

# 1 **Feedbacks between the formation of secondary minerals and the** 2 **infiltration of fluids into the regolith of granitic rocks in different** 3 **climatic zones (Chilean Coastal Cordillera)**

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14

15 **Abstract.** Subsurface fluid pathways and the climate-dependent infiltration of fluids into the subsurface jointly control the  
16 intensity and depth of mineral weathering reactions. The products of these weathering reactions (secondary minerals), such as  
17 Fe(III) oxyhydroxides and clay minerals, in turn exert a control on the subsurface fluid flow and hence on the development of  
18 weathering profiles.

19 We explored the dependence of mineral transformations on climate during the weathering of granitic rocks in two 6 m deep  
20 weathering profiles in Mediterranean and humid climate zones along the Chilean Coastal Cordillera. We used geochemical  
21 and mineralogical methods such as (micro-) X-ray fluorescence, oxalate/dithionite extractions, X-ray diffraction and electron  
22 microprobe mapping to elucidate the transformations involved during weathering. In the profile of the Mediterranean climate  
23 zone, we found a low weathering intensity affecting the profile down to 6 m depth. In the profile of the humid climate zone,  
24 we found a high weathering intensity. Based on our results, we propose mechanisms that can intensify the progression of  
25 weathering to depth. The most important is weathering-induced fracturing (WIF) by Fe(II) oxidation in biotite and precipitation  
26 of Fe(III) oxyhydroxides, and by swelling of interstratified smectitic clay minerals that promotes the formation of fluid  
27 pathways. We also propose mechanisms that mitigate the development of a deep weathering zone, like the precipitation of  
28 secondary minerals (e.g., clay minerals) and amorphous phases that can impede the subsurface fluid flow. We conclude that  
29 the depth and intensity of primary mineral weathering in the profile of the Mediterranean climate zone is significantly  
30 controlled by WIF. It generates a surface-subsurface connectivity that allows fluid infiltration to great depth and hence  
31 promotes a deep weathering zone. Moreover, the water supply to the subsurface is limited in the Mediterranean climate and  
32 thus most of the weathering profile is generally characterized by a low weathering intensity. The depth and intensity of  
33 weathering processes in the profile of the humid climate zone, on the other hand, are controlled by an intense formation of

34 secondary minerals in the upper section of the weathering profile. This intense formation arises from pronounced dissolution  
35 of primary minerals due to the high water infiltration (high precipitation rate) into the subsurface. The secondary minerals, in  
36 turn, impede the infiltration of fluids to great depth and thus mitigate the intensity of primary mineral weathering at depth.  
37 These two settings illustrate that the depth and intensity of primary mineral weathering in the upper regolith are controlled by  
38 positive and negative feedbacks between the formation of secondary minerals and the infiltration of fluids.

39

40 **Keywords:** Coastal Cordillera, feedback, weathering-induced fracturing, secondary minerals, Critical Zone, fluid flow

## 41 **1 Introduction**

42 The formation of weathered material (regolith) from unweathered rock (bedrock) is a key process for shaping Earth's surface.  
43 It is of major importance for making mineral-bound nutrients accessible to the biosphere of the Critical Zone (e.g., Dawson et  
44 al., 2020) and to supply rocks and minerals to the sediment cycle. In this process the in-situ disaggregation and chemical  
45 depletion of weathered rock (saprock) to saprolite plays an essential role. This transformation is a result of fracturing and  
46 mineral dissolution (e.g., Navarre-Sitchler et al., 2015). Both are associated with chemical, physical (e.g., Goodfellow et al.,  
47 2016), and biological weathering processes (e.g., Drever, 1994; Lawrence et al., 2014; Napieralski et al., 2019). These  
48 processes are linked to climate-related parameters such as precipitation rate, fluid flow (water and gases), and biological  
49 activity. Apart from that, the weathering processes and hence the saprolite formation also depend on primary fractures (e.g.,  
50 Molnar et al., 2007; Hynek et al., 2017; Kim et al., 2017; Holbrook et al., 2019; Hayes et al., 2020; Krone et al., 2021; Hampl  
51 et al. 2022a), discontinuity density and tortuosity (Israeli et al., 2021), thermoelastic relaxation (e.g., Nadan and Engelder,  
52 2009) as well as the topographic surface profile (e.g., Rempe and Dietrich, 2014; St. Clair et al., 2015). However, one of the  
53 most fundamental parameters for the regolith formation is the mineral content of the bedrock. The weathering of some of these  
54 primary minerals and the consequent formation of secondary minerals can lead to an amplification of the depth and intensity  
55 (i.e., the parameter describing the elemental loss and relative amount of secondary minerals) of primary mineral weathering  
56 (e.g., Fletcher et al., 2006; Lebedeva et al., 2007; Buss et al., 2008; Behrens et al., 2015; Hampl et al. 2022a). Such mechanisms  
57 comprise (1) a forcing process like the formation of secondary minerals that is triggering (2) a responsive process such as more  
58 intense infiltration of fluids to depth. The latter process reinforces the initial forcing process of secondary mineral formation.  
59 Such a mechanism is therefore called positive feedback between (1) and (2). The formation of secondary minerals can also  
60 have a weathering-impeding effect (e.g., Lohse and Dietrich, 2005; Navarre-Sitchler et al., 2015; Kim et al., 2017; Gerrits et  
61 al., 2021) causing a mitigation of the weathering depth and -intensity. Such mechanisms comprise (1) a forcing process like  
62 the formation of secondary minerals and (2) a responsive process such as reduced infiltration of fluids to depth. The latter  
63 process damps the initial forcing process of secondary mineral formation, and the mechanism is therefore called negative  
64 feedback between (1) and (2).

65 Deciphering the relationship between the formation of secondary minerals and the climatic conditions they were formed under  
66 is a prerequisite for understanding the weathering system. It allows to determine whether feedbacks between the formation of  
67 secondary minerals and the infiltration of fluids affect the intensity and depth of primary mineral weathering. We hypothesize  
68 that a positive feedback loop results in a deep weathering depth, as secondary minerals form fluid pathways by fracturing due  
69 to volume increase. On the other hand, we think that a negative feedback loop leads to a shallow weathering depth, as the  
70 precipitation of secondary minerals seals fluid pathways.

71 To explore such connections and to elucidate the impact of secondary minerals on the development of weathering systems in  
72 different climatic zones, we investigated two 6 m deep weathering profiles in the Chilean Coastal Cordillera. One profile is  
73 located in a Mediterranean (mean annual temperature: 14.9 °C, mean annual precipitation: 436 mm yr<sup>-1</sup>) and another in a humid  
74 climate zone (mean annual temperature: 14.1 °C, mean annual precipitation: 1084 mm yr<sup>-1</sup>) (Scheibe et al., 2023), and both  
75 developed from weathering of granitic rock. Both sites are eroding and the surfaces in the locations are thus constantly turned  
76 over (see compilation of rates and environmental parameters in Oeser and von Blanckenburg (2020) and references therein).  
77 The profiles were sampled in soil pits and complemented with rock samples obtained by deep wireline rotary drilling close to  
78 the soil pits. Samples were investigated by a combination of analytical techniques such as X-ray fluorescence and micro-X-  
79 ray fluorescence as well as oxalate-/dithionite extraction to characterize the geochemical composition, and X-ray diffraction,  
80 magnetic susceptibility measurements, electron microprobe as well as light microscopy to identify the mineral assemblages.  
81 The combined results of these techniques are used to derive weathering-intensifying and -mitigating processes during  
82 subsurface weathering and to elucidate how these processes influence the depth and intensity of weathering in the different  
83 climate zones.

## 84 **2 Study sites**

### 85 **2.1 La Campana (LC)**

86 The soil pit (-33.02833° N, -71.04370° E, 894 m) and the drilling site some 15 m next to it (-33.02833° N, -71.04354° E,  
87 898 m) are located south of the La Campana National Park approximately 60 km NW of Santiago de Chile (Fig. 1a). They are  
88 situated on a ridge with steep slope dip angles of 20–30°.

89 The vegetation can be characterized as Mediterranean sclerophyllous forest with *Cryptocarya alba* and *Lithraea caustica* as  
90 dominant plants (Luebert and Pliscoff, 2006; Oeser et al., 2018; Fig. 1b,c). The annual precipitation rate (measured from April  
91 2016 to April 2020) is 346 mm yr<sup>-1</sup> (Übernicketl et al., 2020) and the Holocene net primary production is 280 ± 50 g C m<sup>-2</sup> yr<sup>-1</sup>  
92 (Werner et al., 2018; Oeser and von Blanckenburg, 2020). Records of long-term meteorological data (e.g., precipitation at  
93 ground level, soil water content, air temperature, relative humidity) from a weather station near the study site can be found in  
94 Übernicketl et al. (2020).

95 The regolith profile developed on top of Upper Cretaceous intrusions of mainly granodiorites and tonalites with subordinate  
96 quartz monzodiorites (Gana et al., 1996). The depths of the soil horizons are A: 0–30 cm, B: 30–83 cm and C (saprolite): >83

97 cm (Fig. 1d). Uplift rates for the north of Santiago de Chile vary between 0.01 and 0.23 mm yr<sup>-1</sup> with a general mean value of  
98 0.13 ± 0.04 (Melnik, 2016). The soil denudation rate in the nearby La Campana National Park is 53.7 ± 3.4 (S-facing slope)  
99 to 69.2 ± 4.6 t km<sup>-2</sup> yr<sup>-1</sup> (N-facing slope) (Oeser et al., 2018) or assuming a material density of 2.6 g cm<sup>-3</sup>, 0.024 mm yr<sup>-1</sup> on  
100 average.

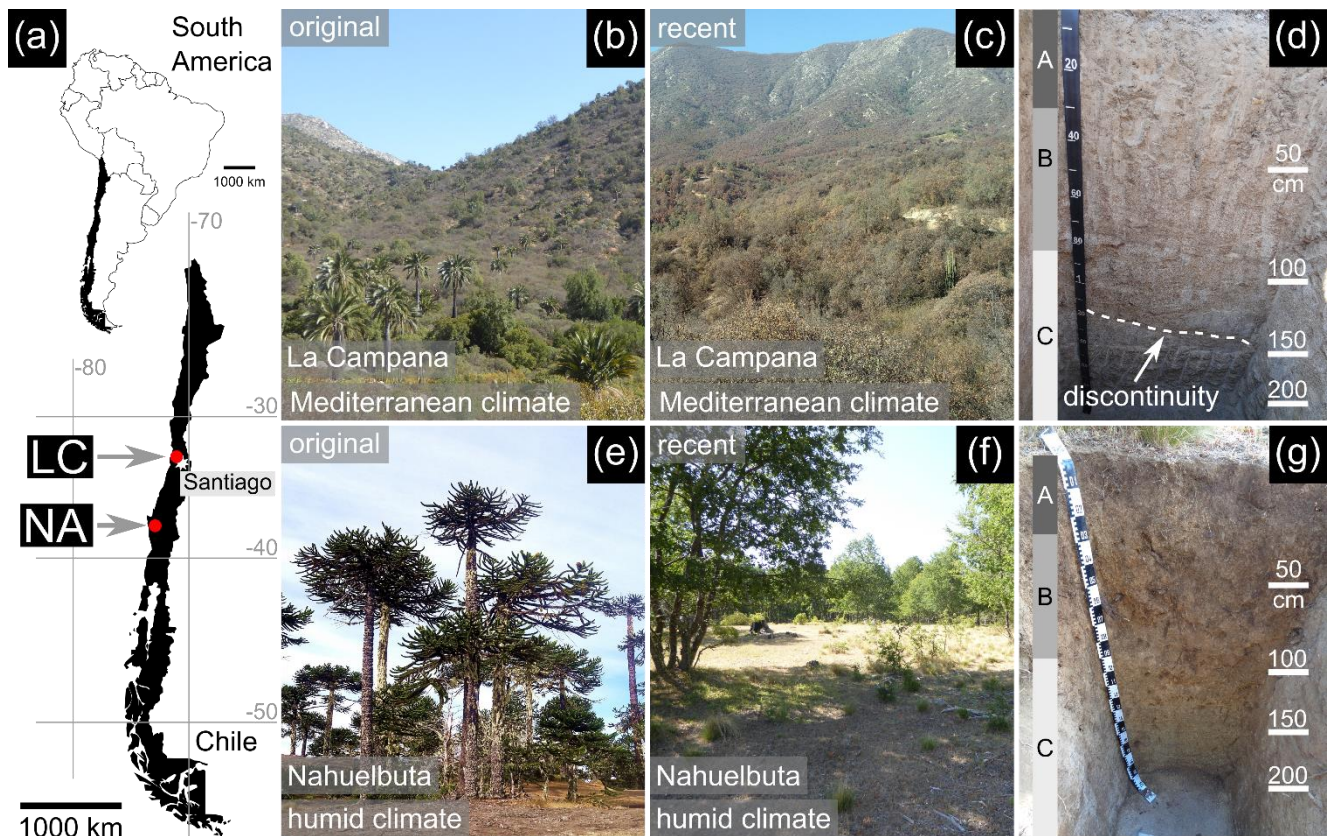
## 101 2.2 Nahuelbuta (NA)

102 The investigated soil pit (-37.79371° N, -72.95065° E, 1113 m) and the drilling site next to it (-37.79381° N, -72.95043° E,  
103 1114 m) are located approximately 20 km west of Angol (Region IX (Araucanía), Province Malleco) in southern Chile (Fig.  
104 1a). The borehole was located on a plateau-like ridge with gently dipping slopes (ca. 10°).

105 The pre-land-use vegetation in the study area resembled the recent vegetation found in the Nahuelbuta National Park which  
106 can be characterized as temperate forest with *Araucaria araucana* as the dominant tree (Luebert and Pliscoff, 2006; Fig. 1e).  
107 However, extensive modern pastoral farming (cow grazing) and fires have converted the ecosystem in the study area to a  
108 sparse forest of deciduous trees such as *Nothofagus obliqua* (see Oeser et al., 2018; Fig. 1f). Numerous signs of burning can  
109 be observed in the field and charcoal is an integral component of the soil down to 25 cm (A horizon). The precipitation rate  
110 (measured from end of March 2016 to April 2020) is 1927 mm yr<sup>-1</sup> (Übernicker et al., 2020) and the Holocene net primary  
111 production is 520 ± 130 g C m<sup>-2</sup> yr<sup>-1</sup> (Werner et al., 2018; Oeser and von Blanckenburg, 2020). Records of long-term  
112 meteorological data (e.g., precipitation at ground level, soil water content, air temperature, relative humidity) from a weather  
113 station near the study site can be found in Übernicker et al. (2020).

114 The regolith profile developed on top of granitoid rocks of the Nahuelbuta central pluton which contains heterogenous  
115 lithological portions (Hervé, 1977; Ferraris, 1979). It is part of the Nahuelbuta Batholith which in turn belongs to the late  
116 Carboniferous Chilean Coastal Batholith (Steenken et al., 2016; Deckart et al., 2013). The depths of the soil horizons are A:  
117 0–25 cm, B: 25–90 cm, and C (saprolite): >90 cm (Fig. 1g). Today's exhumation rates in NA are high (>0.2 mm yr<sup>-1</sup>; Glodny  
118 et al., 2008b), whereas the catchment-wide denudation rate is small (27.4 ± 2.4 mm kyr<sup>-1</sup>; van Dongen et al., 2019) compared  
119 to LC. The soil denudation rate in the nearby Nahuelbuta National Park ranges between 17.7 ± 1.1 (N-facing slope) to 47.5 ±  
120 3.0 t km<sup>-2</sup> yr<sup>-1</sup> (S-facing slope) (Oeser et al., 2018) or assuming a material density of 2.6 g cm<sup>-3</sup>, 0.013 mm yr<sup>-1</sup> on average.  
121 Tectonic fractures in NA can be related to the Lanalhue Fault Zone (see Glodny et al., 2008a).

122



123 **Figure 1: Overview of the study sites and soil profiles.** (a) Position of La Campana (LC) and Nahuelbuta (NA) in Chile. Modified  
 124 map data from [OpenStreetMap](#) (© [OpenStreetMap](#) contributors). (b) Original vegetation in LC (i.e., before human intervention;  
 125 La Campana National Park). (c) Vicinity of the soil pit and drilling site in LC and (d) the first 2 m of the soil profile in LC with  
 126 inscribed soil horizons (A-C). A prominent discontinuity (dashed line) can be found in the depth interval 120–140 cm. (e) The original  
 127 vegetation in NA (i.e., before human intervention; Nahuelbuta National Park) in comparison to (f) the recent vegetation in the  
 128 vicinity of the soil pit and drilling site. (g) The first 2 m of the soil profile in NA with inscribed soil horizons (A-C).

## 129 3 Materials and methods

### 130 3.1 Soil pit sampling, drilling, and sample preparation

131 The sampled 6 m deep soil profiles were located close to the main boreholes at the respective sites. Bulk samples were collected  
 132 in 20 intervals in each soil pit and weighed around 3 kg. Corestones were not encountered in the soil pit profiles of LC and  
 133 NA. By using a rotary splitter (type PT, Retsch) the bulk samples were separated into aliquots (see Hampl et al., 2022b).  
 134 During the drilling campaigns, up to 1.5 m long core runs were recovered by wireline diamond drilling (~80 mm core diameter)  
 135 using potable water as drilling fluid (see Krone et al. (2021) for a detailed description of the drilling technique). Rock samples  
 136 were separated from the core by mechanical methods (angle grinder, hammer and chisel), cut (diamond saw), impregnated  
 137 with blue artificial resin filling the porosity, and subsequently thin-sectioned. Representative bedrock samples were separated  
 138 from the core (diamond saw) and crushed (jaw crusher).

### 139 3.2 Analytical methods and calculations

140 A detailed description of the analytical methods can be found in the accompanying data publication of this study (Hampl et  
141 al., 2022b).

#### 142 3.2.1 X-ray fluorescence (XRF) and micro-X-ray fluorescence ( $\mu$ -XRF)

143 Soil pit samples were ground with an agate disc mill and annealed (950°C for 1h) before adding a lithium borate flux to produce  
144 glass beads in platinum crucibles. The element composition of the glass beads was analysed with a Thermo Scientific ARL  
145 PERFORM<sup>®</sup>X X-ray fluorescence sequential spectrometer (WD-XRF; Thermo Fisher Scientific Inc., U.S.A.). Additional  
146 powder pellets were produced by mixing the ground air-dried samples with wax. The mixtures were pressed and analysed with  
147 a SPECTRO XEPOS energy dispersive X-ray fluorescence spectrometer (ED-XRF, SPECTRO Analytical Instruments GmbH,  
148 Germany). Polished sample slabs of bedrock (Fig. 2) were mapped for the spatial distribution of elements with a  $\mu$ -XRF  
149 spectrometer M4 Tornado (Bruker, Germany).

#### 151 Geochemical calculations

152 Zr contents obtained from the XRF element analyses on powder pellets were used as an immobile element for the calculation  
153 of the chemical depletion fraction (CDF; Riebe et al., 2003; Eq. 1), and the mass transfer coefficient ( $\tau$ ; Anderson et al., 2002;  
154 Eq. 2).

$$156 \text{ CDF} = 1 - \frac{Zr_N^b}{Zr_N^w}, \quad (1)$$

$$158 \tau = \frac{X^w \cdot Zr^b}{X^b \cdot Zr^w} - 1, \quad (2)$$

160  $X^b$  = concentration of element X in the bedrock,  $X^w$  = concentration of element X in the weathered sample,  $Zr^b$  = concentration  
161 of Zr in the bedrock,  $Zr_N^b$  = zirconium content of the bedrock normalized to a LOI-free sum of 100 % (see Hampl et al., 2022b),  
162  $Zr^w$  = concentration of Zr in the weathered sample,  $Zr_N^w$  = zirconium content of the weathered sample normalized to a LOI-  
163 free sum of 100 % (see Hampl et al., 2022b).

165 The chemical index of alteration (CIA; Nesbitt and Young, 1982) was modified to  $\Delta$ CIA (Eq. 3).

$$167 \Delta \text{CIA} = \left[ \left( \frac{Al_2O_3^w}{Al_2O_3^w + CaO^w + Na_2O^w + K_2O^w} \right) - \left( \frac{Al_2O_3^b}{Al_2O_3^b + CaO^b + Na_2O^b + K_2O^b} \right) \right] \cdot 100, \quad (3)$$

169  $w$  = in the weathered sample,  $b$  = in the bedrock.

### 171 **3.2.2 Oxalate- and dithionite extraction**

172 Air-dried bulk samples of <2 mm (dry-sieved) were used for oxalate- and dithionite extractions. The solutions thus obtained  
173 were measured with an ICP-OES iCAP 6300 DUO (Thermo Fisher Scientific, USA) to determine the extractable Fe, Al, and  
174 Si contents. The oxalate extraction employed targets the easily extractable mainly X-ray amorphous Fe(III) oxyhydroxides and  
175 (poorly) crystalline Al-containing minerals (see review by Rennert (2019) and references therein). The dithionite extraction  
176 dissolves crystalline and amorphous iron oxides (McKeague and Day, 1966). In doing so it can (partly) attack Al-bearing  
177 (mineral) phases (see review by Rennert (2019) and references therein).

178 The oxalate extractions were performed after Schwertmann (1964) with an oxalic acid-/oxalate-extraction solution (0.2 M, pH  
179 3.0). After the addition of the solution to the sample and shaking for 2 h in the dark (over-head shaker), the solution was filtered  
180 in a darkened room and immediately measured. The cold dithionite extractions were performed based on Holmgren (1967)  
181 with an extraction solution (mixture of 0.2 M NaHCO<sub>3</sub> and 0.24 M trisodium citrate) and sodium dithionite under oxic  
182 conditions. The resulting mixture of chemicals and sample was shaken for 16 h and centrifuged before the supernatant was  
183 filtered and immediately measured. Additional reference samples, blanks and calibration solutions were also prepared and  
184 measured like the soil pit samples. The results of the samples presented here are the mean of duplicate measurements performed  
185 on two individually extracted sample aliquots.

### 186 **3.2.3 Grain size determination**

187 Sample aliquots were suspended in de-ionized water (<10 μS m<sup>-1</sup>) and dispersed in a rotating overhead shaker (approx. 15 h)  
188 and a subsequent ultrasonic bath before vibrational wet sieving. The >63 μm sieving fractions were dried (50°C, approx. 24  
189 h) and their weight percentages were measured. The clay and silt contents were determined using the <63 μm suspension and  
190 a pipette method. Organic-rich samples were treated with H<sub>2</sub>O<sub>2</sub> to decompose organic matter and sodium pyrophosphate was  
191 used as a dispersion agent to prevent coagulation. Clay (<2 μm) was separated from the <63 μm fraction slurry via  
192 centrifugation.

### 193 **3.2.4 X-ray diffraction (XRD)**

194 Untreated air-dried aliquots of bulk samples were crushed in a porcelain mortar and afterwards processed with a micronisation  
195 XRD-mill McCrone (Retsch, Germany) to obtain a final powder of <10 μm. These powders were mounted to XRD sample  
196 holders by back-loading and X-ray diffraction measurements were performed with a Rigaku SmartLab equipped with a 9 kW  
197 rotating Cu-anode and a HyPix-3000 detector in Bragg-Brentano geometry (3–80° 2θ, scan step: 0.01°, scan speed: 1° min<sup>-1</sup>,  
198 and 60 rpm sample rotation). For the identification and semi-quantitative analyses, the software SmartLab Studio II and the  
199 mineral database PDF-4 Minerals 2021 including reference intensity ratio (RIR) factors were used. Image processing (imageJ;  
200 version 1.53a; Schneider et al., 2012) performed on the μ-XRF element distribution maps in Fig. 2 was used to get a rough

201 compositional information of the mineral content in the sampled bedrock. These analyses were used as a supporting basis for  
202 the semi-quantitative XRD analyses with RIR factors.

203 Clay mineral contents in the samples were quantitatively estimated by combining the results of the grain size determination  
204 with the semi-quantitative results of the XRD analyses. The clay-size fraction (<2  $\mu\text{m}$ ) of which the mass was determined by  
205 sieving/pipetting, was assumed to represent the entire clay mineral content of the sample, while the other size fractions were  
206 considered to be free of clay minerals. This assumed clay mineral content (in wt.%) was combined with the XRD-semi-  
207 quantitative weight percentages of the primary minerals in the same sample to approximate the mineral composition of the  
208 whole soil pit sample (summarized to 100 wt.%). Despite the assumption that only the <2  $\mu\text{m}$  grain size fraction contains clay  
209 minerals, this estimate appears to be the most accurate because there are no matching files in the mineral database used here  
210 that would accurately semi-quantify the identified interstratified clay minerals.

211 The separated clay-size fractions were measured as oriented clay films (texture preparation). A D2 Phaser XRD device  
212 (Bruker) equipped with a Cu-anode was utilized for the measurements. The diffractograms were recorded in Bragg-Brentano  
213 geometry in the range of 3–35° 2 $\theta$  (step width: 0.01° 2 $\theta$ , 0.5 seconds per step). The samples were measured after air-drying,  
214 during ethylene glycol saturation and after a thermal treatment at 550°C for 1 h. Selected samples were also treated with  
215 glycerol and KCl (1 M) to characterize the clay minerals in more detail. The identification was supported by a clay mineral  
216 identification chart (Starkey et al., 1984).

### 217 **3.2.5 Magnetic susceptibility measurements**

218 The magnetic susceptibility was measured on all twenty-one McCrone-milled bulk samples of the LC profile with a KLY-3  
219 Kappabridge (AGICO, Czechia). Measurements were performed in triplicates at room temperature, a frequency of 875 Hz and  
220 a peak magnetic field of 300 A m<sup>-1</sup>.

221 To obtain the magnetite content of the bedrock, a representative 60x60 mm sample slab (Fig. 2a) was mapped with the  $\mu$ -XRF  
222 spectrometer M4 Tornado. The  $\mu$ -XRF map that depicts only the maximum Fe content was used as an approximation of the  
223 magnetite content since magnetite is the mineral with the highest Fe concentration in the rock. Finally, the map was analysed  
224 with the image processing program imageJ (version 1.53a; Schneider et al., 2012) to quantify the magnetite content. The  
225 obtained value was equalled to the measured magnetic susceptibility of the same sample and used to convert the magnetic  
226 susceptibility results of the LC soil pit samples into approximated magnetite contents by the rule of three. The investigated  
227 bedrock of NA contains no magnetite.

### 228 **3.2.6 Light microscopy and electron microprobe analysis (EMPA)**

229 Thin sections were investigated with the light microscope DM750P (Leica, Wetzlar, Germany) equipped with a microscope  
230 camera (Euromex, The Netherlands). Electron microprobe element distribution maps of selected areas were obtained for Al,  
231 Ca, Fe, K, and Mg by using standard wavelength dispersive techniques on a JEOL Superprobe JXA-8230 fitted with a W-  
232 emitter electron gun (accelerating voltage: 15 kV, beam current: 20 nA, beam diameter and step width: 1  $\mu\text{m}$ ).



## 233 **4 Results**

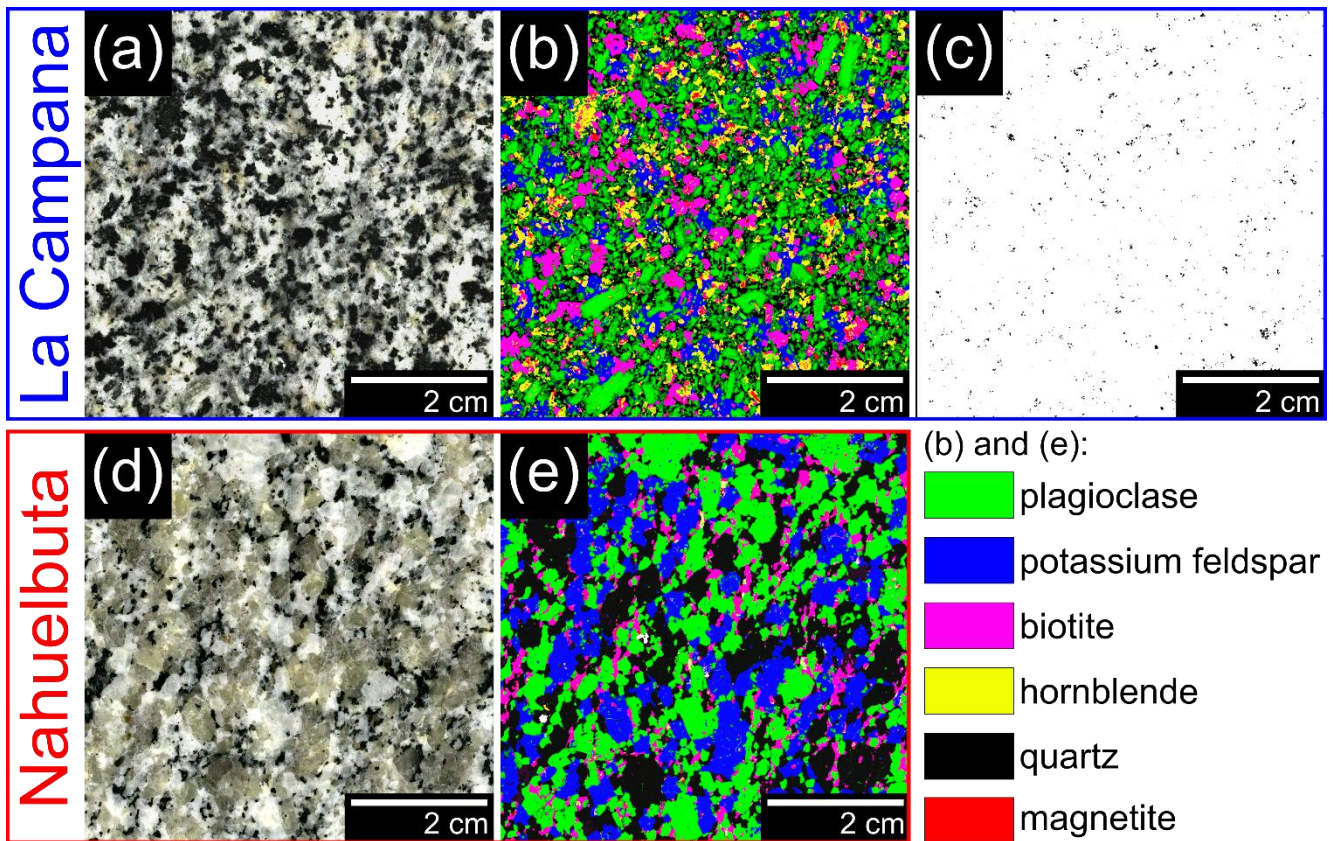
234 The data tables (cited as Table S1–S5) are included in the accompanying data publication (Hampl et al., 2022b).

### 235 **4.1 Bedrock**

236 According to the Streckeisen nomenclature the bedrock of LC can be described as granodiorite and the investigated bedrock  
237 of NA can be described as granite. However, the drill core revealed that the bedrock of NA occasionally contains more mafic  
238 sections. The most abundant minerals in the fine-grained bedrock of LC are plagioclase, quartz, microcline, hornblende, biotite,  
239 and chlorite (Fig. 2a,b). The latter occurs solely and abundantly along with (former) biotite crystals as their hydrothermal  
240 transformation products (i.e., chloritization; e.g., Kogure and Banfield, 2000). Magnetite is a ubiquitous accessory mineral  
241 (Fig. 2c; <1 vol.%) in LC and shows no signs of alteration to hematite (martitisation). Pyrite and chalcopyrite are also observed  
242 in much smaller abundance than magnetite. Mafic xenoliths can frequently be found in the granodiorite of LC.

243 In the coarse-grained Nahuelbuta granite, quartz, plagioclase, microcline, biotite, and chlorite are the main constituents (Fig.  
244 2d,e). In contrast to LC, amphiboles can only be found as an accessory mineral (<1 vol.%) in the investigated bedrock of NA.  
245 Like in LC, biotite is often chloritized. Magnetite and sulfides could not be identified in the investigated rock samples of NA.  
246 Variations in the biotite content, the occurrence of amphibole crystals, differences in fabric (microcline of a few centimetres),  
247 the alternation with mafic portions and the presence of pegmatites in the core make the overall lithology of NA far more  
248 heterogenous compared to LC.

249



250 **Figure 2: Bedrock of the investigated profiles. (a) Bedrock from La Campana (IGSN: GFFJH0095) with (b) a corresponding  $\mu$ -XRF**  
 251 **map reflecting the spatial mineral distribution. (c)  $\mu$ -XRF map of the maximum Fe content (black dots) representing the magnetite**  
 252 **crystals in the bedrock sample slab of La Campana. (d) Typical unweathered granite from Nahuelbuta (IGSN: GFFJH00H0) and**  
 253 **(e) a  $\mu$ -XRF map reflecting the mineral content of the same.**

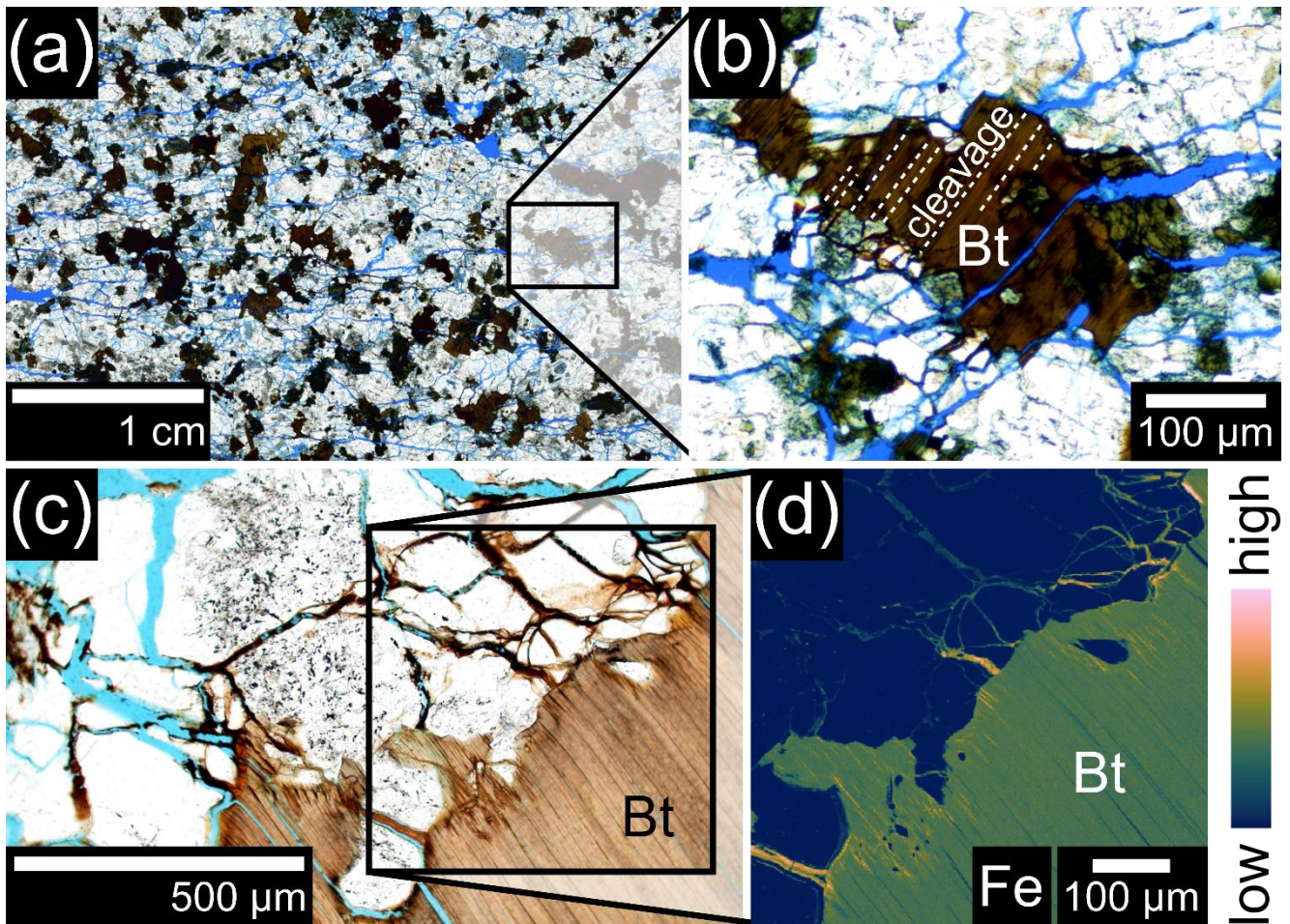
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## 255 4.2 Regolith

### 256 4.2.1 Incipient weathering in rock

257 Weathered rock from the borehole of LC shows abundant indications of weathering-induced fracturing (WIF) due to Fe(II)  
 258 oxidation in biotite, like fanned-out edges or opening due to dilatation (Fig. 3a,b). Secondary minerals like Fe(III)  
 259 oxyhydroxides are subordinate and are mostly associated with biotite. They are detectable as Fe-enrichments at the edge of  
 260 biotite crystals and within the cracks encompassing biotite (Fig. 3c,d). To a minor degree, Fe(III) oxyhydroxides are also  
 261 associated with hornblende. Nevertheless, most micro-fractures in feldspar and quartz of the investigated thin sections are  
 262 solely filled with blue resin and are bare of any secondary minerals.

263

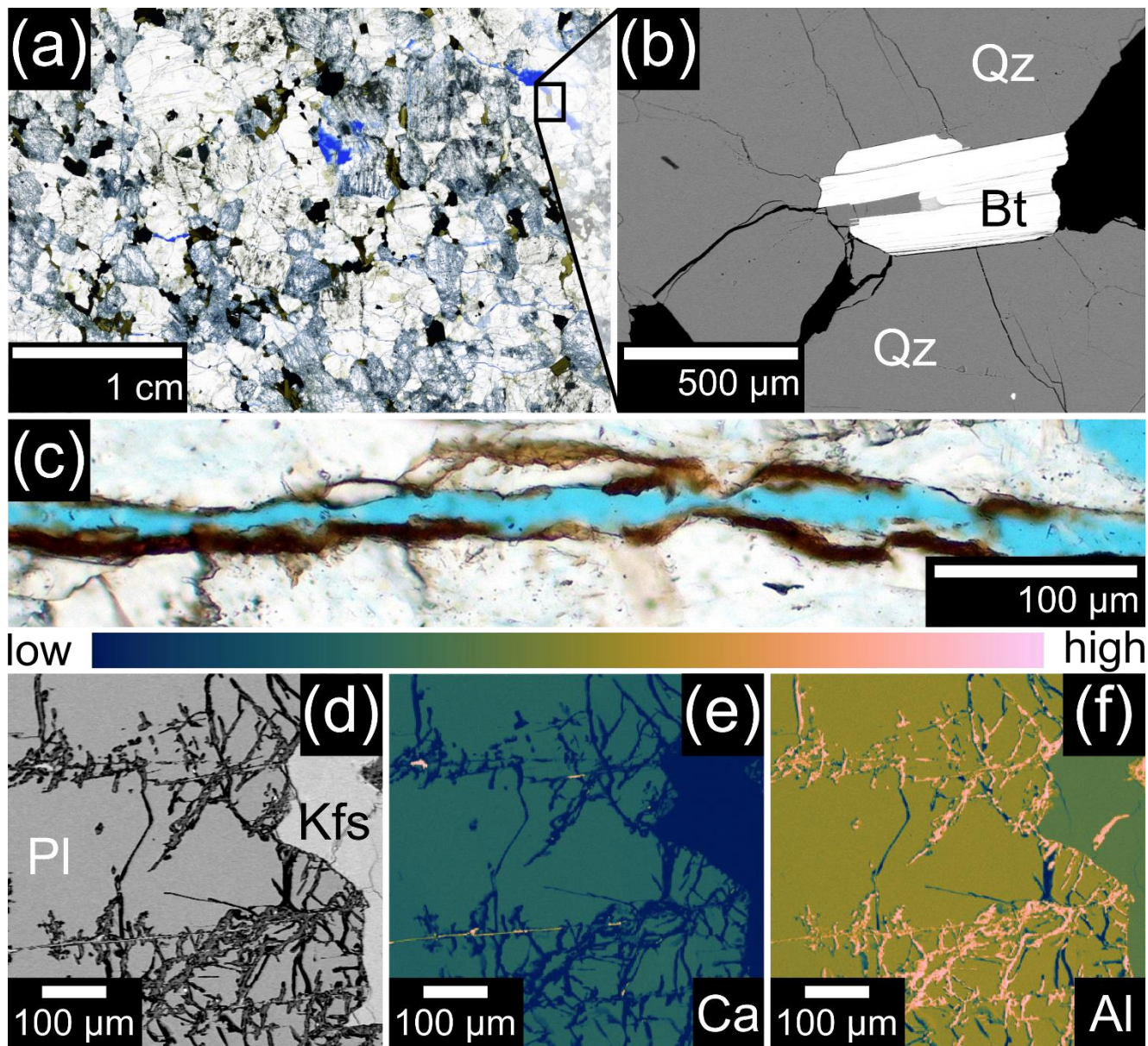


264 **Figure 3: Rock weathering in La Campana (LC; porosity is represented by blue-dyed resin).** (a) Thin section image (transmitted  
 265 **light)** of a weathered rock sample obtained from approx. 27 m depth in the LC drill core (IGSN: GFFJH00HY). (b) A detail image  
 266 **of biotite showing signs of dilatation (dashed lines indicate cleavage planes).** (c) Secondary minerals in cracks around biotite. (d) The  
 267 **electron microprobe map of the contact zone between biotite and quartz/feldspar displays Fe-enrichments at the interface. Bt =**  
 268 **biotite.**

269

270 Indications of WIF around biotite are also present in weathered rock of NA (Fig. 4a,b). However, the cracks are often filled  
 271 and covered with Fe(III) oxyhydroxides and clay minerals as observed with light microscopy (Fig. 4c) and electron microprobe  
 272 investigations. Unlike LC, weathered rock in NA is characterized by distinct Ca-depletion and Al-enrichment in plagioclase  
 273 which indicates partial dissolution (Fig. 4d–f). These alteration sites host secondary minerals covering the newly formed  
 274 surfaces which were formed by the dissolution of the plagioclase.

275



276 Figure 4: Rock weathering in Nahuelbuta (NA). (a) Thin section image (transmitted light) of weathered rock obtained from approx.  
 277 6 m depth in the NA drill core (note that the porosity (blue) is largely associated with weathered plagioclase; IGSN: GFFJH00HX).  
 278 (b) Indications of WIF in quartz (backscattered electron image, EMP). (c) Thin section image (transmitted light) of a crack covered  
 279 with brown Fe(III) oxyhydroxides from approx. 12 m depth (IGSN: GFFJH00J2). (d) Backscattered electron image (EMP) of partly  
 280 dissolved plagioclase and (e) the respective Ca and (f) Al map of the section (IGSN: GFFJH00HX). Qz = quartz, Bt = biotite, Pl =  
 281 plagioclase, Kfs = potassium feldspar.

282

## 283 4.2.2 Saprolite and soil

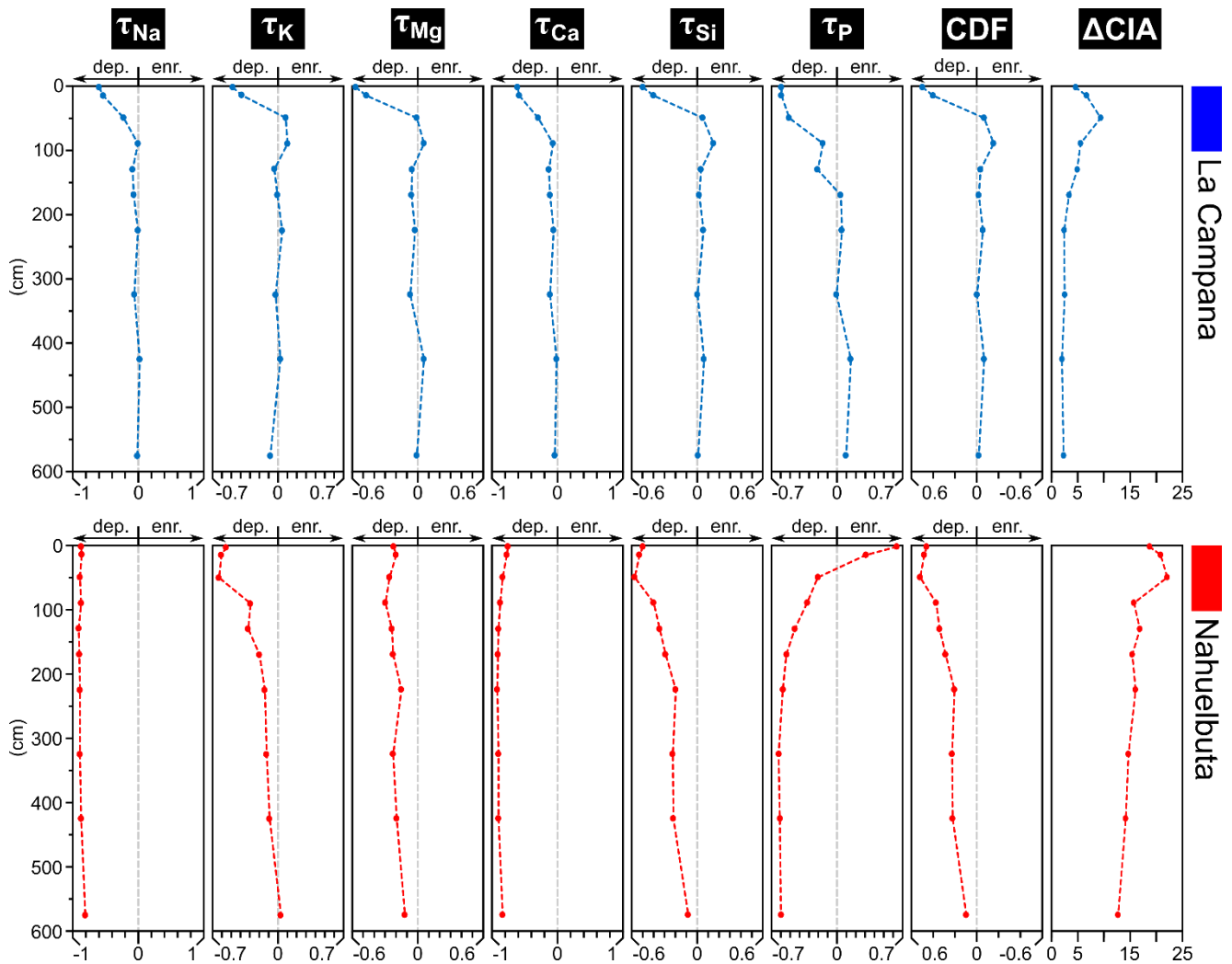
### 284 Chemical alteration

285

286 The mass transfer coefficient  $\tau$  indicates moderate depletion below 80 cm (not smaller than -0.2) in the LC soil pit profile, but  
287 clear depletion in the uppermost few decimetres where Na, K, Mg, Ca, Si and P can reach up to  $\tau = -0.5$  and -0.6 (Fig. 5; Table  
288 S1). A pronounced P depletion can be detected down to 1.4 m depth in LC. The chemical depletion fraction (CDF) of LC and  
289 the bedrock-normalized chemical index of alteration ( $\Delta$ CIA) indicate a weak chemical weathering degree below ca. 0.5–1 m,  
290 but minor chemical depletion was analysed down to the bottom of the 6 m deep profile of LC (see  $\Delta$ CIA; Fig. 5).

291 In contrast, Nahuelbuta is characterized by distinct chemical depletion of Ca and Na (up to  $\tau = -0.9$ ; Fig. 5). K is depleted to a  
292 depth of approximately 5 m, Si to a depth of ~6 m and Mg shows moderate depletion ( $\tau \geq -0.3$ ) throughout the profile. P is  
293 strongly depleted between ca. 2–6 m ( $\tau \sim -0.6$ ) but the P content gradually increases from approx. 3 m depth towards the  
294 surface and is enriched in the uppermost ~20 cm of the soil (A horizon; Fig. 5). The CDF values of NA indicate depletion  
295 down to the bottom of the profile at 6 m depth. The  $\Delta$ CIA of the profile underpins strong chemical alteration compared to the  
296 bedrock (Fig. 5). However, overall chemical depletion decreases towards the bottom of the soil profile and according to the  $\tau$ -  
297 values in 550–600 cm only Na, Ca and P seem to be significantly depleted at >6 m depth.

298

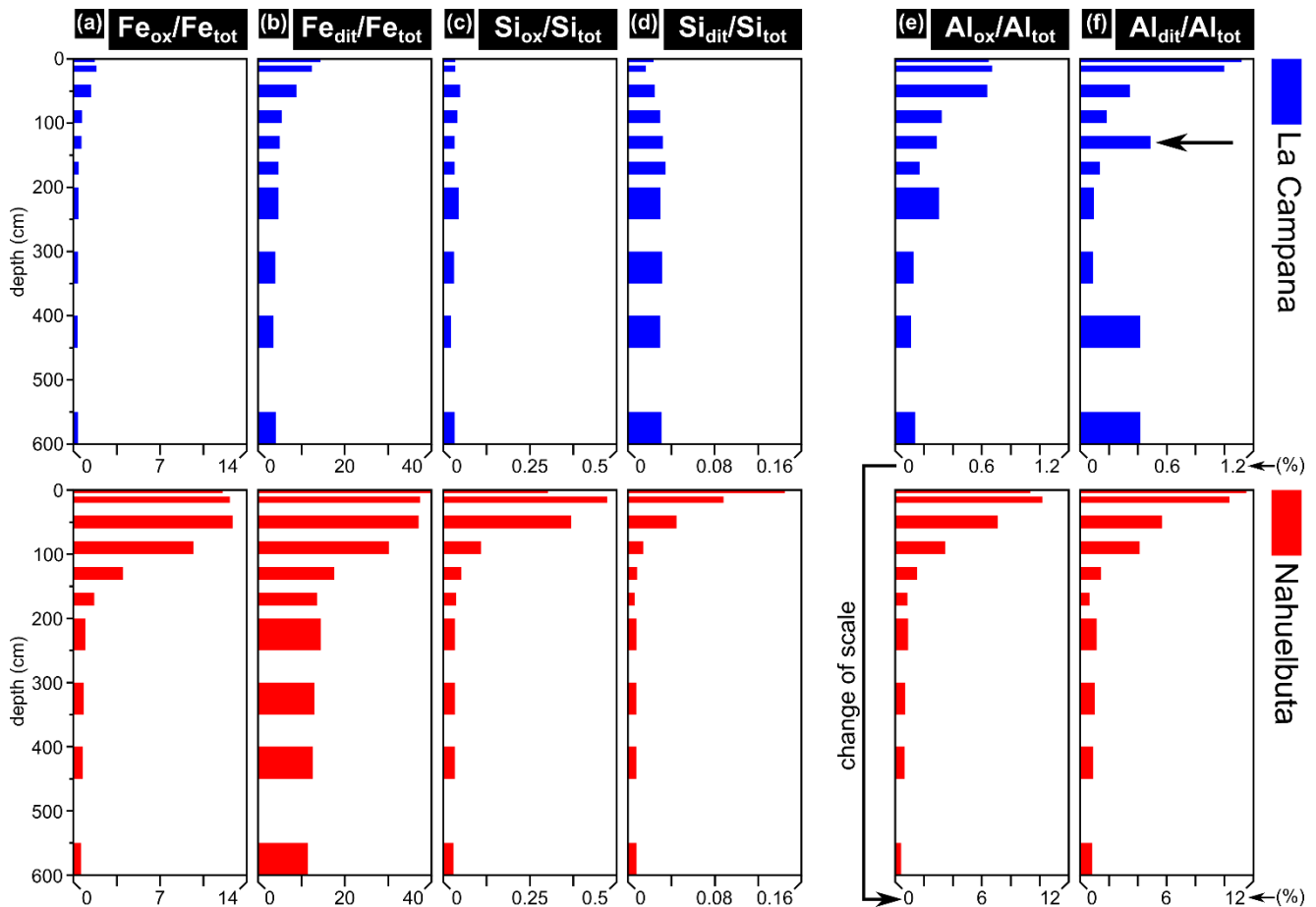


299 **Figure 5:**  $\tau$ -values of Na, K, Mg, Ca, Si, and P as well as the CDF (all based on Zr) and  $\Delta$ CIA values of the soil pit profiles in La  
 300 **Campana (LC) and Nahuelbuta (NA; Table S1).** Note that the scales are equal for the individual indices of LC and NA. dep. =  
 301 **depletion, enr. = enrichment.**

302

303 Since many secondary minerals are formed via a metastable or amorphous precursor (e.g., Steefel and van Cappellen, 1990;  
 304 Hellmann et al., 2012; Behrens et al., 2021), we assume that the extractable Fe, Si, and Al contents are indicative for recent  
 305 weathering of primary minerals (Fig. 6; see chapter 3.2.2 for an assignment of the extractable elements to the minerals they  
 306 likely originate from).

307



308 **Figure 6: Oxalate- and dithionite-extractable Fe, Si and Al contents divided by the respective total element contents of the bulk soil**  
 309 **samples of La Campana (LC) and Nahuelbuta (NA; Table S2). The elevated ratio at 120–140 cm in (f) (arrow) coincides with the**  
 310 **position of a discontinuity in the profile (Fig. 1d). Note that the scales for LC and NA are equal in (a)–(d). The scale in (e) and (f) is**  
 311 **one order of magnitude larger for NA compared to LC.**

312

313 Extractable contents of Fe in LC are moderately elevated in the uppermost meter of the profile (up to  $Fe_{dit}/Fe_{tot} \sim 14\%$ )  
 314 compared to the other depth intervals which show low contents ( $Fe_{dit}/Fe_{tot} < 1\text{ m}$ :  $\sim 4\text{--}5\%$ ; Table S2; Fig. 6a,b). The extractable  
 315 Si-contents show no clear pattern (Fig. 6c,d) whereas oxalate-/dithionite-extractable Al-contents are variable in the profile of  
 316 LC (Fig. 6e,f). The elevated  $Al_{dit}/Al_{tot}$  value in the depth interval 120–140 cm in LC ( $\sim 0.5\%$ ; Fig. 6f) coincides with a  
 317 discontinuity in the saprolite (Fig. 1d) and may indicate more secondary crystalline and amorphous Al-bearing phases in this  
 318 section. The profile in NA is characterized by high amounts of extractable Fe, Si and Al contents which are especially elevated  
 319 in the uppermost meter of the profile ( $Fe_{dit}/Fe_{tot}$  up to  $\sim 40\%$ ,  $Si_{dit}/Si_{tot}$  up to  $\sim 0.14\%$ ,  $Al_{dit}/Al_{tot}$  up to  $\sim 12\%$ ). The extractable  
 320 contents rapidly decrease from the surface towards the bottom of the NA profile and starting at approx. 2 m they are similar  
 321 down to 6 m (Fig. 6).

322 The Fe<sub>2</sub>O<sub>3</sub> content in the investigated bedrock of LC is more than twice as high as that of the NA bedrock, but the oxalate- and  
323 dithionite-extractable Fe contents (and hence the amount of the respective secondary minerals) are far higher in NA (Fig. 6a,b).  
324 The difference between LC and NA is even more pronounced for the extractable Al contents as values in NA can be 10 times  
325 higher than in LC (Fig. 6e,f). The extractable contents in the profiles of both study sites are generally within the range of  
326 previous investigations on soil samples from the La Campana and Nahuelbuta National Parks, but the Fe<sub>dit</sub>/Fe<sub>tot</sub> contents in the  
327 upper profile section of NA in this study are much higher (up to 40 %) than those measured in the Nahuelbuta National Park  
328 (<25 %; Oeser et al., 2018).

329

### 330 **Mineral content and grain sizes**

331

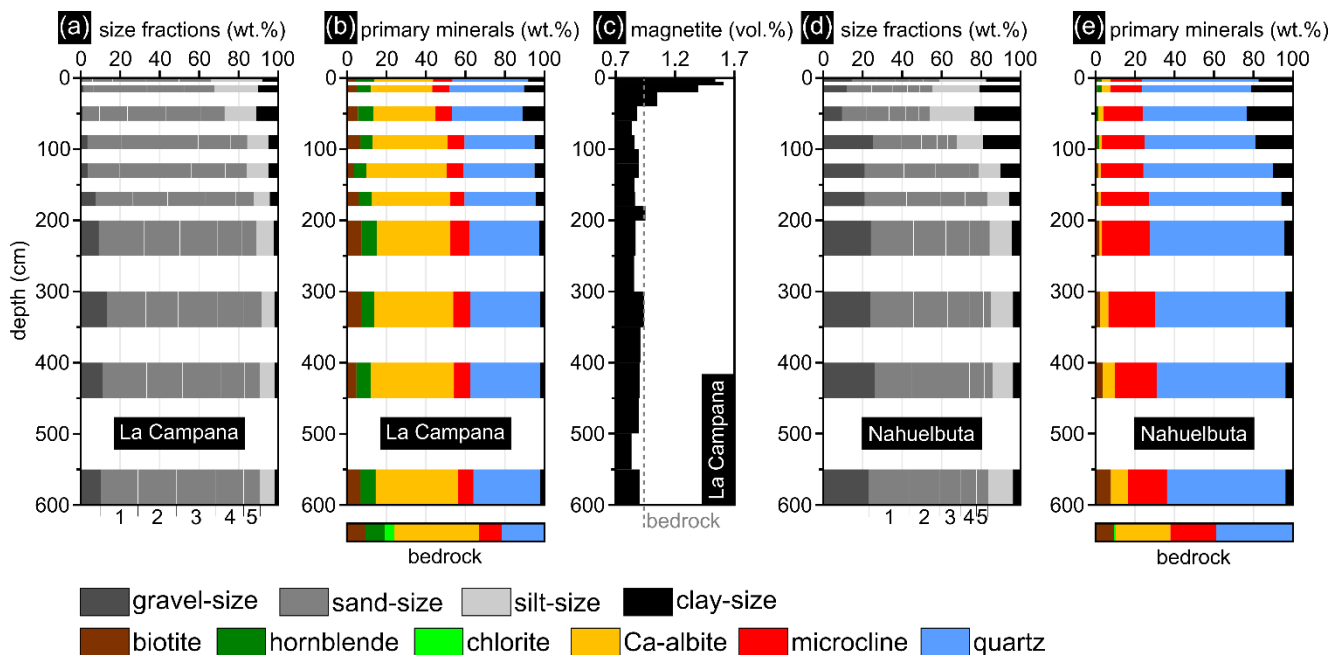
332 The sieving results of LC show a gradual decrease in particle size from the bottom of the profile towards the surface and a  
333 relatively constant sand-size content ranging from 65–80 wt.% with similar portions of the individual sand-size fractions (Fig.  
334 7a). The small geochemical depletion below the uppermost ~2 m of the LC profile (Fig. 5) is also reflected in the little changing  
335 mineral composition of the profile (Fig. 7b). Only the plagioclase (Ca-albite) content slightly decreases from approx. 1 m depth  
336 towards the surface. A small decrease of biotite in the depth interval 120–140 cm coincides with the mentioned discontinuity  
337 of this profile section (Fig. 1d). The abundant chlorite of the investigated bedrock in LC (~5 wt.%) is completely weathered  
338 and absent from the soil pit samples (Fig. 7b).

339 Significant alteration of magnetite (e.g., martitisation) could not be observed in ore microscopic investigations of the magnetic  
340 particles in soil pit samples of LC. Thus, the magnetic susceptibility directly reflects the magnetite content of the samples (e.g.,  
341 Ferré et al., 2012). A relative magnetite enrichment was detected in the uppermost 40 cm of the LC profile (1–1.6 vol.%)  
342 whereas the rest of the profile shows approximately constant magnetite contents (mean ~0.9 vol.%) close to the value of the  
343 investigated bedrock (0.94 vol.%; Fig. 7c). This almost consistent magnetite content underlines the homogeneity of the bedrock  
344 that was weathered in the 6 m deep soil pit (i.e., no mafic dykes, pegmatites, or major xenoliths).

345 The soil pit profile of NA is characterized by a much higher gravel- and silt/clay-size content compared to LC (Fig. 7d). This  
346 reflects the more heterogeneous grain size distribution of the investigated bedrock in NA compared to the bedrock of LC (see  
347 Fig. 2). High clay contents can be detected in the uppermost meter of the NA profile (partly >20 wt.%) and the identified  
348 mineral content of the soil pit samples differs significantly from the mineral content of the investigated bedrock (Fig. 7e). The  
349 plagioclase (Ca-albite) content distinctly decreases from the bottom of the profile towards the surface and the bedrock content  
350 of ~28 wt.% partly decreases down to 1 wt.% in the soil pit. The microcline content on the other hand is relatively uniform.  
351 Just as in LC, the chlorite of the bedrock analysed here (~1 wt.%) is completely weathered in the NA soil pit profile and is  
352 absent from the samples.

353



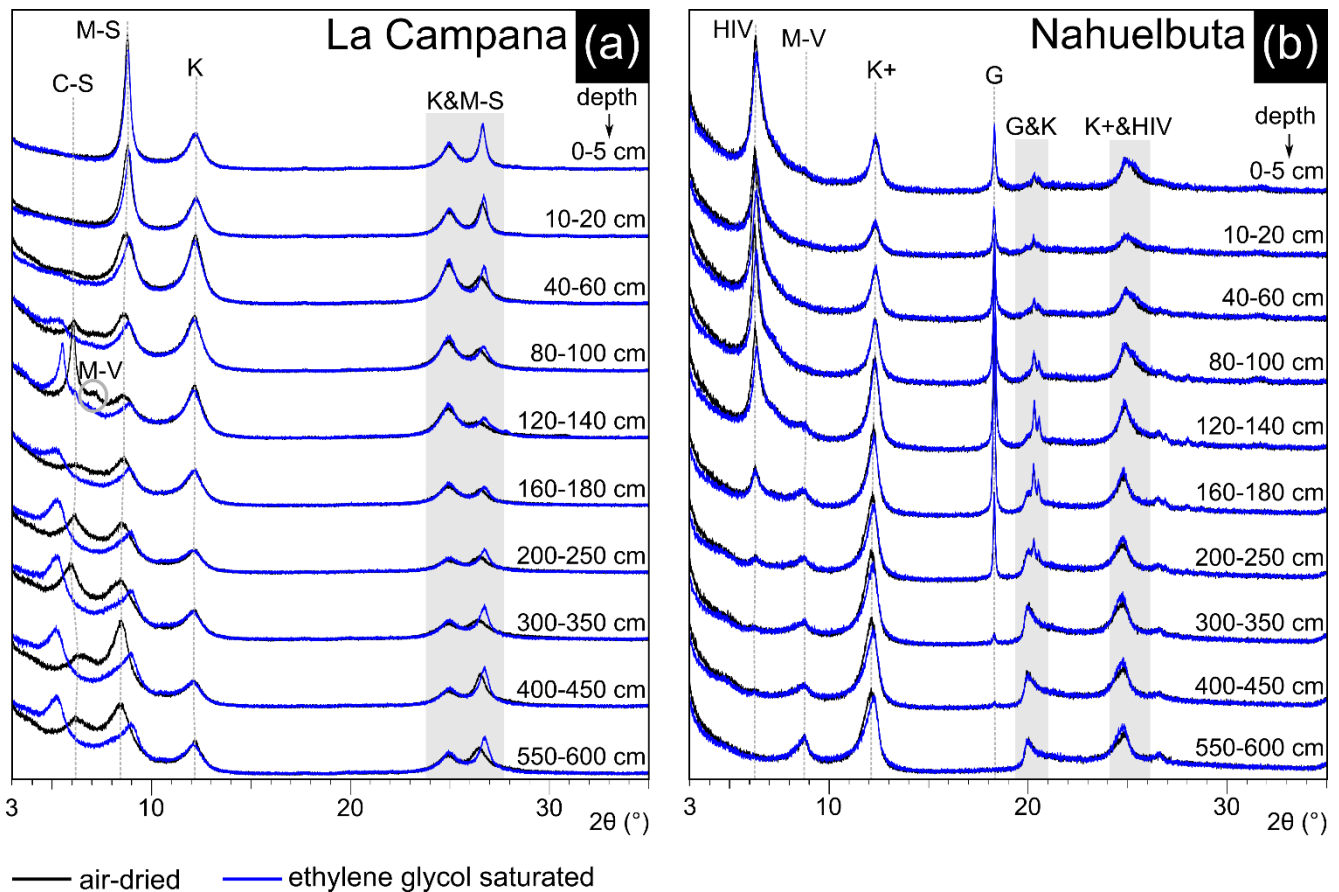


354 **Figure 7: Sieving/pipetting results, semi-quantitative XRD results and approximated magnetite contents of the investigated soil pit**  
 355 **samples in La Campana (LC) and Nahuelbuta (NA). (a) Grain size distribution based on wet-sieving and pipetting, (b) semi-**  
 356 **quantitative XRD and (c) magnetic susceptibility results converted to approximate magnetite contents of the LC profile. (d) Wet-**  
 357 **sieving combined with pipetting results and (e) semi-quantitative XRD results of the NA samples. Semi-quantitative XRD results of**  
 358 **the investigated bedrock samples (see Fig. 2) are given below the results of the soil pit samples. In (a) and (d): 1:  $\leq 2000$  to  $>1000$   $\mu\text{m}$ ,**  
 359 **2:  $\leq 1000$  to  $>500$   $\mu\text{m}$ , 3:  $\leq 500$  to  $>250$   $\mu\text{m}$ , 4:  $\leq 250$  to  $>125$   $\mu\text{m}$ , 5:  $\leq 125$  to  $>63$   $\mu\text{m}$ .**

360

361 The mineral content of the clay-size fraction in LC differs significantly from that in NA (Fig. 8). La Campana is characterized  
 362 by abundant expandable clay minerals (interstratified chlorite-smectite and interstratified mica-smectite) which can largely be  
 363 traced back to the weathering of chlorite and biotite (Fig. 8a). Kaolinite can be found throughout the LC profile whereas  
 364 interstratified mica-vermiculite only occurs in the depth interval of the discontinuity (120–140 cm; see Fig. 1d). The  
 365 expandable portion of the interstratified minerals gradually decreases from the profile bottom towards the surface and cannot  
 366 be detected in the uppermost centimetres of the LC profile. Only mica and kaolinite constitute the clay-size fraction of the  
 367 uppermost part of the profile in LC. The mineral content in the clay-size fraction of NA is characterized by small amounts of  
 368 interstratified mica-vermiculite below 1 m depth and ubiquitous kaolinite which shows small expandable portions below 2 m  
 369 depth. Hydroxy-interlayered vermiculite (HIV) and gibbsite can first be detected in 400–450 cm depth and the content  
 370 increases towards the surface. The main minerals of the clay-size fraction in the uppermost part of the profile are HIV, kaolinite,  
 371 and gibbsite (Fig. 8b).

372



373 **Figure 8: Minerals in the clay-size fraction of the soil pit profiles in La Campana (LC) and Nahuelbuta (NA).** (a) The profile in LC  
 374 features abundant expandable clay minerals. (b) NA is characterized by the presence of gibbsite and vermiculite but very minor  
 375 amounts of expandable clay minerals. C-S = interstratified chlorite-smectite, G = gibbsite, HIV = hydroxy-interlayered vermiculite,  
 376 K = kaolinite, K+ = kaolinite with expandable portions, M-S = interstratified mica-smectite, M-V = interstratified mica-vermiculite.

## 377 5 Discussion

### 378 5.1 Climate-dependent mineral transformations

379 Chemical depletion and mineral transformations are far more pronounced in the profile of NA compared to the profile of LC  
 380 even though the bedrock of LC contains more minerals with higher solubility compared to NA (more plagioclase, biotite,  
 381 chlorite or hornblende in LC than in NA where quartz and potassium feldspar dominate; see e.g., Wilson, 2004; Bandstra et  
 382 al., 2008). The high chemical depletion ( $\tau[\text{Na}, \text{Ca}]$  up to -0.9 and  $\Delta\text{CIA}$  up to 22; Fig. 5) and the occurrence of gibbsite in NA  
 383 are indicative of distinct dissolution of primary minerals (esp. plagioclase; Fig. 7e) and solute removal of alkali and alkaline  
 384 earth metals while immobile Al remains as hydroxide ( $\text{Al}(\text{OH})_3$  = gibbsite). This depletion is assumed to be the result of more  
 385 water infiltration into the subsurface of NA (more precipitation due to humid climate) compared to LC (less precipitation due  
 386 to Mediterranean climate). The measured  $\tau[\text{P}]$  distribution in NA is a clear indication for biologically controlled nutrient uplift

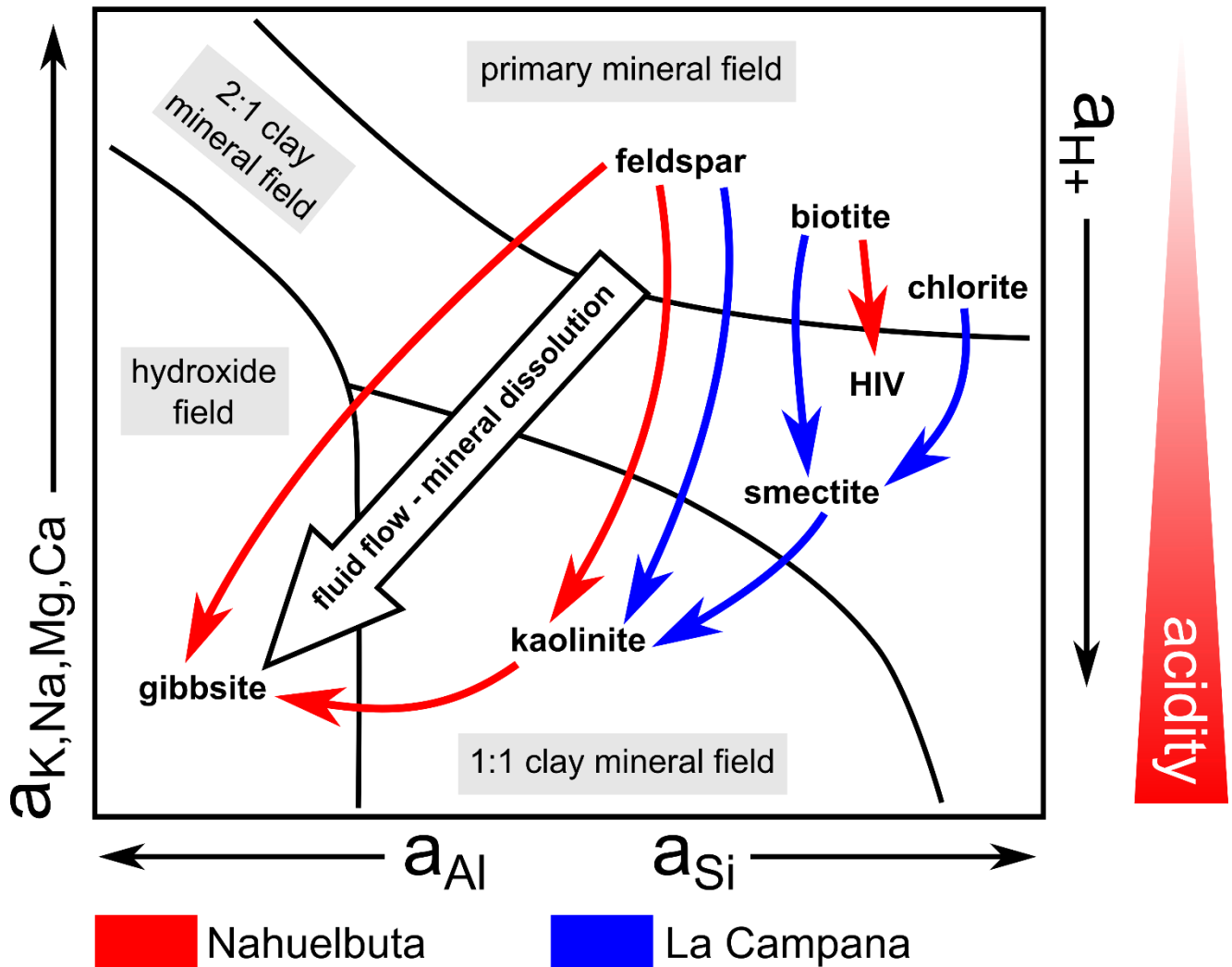
387 and recycling within the topsoil (Jobbágy and Jackson, 2004). We assume that the high precipitation rate in NA leads to more  
388 biomass production by plants, which in turn implies more litter production and a stimulation of biogenic decay that supplies  
389 plants with nutrients. Thus, we concur with the hypothesis that the ecosystem in NA is thriving on nutrient recycling rather  
390 than on an uptake of nutrients that were released by biogenic weathering at depth (Oeser and von Blanckenburg, 2020). Apart  
391 from Ca, Na, and P ( $\tau$ -values in Fig. 5), the chemical depletion successively decreases from the surface towards the bottom  
392 part of the investigated profile in NA. To account for this shallow chemical depletion, we propose that a secondary-mineral-  
393 controlled impeding of the fluid infiltration to depth is playing an important role for the depth of mineral transformations in  
394 NA.

395 Chemical depletion can be detected throughout the investigated profile in LC, but the chemical weathering degree is very low  
396 between 2–6 m depth (Fig. 5) and the mineral transformations in this section of the profile are only minor (Fig. 7b). On the  
397 other hand, distinct mineral dissolution and removal of solutes is testified by the higher magnetic susceptibility values in the  
398 uppermost decimetres of the LC profile. This can be related to a residual accumulation of weathering-resistant magnetite while  
399 other minerals like plagioclase dissolve. The strong chemical depletion in this part of the profile is also reflected by the low  $\tau$ -  
400 and elevated CDF-/ $\Delta$ CIA-values. To account for the detected weak but deep chemical weathering in LC, we propose that a  
401 secondary-mineral-controlled formation of fluid pathways is facilitating the fluid infiltration to depth and is thus an important  
402 control on the chemical weathering reactions in the subsurface.

403 The difference between the profiles is also displayed by the oxalate- and dithionite-extractable Fe, Si, and Al contents. While  
404 high extractable contents especially within the uppermost 2 m of the NA profile are interpreted to indicate considerable  
405 ongoing (recent) transformations of primary to secondary minerals, LC shows comparatively little indications in this regard.  
406 This difference underlines the higher degree of mineral transformations in NA compared to LC which is also reflected in the  
407 mineral content of the clay-size fraction (see Fig. 9). That oxalate- frequently exceeds dithionite-extractable Al contents is  
408 indicative for amorphous phases since oxalate is more effective at extracting amorphous forms of Al (McKeague and Day,  
409 1966). Moreover, the highest contents of the clay-size fraction in the profiles are in good correlation with the elevated  
410 extractable Fe, Si and Al contents and highlight the pronounced mineral transformation in the uppermost part of the profiles.  
411 This size fraction hosts most of the products of primary silicate weathering. Clay-size minerals of NA mainly correspond to  
412 distinct weathering of plagioclase and biotite, whereas in LC they can mainly be associated with chlorite and biotite weathering  
413 (Fig. 9). Feldspar weathers to kaolinite and gibbsite in NA and biotite weathers to hydroxy-interlayered vermiculite (HIV).  
414 Chlorite completely dissolved in the NA profile, whereas both chlorite and biotite in LC weather via interstratified clay  
415 minerals to smectite. Finally, smectite and feldspar likely weather to kaolinite in LC (Fig. 9). The mineral composition of the  
416 clay-size fraction (Fig. 8) is dependent on the bedrock composition (e.g., more chlorite in LC) and the climate-dependent  
417 mineral dissolution (see Fig. 9) in the study sites. However, we argue that the amount of secondary minerals is largely a  
418 function of the climatic conditions that control the weathering intensity via water availability in the study sites.

419 As this study does not consider the entire weathering profile in LC and NA, the interplay between erosion rate and weathering  
420 advance rate (Lebedeva and Brantley, 2020) is not addressed here. However, the different denudation rates in the study areas

421 (mean soil denudation rate in LC: ~ 61, in NA: ~ 33 t km<sup>-2</sup> yr<sup>-1</sup>; Oeser et al., 2018) likely affect the weathering intensity. Due  
 422 to the higher denudation rates in LC compared to NA (Oeser et al., 2018; van Dongen et al., 2019), we hypothesize that the  
 423 residence time of weathered material in the regolith of LC is shorter than in NA. Thus, there is less time for chemical weathering  
 424 in LC. In combination with the lower water availability in LC, this factor might contribute to the lower weathering intensity  
 425 in the regolith of LC compared to NA. This would also concur with the finding that water availability in the soil and soil  
 426 residence time are the limiting factors for weathering processes in dry environments (Schoonejans et al., 2016). NA, on the  
 427 other hand, is characterized by a longer residence time of weathered material. Together with the higher water availability, this  
 428 factor might contribute to the high weathering intensity in the upper regolith of NA. The situation in LC may be comparable  
 429 to an incompletely developed profile, and the situation in NA to a completely developed profile (Reis and Brantley, 2019).  
 430



431 **Figure 9: Schematic diagram showing the transformation of primary minerals to secondary minerals (clay minerals and aluminium**  
432 **hydroxide) depending on the activities of H<sup>+</sup>, Si, Al, K, Na, Mg and Ca. The depletion of the alkali and alkaline earth metals, and**  
433 **the increase of the Al activity are coupled to an increase of the mineral dissolution and the removal of solutes by a higher subsurface**  
434 **fluid flow. Elevated a<sub>H<sup>+</sup></sub>-values (i.e., lower pH) increase the mineral solubility. Modified from Chesworth et al. (2008). HIV = hydroxy-**  
435 **interlayered vermiculite, a = thermodynamic activity**

436

## 437 **5.2 Weathering-intensifying processes**

### 438 **5.2.1 Porosity increase by weathering-induced fracturing and its impact on the weathering depth**

439 Ferrous primary minerals of the LC granodiorite can frequently be identified as initiating locations of micro-cracks. This  
440 observation can be related to weathering-induced fracturing (WIF) due to the increase in volume caused by the oxidation of  
441 Fe(II) in Fe(II)-bearing silicates (e.g., Buss et al., 2008; Behrens et al., 2015; Kim et al., 2017) and the formation of secondary  
442 Fe(III) oxyhydroxides (Fletcher et al., 2006; Lebedeva et al., 2007; Anovitz et al., 2021; Fig. 3d). This process generates and  
443 increases surface areas of primary minerals and in turn accelerates weathering reactions (positive feedback between the  
444 formation of secondary minerals and the infiltration of fluids (esp. O<sub>2</sub> and water) to depth; e.g., Røyne et al., 2008). These  
445 weathering-induced fractures consequently facilitate the presence of surface-derived O<sub>2</sub> in the deep subsurface (Kim et al.,  
446 2017) and the corresponding transport through the saprolite/soil is dominated by advection (Lebedeva et al., 2007). The  
447 bedrock of LC is richer in Fe-bearing minerals than the investigated granite of NA (ca. 25 wt.% in LC and ca. 10 wt.% in NA)  
448 and hosts biotite, hornblende, chlorite, and magnetite as Fe(II) sources. A considerable amount of the total Fe content is bound  
449 in magnetite (roughly 0.7 wt.% of the total Fe<sub>2</sub>O<sub>3</sub> content if the magnetite content of the bulk sample is 1 wt.%). However, we  
450 found no microscopic evidence (no oxidation) nor indications in the magnetic susceptibility results that the Fe(II) in magnetite  
451 is available for weathering reactions. Thus, we conclude that magnetite is stable under the environmental conditions of LC. Of  
452 the three remaining Fe(II)-bearing minerals, biotite was found to be the most important one for the generation of WIF in LC  
453 (see also Buss et al., 2008; Bazilevskaya et al., 2013, 2015) due to its volumetric expansion during weathering (e.g.,  
454 Goodfellow et al., 2016). Although WIF also occurs in NA (Fig. 4b) it does not seem to significantly increase the permeability  
455 of the rock which can be related to the low Fe(II) content of the dominant bedrock (Fe<sub>2</sub>O<sub>3</sub> (total Fe): <3 wt.%; Table S1; see  
456 Kim et al., 2017).

457 Other than that, chlorite is suggested to be an important mineral in the development of the investigated weathering profile in  
458 LC. The original chlorite content of the bedrock in LC has been completely transformed into interstratified chlorite-smectite  
459 in the soil pit profile. We suggest that this transformation plays a significant role for the development of the LC profile since  
460 expandable clay minerals are known to disaggregate rock by swelling (e.g., Dunn and Hudec, 1966; Jiménez-González et al.,  
461 2008). The ensuing fracturing also forms new fluid pathways and new access to reactive surfaces of primary minerals which  
462 in turn fosters weathering reactions (positive feedback mechanism; see e.g., Røyne et al., 2008). Even though expandable clay  
463 minerals can also cause sealing of the subsurface (Kim et al., 2017) we do not regard this effect as significant for LC since  
464 clay contents are very low. However, a minor retardation of the fluid flow from surface to depth due to the expansion of the

465 interstratified clay minerals in LC (Fig. 8a) cannot be excluded (see Kim et al., 2017). In conclusion, we propose that small  
466 amounts of expandable clay minerals like in LC can generate porosity whereas high amounts of expandable clay minerals can  
467 reduce porosity.

468 The feedback mechanism of weathering-induced fracturing is presented here for granodiorite. However, the significance of  
469 this mechanism is not restricted to plutonic rocks. Weathering-induced fracturing requires Fe(II)-bearing minerals such as  
470 biotite and/or potentially the presence of expandable clay minerals that cause the formation of cracks by volume increase  
471 during weathering. This feedback concept is thus transferable to all igneous, metamorphic and sedimentary rocks that contain  
472 these minerals.

### 473 **5.2.2 Increase of weathering intensity by biogenic activity**

474 The formation of secondary minerals such as clay minerals and aluminium hydroxide is among other factors controlled by  
475 biogenic activity since organic acids and an acidity-increase by elevated organic-derived CO<sub>2</sub> contents accelerate dissolution  
476 rates of primary minerals (see e.g., Lucas, 2001; Lawrence et al., 2014). This effect needs to be considered for the organic-rich  
477 and acidic subsurface of NA (see Bernhard et al., 2018). The acidity likely contributes to the high degree of mineral dissolution  
478 in NA (see a<sub>H+</sub> in Fig. 9), which consequently leads to an increased formation of secondary minerals.

479 The depth interval 120–140 cm in LC is characterized by lower amounts of biotite and a different clay mineral composition  
480 compared to the surrounding depth intervals (Fig. 7b; Fig. 8a). This depth interval coincides with a discontinuity crossing the  
481 entire profile width (Fig. 1d). We interpret this plant-root-containing discontinuity in the saprolite as a fracture remnant since  
482 there are no indications of a lithological heterogeneity in this zone (e.g., a significant change in the magnetic susceptibility or  
483 of the primary mineral content; Fig. 7b,c). To explain the lower biotite content and the different clay composition in this part  
484 of the profile, we propose an intensification of weathering reactions in the vicinity of the fracture fostered by the observed  
485 plant roots (e.g., Fimmen et al., 2008; Pawlik et al., 2016; Nascimento et al., 2021). This weathering-promoting mechanism  
486 might account for the increase in interstratified chlorite-smectite and the appearance of interstratified mica-vermiculite (Fig.  
487 8a), while the amount of biotite decreases due to its transformation to secondary minerals (Fig. 7b).

## 488 **5.3 Weathering-mitigating processes**

### 489 **5.3.1 O<sub>2</sub> consumption by Fe-bearing silicates and its impact on the weathering depth and intensity**

490 The granodiorite of LC hosts an abundance of Fe(II)-bearing minerals (Fig. 7b). The Fe<sub>2</sub>O<sub>3</sub> content of the LC bedrock after  
491 subtraction of the inert magnetite-bound Fe<sub>2</sub>O<sub>3</sub> fraction (since 100 % pure magnetite contains 69 % Fe<sub>2</sub>O<sub>3</sub>, 0.94 % magnetite  
492 as analysed in the LC bedrock equals to 0.65 % magnetite-bound Fe<sub>2</sub>O<sub>3</sub> which needs to be subtracted) is 5.34 wt.% (for  
493 comparison: 2.33 wt.% Fe<sub>2</sub>O<sub>3</sub> in NA). Since O<sub>2</sub> is reduced by the oxidation of mineral-bound Fe(II) (e.g., White and Yee,  
494 1985; Perez et al., 2005) and the consequent formation of secondary minerals, the O<sub>2</sub> content and hence oxidative weathering  
495 reactions are expected to decrease from surface to depth. A rapid decrease of the O<sub>2</sub> concentration to depth is characteristic for

496 weathering systems in which O<sub>2</sub> transport is dominated by diffusion (Behrens et al., 2015). Given the observed deep fracturing  
497 due to Fe(II) oxidation (i.e., WIF) in LC and the consequent deep connectivity between the surface and the subsurface (Kim  
498 et al., 2017), the O<sub>2</sub> transport in LC is most likely dominated by advection. As a consequence, diffusive O<sub>2</sub> transport is  
499 insignificant in the upper regolith of LC and the O<sub>2</sub> consumption by Fe(II) oxidation is not limiting the regolith depth in LC  
500 (compare Bazilevskaya et al., 2013). It has been argued that WIF and thus a thicker regolith is more likely when the ratio  
501 pO<sub>2</sub>/pCO<sub>2</sub> in soil water is greater than the ratio of the capacity for O<sub>2</sub> consumption to the capacity for CO<sub>2</sub> consumption in  
502 bedrock (Stinchcomb et al., 2018). In the study sites, decomposition of organic matter is restricted to the topsoil, likely because  
503 organic matter at depth becomes stabilized against microbial decomposition (Scheibe et al., 2023). Thus, we suggest that the  
504 pCO<sub>2</sub> of water in the deeper profile part of LC is low (i.e., pO<sub>2</sub>/pCO<sub>2</sub> is high), and O<sub>2</sub> is not being consumed by organic matter  
505 decomposition but is available for Fe(II) oxidation and hence WIF. The WIF-controlled connectivity between the surface and  
506 the subsurface results in an O<sub>2</sub> availability for oxidative weathering processes at great depth. On the other hand, the weak  
507 chemical weathering in LC is in good agreement with the low precipitation rate (~350 mm yr<sup>-1</sup>; Übernickel et al., 2020). The  
508 low precipitation rate entails a small infiltration of water to depth and hence minor primary mineral dissolution and thus  
509 chemical weathering at depth.

510 The cracks around weathered biotite in the investigated samples of LC are (mainly) filled with Fe(III) oxyhydroxides as  
511 revealed by the high Fe-enrichment detected in electron microprobe maps (Fig. 3d). Newly formed weathering-induced  
512 fractures make the biotite more accessible to surface inputs like water and O<sub>2</sub> which promotes the dissolution of biotite. The  
513 solutes formed as a result migrate along the weathering-induced cracks and precipitate in the vicinity of the biotite crystal as  
514 secondary phases (Fig. 3c). Thus, we propose that the reactive surface of biotite is partly shielded from weathering reactants  
515 (water, O<sub>2</sub>) due to the precipitation of secondary minerals (see e.g., Navarre-Sitchler et al., 2015; Vázquez et al., 2016; Gerrits  
516 et al., 2020; 2021). Combined with the low subsurface water availability in LC causing a low mineral dissolution degree, this  
517 shielding might contribute to the relatively stable biotite content throughout the LC profile (Table S4).

### 518 **5.3.2 Reduction of weathering intensity and -depth by damping of fluid flow**

519 The formation of secondary minerals such as clay minerals (via amorphous and poorly crystalline precursors; see Fig. 6) can  
520 decrease the porosity (e.g., Bazilevskaya et al., 2015; Navarre-Sitchler et al., 2015) formed by WIF and dissolution. Al-rich  
521 phases were found as precipitates in partly dissolved plagioclase of NA (Fig. 4d–f) and within cracks which can often be  
522 identified as weathering-induced. We suggest that the abundant presence of clay minerals and gibbsite in NA restricts the fluid  
523 flow through such fractures and pores. The clay-rich zone in the uppermost metre of the NA soil pit profile (around 50 cm  
524 depth; Fig. 7d) likely acts as a (partially) shielding horizon (impeding vertical flow of surface inputs to the deep subsurface;  
525 see e.g., Lohse and Dietrich, 2005). Clay-rich horizons can therefore influence the dynamic of the subsurface fluid flow and  
526 thus mitigate mineral transformations and chemical weathering at depth. At the same time, these conditions foster a long fluid  
527 residence time in the upper regolith and thus promote the precipitation of secondary minerals such as clay minerals that may  
528 impel the weathering of primary minerals in the upper part of the weathering profile (see Maher, 2010). However, the seasonal

529 sealing of fractures and pore spaces due to an increase of soil moisture and an ensuing clay expansion (Kim et al., 2017) is not  
530 assumed for NA as expandable secondary minerals barely occur in the clay-size fraction of NA (Fig. 8b).  
531 The negative feedback mechanism presented here is demonstrated for granite. However, the concept is essentially based on  
532 newly formed minerals such as clay minerals that inhibit the subsurface fluid flow by blocking pathways. This feedback  
533 mechanism can thus be significant for weathering systems developing from all igneous, metamorphic and sedimentary rocks  
534 where secondary minerals can block the permeable porosity formed by WIF and primary mineral dissolution.

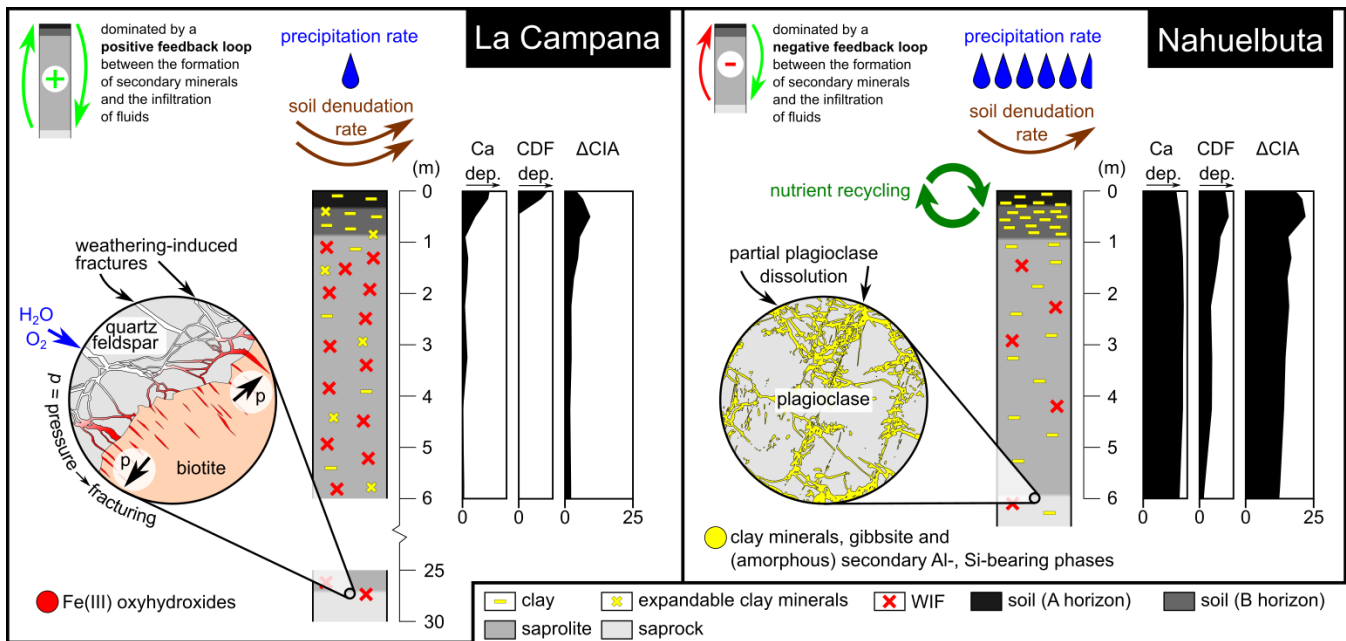
## 535 **6 Conclusions**

536 In two 6 m deep weathering profiles formed on granitic rock in two climatic zones (Mediterranean and humid climate), we  
537 found different degrees of elemental loss by chemical weathering, and different secondary minerals. Under Mediterranean  
538 climate conditions (La Campana), Fe(II)-oxidation, precipitation of Fe(III) oxyhydroxide and clay swelling lead to fracturing  
539 and the formation of fluid pathways. This weathering-induced fracturing (WIF) is likely one of the dominant controls on the  
540 development of the upper regolith as it leads to a deep infiltration of surface inputs (esp. water and O<sub>2</sub>) which in turn causes  
541 further WIF. While the intensity of chemical weathering at the Mediterranean site is low, it was detected throughout the entire  
542 6 m deep profile. This suggests that the weathering front is located at much greater depth in La Campana. The overall low  
543 abundance of secondary minerals can be explained by the low climate-related subsurface water availability in La Campana.  
544 The lack of large quantities of secondary minerals ensures that fractures and porosity generated by WIF remain accessible to  
545 water and gases. Thus, we conclude that the development of the deep but weak chemical weathering in the upper regolith of  
546 La Campana is significantly controlled by two mechanisms: (1) A positive feedback loop between the formation of secondary  
547 minerals and the infiltration of fluids to depth induced by (mainly) biotite weathering (WIF) which leads to a deep surface-  
548 subsurface connectivity for weathering reactants (in particular O<sub>2</sub>). (2) Low subsurface water availability resulting in a low  
549 amount of secondary minerals which would otherwise seal this connectivity.

550 Under humid climate conditions (Nahuelbuta), clay minerals, gibbsite as well as amorphous and poorly crystalline secondary  
551 minerals largely formed due to intense plagioclase dissolution. We link this intense dissolution to the high climate-related  
552 subsurface water availability in Nahuelbuta. The secondary minerals thus formed are suggested to impede the flow of surface  
553 inputs to depth. Moreover, the generally lower amount of Fe(II)-bearing silicates in Nahuelbuta compared to La Campana  
554 results in less WIF and thus fewer fluid pathways. Therefore, we conclude that the development of the weathering profile in  
555 Nahuelbuta is predominantly governed by two mechanisms: (1) Considerable climate-related subsurface water availability and  
556 high biogenic activity which lead to intense weathering of primary minerals in the upper part of the regolith. (2) A negative  
557 feedback loop between the formation of secondary minerals and the infiltration of fluids to depth induced by (mainly)  
558 plagioclase weathering and the ensuing formation of secondary minerals which leads to a poor surface-subsurface connectivity  
559 for weathering reactants. The main findings and factors that are most relevant to the development of the different weathering  
560 systems are summarized in Figure 10.



561 The relationship between precipitation and the degree of chemical weathering along the climate gradient of the Chilean Coastal  
 562 Cordillera was found to be non-linear and non-systematic (Oeser and von Blanckenburg, 2020; Schaller and Ehlers, 2022).  
 563 We argue that a systematic relationship is likely concealed by variations in the mineral content of the bedrocks and the  
 564 associated feedback mechanisms. However, the investigated feedbacks provide a causal explanation for the depth of chemical  
 565 weathering. This study illustrates how the formation of secondary minerals and the infiltration of surface-derived fluids to  
 566 depth are interlinked by positive and negative feedback loops. We demonstrated that these feedback loops and the climatic  
 567 conditions they occur in are important controls on the development of the upper regolith.  
 568



569  
 570 **Figure 10: Schematic summary of the two weathering systems. According to our findings, the regolith of La Campana (LC) is**  
 571 **dominated by a positive feedback loop between weathering-induced fracturing (WIF) and the infiltration of fluids to depth. WIF**  
 572 **creates deep-reaching pathways for fluids (water, O<sub>2</sub>) and hence a good connectivity between the surface and the subsurface.**  
 573 **Moreover, the low water availability in the Mediterranean climate inhibits the formation of large amounts of secondary minerals**  
 574 **(i.e., low weathering intensity) that could seal these pathways. The high denudation rate in LC results in a short residence time of**  
 575 **weathered material in the profile and could therefore contribute to the detected lower weathering intensity (i.e., less chemical**  
 576 **weathering). The regolith of Nahuelbuta (NA), on the other hand, was found to be dominated by a negative feedback loop between**  
 577 **the formation of secondary minerals and amorphous phases, and the infiltration of fluids to depth. These secondary solids are**  
 578 **consequences of the high water availability in NA that results in intense chemical weathering (i.e., high weathering intensity). The**  
 579 **high weathering intensity entails the formation of abundant secondary minerals and amorphous phases that reduce the connectivity**  
 580 **between the surface and the subsurface. The lower denudation rate and thus longer residence time of weathered material in NA**  
 581 **likely contributes to the more intense chemical weathering. dep. = depletion.**  
 582

583 **Data availability**

584 Datasets related to this article can be found in the data publication Hampl et al. (2022b). The data publication is hosted at the  
585 GFZ Data Services and can be downloaded by clicking on “Download data and description” in the field “Files”.  
586

587 **Sample availability**

588 The IGSN-registered samples used in this article are deposited at the Department of Applied Geochemistry (Technische  
589 Universität Berlin) and are listed in the data publication of this paper (Hampl et al., 2022b).  
590

591 **Author contribution**

592 Ferdinand J. Hampl: conceptualization, methodology, investigation, writing – original draft preparation  
593 Ferry Schiperski: methodology, supervision, writing – review & editing  
594 Christopher Schwerdhelm: investigation, writing – review & editing  
595 Nicole Stroncik: investigation, writing – review & editing  
596 Casey Bryce: funding acquisition, writing – review & editing  
597 Friedhelm von Blanckenburg: supervision, writing – review & editing  
598 Thomas Neumann: funding acquisition, supervision, writing – review & editing  
599

600 **Competing interests**

601 The authors declare that they have no conflict of interest.  
602

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611

## 612 **References**

613 Anderson, S., Dietrich, W., and Brimhall, G.: Weathering profiles, mass-balance analysis, and rates of solute loss: Linkages  
614 between weathering and erosion in a small, steep catchment, *Geol. Soc. Am. Bull.*, 114 (9), 1143–1158,  
615 [https://doi.org/10.1130/0016-7606\(2002\)114<1143:WPMBAA>2.0.CO;2](https://doi.org/10.1130/0016-7606(2002)114<1143:WPMBAA>2.0.CO;2), 2002.

616 Anovitz, L.M., Cheshire, M.C., Hermann, R.P., Gu, X., Sheets, J.M., Brantley, S.L., Cole, D.R., Ilton, E.S., Mildner, D.F.R.,  
617 Gagnon, C., Allard, L.F., and Littrell, K.C.: Oxidation and associated pore structure modification during experimental  
618 alteration of granite, *Geochim. Cosmochim. Ac.*, 292, 532–556, <https://doi.org/10.1016/j.gca.2020.08.016>, 2021.

619 Bandstra, J. Z., Buss, H. L., Campen, R. K., Liermann, L. J., Moore, J., Hausrath, E. M., Navarre-Sitchler, A. K., Jang, J.-H.,  
620 and Brantley, S. L.: Compilation of mineral dissolution rates, in: *Kinetics of Water-Rock Interaction*, edited by: Brantley, S.  
621 L., Kubicki, J. D., and White, A. F., Springer New York, 737–823, <https://doi.org/10.1007/978-0-387-73563-4>, 2008.

622 Bazilevskaya, E., Lebedeva, M., Pavich, M., Rother, G., Parkinson, D. Y., Cole, D., and Brantley, S. L.: Where fast weathering  
623 creates thin regolith and slow weathering creates thick regolith, *Earth Surf. Proc. Land.*, 38, 847–858,  
624 <https://doi.org/10.1002/esp.3369>, 2013.

625 Bazilevskaya, E., Rother, G., Mildner, D. F., Pavich, M., Cole, D., Bhatt, M. P., Jin, L., Steefel, C. I., and Brantley, S. L.: How  
626 Oxidation and Dissolution in Diabase and Granite Control Porosity during Weathering, *Soil Sci. Soc. Am. J.*, 79, 55–73,  
627 <https://doi.org/10.2136/sssaj2014.04.0135>, 2015.

628 Behrens, R., Bouchez, J., Schuessler, J. A., Dultz, S., Hewawasam, T., and von Blanckenburg, F.: Mineralogical  
629 transformations set slow weathering rates in low-porosity metamorphic bedrock on mountain slopes in a tropical climate,  
630 *Chem. Geol.*, 411, 283–298, <https://doi.org/10.1016/j.chemgeo.2015.07.008>, 2015.

631 Behrens, R., Wirth, R., and von Blanckenburg, F.: Rate limitations of nano-scale weathering front advance in the slow-eroding  
632 Sri Lankan Highlands, *Geochim. Cosmochim. Ac.*, 311, 174–197, <https://doi.org/10.1016/j.gca.2021.06.003>, 2021.

633 Bernhard, N., Moskwa, L.-M., Schmidt, K., Oeser, R. A., Aburto, F., Bader, M. Y., Baumann, K., von Blanckenburg, F., Boy,  
634 J., van den Brink, L., Brucker, E., Büdel, B., Canessa, R., Dippold, M. A., Ehlers, T. A., Fuentes, J. P., Godoy, R., Jung, P.,  
635 Karsten, U., Köster, M., Kuzyakov, Y., Leinweber, P., Neidhardt, H., Matus, F., Mueller, C. W., Oelmann, Y., Oses, R., Oses,

636 P., Paulino, L., Samolov, E., Schaller, M., Schmid, M., Spielvogel, S., Spohn, M., Stock, S., Stroncik, N., Tielbörger, K.,  
637 Übernicker, K., Scholten, T., Seguel, O., Wagner, D., and Kühn, P.: Pedogenic and microbial interrelations to regional climate  
638 and local topography: New insights from a climate gradient (arid to humid) along the Coastal Cordillera of Chile, *CATENA*,  
639 170, 335–355, <https://doi.org/10.1016/j.catena.2018.06.018>, 2018.

640 Buss, H. L., Sak, P. B., Webb, S. M., and Brantley, S. L.: Weathering of the Rio Blanco quartz diorite, Luquillo mountains,  
641 Puerto Rico: coupling oxidation, dissolution, and fracturing, *Geochim. Cosmochim. Ac.*, 72, 4488–4507,  
642 <https://doi.org/10.1016/j.gca.2008.06.020>, 2008.

643 Chesworth W. et al.: Clay Mineral Formation, in: *Encyclopedia of Soil Science, Encyclopedia of Earth Sciences Series*, edited  
644 by: Chesworth, W., Springer, Dordrecht, Figure C51, [https://doi.org/10.1007/978-1-4020-3995-9\\_108](https://doi.org/10.1007/978-1-4020-3995-9_108), 2008.

645 Dawson, T. E., Hahm, W. J., and Crutchfield-Peters, K.: Digging deeper: what the critical zone perspective adds to the study  
646 of plant ecophysiology, *New Phytol.*, 226, 666–671, <https://doi.org/10.1111/nph.16410>, 2020.

647 Deckart, K., Hervé, F., Fanning, C., Ramírez, V., Calderón, M., and Godoy, E.: U-Pb Geochronology and Hf-O Isotopes of  
648 zircons from the Pennsylvanian Coastal Batholith, South-Central Chile, *Andean Geol.*, 41 (1), 49–82,  
649 <https://doi.org/10.5027/andgeoV41n1-a03>, 2013.

650 Drever, J. I.: The effect of land plants on weathering rates of silicate minerals, *Geochim. Cosmochim. Ac.*, 58, 2325–2332,  
651 [https://doi.org/10.1016/0016-7037\(94\)90013-2](https://doi.org/10.1016/0016-7037(94)90013-2), 1994.

652 Dunn, J. R., and Hudec, P. P.: Water, Clay and Rock Soundness, *Ohio J. Sci.*, 66 (2), 153–168, 1966.

653 Ferraris, F.: Hoja Los Angeles – Angol, Escala: 1:250.000, Carta Geológica de Chile N°5 (Preliminar), Instituto de  
654 Investigaciones Geológicas, OCLC number: 1024799672, 1979.

655 Ferré, E., Michelsen, K., Ernst, W., Boyd, J., and Cañón-Tapia, E.: Vertical zonation of the Barcroft granodiorite, White  
656 Mountains, California: Implications for magmatic processes, *Am. Mineral.*, 97, 1049–1059,  
657 <http://dx.doi.org/10.2138/am.2012.4013>, 2012.

658 Fimmen, R., Richter, D., Vasudevan, D., Williams, M., and West, L.: Rhizogenic Fe-C redox cycling: A hypothetical  
659 biogeochemical mechanism that drives crustal weathering in upland soils, *Biogeochemistry*, 87, 127–141,  
660 <https://doi.org/10.1007/s10533-007-9172-5>, 2008.

661 Fletcher, R. C., Buss, H. L., and Brantley, S. L.: A spheroidal weathering model coupling porewater chemistry to soil  
662 thicknesses during steady-state denudation, *Earth Planet. Sc. Lett.*, 244, 444–457, <https://doi.org/10.1016/j.epsl.2006.01.055>,  
663 2006.

664 Gana, P., Wall, R., and Gutiérrez, A.: Mapa geológico del área de Valparaiso-Curacavi, Región de Valparaiso y Región  
665 Metropolitana, Mapas Geológicos, N° 1, Escala 1:100 000, Servicio Nacional de Geología y Minería (Chile), OCLC number:  
666 43901854, 1996.

667 Gerrits, R., Pokharel, R., Breitenbach, R., Radnik, J., Feldmann, I., Schuessler, J. A., von Blanckenburg, F., Gorbushina, A.  
668 A., and Schott, J.: How the rock-inhabiting fungus *K. petricola* A95 enhances olivine dissolution through attachment, *Geochim.*  
669 *Cosmochim. Ac.*, 282, 76–97, <https://doi.org/10.1016/j.gca.2020.05.010>, 2020.

670 Gerrits, R., Wirth, R., Schreiber, A., Feldmann, I., Knabe, N., Schott, J., Benning, L. G., and Gorbushina, A. A.: High-  
671 resolution imaging of fungal biofilm-induced olivine weathering, *Chem. Geol.*, 559, 119902,  
672 <https://doi.org/10.1016/j.chemgeo.2020.119902>, 2021.

673 Glodny, J., Echtler, H., Collao, S., Ardiles, M., Buron, P., and Figueroa, O.: Differential Late Paleozoic active margin evolution  
674 in South-Central Chile (37° S–40° S) – the Lanalhue Fault Zone. *J. S. Am. Earth Sci.*, 26, 397–411,  
675 <https://doi.org/10.1016/j.jsames.2008.06.001>, 2008a.

676 Glodny, J., Gräfe, K., Echtler, H., and Rosenau, M.: Mesozoic to Quaternary continental margin dynamics in south-central  
677 Chile (36–42°S): The apatite and zircon fission track perspective, *Int. J. Earth Sci.*, 97, 1271–1291,  
678 <https://doi.org/10.1007/s00531-007-0203-1>, 2008b.

679 Goodfellow, B. W., Hilley, G. E., Webb, S. M., Sklar, L. S., Moon, S., and Olson, C. A.: The chemical, mechanical, and  
680 hydrological evolution of weathering granitoid, *J. Geophys. Res.-Earth*, 121, 1410–1435,  
681 <https://doi.org/10.1002/2016JF003822>, 2016.

682 Hampl, F. J., Schiperski, F., Byrne, J. M., Schwerdhelm, C., Kappler, A., Bryce, C., von Blanckenburg, F., and Neumann, T.:  
683 The role of iron-bearing minerals for the deep weathering of a hydrothermally altered plutonic rock in semi-arid climate  
684 (Chilean Coastal Cordillera), *Chem. Geol.*, 604, 120922, <https://doi.org/10.1016/j.chemgeo.2022.120922>, 2022a.

685 Hampl, F. J., Schiperski, F., Schwerdhelm, C., Stroncik, N., Bryce, C., von Blanckenburg, F., and Neumann, T.: Mineralogical  
686 and geochemical data of two weathering profiles in a Mediterranean and a humid climate region of the Chilean Coastal  
687 Cordillera, GFZ Data Services [data set], <https://doi.org/10.5880/figgeo.2022.035>, 2022b.

688 Hayes, N. R., Buss, H. L., Moore, O. W., Krám, P., and Pancost, R. D.: Controls on granitic weathering fronts in contrasting  
689 climates, *Chem. Geol.*, 535, 119450, <https://doi.org/10.1016/j.chemgeo.2019.119450>, 2020.

690 Hellmann, R., Wirth, R., Daval, D., Barnes, J.-P., Penisson, J.-M., Tisserand, D., Epicier, T., Florin, B., and Hervig, R. L.:  
691 Unifying natural and laboratory chemical weathering with interfacial dissolution–reprecipitation: A study based on the  
692 nanometer-scale chemistry of fluid–silicate interfaces, *Chem. Geol.*, 294–295, 203–216,  
693 <https://doi.org/10.1016/j.chemgeo.2011.12.002>, 2012.

694 Hervé, F.: Petrology of the crystalline basement of the Nahuelbuta Mountains, southcentral Chile, in: *Comparative Studies on*  
695 *the Geology of the Circum-Pacific Orogenic Belt in Japan and Chile*, edited by: Ishikawa, T., and Aguirre, I., Japan Society  
696 for the Promotion of Science, Tokyo, 1-51, 1977.

697 Holbrook, S., Marcon, V., Bacon, A., Brantley, S., Carr, B., Flinchum, B., Richter, D., and Riebe, C.: Links between physical  
698 and chemical weathering inferred from a 65-m-deep borehole through Earth’s critical zone, *Sci. Rep.-UK*, 9, 4495,  
699 <https://doi.org/10.1038/s41598-019-40819-9>, 2019.

700 Holmgren, G. G. S.: A Rapid Citrate-Dithionite Extractable Iron Procedure, *Soil Sci. Soc. Am. J.*, 31, 210–211,  
701 <https://doi.org/10.2136/sssaj1967.03615995003100020020x>, 1967.

702 Hynek, S., Comas, X., and Brantley, S. L.: The effect of fractures on weathering of igneous and volcanoclastic sedimentary  
703 rocks in the Puerto Rican tropical rain forest, *Proced. Earth Plan. Sc.*, 17, 972–975,  
704 <https://doi.org/10.1016/j.proeps.2017.01.001>, 2017.

705 Israeli, Y., Salhov, E., and Emmanuel, S.: Impact of textural patterns on modeled rock weathering rates and size distribution  
706 of weathered grains, *Earth Surf. Proc. Land.*, 46, 1177–1187, <https://doi.org/10.1002/esp.5093>, 2021.

707 Jiménez-González, I., Rodríguez-Navarro, C., and Scherer, G. W.: Role of clay minerals in the physicomaterial  
708 deterioration of sandstone, *J. Geophys. Res.*, 113, F02021, <https://doi.org/10.1029/2007JF000845>, 2008.

709 Jobbágy, E. G., and Jackson, R. B.: The uplift of soil nutrients by plants: biogeochemical consequences across scales, *Ecology*,  
710 85, 2380–2389, <https://doi.org/10.1890/03-0245>, 2004.

711 Kim, H., Stinchcomb, G., and Brantley, S.: Feedbacks among O<sub>2</sub> and CO<sub>2</sub> in deep soil gas, oxidation of ferrous minerals, and  
712 fractures: A hypothesis for steady-state regolith thickness, *Earth Planet. Sc. Lett.*, 460, 29–40,  
713 <https://doi.org/10.1016/j.epsl.2016.12.003>, 2017.

- 714 Kogure, T., and Banfield, J. F.: New insights into the mechanism for chloritization of biotite using polytype analysis, *Am.*  
715 *Mineral.*, 85 (8–9), 1202–1208, <https://doi.org/10.1515/am-2000-8-913>, 2000.
- 716 Krone, L. V., Hampl, F. J., Schwerdhelm, C., Bryce, C., Ganzert, L., Kitte, A., Übernickel, K., Dielforder, A., Aldaz, S., Oses-  
717 Pedraza, R., Perez, J. P. H., Sanchez-Alfaro, P., Wagner, D., Weckmann, U., and von Blanckenburg, F.: Deep weathering in  
718 the semi-arid Coastal Cordillera, Chile, *Sci. Rep.-UK*, 11, 13057, <https://doi.org/10.1038/s41598-021-90267-7>, 2021.
- 719 Lawrence, C., Harden, J., and Maher, K.: Modeling the influence of organic acids on soil weathering, *Geochim. Cosmochim.*  
720 *Ac.*, 139, 487–507, <https://doi.org/10.1016/j.gca.2014.05.003>, 2014.
- 721 Lebedeva, M. I. and Brantley, S. L.: Exploring an 'ideal hill': how lithology and transport mechanisms affect the possibility of  
722 a steady state during weathering and erosion. *ESPL*, 45(3), 652-665, <https://doi.org/10.1002/esp.4762>, 2020.
- 723 Lebedeva, M. I., Fletcher, R. C., Balashov, V. N., and Brantley, S. L.: A reactive diffusion model describing transformation  
724 of bedrock to saprolite, *Chem. Geol.*, 244, 624–645, <https://doi.org/10.1016/j.chemgeo.2007.07.008>, 2007.
- 725 Lohse, K. A., and Dietrich, W. E.: Contrasting effects of soil development on hydrological properties and flow paths, *Water*  
726 *Resour. Res.*, 41, W12419, <https://doi.org/10.1029/2004WR003403>, 2005.
- 727 Lucas, Y.: The Role of Plants in Controlling Rates and Products of Weathering: Importance of Biological Pumping, *Annu.*  
728 *Rev. Earth Pl. Sc.*, 29, 135–163, <https://doi.org/10.1146/annurev.earth.29.1.135>, 2001.
- 729 Luebert, F., and Plissock, P.: Sinópsis bioclimática y vegetal de Chile, Editorial Universitaria, Santiago de Chile, ISBN  
730 956-11-1832-7, 2006.
- 731 Maher, K.: The dependence of chemical weathering rates on fluid residence time, *EPSL*, 294, 1–2, 101-110,  
732 <https://doi.org/10.1016/j.epsl.2010.03.010>, 2010.
- 733 McKeague, J. A., and Day, J. H.: Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of  
734 soils, *Can. J. Soil Sci.*, 46 (1), 13–22, <https://doi.org/10.4141/cjss66-003>, 1966.
- 735 Melnick, D.: Rise of the central Andean coast by earthquakes straddling the Moho, *Nat. Geosci.*, 9, 401–407,  
736 <https://doi.org/10.1038/ngeo2683>, 2016.
- 737 Molnar, P., Anderson, R. S., and Anderson, S. P.: Tectonics, fracturing of rock, and erosion, *J. Geophys. Res.*, 112, F03014,  
738 <https://doi.org/10.1029/2005JF000433>, 2007.

- 739 Nadan, B. J., and Engelder, T.: Microcracks in New England granitoids: A record of thermoelastic relaxation during  
740 exhumation of intracontinental crust, *Geol. Soc. Am. Bull.*, 121, 80–99, <https://doi.org/10.1130/b26202.1>, 2009.
- 741 Napieralski, S. A., Buss, H. L., Brantley, S. L., Lee, S., Xu, H., and Roden, E. E.: Microbial chemolithotrophy mediates  
742 oxidative weathering of granitic bedrock, *P. Natl. Acad. Sci. USA*, 116, 26394–26401,  
743 <https://doi.org/10.1073/pnas.1909970117>, 2019.
- 744 Nascimento, D. L., Abrahão, A., Lambers, H., Teodoro, G. S., Ladeira, F. S. B., de Britto Costa, P., Oliveira, R. S., and de  
745 Farias, C. H. B.: Biogeomorphological evolution of rocky hillslopes driven by roots in campos rupestres, Brazil,  
746 *Geomorphology*, 395, 107985, <https://doi.org/10.1016/j.geomorph.2021.107985>, 2021.
- 747 Navarre-Sitchler, A., Brantley, S. L., and Rother, G.: How Porosity Increases During Incipient Weathering of Crystalline  
748 Silicate Rocks, *Rev. Mineral. Geochem.*, 80 (1), 331–354, <https://doi.org/10.2138/rmg.2015.80.10>, 2015.
- 749 Nesbitt, H., and Young, G.: Early Proterozoic climates and plate motions inferred from major element chemistry of lutites,  
750 *Nature*, 299, 715–717, <https://doi.org/10.1038/299715a0>, 1982.
- 751 Oeser, R. A., Stroncik, N., Moskwa, L.-M., Bernhard, N., Schaller, M., Canessa, R., van den Brink, L., Köster, M., Brucker,  
752 E., Stock, S., Fuentes, J. P., Godoy, R., Matus, F. J., Osés Pedraza, R., Osses McIntyre, P., Paulino, L., Seguel, O., Bader, M.  
753 Y., Boy, J., Dippold, M. A., Ehlers, T. A., Kühn, P., Kuzyakov, Y., Leinweber, P., Scholten, T., Spielvogel, S., Spohn, M.,  
754 Übernickel, K., Tielbörger, K., Wagner, D., and von Blanckenburg, F.: Chemistry and microbiology of the Critical Zone along  
755 a steep climate and vegetation gradient in the Chilean Coastal Cordillera, *CATENA*, 170, 183–203,  
756 <https://doi.org/10.1016/j.catena.2018.06.002>, 2018.
- 757 Oeser, R. A., and von Blanckenburg, F.: Do degree and rate of silicate weathering depend on plant productivity?  
758 *Biogeosciences*, 17, 4883–4917, <https://doi.org/10.5194/bg-17-4883-2020>, 2020.
- 759 Pawlik, Ł., Phillips, J. D., and Šamonil, P.: Roots, rock, and regolith: Biomechanical and biochemical weathering by trees and  
760 its impact on hillslopes – A critical literature review, *Earth-Sci. Rev.*, 159, 142–159,  
761 <https://doi.org/10.1016/j.earscirev.2016.06.002>, 2016.
- 762 Perez, J. R., Banwart, St. A., and Puigdomenech, I.: The kinetics of  $O_{2(aq)}$  reduction by structural ferrous iron in naturally  
763 occurring ferrous silicate minerals, *Appl. Geochem.*, 20, 2003–2016, <https://doi.org/10.1016/j.apgeochem.2005.07.001>, 2005.
- 764 Reis, F. D. A. A. and Brantley, S. L.: The impact of depth-dependent water content on steady state weathering and eroding  
765 systems. *Geochim. Cosmochim. Acta*, 244, 40–55, <https://doi.org/10.1016/j.gca.2018.09.028>, 2019.



- 766 Rempe, D. M., and Dietrich, W. E.: A bottom-up control on fresh-bedrock topography under landscapes, *P. Natl. Acad. Sci.*  
767 *USA*, 111 (18), 6576–6581, <https://doi.org/10.1073/pnas.1404763111>, 2014.
- 768 Rennert, T.: Wet-chemical extractions to characterise pedogenic Al and Fe species – a critical review, *Soil Res.*, 57, 1–16,  
769 <https://doi.org/10.1071/SR18299>, 2019.
- 770 Riebe, C. S., Kirchner, J. W., and Finkel, R. C.: Long-term rates of chemical weathering and physical erosion from cosmogenic  
771 nuclides and geochemical mass balance, *Geochim. Cosmochim. Ac.*, 67, 4411–4427, [https://doi.org/10.1016/S0016-](https://doi.org/10.1016/S0016-772)  
772 [7037\(03\)00382-X](https://doi.org/10.1016/S0016-7037(03)00382-X), 2003.
- 773 Røyne, A., Jamtveit, B., Mathiesen, J., and Malthe-Sørenssen, A.: Controls on rock weathering rates by reaction-induced  
774 hierarchical fracturing, *Earth Planet. Sc. Lett.*, 275, 364–369, <https://doi.org/10.1016/j.epsl.2008.08.035>, 2008.
- 775 Schaller, M., and Ehlers, T. A.: Comparison of soil production, chemical weathering, and physical erosion rates along a climate  
776 and ecological gradient (Chile) to global observations, *Earth Surf. Dynam.*, 10, 131–150, [https://doi.org/10.5194/esurf-10-131-](https://doi.org/10.5194/esurf-10-131-777)  
777 [2022](https://doi.org/10.5194/esurf-10-131-2022), 2022.
- 778 Scheibe, A., Sierra, C. A., Spohn, M.: Recently fixed carbon fuels microbial activity several meters below the soil surface.  
779 *Biogeosciences*, 20, 827-838, <https://doi.org/10.5194/bg-20-827-2023>, 2023.
- 780 Schneider, C. A., Rasband, W. S., and Eliceiri, K. W.: NIH Image to ImageJ: 25 years of image analysis, *Nat. Methods*, 9 (7),  
781 671–675, <https://doi.org/10.1038/nmeth.2089>, 2012.
- 782 Schoonejans, J., Vanacker, V., Opfergelt, S., Ameijeiras-Mariño, Y., Christl, M.: Kinetically limited weathering at low  
783 denudation rates in semiarid climatic conditions. *J. Geophys. Res. Earth Surf.*, 121, 336–350,  
784 <https://doi.org/10.1002/2015JF003626>, 2016.
- 785 Schwertmann, U.: Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung, *Zeitschrift für*  
786 *Pflanzenernährung, Düngung, Bodenkunde*, 105, 194–202, <https://doi.org/10.1002/jpln.3591050303>, 1964.
- 787 Starkey, H. C., Blackmon P. D., and Hauff P. L. The routine mineralogical analysis of clay-bearing samples, *U.S. Geological*  
788 *Survey Bulletin*, 1563, <https://doi.org/10.3133/b1563>, 1984.
- 789 St. Clair, J., Moon, S., Holbrook, W. S., Perron, J. T., Riebe, C. S., Martel, S. J., Carr, B., Harman, C., Singha, K., and Richter,  
790 D.: Geophysical imaging reveals topographic stress control of bedrock weathering, *Science*, 350 (6260), 534–538,  
791 <https://doi.org/10.1126/science.aab2210>, 2015.

792 Steefel, C. I., and van Cappellen, P.: A new kinetic approach to modeling water-rock interaction: The role of nucleation,  
793 precursors, and Ostwald ripening, *Geochim. Cosmochim. Ac.*, 54 (10), 2657–2677, [https://doi.org/10.1016-](https://doi.org/10.1016/0016-7037(90)90003-4)  
794 7037(90)90003-4, 1990.

795 Steenken, A., Rabbia, O., and Hernández, L.: The Emplacement of the Nahuelbuta Batholith in an Active Continental Margin  
796 (Central Chile), XVIII Congreso Peruano de Geología, Lima, Peru, 2016.

797 Stinchcomb, G. E., Kim, H., Hasenmueller, E. A., Sullivan, P. L., Sak, P. B., and Brantley, S. L.: Relating soil gas to weathering  
798 using rock and regolith geochemistry. *Am. J. Sci.*, 318, 727-763, <https://doi.org/10.2475/07.2018.01>, 2018.

799 Übernicker, K., Ehlers, T. A., Ershadi, M. R., Paulino, L., Fuentes Espoz, J.-P., Maldonado, A., Oses-Pedraza, R., and von  
800 Blanckenburg, F.: Time series of meteorological station data in the EarthShape study areas in the Coastal Cordillera, Chile,  
801 GFZ Data Services [data set], <https://doi.org/10.5880/fidgeo.2020.043>, 2020.

802 van Dongen, R., Scherler, D., Wittmann, H., and von Blanckenburg, F.: Cosmogenic  $^{10}\text{Be}$  in river sediment: where grain size  
803 matters and why, *Earth Surf. Dynam.*, 7, 393–410, <https://doi.org/10.5194/esurf-7-393-2019>, 2019.

804 Vázquez, M., Ramírez, S., Morata, D., Reich, M., Braun, J.-J., and Carretier, S.: Regolith production and chemical weathering  
805 of granitic rocks in central Chile, *Chem. Geol.*, 446, 87–98, <https://doi.org/10.1016/j.chemgeo.2016.09.023>, 2016.

806 Werner, C., Schmid, M., Ehlers, T. A., Fuentes-Espoz, J. P., Steinkamp, J., Forrest, M., Liakka, J., Maldonado, A., and Hickler,  
807 T.: Effect of changing vegetation and precipitation on denudation – Part 1: Predicted vegetation composition and cover over  
808 the last 21 thousand years along the Coastal Cordillera of Chile, *Earth Surf. Dynam.*, 6, 829–858, [https://doi.org/10.5194/esurf-](https://doi.org/10.5194/esurf-6-829-2018)  
809 6-829-2018, 2018.

810 White, A. F., and Yee, A.: Aqueous oxidation-reduction kinetics associated with coupled electron transfer from iron-containing  
811 silicates at 25°C, *Geochim. Cosmochim. Ac.*, 49, 1263–1275, [https://doi.org/10.1016/0016-7037\(85\)90015-8](https://doi.org/10.1016/0016-7037(85)90015-8), 1985.

812 Wilson, M. J.: Weathering of the primary rock-forming minerals: processes, products and rates, *Clay Miner.*, 39, 233–266,  
813 <https://doi.org/10.1180/0009855043930133>, 2004.