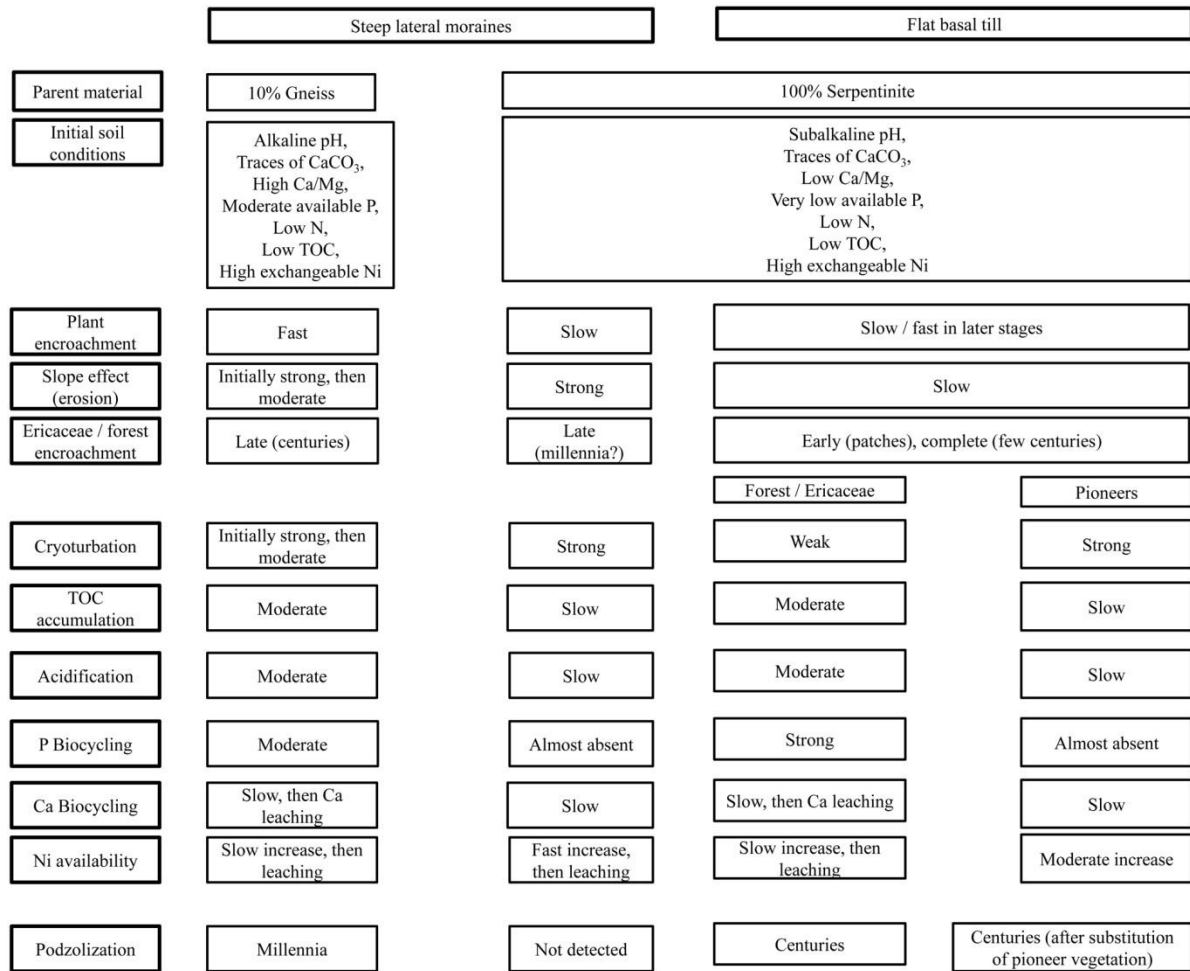
806 Fig. 5: Different Ca/Mg ratio in subsurface and surface horizons, indicated by the ratio
 807 between their respective values, in the western lateral moraines (a); ratio of exchangeable Ni
 808 (b) and TOC concentrations (c) in subsurface and surface horizons under climax or quasi-
 809 climax vegetation, the pH value decrease since moraine deposition, evidenced by the
 810 difference between the initial pH values and the value in each surface horizons, under pioneer
 811 plant communities or under other vegetation types (d). The dominance of ericaceous shrubs in
 812 the understory was used as indicator of climax plant communities. $p < 0.05$.



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814

815 Fig. 6: Conceptual diagram of factors influencing the speed of soil formation processes in the
 816 Verra Grande proglacial area.

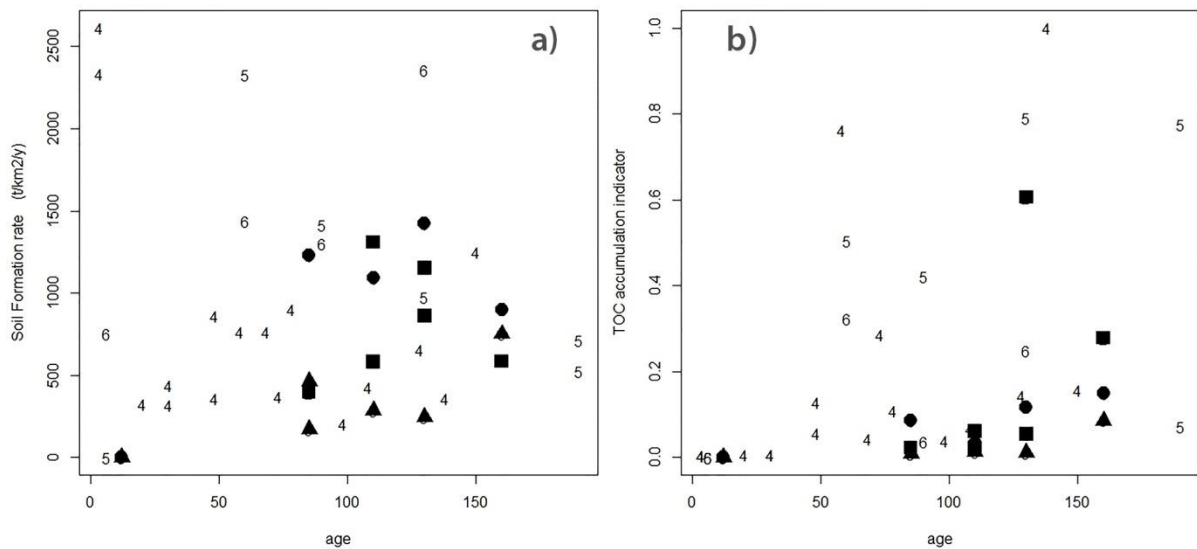


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820 Fig. 7: Soil formation rate according to the method described by Egli et al. (2014) and the
 821 TOC accumulation index (TOCind) in Verra Grande forefield (the eastern, western and
 822 central moraine systems are represented by respectively full circles, triangles and squares), in
 823 the Morteratsch forefield (number 4, from Egli et al. 2012 and Egli et al. 2014) and in the Lys
 824 forefield (number 5 for forest habitats and number 6 for subalpine grassland, from D'Amico et
 825 al. 2014a).



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Table 1: main environmental properties of the study sites

site ^a	Year of deposition ^b	Elevation (m a.s.l.)	Aspect (°N)	Slope steepness (%)	bare soil (%)	Tree cover (%)	Parent material ^c
C2	1950	2255	200	1	40	30	SP
C3*	1880	2132	180	3	50	80	SP
C4	1921	2185	180	3	25	10	SP
C5	1921	2235	180	5	40	10	SP
C6*	1921	2235	180	8	20	20	SP
C7	1861	2120	180	3	40	60	SP
C8*	~1820-1300?	2080	160	10	0	80	SP
E1	2000	2318	270	35	50	0	SP (10% GN)
E2	1950	2260	250	25	20	5	SP (10% GN)
E3	1921	2275	260	35	30	5	SP (10% GN)
E4	1861	2285	260	30	1	5	SP (10% GN)
E5	1821	2250	300	30	0	5	SP (10% GN)
E6*	LG	2200	300	30	0	60	SP (<5% GN)

W1	2000	2315	90	35	99	0	SP
W2	1950	2252	60	10	85	0	SP
W3	1950	2257	60	30	40	30	SP
W4	1921	2260	240	30	75	0	SP
W5	1861	2265	240	30	50	0	SP
W6	1821	2225	300	35	20	1	SP
W7*	LG	2230	110	30	0	60	SP

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831 ^a: high ericaceous cover in the understory is evidenced by the * next to the site symbol

832 ^b: LG: Late Glacial, around 11500 years BP

833 ^b: SP: serpentinite, GN: gneiss

834

835 Table 2: selected macromorphological properties of the soils along the Verra Grande
 836 chronosequence. Oi horizons, 0.5 to 3 cm thick, were omitted from the list.

Site	Horizon	Depth (cm)	Color (Munsell, dry)	Structure ^a	Roots ^b	Rock fragments ^c (%)	Silt caps ^d
W1	C	0-25+	Gley1-6/10Y	AB	A	60	1
W2	A	0.5-3	5Y 5/2	GR, 2, w	A	30	
	C	3-21	5Y 5/1	L, 2, w	C	60	
	2C	21-35+	Gley1-6/10Y	L, 4, s	A	10	1
W3	AC	0-7	5Y 5/2	GR, 2, w	S	70	
	C	7-20+	Gley1-6/10Y	L, s, m		70	1
W4	O (biotic crust)	discontinuous					
	A	0-3	5Y 4/2	GR, 2, w	A	30	
	AC	3-10	5Y 5/2	GR, 2, w			
	C1	10-17	5Y 5/1	GR, 2, w	S	60	1
	C2	17-30+	Gley1-5/10Y	L, 4, w	A	60	1
W5	O (biotic crust)	0-0.4	2.5Y 2/1				
	A	0.4-4	5Y 5/1	GR, 2, w	AA	50	
	C1	4-17	Gley1-6/10Y	GR, 1, w	S	60	1
	C2	17-30+	Gley1/G	VS		70	2
W6	O (biotic crust)	0-0.2	2.5Y 2/1				
	A	0.2-8	2.5Y 2.5/1	GR, 2, w	AA	50	
	CA	8-19	5Y 4/1	GR, 2, w	A	70	
	C	19-40+	5Y 5.5/1	VS	S	80	2
W7	Oe/Oa	2-3					
	A	3-10	2.5Y 3.5/3	GR, 1, w	AA	10, WW	
	Bw	10-24	2.5Y 5.5/6	SP, w, fi	A	60	
	C	24-35+	2.5Y 5/3	SP, s, m	C	60	
E1	C1	0-8	5Y 5/1	AB	C	50	
	C2	8-30+	Gley1-6/10Y	AB	S	50	1
E2	Oe	0-1	10YR 2/1		A	0	
	A	1-9	5Y 4/3	GR, 1, w	A	30	
	AC	9-20	5Y 4/1	AB	A	60	
	C	20-40+	Gley1-4/10Y	AB	S	50	2
E3	A	0-3	5Y 3/2	GR, 1, w	A	50	
	CA	3-23	5Y 4/1	GR, 1, w	C, m	50	
	C	23-40+	Gley1-5/10Y	VS	S	60	2
E4	Oe	0-2	10YR 2/1	GR, 2, w	A		
	A	2-12	5Y 4/2 (60%), 2.5Y 3/2 (40%)	GR, 2, w	A	50	
	CA	12-30	5Y5/2	GR-SP, 2, w	C, m	60	2
	C	30-40+	Gley1-5/10Y	VS	S	90	3
E5	Oa	1-2	10YR 2/1	M	AA		
	AC	2-13	2.5Y 5/3	SP, 2, m	C, m	60	2

E6	C	13-50+	5Y 5/1	VS, s	C	70	3
	Oe	2-5					
	Oa	5-12	7.5YR 2/1	M			
	E	12-21	10YR 6/2	L, 4, w	C	10 WW	
	Bs1	21-42	7.5YR 5/4	SP, 3, m	C, co	20 WW	
	Bs2	42-63+	7.5YR 5/4	SP, 3, m	S, C, co	50 W	
C2	A	0.5-7	5Y 5/2	GR, 2, w	A	30	
	C	7-30+	5Y 5/1	L, 2, w	C	60	1
C3	Oe	4-7			A		
	A	7-10	5Y 4/2	GR, 2, w	A	50	
	AB	10-18	2.5Y 5/3	SP, 2, m	C	50	
	C	18-30+	Gley1-5/10Y	VS	S	70	2
	Oe	0-2	10YR 2/1	GR			
C4	A	2-8	2.5Y 4/2	GR, 2, w	C	50	
	C1	8-21	5Y 5/1	L, 2, w	C	50	2
	C2	21-35	5Y 5/1	VS	S	60	3
C5	Oe	0.5-3					
	A	3-7	Gley1 4/1	GR, 2, w	C	50	
	CA	7-21	5Y 5/1	GR, 2, w	C	60	
	C	21-32+	Gley1 5/5GY	VS	S	60	1
C6	Oe	1-4		M			
	A	4-9	2.5Y 2.5/1	GR, 2, w	C	40	
	AC	9-25	5Y 4/1	GR, 2, w	S	60	
	C	25-34+	5Y 5/1	VS	S	70	
C7	Oe	1-2					
	Oa	2-4			AA		
	A1	4-8	5Y 4/2 (2.5Y 3/2, 30%)	GR, 2, w	A	30	
	AC	8-18	5Y 5/2	GR, 2, w	C, m	60	1
	C	18-23+	Gley1-5/10Y	VS, cemented	S	60	3
C8	Oe-Oa	3-9	7.5YR 2/1	M	A		
	E	9-13	2.5Y 5/2	L, 3, w	A, m	20, WW	
	Bs	13-21	10YR 4/3	GR, 3, w	C	50, W	
	C	21-50+	5Y 5/1	VS	S	60	3

837

838 ^a GR: granular; PL: platy; PS: subangular blocky; MA: massive; RS: rock structure; AB:
839 absent; M: matted (O horizons). 1: very fine; 2: fine; 3: medium; 4: coarse. W: weak; m:
840 moderate; s: strong.

841 ^b AA: very abundant; A: abundant; C: common; S: scarce. m: mid-sized roots; co: coarse
842 roots.

843 ^cW: weathered; WW: highly weathered

844 ^d1: silt caps up to 1 mm thick, visible on few rock fragments; 2: silt caps up to 2 mm thick,

845 visible on many rock fragments; 3: silt caps up to 2 mm thick, visible on most rock fragments

846 Table 3: Ammonium oxalate- (Fe_{ox} , Al_{ox}) and dithionite-citrate-bicarbonate (Fe_d , Al_d)
 847 extractable Fe and Al in the oldest soils from the Western, Eastern and Central parts of the
 848 study area.

		$\text{Fe}_{\text{ox}}(\text{g kg}^{-1})$	$\text{Al}_{\text{ox}}(\text{g kg}^{-1})$	$\text{Fe}_d(\text{g kg}^{-1})$	$0.5\text{Fe}_{\text{ox}}+\text{Al}_{\text{ox}}$ (%)
W7	A	1.90	0.30	12.93	0.12
	Bw	1.53	0.27	13.40	0.10
	BC	1.02	0.28	7.52	0.08
E6	E	4.66	1.48	9.84	0.38
	Bs1	10.07	2.86	20.10	0.79
	Bs2	11.25	3.21	21.25	0.88
C8	E	3.85	0.25	4.70	0.22
	Bs	6.85	0.35	11.60	0.37
	C	4.23	0.20	3.15	0.23

849

850

851 Table 4: Chemical properties of the soils along the Verra Grande chronosequence. When a
 852 cell is empty the property was not determined.

Profile	Horizon	pH	CaCO ₃ g kg ⁻¹	C g kg ⁻¹	C/N	Mg cmol.kg ⁻¹	Ca/Mg	Ni _{ex} mg kg ⁻¹	P _{olsen} mg kg ⁻¹
W1	C	7.4	4.0	5.0		0.39	0.55	6.99	0.06
W2	A	6.9	0.0	6.1	15.3	0.66	0.73	23.88	0.17
	C	7.5	0.0	1.0		0.41	0.88	12.21	
	2C	7.6	1.2	0.1					
W3	AC	7.3	0.0	2.6	8.7	1.17	0.98	37.37	0.09
	C	7.8	0.0	1.5		4.35	0.06	24.12	
W4	O (bioticcrust)	7.0		19.3	14.9	1.74	0.89	76.43	
	A	6.9	0.0	3.5	11.7	0.74	0.63	63.42	0.24
	AC	7.1	0.0	2.3	11.1	0.32	1.03	46.02	
	C1	7.4	2.0	1.2	9.8	0.25	1.12	19.21	
	C2	7.5	3.2	0.2		0.38	1.16	18.99	
W5	O (bioticcrust)	6.5		16.8	14	2.07	0.66	4.62	
	A	6.9	0.0	4.0	13.3	0.97	0.64	77.16	0.35
	C1	7.6	1.1	1.0		0.36	0.86	39.41	
	C2	7.5	0.9	bdl		0.24	1.09	13.79	
W6	O (bioticcrust)	5.9		32.1	15.1				
	A	5.9		13.2	14.3	2.62	0.61	133.43	1.50
	CA	7.0	4.0	5.4	15.1	1.21	0.65	62.21	
	C	7.1	2.1	0.6		0.44	0.97	40.82	
W7	Oe/Oa	5.6		296.0	23.7				
	A	6.2		18.2	21.5	3.93	0.45	8.70	0.98
	Bw	6.3		12.6	21	3.59	0.43	9.02	
	C	6.4		3.0	15	1.99	0.40	2.63	
E1	C1	7.9	1.0	4.0	12.9	0.39	1.75	6.41	0.72
	C2	8.0	5.0	0.5		1.68	1.08	3.16	
E2	A	6.9	0.0	19.5	19.5	0.92	0.95	31.94	0.12
	AC	7.8	1.0	5.1	12.8	0.88	1.06	19.22	
	C	7.8	1.0	0.2		1.25	0.43	4.61	
E3	A	6.8	0.0	11.3	14.1	2.11	0.77	37.72	1.06
	CA	7.2	0.0	1.7	8.5	1.50	0.39	11.54	
	C	7.6	0.0	0.2	20	1.38	0.40	6.28	
E4	A	6.7	0.0	17.3	12.4	1.97	0.89	41.33	0.71
	CA	6.8	0.0	3.1	10.3	1.89	0.41	9.18	
	C	6.7	0.0	1.4		1.08	0.44	8.51	
E5	Oa	6.3		86.6	12.7				
	AC	6.3	4.0	18.6	14.1	2.59	0.66	26.95	1.71
	C	7.1	4.0	2.8	9.3	1.55	0.61	13.23	
E6	Oe	4.8		295.4	24.6				
	Oa	4.6		175.0	22.2				
	E	4.9		22.1	28.5	6.27	0.16	10.77	5.92

	Bs1	5.4		17.7	18.9	5.15	0.10	14.11	
	Bs2	5.6		17.7	16.2	4.99	0.11	16.94	
C2	A	7.1	0.0	6.7	16.5	1.17	0.98	37.33	0.17
	C	7.6	3.0	2.1	19.2	0.68	0.66	19.00	
C3	A	6.6	0.0	21.1	24.4	4.65	0.70	40.73	0.1
	AB	6.9	0.0	7.0	17.5	1.41	0.46	33.49	
	C	7.0	0.0	2.3	23	1.26	0.44	63.31	
C4	A	6.6	3.0	7.0	17.4	1.43	0.67	60.71	0.27
	C1	7.6	2.0	3.0	14.9	1.96	0.38	17.64	
	C2	7.7	6.0	1.1		1.61	0.29	3.36	
C5	Oe	6.5		281.0	23.93				
	A	6.7	0.0	11.4	19.0	1.66	0.70	39.86	0.09
	CA	7.2	1.0	4.3	20.6	1.01	0.48	56.29	
	C	7.3	2.0	2.4	15.3	1.13	0.42	39.11	
C6	Oe	5.9		305.5	26.1				
	A	6.1	0.0	7.3	24.4	1.38	0.43	35.86	1.31
	AC	6.7	0.0	14.7	22.8	3.00	0.46	51.58	
	C	7.0	0.0	3.4	18.64	2.21	0.44	48.21	
C7	Oa	6.3		241.1	25.1				
	A1	6.4	0.0	10.1	20.0	2.35	0.66	13.35	0.66
	AC	7.1	0.0	2.3	11.5	1.38	0.37	5.22	
	C	7.1	0.0	1.1		1.21	0.34	1.89	
C8	Oe-Oa	5.8		210.5	19.5				
	E	6.1		11.7	16.7	1.03	0.78	39.86	1.91
	Bs	6.6	0.0	15.4	17.1	3.71	0.37	50.10	
	C	7.1	0.0	2.5	12.5	2.16	0.34	30.84	

853

854 Bdl: below instrumental detection limit

855

856 Table 5: Pearson's correlation coefficient among chemical and site properties in the Verra
 857 Grande soil chronosequence

	pH	Ca _{ex}	Mg _{ex}	K _{ex}	Ca _{ex} /Mg _{ex}	Ni _{ex}	TOC	C/N	P _{Olsen}	age	slope	asp	tcov	NS	NIBA
Ca _{ex}	-0.11	1													
Mg _{ex}	<u>-0.72</u>	<u>0.57</u>	1												
K _{ex}	-0.24	<u>0.88</u>	<u>0.53</u>	1											
Ca _{ex} /Mg _{ex}	<u>0.71</u>	0.24	<u>-0.47</u>	0.21	1										
Ni _{ex}	-0.17	0.00	-0.12	0.12	-0.11	1									
TOC	<u>-0.53</u>	<u>0.73</u>	<u>0.78</u>	<u>0.61</u>	-0.23	-0.04	1								
C/N	<u>-0.62</u>	0.33	<u>0.77</u>	0.34	-0.43	-0.35	<u>0.65</u>	1							
P _{Olsen}	<u>-0.75</u>	0.16	<u>0.8</u>	0.22	-0.42	-0.12	<u>0.52</u>	<u>0.58</u>	1						
Age	<u>-0.58</u>	0.07	<u>0.72</u>	0.05	<u>-0.48</u>	-0.33	0.36	<u>0.63</u>	<u>0.67</u>	1					
Tree cover	<u>-0.52</u>	0.38	<u>0.59</u>	<u>0.5</u>	-0.3	-0.29	<u>0.54</u>	<u>0.72</u>	<u>0.46</u>	<u>0.46</u>	-0.41	-0.22	1		
Bare soil	<u>0.68</u>	-0.32	<u>-0.49</u>	-0.36	0.17	-0.06	<u>-0.56</u>	-0.33	<u>-0.49</u>	-0.42	-0.04	<u>-0.44</u>	-0.36	1	
NIBA	-0.43	-0.11	0.25	-0.10	-0.3	-0.24	0.13	<u>0.53</u>	0.32	0.41	-0.19	-0.24	0.42	-0.11	1
pHBA	-0.26	-0.19	0.01	-0.19	-0.21	-0.10	0.09	0.32	0.07	-0.06	<u>-0.47</u>	0.04	0.10	-0.25	-0.01
camgBA	0.14	<u>-0.48</u>	-0.28	<u>-0.54</u>	-0.28	0.31	-0.3	-0.26	-0.27	-0.05	0.25	0.00	<u>-0.45</u>	0.43	0.07
Ericaceae	<u>-0.68</u>	-0.10	<u>0.49</u>	0.04	<u>-0.45</u>	-0.26	0.27	<u>0.54</u>	<u>0.66</u>	<u>0.75</u>	0.01	-0.03	<u>0.65</u>	<u>-0.55</u>	<u>0.64</u>

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