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13 **Metals and secondary metabolites in saxicolous lichen communities on ultramafic and non-**
14 **ultramafic rocks of the Western Italian Alps**

15
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51 **Abstract:**

52 There is a long history of studies on lichens found in ultramafic habitats, but comparisons between
53 lichen communities on different ultramafic lithologies are scant, and potential metabolic adaptations
54 to the multiple edaphic stresses of ultramafic substrates have been widely neglected. The current
55 work is the first to characterise differences in the abundance and structure of saxicolous lichen
56 communities on different ultramafic lithologies (dunite, lherzolite, and serpentinite), analysed in
57 two areas of the Western Alps (NW-Italy). Differences between communities on various ultramafic
58 lithologies were observed, including differences between a mafic control (Mg-Al metagabbro);
59 however, factors other than the substrate were observed to drive more remarkable differences
60 between lichen communities on ultramafics of alpine and prealpine areas. XRF analyses
61 demonstrated that the mineral composition of different lithologies is reflected by metal contents in
62 crustose lichens, with weathering processes accounting for relative shifts in elemental abundances
63 between rocks and thalli. A TLC screening of lichen secondary metabolites (LSM), which are
64 thought to regulate metal and pH homeostasis in thalli, revealed lithological vicariance among
65 dominant lichen species with different LSM patterns and intraspecific variability in LSM
66 production associated with differences in lithology and location. In particular, the presence or
67 absence of norstictic acid in species or lineages/individuals on the different lithologies, in
68 relationship to concentrations of Fe, Mg, and Ni contents in lichen thalli, was recognized as a
69 metabolic adaptation to metal stress. Pull-up tests revealed that physical factors such as a
70 differential surface disaggregation may contribute more toward differences observed in lichen
71 abundance on the different lithologies investigated.

72

73 **Running title:**

74 Metals and secondary metabolites in lichens on ultramafics

75

76 **Summary text:**

77 This work is the first to compare lichen colonisation on different ultramafic lithologies, exploring
78 metabolic adaptation to substrate-related metal stress. Physical factors such as surface
79 disaggregation determine lichen abundance on the different lithologies, while the presence or
80 absence of certain secondary metabolites accounts for a community-level adaptation to different
81 metal concentrations in the colonised rocks. This research contributes to our knowledge of
82 biological adaptation to metal stresses in natural environments and of the ecological significance of
83 lichen secondary metabolites.

84

85 **Keywords:**

86 lichen diversity, metal stress, norstictic acid, SDR analysis, serpentine ecosystem, X-ray
87 fluorescence

88

89

90 **Introduction**

91 The peculiarity of plant communities on ultramafic substrates has been long-recognised, with some
92 recurrent traits being low levels of individual species abundance and overall species diversity,
93 abundance of endemic species, range extensions and disjunctions, ecotypic differentiation, and
94 xeromorphic adaptations (Roberts and Proctor 1992). The characterisation of these unique floras
95 has grown due to our improved understanding of their physiological adaptation to the edaphic
96 stressors of ultramafic soils, stressors such as high concentrations of heavy metals (e.g. Co, Cr, Ni),
97 a paucity of essential nutrients (e.g. K, N, P, and S), a high Mg:Ca ratio, and drought (Kazakou *et*
98 *al.* 2008). Advances in molecular methods have particularly contributed to ultramafic ecosystems
99 becoming model systems for the study of plant adaptation to environmental stress (Brady *et al.*
100 2005; Harrison and Rajakaruna 2011). Nevertheless, researchers still debate whether some
101 physiological and ecological traits that are associated with serpentine tolerance or endemism are
102 plastic responses to edaphic conditions or are genetically based (Kay *et al.* 2011).

103 Studies on lichens found on ultramafic substrates also have a long history, with a prominent feature
104 being the search for similarities between the ecological characteristics displayed by plant
105 communities on ultramafic substrates and those of the lichen biota. However, with few exceptions,
106 lichen communities found on ultramafic substrates display high species diversity and cover values,
107 often appearing richer than on adjacent, non-ultramafic substrates (Favero-Longo *et al.* 2004;
108 Favero-Longo 2014, with refs. therein). Unlike vascular plants, which display high rates of
109 endemism on ultramafic substrates, only one lichen species has been reported to occur exclusively
110 on serpentinites: *Porpidia nadvornikiana* (Vězda) Hertel & Knoph (Fryday 2005). Lichens also do
111 not display the proliferation of ecotypes or peculiar morphologies that often characterises the
112 vascular plant flora of ultramafic areas. Lichen ecotypes demonstrating peculiar morphologies on
113 ultramafic soils were reported in early works, but these have not been confirmed, and new
114 ultramafic ecotypes have not been described recently (Favero-Longo 2014).

115 Surprisingly, studies of lichens found on ultramafic substrates have been generally limited to
116 communities on serpentinised ultramafic rocks and serpentine soils, while little information is
117 available on lichen communities of non-serpentinised ultramafics (i.e. peridotites s.l.). This is worth
118 noting, as the different mineral composition and weathering processes which characterise
119 peridotites may result in different edaphic conditions for lichens relative to those of serpentinised
120 ultramafics. Peridotites consist of varying quantities of olivine [(Mg, Fe)₂SiO₄], Ca-poor pyroxene
121 [orthopyroxene: (Mg, Fe)₂Si₂O₆], and Ca-rich pyroxene [clinopyroxene: Ca(Mg, Fe)Si₂O₆],
122 whereas serpentinites consist mostly of serpentine [the metamorphic product of olivine and
123 orthopyroxene: Mg₃Si₂O₅(OH)₄] with greater or lesser quantities of clinopyroxene and magnetite
124 [Fe²⁺Fe³⁺₂O₄] (O’Hanley, 1996). Olivine and orthopyroxene show a higher propensity for
125 weathering (i.e. lower stability) relative to serpentine and clinopyroxene (Wilson 2004; Kierczak *et*
126 *al.* 2007).

127 Some researchers have studied lichen-substrate interactions on ultramafics in terms of
128 biodeterioration processes (Favero-Longo *et al.* 2013 with refs. therein); however, the physiological
129 mechanisms which allow lichens to tolerate the stressors of ultramafic substrates have been widely
130 neglected. As desiccation-tolerant and mostly oligotrophic organisms (Nash 2008), the tolerance of
131 lichen species to high concentrations of heavy metals and high Mg:Ca ratios found on ultramafic
132 substrates is of particular interest. Studies on lichen thalli exposed to airborne metal pollution or
133 from metal-rich mine spoils or metal-polluted soils have documented varying patterns of
134 physiological response, depending on the species and concentration of the metals in question, the
135 species involved in the lichen symbiosis (i.e. the mycobiont and the photobiont), and environmental
136 conditions (Purvis and Pawlik-Skowrońska 2008; Bačkor and Loppi 2009). At the cellular level,
137 glutathione and antioxidant stress proteins, together with phytochelatins synthesised by photobionts,
138 have been shown to have a major role in limiting the toxicity of heavy metals (Bačkor and Fahselt
139 2008). Different patterns of intracellular metal compartmentalisation have also been documented,
140 but extracellular binding and biomineralisation processes have been recognised as the crucial

141 avoidance strategies in lichens exposed to high concentrations of metal levels (Purvis and Pawlik-
142 Skowrońska 2008). Extracellular polymeric substances, cell wall chitin, melanins, and low-
143 molecular weight primary metabolites (mostly oxalic acid) have been shown to be variously
144 involved in metal immobilisation and tolerance (Favero-Longo 2014). Some of the polyphenolic
145 secondary metabolites produced by lichens (i.e. lichen secondary metabolites, LSM), most of them
146 unique to these symbiotic organisms (Elix and Stocker-Wörgötter 2008), also form metal-organic
147 complexes in thalli growing on metalliferous substrates, thus contributing to the metal avoidance
148 strategy (Purvis and Pawlik-Skowrońska 2008). However, contrasting patterns of LSM
149 concentrations have been reported in lichen thalli growing on metal-rich and control sites, calling
150 into question the mechanisms of the protective action of LSM against metal toxicity (Bačkor *et al.*
151 2011; Pawlik-Skowrońska and Bačkor 2011). The role of LSM in the metal homeostasis of lichens
152 has been widely documented by Hauck and colleagues who showed that the type and abundance of
153 LSM produced by lichen species influence their specificity for specific pH conditions and metal
154 availability (Hauck *et al.* 2007, 2009, 2010, 2013). In particular, LSM activity may be related to
155 extracellular exclusion processes, but also to temporary chelating processes which, through a
156 largely unknown mechanism, favour metal uptake (Hauck *et al.* 2009). The production of a LSM,
157 having a certain ion specificity and a pH-dependent water soluble fraction, may be thus
158 advantageous on substrates with low concentrations of metals required for nutrition. Alternatively,
159 the production of LSM may be disadvantageous on substrates with high concentrations of the same
160 metals, potentially increasing metal-availability to toxic levels (Hauck *et al.* 2013). Such a
161 hypothesis could offer a comprehensive explanation of the ecophysiological role of LSM in metal
162 tolerance; however, no studies have focused on this aspect of lichen communities found on
163 ultramafic substrates.
164

165 *Aims*

166 In this paper, saxicolous lichen communities from two ultramafic areas of the Western Alps (NW-
167 Italy) were studied. The ultramafic areas contained well-preserved mantle peridotites and/or
168 serpentinites. The first area, Mt. Musiné in the Lanzo peridotite massif, contained dunites
169 (peridotites with >90% modal olivine), lherzolites-harzburgites (peridotites with various amounts of
170 olivine, orthopyroxene and \pm clinopyroxene), and serpentinites (serpentinised peridotites with major
171 serpentine \pm clinopyroxene). The second area, the Monviso meta-ophiolite massif, contained
172 serpentinites and, as a comparison, Mg-Al metagabbros (a non-ultramafic ophiolitic lithology).
173 Lichen abundance and diversity were documented from saxicolous lichen communities found on
174 the different lithologies of the two areas. In addition, metal concentrations and lichen secondary
175 metabolites were examined by X-ray fluorescence spectrometry and thin layer chromatography,
176 respectively, in the thalli of the dominant lichen species found on the different lithologies. Physical
177 weathering of rocks was evaluated in terms of surface disaggregation using pull-up tests.
178 The first research aim (a) was to compare lichen diversity and abundance on the different ultramafic
179 and non-ultramafic lithologies. The second research aim (b) was to examine the relationship
180 between the chemical composition of the rock substrate and the metal contents of dominant lichen
181 species. The third research aim (c) was to test the hypothesis that LSM in lichens from the different
182 lithologies will vary depending on rock chemistry and the related metal contents in thalli. The
183 fourth and final research aim (d) was to evaluate how chemical (i.e. rock composition) and physical
184 (i.e. surface disaggregation) features of the different lithologies may contribute to observed
185 colonisation patterns.

186

187 **Material and methods**

188 *Study sites*

189 Two areas of the Western Alps with abundant ultramafic lithologies were selected to examine
190 lichen colonisation on serpentinites in comparison with that on non-serpentinised peridotites (Area

191 A: Mt. Musiné in the Lanzo peridotite massif) and on a mafic ophiolitic lithology (Area B: Monviso
192 meta-ophiolite massif) (Fig. 1a, b; also see Supplementary Material 1).

193 The Lanzo peridotite massif (Area A), located along the inner part of the metamorphic belt of the
194 Western Alps, at its boundary with the Po Plain, is one of the largest bodies of peridotites in the
195 world (Elter 2005). The study area was located on the ultramafic outcrops of the south-eastern ridge
196 of Mt. Musiné (Area A: approx. 0.01 km², from 800 to 1100 m a.s.l.; Fig. 1c), in the southern Lanzo
197 massif, located 20 km north-west of the city of Turin. These outcrops are characterised by
198 exceptionally well-preserved mantle peridotites (Elter *et al.* 2005). Lherzolites enriched in Ca-rich
199 plagioclase (major olivine, clinopyroxene, and orthopyroxene; minor Ca-rich plagioclase and
200 spinel) are the dominant lithology, locally including metre-thick bands of harzburgites (major
201 olivine and orthopyroxene; minor clinopyroxene, spinel, and Mg-chlorite) and decametre-wide
202 bodies of dunites (major olivine; minor spinel, Mg-chlorite, orthopyroxene, and phlogopite). Tiny
203 pods of serpentinites (major antigorite serpentine, partially or completely replacing olivine and
204 orthopyroxene; minor clinopyroxene and magnetite) also occur. The climate is transitional between
205 a temperate-continental climate (characteristic of the Po Plain) and a pre-alpine climate, with higher
206 precipitation. Rock outcrops are mostly surrounded by xero-thermic pastures, flanked by *Pinus*
207 *nigra* revegetation stands and mesophilous coppice forest stands at lower and higher altitudes,
208 respectively.

209 The Monviso massif (Area B) is arguably the most representative of several ophiolite bodies in the
210 Alps that are relics of oceanic crust formed during the opening of the Mesozoic Tethys and which
211 underwent metamorphism during Alpine subduction. These ophiolite bodies now sparsely overlie
212 the continental tectonic units of the Western Alps, topographically isolated at altitudes higher than
213 those of the Lanzo massif (Rolfo *et al.* 2014). The Monviso massif was chosen as the second study
214 area because it encompasses the entire lithological spectrum of ophiolites, allowing for a
215 comparison of lichen colonisation on both petrographically well characterised serpentinites and
216 associated mafic lithologies (Rolfo *et al.* 2014), a possibility not offered by any serpentinite body

217 localised in the same altitudinal range of Mt. Musiné (Area A). In particular, investigations focused
218 on the north- to northeast-facing slope above the Po River Springs, at Pian del Re (Area B: approx.
219 0.015 km², at 2100 m a.s.l.; Fig. 1d), characterised by outcrops of serpentinites and metric blocks of
220 Mg-Al metagabbros from overhanging cliffs. The serpentinite derives from primary spinel
221 lherzolite and mainly consists of antigorite serpentine ± clinopyroxene, with minor Mg-rich chlorite
222 and magnetite, Fe-Ni alloys, and sulphides as ore minerals (Spandler *et al.* 2011; Rolfo *et al.* 2015).
223 The metagabbro mainly consists of a whitish matrix with abundant Ca- (e.g. zoisite, tremolite) and
224 Mg- (e.g. Mg-chlorite, talc) silicate minerals, and in which bright-green porphyroclasts of Cr-
225 omphacite pyroxene also occur (Spandler *et al.* 2011; Rolfo *et al.* 2015). The area, which has been
226 included in the World Network of Biosphere Reserves (UNESCO's Man and the Biosphere
227 Programme; www.unesco.org), has a typical alpine climate and is characterised by alpine grassland.

228

229 *Sampling and analysis of lichen diversity*

230 In Area A, nine macroplots (10 m × 10 m) were haphazardly located on outcrop areas of the
231 different ultramafic lithologies, their distribution following the respective lithology abundance (n=2
232 on dunite, Dun; n=5 on lherzolite-harzburgite, Lhe; n=2 on serpentinite, Ser_A) and accessibility
233 limitations. In Area B, six macroplots (10 m × 10 m) were also haphazardly located on areas
234 including serpentinite outcrops and blocks (n=3, Ser_B) and Mg-Al metagabbro blocks (n=3, MMg).
235 Rock samples were collected from each of the macroplots, and thin sections of selected rock
236 samples were petrographically characterised using an Olympus BX-60 transmitted light polarising
237 microscope.

238 Within each macroplot, three independent 50 cm × 50 cm plots were established on randomly
239 selected rock surfaces sharing similar (micro-)environmental features (e.g. direct solar irradiation,
240 regular micromorphology, absence of cracks, slope < 30°, height from the ground > 50 cm to avoid
241 plant interactions). Each plot was surveyed using a square grid divided into 25 quadrats (10 cm × 10
242 cm). Total lichen cover within each plot was estimated visually. The frequency of each species in

243 each plot was calculated as the sum of its occurrences within the grid quadrats. Species density and
244 total species frequency (i.e. the sum of the frequency values calculated for all the species through
245 the square grid) were calculated at the plot level. Specimens of lichens collected from the plots were
246 identified in the laboratory, following Wirth (1995), Smith *et al.* (2009), and monographic
247 descriptions and were deposited at the Herbarium of the University of Torino (TO). Nomenclature
248 follows Nimis and Martellos (2008).

249 The relative importance of components of γ -diversity [i.e. similarity (S), relativised richness
250 difference (D), and relativised species replacement (R)] was evaluated for all combinations of plots.
251 The plot-level matrix of species presence/absence was analyzed with SDR Simplex software (2001)
252 using the Simplex method (SDR Simplex; Podani and Schmera 2011). Similarity (S) was calculated
253 following the Jaccard coefficient of similarity:

$$254 S_{\text{Jac}} = a/n$$

255 where a is the number of species shared by the two plots, and n is the total number of species.

256 The relativised richness difference (D) was calculated as the ratio of the absolute difference
257 between the species numbers of each site (b , c) and the total number of species, n :

$$258 D = |b-c|/n$$

259 Relativised species replacement (R) was calculated as:

$$260 R = 2 * \min \{b, c\}/n$$

261 A relativised β -diversity as the sum of R+D, a relativised richness agreement as the sum of R+S,
262 and a relativised nestedness as the sum of S+D were also calculated for each pair of plots following
263 Podani and Schmera (2011).

264

265 *X-ray fluorescence spectrometry*

266 Metal contents (percent weight of Mg, Al, Si, Ca, Cr, Fe, Ni) were quantified in the medulla of
267 thalli of the dominant species from each of the different ultramafic and non-ultramafic lithologies
268 using X-ray fluorescence spectrometry (XRF). The following species were examined (lithologies

269 for each species are listed in brackets): *Aspicilia caesiocinerea* (Lhe, Ser_A, MMg), *A. cinerea* (Dun,
270 Ser_B), *Candelariella vitellina* (all), *Lecanora bicincta* (Lhe), *Lecanora polytropa* (Dun, Ser_A, Ser_B,
271 MMg), *Lecidella* cfr. *carpathica* (Dun, Lhe, Ser_A, Ser_B), *Rhizocarpon geographicum* (all
272 lithologies), *R. polycarpum* (Ser_B), *R. reductum* (Dun, Lhe, Ser_A), *Umbilicaria cylindrica* (MMg,
273 Ser_B), *Xanthoparmelia* gr. *stenophylla* (Dun, Lhe, Ser_A). Analyses were performed on thalline
274 cross-sections dissected under a stereomicroscope using a minimum of 5 specimens per species per
275 lithology ($n_{\text{tot}}=207$). Cross-sections were analysed using a Micro-XRF Eagle III-XPL
276 (Röntgenanalytik Messtechnik GmbH, Germany). To obtain results representative of total metal
277 contents of the medulla, including crystalline inclusions and extracellularly bound cations, washing
278 steps were avoided. The XRF system included a Rh X-ray tube, a liquid nitrogen cooled ultrapure
279 Si detector with an active area of 30 mm² and a 5 µm beryllium window, two CCD video cameras
280 and primary filters to optimise the peak to background ratio in the energetic range of interest (see
281 Vaggelli *et al.* 2014 for additional details). Analyses were performed on 130 × 130 µm² areas of
282 each sample under the following analytical conditions: voltage 30 KV, beam current 300 µA, live
283 time 60.0 seconds. Average metal contents of the different lithologies were quantified by
284 performing spot analyses on the thin sections representative of the different macroplots (at least ten
285 analyses per lithology; $n_{\text{tot}}=52$) using the same analytical conditions as for lichen thalli.
286 Analytical results, encompassing metal contents in rocks and in lichens, including intrathalline
287 mineral deposits and extracellularly bound and intracellularly compartmentalised metals, were
288 uniformly expressed as the percent weight of elements (normalised to 100% after the exclusion of
289 P, S, K in thalline analyses) to allow correlation analyses. An ordination of lithologies and species
290 on the basis of their metal contents was performed using principal co-ordinate analysis (PCoA-I,
291 symmetric scaling without post-transformation of scores) with the software CANOCO 4.5 (Ter
292 Braak and Šmilauer 2002). XRF results were statistically analysed using Systat 10.2 (Richmond,
293 CA, USA) to compare metal contents between the different lithologies, between the same lichen
294 species found on different lithologies, and between different species on the same lithology using

295 analysis of variance (ANOVA) with post-hoc Tukey's test. Correlations between metal contents in
296 lichens and their rock substrate were assessed using Pearson correlation.

297

298 *Thin layer chromatography*

299 Patterns of lichen secondary metabolites in the dominant lichen species on each of the different
300 ultramafic and non-ultramafic lithologies were examined by thin layer chromatography (TLC;
301 Orange *et al.* 2010). The following species were examined (with respective lithologies listed in
302 parentheses): *Aspicilia caesiocinerea* (Lhe, Ser_A, MMg), *A. cinerea* (Dun, Ser_B), *Candelariella*
303 *vitellina* (all), *Lecidella cfr. carpathica* (Dun, Lhe, Ser_A, Ser_B), *Rhizocarpon geographicum* (all), *R.*
304 *polycarpum* (Ser_B), *R. reductum* (Dun, Lhe, Ser_A). At least five specimens per lithology (from
305 different macroplots) were extracted with acetone. Silicagel SIL G-25 UV254 (Macherey-Nagel;
306 Düren, Germany) was used as the support on glass plates and a solution of toluene and acetic acid
307 (170:30) was used as the solvent ("Solvent C" sensu Orange *et al.* 2010) for compound separation.
308 The developed chromatograms were examined using a UV lamp manufactured by Spectroline
309 Longlife™ (254 nm and 365 nm wavelengths) with fluorescence analysis cabinet (without spray
310 reagents). The R_f of the observed spots were defined with reference to reference compounds (i.e.
311 norstictic acid extracted from *Pleurosticta acetabulum* (Neck.) Elix & Lumbsch and usnic acid
312 produced by Sigma-Aldrich (St Luis, MO, USA). For each species, a matrix of the
313 presence/absence of spots observed on the chromatogram of each specimen was used to perform an
314 ordination of specimens collected on the different lithologies on the basis of their metabolite
315 patterns using principal co-ordinate analysis (PCoA-IIa/e; Ter Braak and Šmilauer, 2002). The
316 matrix of spot presence/absence and a matrix of metal contents of thalli from each lithology were
317 used to analyse the metabolite(species)-metal(environment) relationships at the lithology level
318 through a canonical correspondence analysis (CCA), which partitions variation explained by each
319 variable and constructs a model of significant variables (CCA using biplot scaling for inter-species
320 distances, Hill's scaling for inter-sample distances; choosing forward selection of variables option;

321 performing Monte Carlo permutation test on the first and all ordination axes; Ter Braak and
322 Verdonschot 1995). PCoA and CCA analyses were performed using CANOCO 4.5 (Ter Braak and
323 Šmilauer, 2002). The goal of these analyses was the comparison of metabolic patterns in different
324 specimens; the identification of all the different spots was beyond the aim of the study and would
325 require the use of more advanced chromatographic techniques (see Parrot *et al.* 2013). Given this
326 premise, R_f values reported by Orange *et al.* (2010) and control species were used as references for
327 the identification of some spots.

328

329 *Pull-up tests*

330 A pull-up test using adhesive tape (3M 396, 3M[®], Italy) was applied to compare the disaggregation
331 of bare surfaces of the different lithologies, following a protocol currently used on manmade
332 substrates (Favero-Longo *et al.* 2009, with refs. therein). Tape was applied to a bare surface
333 averaging 5 cm × 50 cm in extent (n = 7 per lithology). Gravimetric (Kern EG240 balance; Kern,
334 Germany) and image (WinCAM Pro 2007d software; Regent's Instrument, Canada) analyses were
335 performed to quantify weight and abundance of the detached materials. The results were
336 statistically analysed by ANOVA with post hoc Tukey test (Systat 10.2, Richmond, CA, USA).

337

338 **Results**

339 *Lichen diversity and abundance*

340 Rich communities of saxicolous lichens were observed throughout the survey (total gamma-
341 diversity: 57 species; average cover: 56.5%), but significant differences in diversity and abundance
342 were observed in the two study areas (A, B) and on the different lithologies (Table 1a).

343 Outcrops in the alpine Area B displayed twice the average cover values of those in the prealpine
344 Area A (80.6% vs. 40.4%), together with a slightly higher abundance in total species diversity (37
345 vs. 31), species density per plot (12.3 vs. 9.6) and total species frequencies per plot (142.0 vs.
346 106.2). Communities on Ser_B and MMg did not show significant differences in either diversity or
347 abundance: relatively higher values of species diversity (28 vs. 24) and average cover values

348 (71.4% vs. 89.8%) were observed for the former and the latter, respectively. Ser_A showed a lichen
349 abundance similar to Ser_B (average cover: 61.0%; species frequency per plot: 126.2), while
350 significantly lower values characterised Lhe (38.6%; 109.7) and even lower values characterised
351 Dun (24.2%; 69.7).

352 A set of three crustose species (*Rhizocarpon geographicum*, *Candelariella vitellina*, *Lecanora*
353 *polytropa*) were dominant on nearly all of the ultramafic and mafic lithologies of Areas A and B,
354 displaying maximum average frequencies in plots (>65%) and grid quadrats (>30%), and thus
355 accounting for the similar γ -diversity components calculated for the ultramafic substrates
356 (Dun+Lhe+Ser_A+Ser_B) and for all substrates combined (including MMg; Tables 1b and 2; detailed
357 comments on SDR scores can be found in Supplementary Material 2). Another seven species, five
358 of which shared high frequency values in plots (>33%) and grid quadrats (>17%), occurred in both
359 Areas A and B, while all other species (82%) were exclusive to one of the two Areas. Accordingly,
360 lower similarity (S) and higher species replacement (R) and richness difference (D) characterised
361 the relevés on ultramafic rocks (Dun, Lhe, Ser_A, Ser_B), with respect to the dataset of Area B (Ser_B,
362 MMg). This indicates higher community similarity between ultramafic and mafic rocks within the
363 same area relative to the similarity of communities on ultramafic lithologies in different areas (also
364 see the PCoA-III analysis for the species presence/absence matrix in Supplementary Material 3).

365 Nevertheless, higher species replacement and lower similarity calculated for the entirety of Area B
366 relative to values calculated for the individual MMg and Ser_B datasets suggests that lichen
367 communities on the two substrates may be distinct, primarily marked by the exclusive occurrence of
368 some species (e.g. the dominant *Aspicilia caesiocinerea* and *Lecidella carpathica*, but also
369 *Staurothele areolata* and *Aspicilia contorta* on Ser_B; the dominant *Aspicilia cinerea* and
370 *Rhizocarpon viridiatrum*, but also *Bellemeria alpina* and *Orphniospora mosigii* on MMg). On the
371 other hand, the closeness of values of S, D, and R calculated for the entirety of the prealpine Area A
372 and for the three included ultramafic lithologies indicated a higher homogeneity of communities.
373 High values of richness agreement ($S+R \geq 80\%$) were calculated through the overall survey and,

374 separately, in Areas A and B; the highest richness difference (D) was observed in the species-poor
375 communities on Dun.

376

377 *Metal contents in rocks and lichens*

378 XRF analyses on the metal contents of the five lithologies (Table 2a) highlighted significant
379 differences, which were most noteworthy on MMg. This mafic lithology displayed higher
380 concentrations of Si and Ca and lower concentrations of Mg and heavy metals (Cr, Fe, Ni) relative
381 to the ultramafic lithologies. Ser_A and Ser_B were very similar and, together with Dun, had relatively
382 higher Mg concentrations relative to Lhe. Lhe was richer in Al and Ca, thus displaying an
383 intermediate composition between the other ultramafic lithologies (Ser_A, Ser_B, Dun) and the mafic
384 lithology (MMg). No significant differences were observed in Fe concentrations, although relatively
385 higher values were measured in Dun and Lhe. The highest Ni and Cr concentrations were detected
386 in Dun and Ser_B, respectively.

387 Relationships between the metal contents in the different lithologies and in the associated thalli of
388 the dominant lichen species were visualised through PCoA-I (Fig. 2). The analysis extracted four
389 components which explained 99.9% of the total variance and ordinated lithologies and lichens
390 according to their metal contents. The first axis (61.8% of the total variance) was positively
391 correlated with Ca and separated species secreting oxalic acid (*Xanthoparmelia stenophylla* and
392 *Lecanora polytropa*). These species had high Ca concentrations in their thalli in the form of
393 insoluble oxalates, despite of the relatively low Ca concentrations in each of the investigated
394 lithologies. The other species scattered along the second axis (26.4%), displaying lower Mg
395 concentrations and higher Al, Ca, and Fe concentrations relative to those of their substrates. The
396 crustose species examined on Ser_A, Ser_B, and Dun clustered together in the high and central part of
397 the diagram, reflecting the higher Mg concentrations of their colonised substrates. Crustose species
398 on MMg clustered together in the lower side of the diagram, following the higher Si and Al
399 concentrations and lower Mg concentrations of their lithology. By contrast, crustose species from

400 Lhe clustered together in an intermediate position, following the intermediate composition of their
401 substrate. Average metal contents in the crustose species (having excluded *Lecanora polytropa*
402 because of its Ca-oxalate content, Table 2b) and those of their respective substrates displayed
403 extremely high correlation values ($R^2 > 0.95$ for Mg and Al; > 0.85 for Si and Fe; > 0.80 for Ni; > 0.75
404 for Ca and Cr; Table 2c). The chemical contents of the foliose *Umbilicaria cylindrica* showed a
405 minor relationship with their substrate, with thalli on Ser_B clustering together with those on MMg in
406 the lower part of the diagram. Significant variability in metal concentrations was detected between
407 the same species on different substrates, mostly following the same patterns observed for crustose
408 lichens as a whole (Table 2d). Only minor differences were detected between different species on
409 the same lithology (analytical results are provided in Supplementary Material 4).

410

411 *Patterns of lichen secondary metabolites*

412 We outline here the similarity of metabolite patterns characterising the different species on the
413 different lithologies (n_{tot} metabolites=48; additional details are provided in Supplementary Material
414 5). As noted previously, the identification of metabolites was limited to some noteworthy
415 compounds for which control species were available for comparisons.

416 At the community level, the analysis of metabolic patterns disclosed a complex framework of (i)
417 lithological vicariance of species with different metabolic patterns (*A. cinerea* and *A. caesiocinerea*)
418 and (ii) intraspecific variability in the occurrence of certain metabolites, which could not be
419 associated to any microscopic morphological differences but appeared to be completely or partially
420 associated to the investigated lithologies (*R. reductum*, *R. geographicum*) and/or the two study areas
421 (A, B; *L. carpathica*, *C. vitellina*).

422

423 TLC on *Aspicilia* specimens highlighted a strong difference in the metabolic patterns of populations
424 occurring on Lhe, Ser_A, and MMg, with all thalli producing norstictic acid and related compounds
425 (connorstictic, cfr. substictic) assignable to *A. cinerea*, whereas those specimens on Dun and Ser_B

426 never secreted norstictic acid, but rather contained an undefined substance with $R_f=22$ and were
427 recognised as *A. caesiocinerea* (PCoA-IIa in Fig. 3a; detailed comments are provided in
428 Supplementary Material 6a). In CCA-a (Fig. 4a; detailed comments and scores are provided in
429 Supplementary Material 6a), norstictic acid and related compounds showed a negative correlation
430 with Ni (the environmental factor exhibiting the highest conditional effect according to forward
431 selection), Fe, and Mg, and a positive correlation with Si, Al, Ca, and Cr. The undefined substance
432 with $R_f=22$ displayed opposite correlations.

433 TLC on *Candelariella vitellina* revealed differences in the populations between Areas A and B.
434 Spots at $R_f=90$, 88, and 7, assigned to pulvinic dilactone, calycin, and pulvinic acid, respectively,
435 were observed in each of the specimens. However, specimens from Area A displayed an orange
436 spot at $R_f=48$, whereas specimens from Area B displayed a yellow spot at $R_f=10$ (PCoA-IIb in Fig.
437 3b; detailed comments are provided in Supplementary Material 6b). In CCA-b (Fig. 4b; detailed
438 comments and scores are provided in Supplementary Material 6b), these two metabolites showed
439 maximum positive correlation with Ca (exhibiting the highest conditional effect) and Si,
440 respectively.

441 Each of the specimens of *Lecidella* collected on the four ultramafic substrates displayed a common
442 signature of three metabolites, with $R_f=79$ (yellowish=atranorin), 63 (brown violet), and 49 (dull
443 red). Remarkably, these spots did not show R_f values and spot colours completely compatible with
444 the metabolites expected in the species of *Lecidella* widely reported on siliceous rocks of the Alps,
445 namely *Lecidella carpathica* (atranorin: $R_f=79$, yellowish; diploicin: $R_f=67$, colourless; thuringione:
446 $R_f=48$, bright orange). On the other hand, these spots were compatible with the metabolites of
447 *Lecidella granulosa* (syn. *L. chodatii*; in Leuckert and Knoph 1992), which has been reported
448 from the central Alps on base-rich siliceous rocks (Nimis and Martellos 2008). However,
449 anatomical features of apothecia were compatible with those described for *L. carpathica* (e.g. red-
450 brown hypothecium) and not with those of *L. granulosa* (e.g. colourless to light brown
451 hypothecium; Kantvilas and Elix 2013). Specimens from Area B mostly produced an additional

452 metabolite with $R_f=38$, compatible with (iso-)artothelin (PCoA-IIc in Fig. 3c; detailed comments
453 are provided in Supplementary Material 6c). In CCA-c (Fig. 4c; detailed comments and scores are
454 provided in Supplementary Material 6c), the occurrence of this metabolite was positively correlated
455 along the first axis with Cr, having the highest conditional effect, and separated Ser_B from the other
456 lithologies.

457 TLC on *Rhizocarpon geographicum* revealed the production of rhizocarpic acid in all the specimens
458 and the production of psoromic acid in all but four specimens (three of these occurred on Ser_B).

459 Undefined metabolites with $R_f=20$ and $R_f=28$ variously occurred on the different lithologies, while
460 others with $R_f=1$ and $R_f=63$, mostly, but not exclusively, characterised the population on MMg
461 (PCoA-IIId in Fig. 3d; detailed comments are provided in Supplementary Material 6d). It is worth
462 noting that the same metabolite patterns also characterised the populations of *R. viridiatrum* on Lhe
463 and Dun in Area A and on MMg in Area B (data not shown). In CCA-d (Fig. 4d; detailed comments
464 are provided in Supplementary Materials 6d), the metabolites with $R_f=1$ and $R_f=63$ were positively
465 correlated with Al (exhibiting the highest conditional effect), Ca, and Si, and were negatively with
466 Cr, Ni, and Mg.

467 Each of the specimens of *Rhizocarpon reductum* found on the three lithologies of Area A produced
468 stictic acid. Norstictic and rhizocarpic acids were present in all specimens from Lhe, but only in a
469 subset of those from Dun and Ser_A . Similarly, on Ser_B , all specimens of *R. polycarpum* contained
470 stictic acid, but only one and two specimens produced norstictic and rhizocarpic acids, respectively
471 (PCoA-IIe in Fig. 3e; detailed comment are provided in Supplementary Material 6e). In CCA-e
472 (Fig. 4e; detailed comment are provided in Supplementary Material 6e), both norstictic and
473 rhizocarpic acids were negatively correlated with Fe (exhibiting the highest conditional effect) and
474 Mg; they were positively correlated with Al, Si, and Ca.

475

476 *Rock-surface disaggregation*

477 Bare surfaces of the different lithologies displayed varying disaggregation patterns. Gravimetric
478 analyses (Fig. 5) displayed higher surface disaggregation on Dun and MMg (approximately 0.4 g
479 cm⁻² of detached mineral fraction) relative to Lhe (0.1 g cm⁻²), with serpentinites in the two areas
480 displaying intermediate values (approximately 0.2 g cm⁻²). However, the image analysis (Fig. 5;
481 additional details are provided in Supplementary Material 7) indicated that the detachment of few
482 millimetre-scale mineral fragments commonly characterised Ser_A, Ser_B, and MMg, whereas a
483 yellowish-rust micrometre-scale mineral powder, likely related to olivine weathering, was
484 uniformly detached from the Dun surface. On Lhe, powdering areas alternated with resistant
485 phenocrysts of fresh pyroxene, giving the surface a lumpy appearance.

486

487 **Discussion**

488 Conflicting information on the richness and peculiarity of the lichen biota of ultramafic substrates is
489 reported in the literature (Favero-Longo *et al.* 2004; Favero-Longo 2014). In this paper, (a)
490 investigations on the lichen colonisation of different types of ultramafic rocks, including
491 serpentinites, but also non-serpentinised peridotites, highlight that differences in lichen abundance
492 and community structure characterise the different lithologies, potentially accounting for the
493 disparate reports in the literature. The results presented here identified differences between lichen
494 communities on ultramafic and mafic substrates, but factors other than the substrate drive more
495 remarkable differences between lichen communities on ultramafics of alpine and prealpine areas. In
496 this paper, we also demonstrate that (b) mineral compositions of the different ultramafic and mafic
497 rocks are reflected by different metal contents in the lichen thalli of dominant crustose species, with
498 weathering processes likely accounting for relative shifts in elemental abundances. The analysis of
499 LSM patterns reveals (c) lithological vicariance of dominant lichen species with different metabolic
500 patterns and intraspecific variability in the occurrence of certain metabolites completely or partially
501 associated with lithology and/or the study area (Area A, B). According to the hypothesis on a role
502 of LSM in regulating metal and/or pH homeostasis in lichens (Hauck *et al.* 2007, 2013), the

503 presence/absence of certain metabolites, such as norstictic acid, affects the compatibility of lichen
504 species or lineages/individuals with the metal contents of different lithologies. Other adaptive roles
505 of LSM (e.g. photoprotection) may account for the various occurrences of other metabolites
506 between the two study areas (Area A, B). Owing to the metabolic adaptation of lichen communities
507 to chemical factors in their substrate, (d) physical factors, such the degree of surface disaggregation,
508 may explain differences observed in the lichen abundance on different lithologies.

509

510 *Lichen communities on different ultramafic lithologies (a)*

511 Most studies on lichens of ultramafic substrates have described saxicolous communities rich in
512 species and with high cover values; however, studies from some areas have reported a paucity of
513 species and low cover values (Favero-Longo *et al.* 2004). Here we show that within a given area
514 (the prealpine Area A) lichen communities display higher cover values, species density, and species
515 frequencies on serpentinites relative to non-serpentinised peridotites (lherzolites > dunites). Of the
516 five previous studies reporting lichen poorness on ultramafics, two specifically dealt with lichens on
517 non-serpentinised ultramafics (Gilbert 1983; Gallo and Piervittori 1987) and other two considered
518 areas with both serpentinised and non-serpentinised peridotites (Zahlbrückner 1907; Suza 1927). A
519 similar, high level lichen abundance on each of the serpentinites investigated at the prealpine and
520 alpine levels of Areas A and B corroborates the results of other studies of lichen communities on
521 serpentinite lithologies in the Alps and other alpine-arctic regions, confirming that serpentinite
522 lithologies are capable of supporting rich lichen communities (Favero-Longo *et al.* 2004 with refs.
523 therein; Favero-Longo and Piervittori 2009; Paukov 2009). Similar levels of species diversity and
524 cover on serpentinites and adjacent Mg-Al metagabbros, a mafic lithology, supports the hypothesis
525 that saxicolous lichen communities found on ultramafic lithologies do not display the characteristic
526 low diversity and cover which is generally reported for plant communities found on ultramafics.
527 Further supporting this hypothesis, the SDR analyses showed high levels of richness agreement

528 (>80%) overall and within Area B (in both cases including the comparison between MMg and the
529 ultramafic lithologies).

530 The observed dominance of a set of few species sharing xerophytism, occurrence in sun exposed
531 sites, and avoidance of calcareous substrates (see ecological indices of dominant species in Nimis
532 and Martellos 2008) is usually reported for lichen communities on serpentinites (Favero-Longo *et*
533 *al.* 2004); however, this condition generally characterises lichen communities on all of the silicate
534 rocks (Wirth 1995; Smith *et al.* 2009). On the other hand, in the case of Area B, the occurrence of
535 species restricted to one of either the ultramafic or mafic substrates corroborates reports by several
536 authors suggesting that lichen communities on serpentinites may have unique species assemblages
537 relative to those of other lithologies (e.g. Sirois *et al.* 1987; Rajakaruna *et al.* 2012). However, the
538 fact that lichen communities on the ultramafic substrate Ser_B displayed higher similarity with those
539 on the mafic substrate MMg relative to those on the ultramafic substrates of Area A suggests that
540 environmental factors other than substrate may prevail in selecting lichen functional traits and
541 driving the community composition. In the current study, these differences may be due in part to the
542 difference in altitude between the prealpine and the alpine areas (also see Giordani *et al.* 2014 on
543 Mediterranean lichen communities).

544

545 *Relationships between metal contents in rocks and lichens (b)*

546 Although rock chemistry, together with texture and moisture capacity, has long been suggested as
547 the main factor driving the diversity of saxicolous lichen communities on different lithologies
548 (Brodo 1973), studies which correlate rock mineralogy and chemistry with lichen communities are
549 rare (Rajakaruna *et al.* 2012, with refs. therein). Rajakaruna and colleagues correlated lichen
550 community composition on ultramafic and non-ultramafic rocks with XRF chemical analyses
551 directly performed on the rock substrates, but only a weak correlation was detected. However, the
552 report did not perform XRF analyses on lichen thalli and high levels of metals in the rock substrates
553 can only be considered a proxy measure of the effective metal stress affecting lichen physiology

554 (Bačkor and Fahselt 2004; Favero-Longo 2014). In this paper, XRF analyses show a high
555 correlation between the metal contents in the thalli of crustose lichens and in their respective
556 lithologies. This correlation is an obvious consequence of ion uptake, but also (and likely more
557 significantly) of the entrapment of mineral particles following the disaggregation of surficial rock
558 layers (Adamo and Violante 2000). However, the shift in metal contents between lichen thalli and
559 fresh rock (see PCoA-I) suggests that there may not be a direct relationship between the metal
560 content of fresh rock and the metal content of lichens (see Brodo 1973). additional processes such
561 as surface weathering affecting the availability of metals. In particular, differences between the Mg
562 contents of rocks and the lichens found on them agree with the weathering trend reported in
563 pedogenetic processes on ultramafics, which is characterised by lower Mg contents in soils relative
564 to the parent rock following the leaching of Mg from olivine, orthopyroxene, and serpentine (e.g.
565 Kierczak *et al.* 2007). These differences also agree with reports of the selective leaching of Mg
566 from serpentine minerals entrapped in lichen thalli (Favero-Longo *et al.* 2013). Occurrence of clay
567 minerals and iron oxyhydroxides widely documented at the interface between lichens and rocks
568 (Adamo and Violante 2000), including serpentinites (Favero-Longo *et al.* 2005), likely accounts for
569 the high Al and Fe contents in thalli. Micro-pedogenetic processes of ultramafics at the scale of the
570 lichen-rock interface remain largely unstudied. Specific differences are likely to occur in the
571 dissolution of primary minerals and the formation of secondary minerals on different parent
572 lithologies and in different climatic conditions (e.g. in the prealpine and alpine areas), as has been
573 documented at a larger scale for soils developing on peridotite and serpentinite lithologies in cold
574 and warm ecosystems (Echevarria 2014).

575 Nevertheless, with the exception of *Lecanora polytropa*, crustose lichens on the different lithologies
576 generally have metal contents which reflect those of their colonised substrate, accounting for
577 changes due to surface weathering, and represent different tasks for the physiological regulation of
578 metal homeostasis in thalli. The chemical composition of lichen species secreting oxalic acid
579 (*Lecanora polytropa*, but also the foliose *Xanthoparmelia stenophylla*) is strongly divergent from

580 that of its colonised substrate due to their accumulation of Ca in the form of Ca-oxalates which are
581 three orders of magnitude less soluble than Mg-oxalate. This process has previously been
582 recognised as a potential detoxification mechanism (Adamo and Violante 2000).

583

584 *Relationships between lichen metal contents and secondary metabolite patterns (c)*

585 Studies on lichens found in heavy-metal rich habitats have progressively strengthened the
586 hypothesis that LSM plays a role in metal and pH homeostasis (Hauck *et al.* 2013). Studies on the
587 effect of LSM on Fe absorption highlighted the fact that saxicolous lichens found on Fe-rich mine
588 substrates do not produce LSM that may excessively increase Fe-(III) or Fe-(II) absorption (Hauck
589 *et al.* 2007). Hauck and colleagues (2007) documented that norstictic acid increases Fe(III)-
590 absorption, but significantly reduces absorption of Fe-(II), which is a more mobile and prevailing
591 ion species under the acidic conditions found in iron slags. However, they also showed that the
592 secretion of norstictic acid, because of its pK_{a1} , may limit the acidity tolerance of lichens (Hauck *et*
593 *al.* 2010). Accordingly, *Acarospora smaragdula*, a species which has been variously reported in
594 literature with and without norstictic acid, was shown to lack the metabolite when it occurred on
595 acidic iron-rich slags (Wedin *et al.* 2009). At pH >7.5 norstictic acid has affinity for, and likely
596 supports the uptake of, Cu-(II), Fe-(III), Mn-(II), and Zn-(II), which are hardly available at high pH,
597 whereas norstictic does not readily form complexes with Mg-(II) or Fe-(II) at pH >7.5 (Hauck *et al.*
598 2010).

599 In this paper, we demonstrated differences in metabolic patterns between dominant lichens on the
600 ultramafic lithologies included in the study and the Mg-Al metagabbros and suggest that these
601 differences should be considered in light of Hauck's hypothesis on the homeostatic role of LSM.
602 Analyses on *Aspicilia* show a clear vicariance of norstictic-lacking (*A. caesiocinerea*) and
603 norstictic-containing (*A. cinerea*) thalli on Dun+Ser_B and Lhe+Ser_A+MMg, respectively. In the
604 alpine Area B, a similar pattern of metabolite occurrence was observed, with an abundance of the
605 norstictic acid producers *Bellemeria alpina* and *Orphniospora mosigii* on MMg compared with

606 their conspicuous absence on adjacent blocks of serpentinites. On the ultramafics of Area A,
607 norstictic acid secretion was detected in *Rhizocarpon reductum*, being a fixed trait of specimens on
608 Lhe, but only occurring in a subset of specimens on Dun and Ser_A. The production of norstictic acid
609 by both *Aspicilia* and *Rhizocarpon reductum* was shown to be negatively correlated with Fe through
610 CCA analyses, suggesting that its potential contribution toward the uptake of Fe-(III) may be a
611 disadvantageous trait (Hauck *et al.* 2007, 2010). Moreover, the production of norstictic acid is also
612 negatively correlated with Ni, whose absorption by the metabolite is not documented, and with Mg,
613 which does not readily form complexes (Hauck *et al.* 2010). Conversely, norstictic acid shows a
614 slight positive correlation with Ca. This suggests that, in the case of ultramafic lithologies, the
615 potential homeostatic role (or toxic potency) of a specific metabolite must be considered in light of
616 multiple ions, including those of Mg, heavy metals, and competing cations such as Ca (see Hauck *et*
617 *al.* 2007).

618 Podzolisation processes yielding acidic pH values have been locally documented on ultramafics of
619 the Western Alps (D'Amico *et al.* 2008). It is likely that a similar condition occurs via weathering
620 processes at the interface between lichens and specific ultramafic substrates, resulting in relatively
621 low pH conditions that contribute to make disadvantageous the secretion of norstictic acid, as has
622 been documented elsewhere (Hauck *et al.* 2010).

623 Rhizocarpic acid is known to play a similar, although lesser effect in increasing and decreasing the
624 absorption of Fe-(III) and Fe-(II), respectively (Hauck *et al.* 2007). Accordingly, *Rhizocarpon*
625 *reductum* displayed a negative correlation between rhizocarpic acid and Fe. In *Rhizocarpon*
626 *geographicum*, however, rhizocarpic acid was present in every specimen. Research into the
627 potential competitive or homeostatic role that could be played by psoromic acid and the other
628 undefined metabolites that variously occurred in different subsets of *R. geographicum* specimens
629 ($R_f=20$, $R_f=28$) or on particular lithologies ($R_f=63$ and $R_f=1$, on MMg) could clarify this difference
630 in the production of rhizocarpic acid. Admittedly, rhizocarpic acid also plays a photoprotective role

631 (Hidalgo *et al.* 2002), and its presence or absence cannot be directly linked to its homeostatic
632 potency.

633 Similarly, in *Lecidella*, the exclusive occurrence of the unknown metabolite with $R_f=38$ on Ser_B,
634 likely assignable to (iso-)arthothelin, may be linked to a higher demand for photoprotection in the
635 alpine Area B, which is located approximately 1000 m higher in elevation than Area A. (Iso-
636)arthothelin is a xanthone, a group of photoprotective metabolites, for which a chelating activity
637 potentially related to a homeostatic role has not been characterised. Nevertheless, it is noteworthy
638 that all of the specimens of *Lecidella* found on ultramafic lithologies, but not those found on MMg,
639 displayed a metabolic pattern including only xanthenes (thiophanic acid and chodatol) and
640 atranorin, a metabolite that decreases the absorption of Fe-(III) and increases that of Fe-(II) (Hauck
641 *et al.* 2007). This pattern, previously reported for *L. granulosa* on base-rich siliceous rocks of the
642 Central Alps (Nimis and Martellos, 2008), differs from that reported for *L. carpathica* in the
643 absence of diploicin, a depsidone (as is norstictic acid) displaying anionic functions potentially
644 involved in metal chelation (Huneck and Yoshimura 1996).

645 Pulvinic acid derivatives (pulvinic acid, calycin, pulvic acid lactone) were found in all of the
646 specimens of *Candelariella vitellina* collected. These yellow metabolites are well known for their
647 photoprotective action, but have also been documented to have a significant role in metal binding
648 (Hauck *et al.* 2009). In particular, pulvinic acid was shown to increase the absorption of Fe-(III)
649 and, differing from norstictic acid, that of Fe-(II) (Hauck *et al.* 2007). The metal-complex formation
650 of pulvinic acid is pH dependent, and chelation of Fe-(II), Fe-(III), and Mg increases at pH >8. The
651 ability to increase the uptake of Fe-(II), which is not readily available at high pH levels due to its
652 rapid oxidation to Fe-(III), may discriminate its homeostatic properties from those of norstictic acid.
653 This may make the occurrence of pulvinic acid advantageous in this species that is ubiquitous on
654 siliceous rocks.

655

656 *Chemical vs. physical stress factors for lichens on ultramafics (d)*

657 The observed metabolic patterns, with particular focus on norstictic acid, suggest that lichen
658 communities can physiologically face the differences in the metal content characterising the diverse
659 ultramafic (and non-ultramafic) lithologies. A physical rather than chemical factor may thus control
660 the higher lichen abundance on Ser_B, MMg > Ser_A > Lhe > Dun. Dunites and lherzolites contain
661 olivine and various amounts of orthopyroxene which are highly subject to surface weathering,
662 yielding the formation of Fe-oxyhydroxide deposits (Wilson 2004) and favouring a surface
663 powdering. This behaviour, which is less pronounced in the serpentinites (mostly at the alpine layer,
664 where weathering processes are slower), results in higher instability of the non-serpentinised
665 surfaces (reduced in lherzolites by the occurrence of more stable clinopyroxene phenocrysts)
666 making them less suitable for the establishment of lichen spores and propagules. Similarly
667 serpentinites in other areas of the Western Alps host richer communities than associated calcareous
668 schists which display lower surface stability (Favero-Longo and Piervittori 2009).
669 Further investigations are needed to clarify whether the reported differences in secondary
670 metabolite patterns are plastic responses or are genetically based (see Kay *et al.* 2011 on higher
671 plants). In the case of *Aspicilia*, molecular investigations highlighted a clear phylogenetic
672 divergence between *A. caesiocinerea* (*Circinaria caesiocinerea*) and *A. cinerea* (Nordin *et al.*
673 2010). However, the reported occurrence of norstictic acid-producing and norstictic acid-lacking
674 thalli on blocks of Mg-Al metagabbros and serpentinites separated by less than 1 m, respectively,
675 invite further investigations.

676

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- 819

820 Table 1. Diversity and abundance of saxicolous lichens on the different lithologies of Area A (Mt.
 821 Musiné: dunite, Dun; lherzolite-harzburgite, Lhe; serpentinite, Ser_A) and Area B (Monviso:
 822 serpentinite, Ser_B; Mg-Al metagabbro, MMg). (a) Overall parameters. For each parameter,
 823 according to Tukey's test, values which do not share at least one letter are statistically different
 824 (capital letters: differences between areas; small letters: differences between lithologies). (b)
 825 Specific abundance in different areas and on different lithologies based on frequency data
 826 calculated per plot (50 x 50 cm) and per grid quadrat (10 x 10 cm) (frequencies >50% in bold;
 827 nomenclature follows Nimis and Martellos 2008).

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(a)	Tot	Area A	Area B	Dun	Lhe	Ser _A	Ser _B	MMg								
Total cover (%)	56.5	40.4 (A)	80.6 (B)	24.2 (a)	38.6 (a)	61.0 (b)	71.4 (bc)	89.8 (c)								
Species richness (gamma-diversity)	57	31	37	17	23	22	28	24								
Exclusive species		20	26	2	3	2	8	6								
Species density/plot	10.7	9.6 (A)	12.3 (B)	8.2 (a)	9.7 (ab)	10.5 (ab)	12.9 (b)	11.8 (ab)								
Minimum & maximum species density/plot	5-17	5-15	9-17	5-12	6-15	9-11	9-17	10-15								
Total species frequencies/plot	119.5	106.2 (A)	142.0 (B)	69.7 (a)	109.7 (b)	126.2 (bc)	135.9 (bc)	148.1 (c)								
Minimum & maximum species frequencies/plot	59-186	59-173	115-186	59-85	73-173	97-160	115-160	120-186								
(b)	% (Frequency in 50 cm x 50 cm plots)								% (Frequency in 10 cm x 10 cm quadrats)							
Species	Tot	Area A	Area B	Dun	Lhe	Ser _A	Ser _B	MMg	Tot	Area A	Area B	Dun	Lhe	Ser _A	Ser _B	MMg
<i>Candelariella vitellina</i>	97.8	100.0	94.4	100.0	100.0	100.0	100.0	88.9	82.6	97.8	59.8	99.3	97.3	97.3	92.0	27.6
<i>Rhizocarpon geographicum</i>	91.1	85.2	100.0	33.3	100.0	100.0	100.0	100.0	67.2	50.4	92.4	2.7	61.1	71.3	95.1	89.8
<i>Lecidella</i> cfr. <i>carpathica</i>	73.3	88.9	50.0	83.3	93.3	83.3	100.0	0.0	22.5	24.3	19.8	14.0	28.5	24.0	39.6	0.0
<i>Lecanora polytropa</i> (incl. v. <i>intricata</i>)	66.7	44.4	100.0	83.3	40.0	16.7	100.0	100.0	30.5	10.1	61.1	28.7	5.9	2.0	24.9	97.3
<i>Aspicilia cinerea</i>	64.4	74.1	50.0	0.0	93.3	100.0	0.0	100.0	48.5	55.3	38.4	0.0	72.3	68.0	0.0	76.9
<i>Xanthoparmelia</i> gr. <i>stenophylla</i>	42.2	70.4	0.0	50.0	66.7	100.0	0.0	0.0	17.3	28.9	0.0	3.3	24.0	66.7	0.0	0.0
<i>Lecidea confluens</i>	35.6	0.0	88.9	0.0	0.0	0.0	77.8	100.0	10.8	0.0	26.9	0.0	0.0	0.0	20.4	33.3
<i>Rhizocarpon viridiatrum</i>	35.6	25.9	50.0	16.7	40.0	0.0	0.0	100.0	25.9	14.2	43.3	0.7	25.3	0.0	0.0	86.7
<i>Aspicilia caesiocinerea</i>	33.3	22.2	50.0	100.0	0.0	0.0	100.0	0.0	27.0	16.9	42.2	76.0	0.0	0.0	84.4	0.0
<i>Rhizocarpon reductum</i>	33.3	55.6	0.0	33.3	66.7	50.0	0.0	0.0	18.4	30.7	0.0	9.3	38.7	32.0	0.0	0.0
<i>Buellia leptoclina</i>	26.7	40.7	5.6	66.7	33.3	33.3	0.0	11.1	2.0	3.1	0.4	4.7	2.9	2.0	0.0	0.9
<i>Caloplaca irrubescens</i>	26.7	44.4	0.0	50.0	33.3	66.7	0.0	0.0	4.3	7.1	0.0	3.3	6.1	13.3	0.0	0.0
<i>Caloplaca arenaria</i>	24.4	40.7	0.0	50.0	40.0	33.3	0.0	0.0	4.0	6.7	0.0	6.0	8.0	4.0	0.0	0.0
<i>Porpidia crustulata</i>	24.4	0.0	61.1	0.0	0.0	0.0	100.0	22.2	11.5	0.0	28.7	0.0	0.0	0.0	55.6	1.8
<i>Rinodina milvina</i>	24.4	0.0	61.1	0.0	0.0	0.0	88.9	33.3	6.6	0.0	16.4	0.0	0.0	0.0	30.7	2.2
<i>Umbilicaria cylindrica</i>	24.4	0.0	61.1	0.0	0.0	0.0	22.2	100.0	9.7	0.0	24.2	0.0	0.0	0.0	2.7	45.8
<i>Bellemeria alpina</i>	20.0	0.0	50.0	0.0	0.0	0.0	0.0	100.0	14.1	0.0	35.3	0.0	0.0	0.0	0.0	70.7
<i>Lecidea fuscoatra</i>	20.0	0.0	50.0	0.0	0.0	0.0	33.3	66.7	4.0	0.0	10.0	0.0	0.0	0.0	1.8	18.2
<i>Aspicilia contorta</i> ssp. <i>hoffmanniana</i>	17.8	11.1	27.8	0.0	20.0	0.0	55.6	0.0	2.9	3.4	2.2	0.0	6.1	0.0	4.4	0.0
<i>Buellia badia</i>	17.8	29.6	0.0	50.0	26.7	16.7	0.0	0.0	2.1	3.6	0.0	7.3	2.4	2.7	0.0	0.0
<i>Caloplaca festivella</i>	17.8	0.0	44.4	0.0	0.0	0.0	77.8	11.1	8.6	0.0	21.6	0.0	0.0	0.0	42.7	0.4
<i>Lecanora bicincta</i>	15.6	25.9	0.0	0.0	26.7	50.0	0.0	0.0	1.5	2.5	0.0	0.0	2.7	4.7	0.0	0.0
<i>Staurothele areolata</i>	15.6	0.0	38.9	0.0	0.0	0.0	77.8	0.0	3.6	0.0	9.1	0.0	0.0	0.0	18.2	0.0
<i>Acarospora veronensis</i>	13.3	0.0	33.3	0.0	0.0	0.0	22.2	44.4	1.5	0.0	3.8	0.0	0.0	0.0	1.8	5.8
<i>Catillaria chalybeia</i>	13.3	22.2	0.0	16.7	33.3	0.0	0.0	0.0	2.1	3.6	0.0	2.0	5.6	0.0	0.0	0.0
<i>Orphniospora mosigii</i>	13.3	0.0	33.3	0.0	0.0	0.0	0.0	66.7	3.3	0.0	8.2	0.0	0.0	0.0	0.0	16.4
<i>Xanthoparmelia</i> gr. <i>conspersa</i>	13.3	22.2	0.0	0.0	40.0	0.0	0.0	0.0	9.0	15.0	0.0	0.0	26.9	0.0	0.0	0.0
<i>Xanthoparmelia</i> gr. <i>pulla</i>	13.3	18.5	5.6	0.0	0.0	83.3	11.1	0.0	5.1	8.3	0.2	0.0	0.0	37.3	0.4	0.0
<i>Lecanora cenisia</i>	11.1	0.0	27.8	0.0	0.0	0.0	22.2	33.3	1.8	0.0	4.4	0.0	0.0	0.0	6.2	2.7
<i>Protoparmeliopsis muralis</i>	11.1	14.8	5.6	0.0	0.0	66.7	11.1	0.0	3.8	5.9	0.7	0.0	0.0	26.7	1.3	0.0
<i>Xanthoparmelia verruculifera</i>	11.1	18.5	0.0	0.0	33.3	0.0	0.0	0.0	1.6	2.7	0.0	0.0	4.8	0.0	0.0	0.0
<i>Acarospora impressula</i>	8.9	14.8	0.0	0.0	20.0	16.7	0.0	0.0	1.6	2.7	0.0	0.0	4.3	1.3	0.0	0.0
<i>Brodoa intestiniformis</i>	8.9	0.0	22.2	0.0	0.0	0.0	22.2	22.2	0.8	0.0	2.0	0.0	0.0	0.0	2.7	1.3
<i>Parmelia saxatilis</i>	8.9	14.8	0.0	0.0	13.3	33.3	0.0	0.0	1.2	2.1	0.0	0.0	0.8	7.3	0.0	0.0
<i>Physcia tribacia</i>	8.9	14.8	0.0	16.7	13.3	16.7	0.0	0.0	1.8	3.0	0.0	0.7	1.6	8.7	0.0	0.0
<i>Polysporina simplex</i>	8.9	14.8	0.0	0.0	20.0	16.7	0.0	0.0	5.8	9.6	0.0	0.0	11.5	14.7	0.0	0.0
<i>Lecanora rupicola</i>	6.7	0.0	16.7	0.0	0.0	0.0	33.3	0.0	0.9	0.0	2.2	0.0	0.0	0.0	4.4	0.0
<i>Rhizocarpon polycarpum</i>	6.7	0.0	16.7	0.0	0.0	0.0	22.2	11.1	0.4	0.0	1.1	0.0	0.0	0.0	1.3	0.9
<i>Umbilicaria deusta</i>	6.7	0.0	16.7	0.0	0.0	0.0	22.2	11.1	2.8	0.0	6.9	0.0	0.0	0.0	5.8	8.0
<i>Verrucaria nigrescens</i>	6.7	11.1	0.0	33.3	0.0	16.7	0.0	0.0	2.9	4.9	0.0	17.3	0.0	4.7	0.0	0.0
<i>Caloplaca grimmiae</i>	4.4	7.4	0.0	0.0	13.3	0.0	0.0	0.0	0.4	0.6	0.0	0.0	1.1	0.0	0.0	0.0
<i>Lecanora dispersa</i>	4.4	7.4	0.0	0.0	6.7	16.7	0.0	0.0	0.9	1.5	0.0	0.0	0.8	4.7	0.0	0.0
<i>Protoparmelia badia</i>	4.4	0.0	11.1	0.0	0.0	0.0	11.1	11.1	0.2	0.0	0.4	0.0	0.0	0.0	0.4	0.4
<i>Rhizocarpon geminatum</i>	4.4	0.0	11.1	0.0	0.0	0.0	22.2	0.0	0.8	0.0	2.0	0.0	0.0	0.0	4.0	0.0
<i>Buellia aethalea</i>	2.2	3.7	0.0	0.0	0.0	16.7	0.0	0.0	1.4	2.4	0.0	0.0	0.0	10.7	0.0	0.0
<i>Buellia stellulata</i>	2.2	3.7	0.0	16.7	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.7	0.0	0.0	0.0	0.0
<i>Caloplaca cacuminum</i>	2.2	0.0	5.6	0.0	0.0	0.0	11.1	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.4	0.0
<i>Ionaspis chrysophana</i>	2.2	0.0	5.6	0.0	0.0	0.0	0.0	11.1	0.6	0.0	1.6	0.0	0.0	0.0	0.0	3.1
<i>Koerberiella wimmeriana</i>	2.2	0.0	5.6	0.0	0.0	0.0	11.1	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.4	0.0
<i>Lecanora flotowiana</i>	2.2	0.0	5.6	0.0	0.0	0.0	0.0	11.1	0.2	0.0	0.4	0.0	0.0	0.0	0.0	0.9
<i>Physcia dubia</i>	2.2	0.0	5.6	0.0	0.0	0.0	11.1	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.4	0.0
<i>Rhizocarpon distinctum</i>	2.2	0.0	5.6	0.0	0.0	0.0	11.1	0.0	0.2	0.0	0.4	0.0	0.0	0.0	0.9	0.0
<i>Schaereria fuscocinerea</i>	2.2	0.0	5.6	0.0	0.0	0.0	0.0	11.1	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.4
sterile white thallus	2.2	0.0	5.6	0.0	0.0	0.0	0.0	11.1	0.2	0.0	0.4	0.0	0.0	0.0	0.0	0.9
sterile white-greenish	2.2	3.7	0.0	0.0	0.0	16.7	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.7	0.0	0.0
<i>Verrucaria</i> cfr. <i>dolosa</i>	2.2	3.7	0.0	16.7	0.0	0.0	0.0	0.0	0.4	0.6	0.0	2.7	0.0	0.0	0.0	0.0
<i>Xanthoria elegans</i>	2.2	0.0	5.6	0.0	0.0	0.0	11.1	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.4	0.0

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831 Table 2. Percentage contribution from the SDR Simplex analyses of saxicolous lichen communities
 832 in the two study areas. Results are reported for the entire dataset and, separately, for Area A (Mt.
 833 Musiné) and Area B (Monviso) for the five lithologies (abbreviations in Table 1) and for the overall
 834 ultramafics (Dun+Lhe+Ser_A+Ser_B).

Dataset	Similarity (S)	Species replacement (R)	Richness difference (D)	Relativized beta-diversity (R+D)	Relativized richness agreement (S+R)	Relativized nestedness (S+D)
All areas	28.36	52.91	18.73	71.64	81.27	47.09
Area A	36.75	42.61	20.64	63.25	79.36	57.39
- Dun	41.08	30.85	28.08	58.92	71.92	69.15
- Lhe	42.91	34.89	22.20	57.09	77.80	65.11
- Ser _A	50.60	40.94	8.46	49.40	91.54	59.06
Area B	41.59	42.87	15.54	58.41	84.46	57.13
- Ser _B	56.38	21.72	21.90	43.62	78.10	78.28
- MMg	62.97	24.34	12.69	37.03	87.31	75.66
All ultramafics	31.07	48.16	20.76	68.93	79.24	51.84

835
836

837 Table 3. XRF analyses of metal contents (av. weight % \pm standard error) in (a) the five investigated
 838 lithologies (abbreviations in Table 1), (b) lichen thalli on the different lithologies (average values of
 839 crustose species, excluding *Lecanora polytropa*), (d) thalli of *Aspicilia caesiocinerea* (A. cae) and
 840 *Aspicilia cinerea* (A. cin), *Candelariella vitellina* (C. vit), *Lecanora polytropa* (L. pol) and
 841 *Lecanora bicincta* (L. bic), *Lecidella* cfr. *carpathica* (L. car.), *Rhizocarpon geographicum* (R. geo),
 842 *Rhizocarpon reductum* (R. red), *Rhizocarpon polycarpum* (R. pol), *Umbilicaria cylindrica* (U. cyl),
 843 and *Xanthoparmelia* gr. *stenophylla* (X. ste) on the different lithologies. (c) Pearson correlation
 844 between av. metal contents in lithologies and lichen thalli (average values per lithology). According
 845 to Tukey's test, metal contents measured for the different lithologies/thalli which do not share at
 846 least one letter are statistically different.

(a) Rocks									
	Mg	Al	Si	Ca	Cr	Fe	Ni		
Dun	39.8 (\pm 3.2) bc	1.7 (\pm 0.4) a	33 (\pm 1) b	0.6 (\pm 0.2) c	0.3 (\pm 0.2)	23.3 (\pm 3.2)	1.1 (\pm 0.2) a		
Lhe	32.3 (\pm 2.3) b	5.9 (\pm 1.1) bc	35.6 (\pm 1.3) b	6 (\pm 1.6) b	0.9 (\pm 0.4)	18.2 (\pm 2.4)	0.7 (\pm 0.1) ab		
SerA	43.8 (\pm 0.7) c	1.2 (\pm 0.1) a	39.2 (\pm 1.2) b	0.7 (\pm 0.5) bc	0.2 (\pm 0.1)	14.3 (\pm 1.4)	0.5 (\pm 0.1) bc		
SerB	41.8 (\pm 0.5) bc	2.3 (\pm 0.3) ab	40.6 (\pm 1.4) ab	0.2 (\pm 0) bc	1 (\pm 0.1)	14.1 (\pm 1.6)	0.1 (\pm 0) c		
MMg	12.4 (\pm 1.6) a	9.2 (\pm 0.8) c	48.5 (\pm 3.6) a	16.4 (\pm 1.6) a	0.2 (\pm 0)	12.8 (\pm 1.8)	0 (\pm 0) c		
(b) Lichens									
	Mg	Al	Si	Ca	Cr	Fe	Ni	Mg/Ca	Mg/Fe
Dun	19 (\pm 1.3) c	6.5 (\pm 0.5) c	35.4 (\pm 1.6) b	3.3 (\pm 1)	0.9 (\pm 0.6)	33.7 (\pm 1.8) a	0.8 (\pm 0.1) a	9.5 (\pm 1.1) ab	0.6 (\pm 0.1)
Lhe	10.5 (\pm 0.9) b	10 (\pm 0.5) b	45.1 (\pm 1.4) d	5.5 (\pm 0.7)	0.9 (\pm 0.3)	27.5 (\pm 1.6) ab	0.2 (\pm 0.1) b	3.2 (\pm 0.5) b	1 (\pm 0.6)
SerA	21.3 (\pm 1.9) c	7 (\pm 0.6) c	39.4 (\pm 1.4) bc	4.6 (\pm 0.6)	0.6 (\pm 0.1)	26.2 (\pm 2) bc	0.4 (\pm 0.1) b	11.9 (\pm 3.2) a	1.2 (\pm 0.2)
SerB	22.4 (\pm 2.5) c	8.2 (\pm 0.9) bc	44.3 (\pm 1.4) cd	4.9 (\pm 1.3)	1 (\pm 0.1)	18.8 (\pm 1.5) c	0.3 (\pm 0.1) b	13.7 (\pm 3.3) a	1.5 (\pm 0.2)
MMg	3.3 (\pm 0.7) a	13.8 (\pm 0.6) a	54 (\pm 2.9) a	6.2 (\pm 1.1)	0.2 (\pm 0.1)	22.4 (\pm 2.4) bc	0 (\pm 0) b	0.9 (\pm 0.2) b	0.1 (\pm 0)
(c) Rock-Lichen correlation									
	Mg	Al	Si	Ca	Cr	Fe	Ni		
	0.959	0.981	0.866	0.794	0.765	0.886	0.848		
(d) Species									
	Mg	Al	Si	Ca	Cr	Fe	Ni	Mg/Ca	Mg/Fe
A. cae - Dun	17.1 (\pm 3) bc	5.3 (\pm 0.8) c	31 (\pm 4.5) c	1.9 (\pm 0.2)	0.3 (\pm 0)	42.5 (\pm 6.4) c	1.3 (\pm 0.4) a	10.3 (\pm 3.2) ab	0.5 (\pm 0.1) a
A. cin.Lhe	10.9 (\pm 2.3) ab	9.2 (\pm 0.8) b	45.2 (\pm 3.2) b	4.1 (\pm 1.2)	1.8 (\pm 1.4)	28.3 (\pm 3.3) bc	0.2 (\pm 0.2) b	5.1 (\pm 2.4) ab	0.5 (\pm 0.1) a
A. cin.SerA	24.5 (\pm 3.4) cd	4.9 (\pm 0.7) c	36.1 (\pm 1.8) bc	3.6 (\pm 1.1)	0.8 (\pm 0.2)	29.1 (\pm 3.1) bc	0.3 (\pm 0.1) b	12 (\pm 3.6) ab	1 (\pm 0.2) a
A. cae.SerB	36.1 (\pm 2.4) d	3.5 (\pm 0.7) c	42 (\pm 1.5) bc	5.2 (\pm 2.5)	1.4 (\pm 0.2)	11.8 (\pm 1) a	0.1 (\pm 0) b	20.2 (\pm 9) b	3.2 (\pm 0.5) b
A. cin.MMg	2.8 (\pm 1.2) a	13.1 (\pm 0.3) a	61.3 (\pm 2.1) a	6.8 (\pm 0.6)	0.1 (\pm 0.1)	15.7 (\pm 1.5) ab	0 (\pm 0) b	0.4 (\pm 0.2) a	0.2 (\pm 0.1) a
C. vit.Dun	17.8 (\pm 2) b	8.8 (\pm 0.8)	38.3 (\pm 2.5) a	2.6 (\pm 0.2)	0.3 (\pm 0.1)	30.9 (\pm 2.5)	0.7 (\pm 0.3)	7.3 (\pm 1.1)	0.6 (\pm 0.1)
C. vit.Lhe	9.5 (\pm 2) ab	13.4 (\pm 1.4)	48.8 (\pm 1.2) b	4.5 (\pm 1)	0.5 (\pm 0.1)	23.1 (\pm 1.7)	0.3 (\pm 0.1)	3.5 (\pm 1)	0.4 (\pm 0.1)
C. vit.SerA	15.3 (\pm 1.9) b	10.1 (\pm 0.9)	41.2 (\pm 3.6) ab	4.8 (\pm 0.5)	0.7 (\pm 0.2)	26.6 (\pm 3.3)	0.7 (\pm 0.1)	3.6 (\pm 0.7)	0.6 (\pm 0.1)
C. vit.SerB	15.3 (\pm 4) b	11.9 (\pm 1.6)	47.7 (\pm 2.3) ab	2.5 (\pm 0.6)	0.6 (\pm 0.1)	21.8 (\pm 3.4)	0.1 (\pm 0.1)	8.6 (\pm 3.9)	0.8 (\pm 0.2)
C. vit.MMg	4.3 (\pm 0.4) a	14.3 (\pm 0.4)	51.3 (\pm 2.8) b	2.5 (\pm 0.4)	0.3 (\pm 0)	27.1 (\pm 3.8)	0 (\pm 0)	1.9 (\pm 0.2)	0.2 (\pm 0)
L. car.Dun	25.9 (\pm 1.4) a	4.6 (\pm 0.6) a	32.1 (\pm 2.2) a	1.7 (\pm 0.1)	0.2 (\pm 0) b	33.9 (\pm 2.3) a	1.1 (\pm 0.2) a	16 (\pm 1.3) bc	0.8 (\pm 0.1) ab
L. car.Lhe	7.2 (\pm 1.2) c	10.9 (\pm 0.3) b	46.3 (\pm 2.2) b	5.9 (\pm 1.5)	0.5 (\pm 0.1) b	29.2 (\pm 2.8) ab	0 (\pm 0) b	1.6 (\pm 0.4) a	0.3 (\pm 0) a
L. car.SerA	14.2 (\pm 3) bc	9.6 (\pm 1) b	39.1 (\pm 5.4) ab	6.6 (\pm 2.3)	0.2 (\pm 0.1) b	29.9 (\pm 6.2) ab	0.2 (\pm 0.1) b	4.1 (\pm 1.5) ab	0.7 (\pm 0.2) ab
L. car.SerB	23.2 (\pm 6.1) ab	8.2 (\pm 1.9) ab	48.6 (\pm 2.7) b	2 (\pm 0.5)	0.9 (\pm 0.2) a	17.1 (\pm 1.7) b	0 (\pm 0) b	1.9 (\pm 10.2) c	1.5 (\pm 0.5) b
L. pol.Dun	10.9 (\pm 2.5) b	4.9 (\pm 0.7) b	21.7 (\pm 3.2) a	41.5 (\pm 8.5) a	0.4 (\pm 0.1)	19.7 (\pm 3.2) ab	0.6 (\pm 0.2) a	0.4 (\pm 0.2) b	0.5 (\pm 0.1) b
L. bic.Lhe	7.6 (\pm 1.9) b	8.8 (\pm 1.3) b	44.9 (\pm 3.4) b	9.9 (\pm 3.1) b	0.6 (\pm 0.2)	27.9 (\pm 1.6) b	0.2 (\pm 0.1) ab	1.4 (\pm 0.5) b	0.3 (\pm 0.1) b
L. pol.SerA	12.9 (\pm 4.6) ab	8.2 (\pm 1.4) ab	43.6 (\pm 6) b	4.9 (\pm 10.9) ab	0.4 (\pm 0.1)	19.5 (\pm 2.2) ab	0.1 (\pm 0.1) ab	5.3 (\pm 3.9) ab	0.6 (\pm 0.2) b
L. pol.SerB	27.7 (\pm 6.2) a	4.4 (\pm 1.1) b	38.1 (\pm 5.7) ab	6.4 (\pm 11.7) ab	1 (\pm 0.1)	12.3 (\pm 2.6) a	0 (\pm 0) b	5.2 (\pm 13.7) a	2.6 (\pm 0.7) a
L. pol.MMg	4.9 (\pm 0.5) b	14.3 (\pm 1.3) a	51.8 (\pm 0.9) b	4.4 (\pm 0.8) b	0.3 (\pm 0)	23.9 (\pm 2) b	0 (\pm 0) b	1.2 (\pm 0.2) b	0.2 (\pm 0) b
R. geo.Dun	16.6 (\pm 4.1) ab	6.2 (\pm 1.3) a	36.7 (\pm 4.7)	7.9 (\pm 4.5)	3.2 (\pm 2.7)	29 (\pm 2.4)	0.4 (\pm 0.2) ab	5.2 (\pm 2.5) ab	0.6 (\pm 0.2) b
R. geo.Lhe	12 (\pm 1.8) b	6.7 (\pm 0.7) a	36.9 (\pm 3.2)	8.2 (\pm 2.5)	1.1 (\pm 0.2)	34.1 (\pm 4.9)	0.3 (\pm 0.1) b	2 (\pm 0.3) b	0.5 (\pm 0.1) b
R. geo.SerA	28.2 (\pm 5.5) a	4.7 (\pm 1) a	41.7 (\pm 2)	4.4 (\pm 1.8)	0.5 (\pm 0.2)	19.9 (\pm 5.3)	0.3 (\pm 0.1) b	5.9 (\pm 12.4) a	2.4 (\pm 0.8) a
R. geo.SerB	18.7 (\pm 4.3) ab	8 (\pm 1.4) a	36.5 (\pm 1.9)	7.6 (\pm 2.8)	1.4 (\pm 0.2)	26.8 (\pm 3.7)	1 (\pm 0.3) a	4.4 (\pm 2) ab	0.8 (\pm 0.2) b
R. geo.MMg	2.6 (\pm 1.8) b	13.9 (\pm 1.9) b	49.5 (\pm 7.3)	9.3 (\pm 2.5)	0.2 (\pm 0.2)	24.3 (\pm 5.1)	0 (\pm 0) b	0.3 (\pm 0.2) ab	0.1 (\pm 0.1) b
R. red.Dun	15.3 (\pm 0.9)	11.8 (\pm 0.1) ab	46.7 (\pm 1.8)	2.5 (\pm 0.2)	0.6 (\pm 0)	23.1 (\pm 2.6)	0.1 (\pm 0.2)	8.1 (\pm 0.4)	0.6 (\pm 0.1)
R. red.Lhe	13.1 (\pm 2.3)	10.2 (\pm 0.9) b	50.4 (\pm 3.9)	4 (\pm 0.7)	0.5 (\pm 0.2)	21.1 (\pm 3.5)	0.3 (\pm 0.1)	4.3 (\pm 1.1)	4 (\pm 3.4)
R. red.SerA	24.2 (\pm 4.1)	5.4 (\pm 0.9) a	38.4 (\pm 2.8)	3.5 (\pm 1)	0.6 (\pm 0.2)	26.8 (\pm 3.5)	0.5 (\pm 0.2)	13 (\pm 5.4)	1 (\pm 0.2)
R. pol.SerB	17.9 (\pm 7)	9.8 (\pm 2.6) ab	47.4 (\pm 3.4)	8 (\pm 6.1)	0.6 (\pm 0.3)	16.3 (\pm 2.3)	0.1 (\pm 0)	13 (\pm 9)	1.1 (\pm 0.4)
U. cyl.SerB	2.1 (\pm 1)	17 (\pm 0.7)	45.4 (\pm 5.1)	5.6 (\pm 1)	0 (\pm 0)	29.9 (\pm 6.8)	0 (\pm 0)	0.3 (\pm 0.2)	0.1 (\pm 0.1)
U. cyl.MMg	0 (\pm 0)	14.6 (\pm 1.9)	42.4 (\pm 7.8)	2.1 (\pm 0.7)	0 (\pm 0)	40.9 (\pm 9.1)	0 (\pm 0)	0 (\pm 0)	0 (\pm 0)
X. ste.Dun	1.6 (\pm 1.6)	2 (\pm 0.5) a	5.8 (\pm 1.1) a	80.7 (\pm 5.5) a	0.5 (\pm 0.4)	9.4 (\pm 3.9)	0 (\pm 0)	0 (\pm 0)	0.2 (\pm 0.2)
X. ste.Lhe	8.7 (\pm 2.6)	5.6 (\pm 0.6) b	22.4 (\pm 2.8) b	41.5 (\pm 4.6) b	1.6 (\pm 0.4)	19.6 (\pm 3.6)	0 (\pm 0)	0.3 (\pm 0.1)	0.7 (\pm 0.2)
X. ste.SerA	6.2 (\pm 0.9)	4.5 (\pm 1.1) ab	14.7 (\pm 4.1) ab	55.2 (\pm 8.4) b	0.4 (\pm 0.4)	17.1 (\pm 5.2)	0 (\pm 0)	0.1 (\pm 0)	0.5 (\pm 0.1)

849 **Figure captions**

850

851 Fig. 1. Location (a, b) and geological setting (c, d) of the study areas A (Mt. Musiné, c, simplified
 852 from Elter *et al.* 2005) and B (Monviso Massif, d, simplified from Rolfo *et al.* 2015). Squares
 853 indicate the surveyed plots on dunites (black), lherzolites (dark grey), serpentinites (light grey), and
 854 Mg-Al metagabbros (white).

855

856 Fig. 2. Ordination of lithologies and lichens on the basis of their metal contents (av. weight %)
 857 measured by XRF.

858

859 Fig. 3. Ordination of specimens of *Aspicilia cinerea*-*A. caesiocinerea* (a), *Candelariella vitellina*
 860 (b), *Lecidella carpathica* (c), *Rhizocarpon geographicum* (d), and *Rhizocarpon reductum*-*R.*
 861 *polycarpum* (e) from different lithologies (abbreviations in Table 2) on the basis of their secondary
 862 metabolite patterns (matrix of presence/absence of metabolites with a certain R_f and colour under
 863 short UV length: identified metabolites listed in the low right corner, details in Supplementary
 864 Material 5).

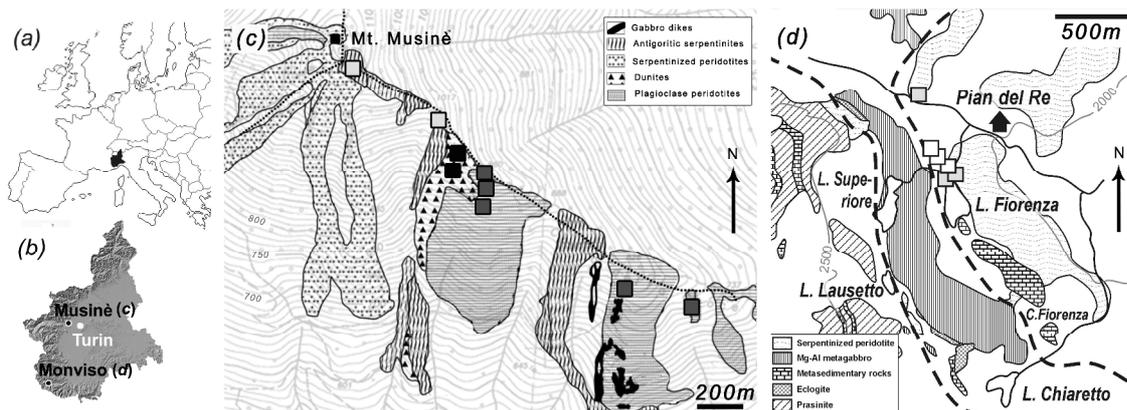
865

866 Fig. 4. Factorial maps in the canonical correspondence analysis (CCA) showing the position of
 867 lichen secondary metabolites (crosses; identified metabolites listed in the low right corner, details in
 868 Supplementary Material 5) and av. metal contents in lichen thalli (symbols according to Fig. 2)
 869 together with the contributions of the different metals. (a) *Aspicilia caesiocinerea* and *A. cinerea*;
 870 (b) *Candelariella vitellina*; (c) *Lecidella* cfr. *carpathica*; (d) *Rhizocarpon geographicum*; and (e)
 871 *Rhizocarpon reductum* and *R. polycarpum*. All the extracted axes displayed in the figure were
 872 significant according to Monte Carlo test. Environmental factors (metals) exhibiting conditional
 873 effects are listed on the diagrams.

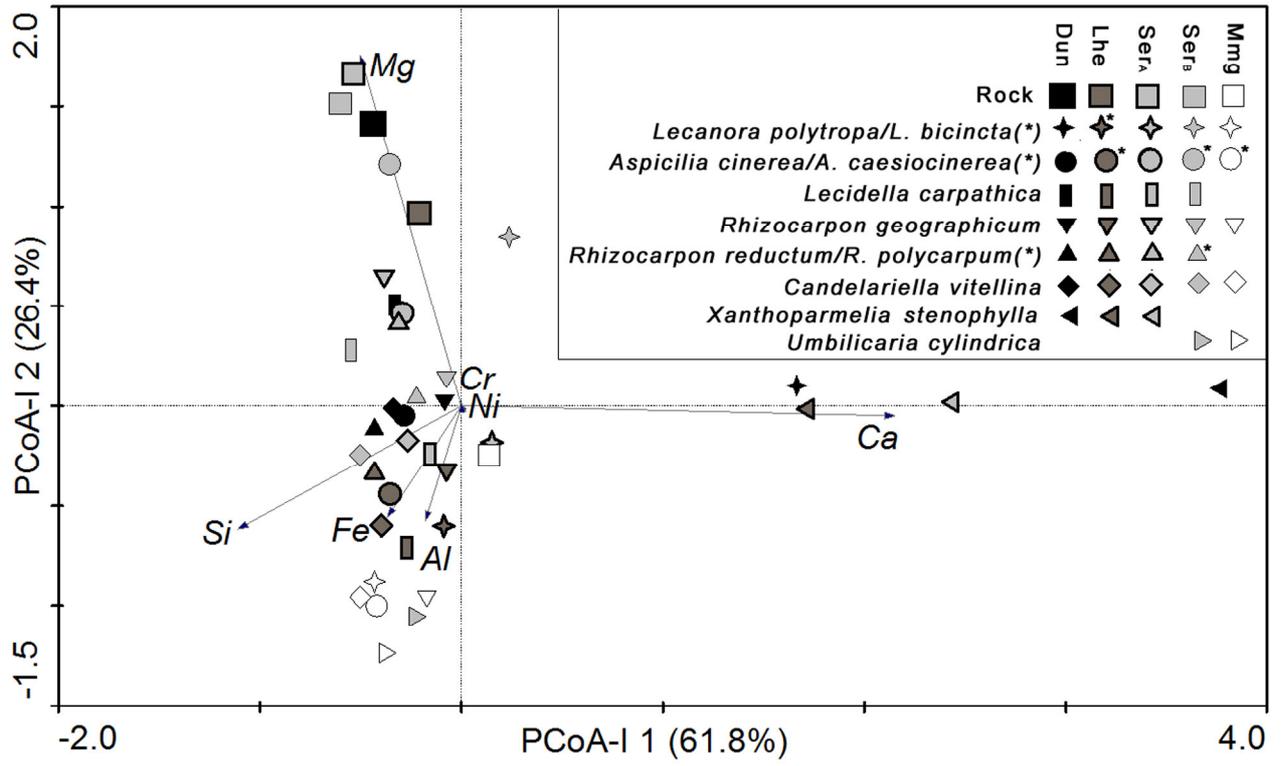
874

875 Fig. 5. Mineral fraction detached from the bare surface of the different lithologies (abbreviations in
 876 Table 2) by pull-up tests: weight (dark grey columns) and abundance (light grey columns) of
 877 detached fragments (av. \pm standard error). According to Tukey's test, columns not sharing at least
 878 one letter are statistically different.

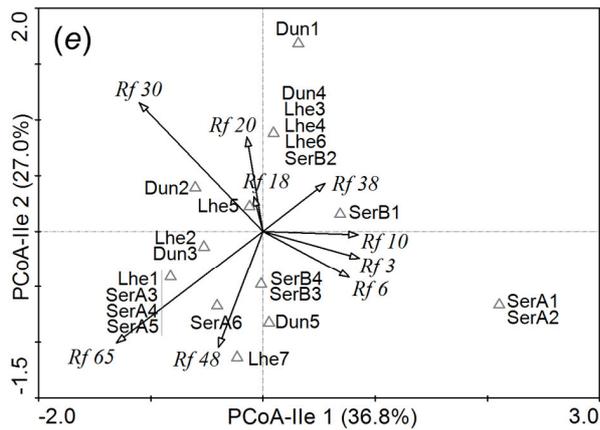
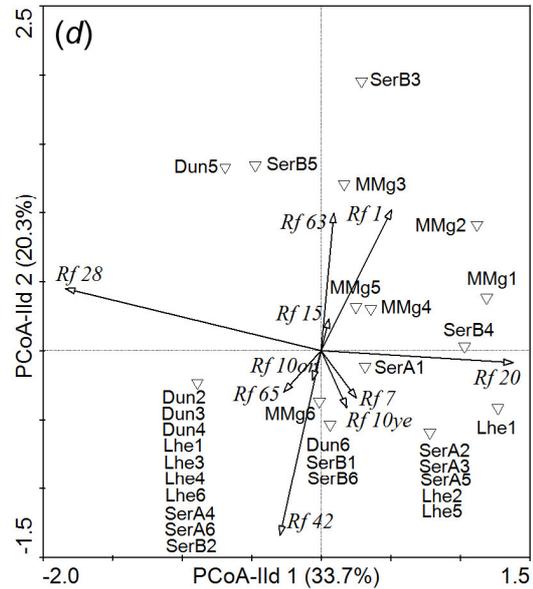
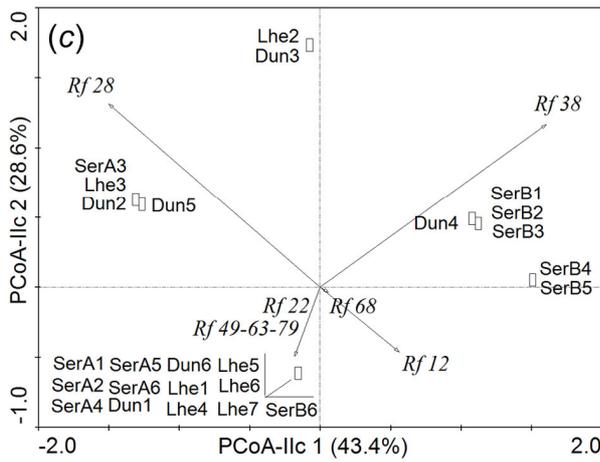
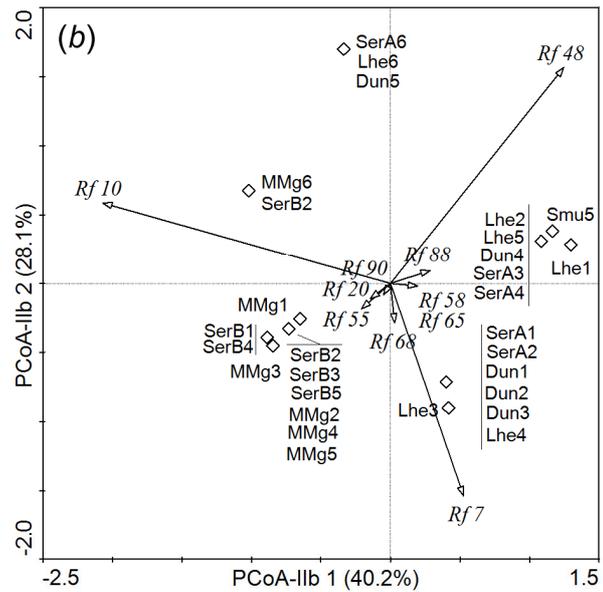
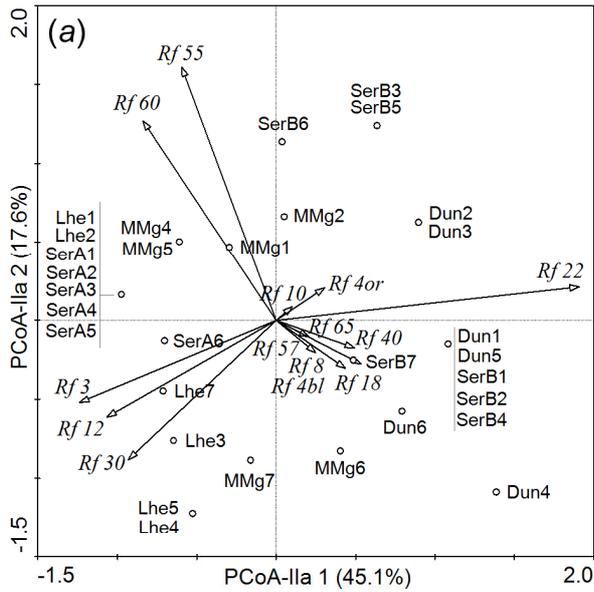
879



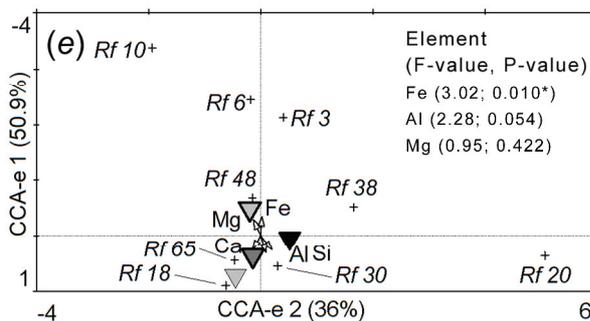
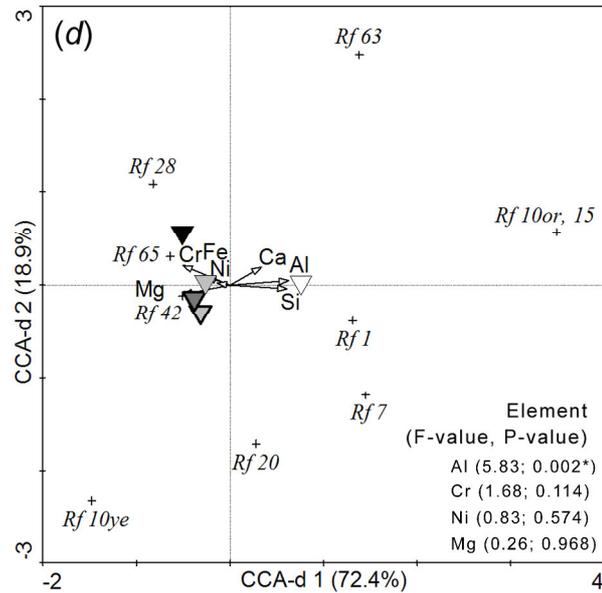
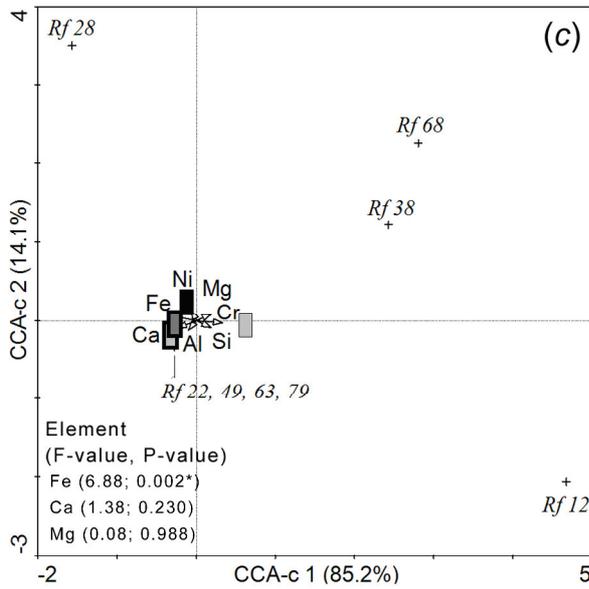
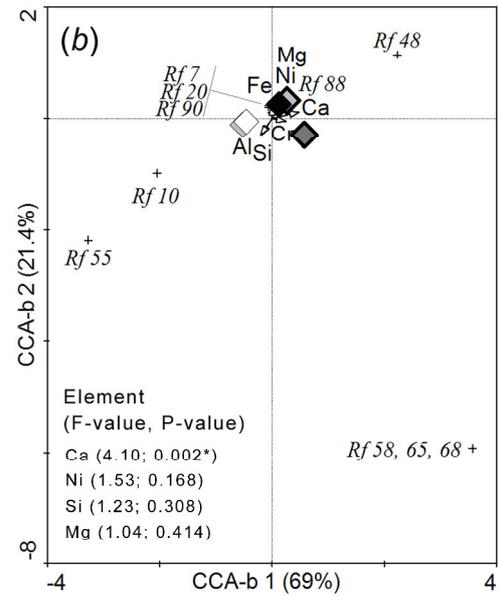
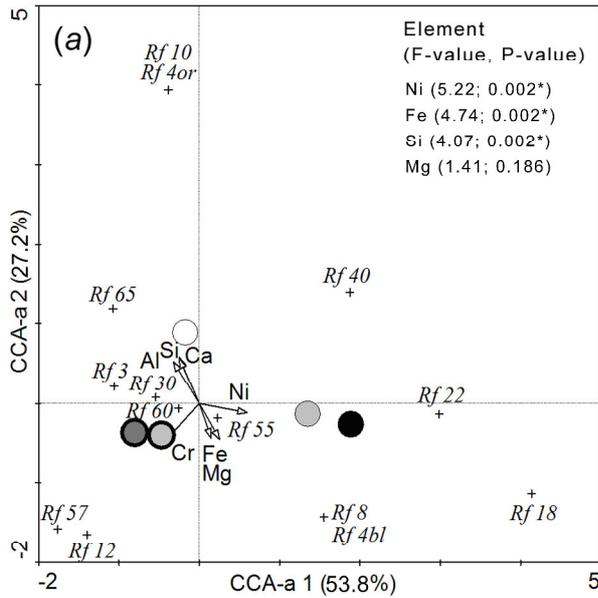
880



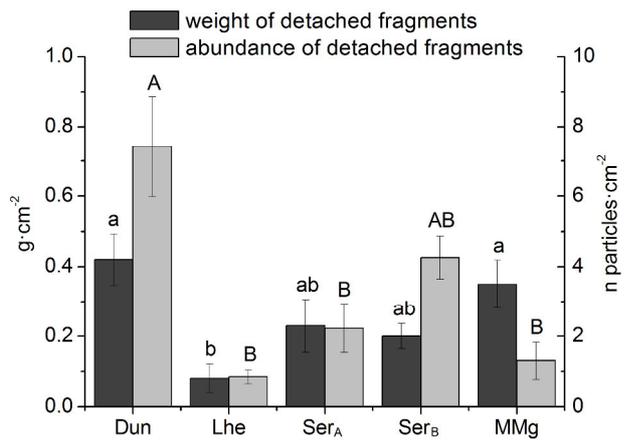
881



- (a) *Rf 3*: connorstictic ac. *Rf 12*: cfr. substictic ac. *Rf 30*: norstictic ac.
- (b) *Rf 7*: pulvinic ac. *Rf 88*: calycin *Rf 90*: pulvic acid lactone
- (c) *Rf 38*: cfr. (iso-)arthotelin *Rf 49*: cfr. thiophanic ac. *Rf 63*: cfr. chodatin *Rf 68*: cfr. 2,5,7 trichloro-3-O-methylnorlichexanthone *Rf 79*: atranorin
- (d) *Rf 42*: psoromic ac. *Rf 65*: rhizocarpic ac.
- (e) *Rf 3*: connorstictic ac. *Rf 12*: cfr. substictic ac. *Rf 18*: stictic ac. *Rf 30*: norstictic ac. *Rf 65*: rhizocarpic ac.
- Others: non identified



- (a)** *Rf* 3: connorstictic ac.
Rf 12: cfr. substictic ac.
Rf 30: norstictic ac.
- (b)** *Rf* 7: pulvinic ac.
Rf 88: calycin
Rf 90: pulvic acid lactone
- (c)** *Rf* 38: cfr. (iso-)arthotelin
Rf 49: cfr. thiophanic ac.
Rf 63: cfr. chodatin
Rf 68: cfr. 2,5,7 trichloro-3-O-methylnorlichexanthone
Rf 79: atranorin
- (d)** *Rf* 42: psoromic ac.
Rf 65: rhizocarpic ac.
- (e)** *Rf* 3: connorstictic ac.
Rf 12: cfr. substictic ac.
Rf 18: stictic ac.
Rf 30: norstictic ac.
Rf 65: rhizocarpic ac.
 Others: non identified



884