

1 **The importance of mineral determinations to PROFILE base**
2 **cation weathering release rates: A case study**

3 Sophie Casetou-Gustafson¹, Cecilia Akselsson², Stephen Hillier^{1,3}, Bengt A. Olsson¹,
4

5 ¹Department of Ecology, Swedish University of Agricultural Sciences, (SLU), P.O. Box 7044, SE-750 07
6 Uppsala, Sweden

7 ²Department of Physical Geography and Ecosystem Science, Lund University, Sölvegatan 12, SE-223 62 Lund,
8 Sweden

9 ³The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, United Kingdom

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11 *Correspondence to:* Sophie Casetou-Gustafson (Sophie.Casetou@slu.se)

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17 Abstract

18 Accurate estimates of base cation weathering rates in forest soils are crucial for policy decisions on sustainable
19 biomass harvest levels and for calculations of critical loads of acidity. The PROFILE model is one of the most
20 frequently used methods to quantify weathering rates, where the quantitative mineralogical input has often been
21 calculated by the A2M (“Analysis to Mineralogy”) program based solely on geochemical data. The aim of this
22 study was to investigate how uncertainties in quantitative mineralogy, originating from modeled mineral
23 abundance and assumed stoichiometry, influence PROFILE weathering estimate, by using measured quantitative
24 mineralogy by X-ray powder diffraction (XRPD) as a reference. Weathering rates ~~This study explored the~~
25 ~~influence of uncertainty in quantitative mineralogy on PROFILE base cation (Ca, Mg, K, Na) weathering rates~~
26 ~~obtained using normative mineralogy compared to those obtained using measured mineralogy, which was taken~~
27 ~~as a reference. Weathering rates~~ were determined for two sites, one in Northern (Flakaliden) and one in Southern
28 (Asa) Sweden. At each site, 3–4 soil profiles were analyzed at 10 cm depth intervals. Normative quantitative
29 mineralogy was calculated from geochemical data and qualitative mineral data with the A2M “Analysis to
30 Mineralogy” program (‘A2M’) using two sets of qualitative mineralogical data inputs to A2M: 1) A site-specific
31 mineralogy ~~calculated based on information about mineral identification by and mineral chemical composition as~~
32 ~~determined directly by XRPD and electron microprobe analyses (EMPA) determined from X ray powder~~
33 ~~diffraction (XRPD) analyses, and 2) regional mineralogy, representing the assumed minerals~~ present identity and
34 assumed mineral chemical compositions for larger geographical areas in Sweden, as per previous published
35 studies. ~~For the site specific mineral input the precise elemental compositions of minerals were determined by~~
36 ~~microprobe analysis, whereas for the regional mineralogy the compositions were as assumed in previous studies.~~
37 ~~A2M does not provide a unique mineralogical solution and one thousand random mineralogical solutions were~~
38 ~~calculated by A2M for each soil unit in order to include the full space of quantitative mineralogies in model~~
39 ~~outcome, all equally possible. A corresponding number of PROFILE runs were made to estimate weathering rates.~~
40 ~~The contribution of individual minerals to the release of base cations was also quantified by using a version of~~
41 ~~PROFILE which outputs this detail. A discrepancy between weathering rates calculated from XRPD data (W_{XRPD})~~
42 ~~and weathering rates based on A2M (W_{A2M}) was only considered significant if the former was outside the full~~
43 ~~range of the latter.~~ Arithmetic means of the weathering rates determined from A2M inputs (W_{A2M}) were generally
44 in relatively close agreement with those (W_{XRPD}) determined by inputs based on direct XRPD and EMPA
45 measurements W_{XRPD} . The hypothesis that using site-specific instead of regional mineralogy will improve the
46 confidence in mineral data input to PROFILE was supported for Flakaliden. However, at Asa, site-specific
47 mineralogies reduced the discrepancy for Na between W_{A2M} and W_{XRPD} but produced larger and significant
48 discrepancies for K, Ca and Mg. For Ca and Mg the differences between weathering rates based on different
49 mineralogies could be explained by differences in the content of some specific Ca- and Mg-bearing minerals, in
50 particular amphibole, apatite, pyroxene and illite. ~~It was concluded that i~~ Improving the accuracy precision in the
51 determination of content of these minerals would reduce weathering uncertainties. High uncertainties in
52 mineralogy, due for example to different A2M assumptions, had surprisingly little effect on the predicted
53 weathering ~~from of~~ Na- and K-bearing minerals. This can be explained by the fact that the weathering rate
54 constants for the minerals involved, e.g. K-feldspar and micas, are similar in PROFILE. Improving the description
55 of the dissolution rate kinetics of the plagioclase mineral group as well as major K-bearing minerals (K-feldspars

56 and micas) should be a priority to help improve of particular importance to future weathering estimates with the
57 PROFILE model.-

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60 **Definitions and abbreviations**

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62 Mineralogy = the identity (specific mineral or mineral group) and stoichiometry (specific mineral chemical
63 composition) of minerals that are present at a certain geographic unit, a particular site (*site-specific mineralogy*)
64 or a larger geographic province (*regional mineralogy*)

65 Quantitative mineralogy= the quantitative information (wt.%) on the abundance of specific minerals in
66 the soil.

67 **Abbreviations:**

68 M_{XRPD} = quantitative mineralogy based on XRPD (amount) and electron microprobe analysis (composition)

69 $M_{A2M-reg}$ = quantitative mineralogy calculated with the A2M model and using regional mineralogy [input](#)

70 $M_{A2M-site}$ = quantitative mineralogy calculated with the A2M model and using site-specific mineralogy [input](#)

71 W_{XRPD} = weathering rate based on quantitative mineralogy determined by [direct](#) XRPD and electron microprobe
72 analysis

73 W_{A2M} = weathering rate based on quantitative mineralogy determined by the A2M model (unspecific mineralogy
74 [input](#))

75 $W_{A2M-reg}$ = weathering rate based on quantitative mineralogy determined by the A2M model, and assuming regional
76 mineralogy [input](#).

77 $W_{A2M-site}$ = weathering rate based on quantitative mineralogy determined by the A2M model and assuming site-
78 specific mineralogy [input](#).

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82 1. Introduction

83 The dissolution of minerals [in soils and rocks](#) during weathering represents, together with deposition, the most
84 important long-term supply of base cations for plant growth as well as acting as a buffer against soil and water
85 acidification. Quantifying weathering rates is therefore of key importance to guide modern forestry demands on
86 biomass removal by helping to identify threshold levels [that are of sustainable for](#) base cation removal from soils
87 and waters. With the introduction of the harvest of forest biomass for energy production that includes whole tree
88 harvest and stump extraction, about 2–3 times more nutrients are exported from the forest compared to stem-only
89 harvest. As a result, issues of acidification and base cation supply are exacerbated and the sustainability of this
90 practice is questioned (Röser, 2008; de Jong et al. 2017). Regional nutrient balance calculations for Sweden have
91 indicated that net losses of base cations from forest soils can occur in stem-only harvest scenarios, and this trend
92 ~~would be was~~ substantially exacerbated and ~~became~~ more frequent in whole-tree harvesting scenarios, largely due
93 to low weathering rates (Sverdrup and Rosén, 1998; Akselsson et al., 2007a,b). ~~Furthermore, T~~the same effect
94 ~~occurred~~ both under current and projected future climate conditions (Akselsson et al., 2016).

95 The weathering rates included in these nutrient balance calculations are in most cases based on the PROFILE
96 model. This ~~is a process-oriented model calculating steady-state weathering rates using transition state theory and~~
97 ~~physical and geochemical properties of the soil such as temperature, soil moisture, soil mineralogy and~~
98 ~~concentrations of base cation, hydrogen and organic acids. model is the most used mechanistic tool to calculate~~
99 ~~steady-state chemical weathering at the interface of soil minerals and their surrounding liquid solution~~ (Sverdrup,
100 1996). ~~This model has~~ has been widely applied in Europe, [Canada](#) and the US during the last several decades
101 or more of weathering research (Olsson et al., 1993; Langan et al., 1995; Kolka et al., 1996; Starr et al., 1998;
102 Sverdrup and Rosén, 1998; [Koseva et al., 2010](#); Whitfield et al., 2006; Akselsson et al., 2007a; [Koseva et al., 2010](#);
103 Stendahl et al., 2013). In ~~a few some~~ cases nutrient balance calculations have also been based on the depletion
104 method (Olsson et al., 1993).

105 Reliable weathering rate estimates are crucial for the accuracy of future nutrient budget calculations (Futter et al.,
106 2012). Regarding the accuracy of the PROFILE model, the importance of high accuracy in physical input
107 parameters for the modelled weathering rate outputs has been highlighted by Hodson et al. (1996) and Jönsson et
108 al. (1995). Among the ~~variousse~~ parameters Hodson et al. (1996) noted that the weathering response of the entire
109 soil profile depends critically on its mineralogy ~~and as such any choice of the model user about mineralogical input~~
110 ~~data would may affect the model outcome significantly~~ (Hodson et al., 1997). ~~In most cases the mineralogical input~~
111 ~~to the PROFILE model is also derived by modelling. However, yet~~ little attention has been given to the influence
112 of modelled versus directly measured mineralogical input data on calculated base cation release rates.

113 The most widely used method for direct quantitative mineralogical analysis of soil samples is X-ray powder
114 diffraction, and the ~~accuracy~~ that can be achieved has been demonstrated in round robin tests most notably the
115 Reynolds Cup (McCarty, 2002; Kleeberg, 2005; Omotoso et al., 2006, Raven and Self, 2017). Casetou-Gustafson
116 et al. (2018) made some independent assessment of the accuracy of their own XRPD data by geochemical cross
117 validation (i.e. the mineral budgeting approach of Andrist-Rangel et al., 2006). Nonetheless, we should stress that
118 like all analytical methods the determined weight fractions of minerals identified in a soil sample by XRPD will
119 have an associated uncertainty, ~~and, a~~ Additionally, minerals present in minor amounts, nominally < 1% by weight,
120 may fall below the lower limit of detection of the XRPD method.

121 Due mainly to the relative ease of measurement and consequent ready availability of total element geochemical
122 data on soils, indirect methods of determining quantitative soil mineralogy, such as so called ‘normative’
123 geochemical calculations have been widely used to generate mineralogical data for use in the PROFILE model.
124 One such method is the normative “Analysis to Mineralogy” (A2M) program (Posch and Kurz, 2007) that has
125 commonly been used in PROFILE applications (Stendahl et al., 2013; Zanchi et al., 2014, ~~this issue~~; Yu et al.,
126 2016; 2018; Kronnäs et al., 2019). Based on a quantitative geochemical analysis of a soil sample, typically
127 expressed in weight percent oxides, as well as ~~and also~~ on some assessment of the available minerals in the soil
128 sample (minerals present) and their stoichiometry (chemical compositions), A2M calculates all possible
129 mineralogical compositions for the soil sample. ~~Thus~~ the A2M output for a given soil sample input has multiple
130 solutions and can be described as a multidimensional mineralogical solution space. This necessitates a choice when
131 using A2M output in applications such as weathering rate studies, the convention for which has been to use the
132 geometric mean mineralogical compositions e.g. Stendahl et al. 2013. Casetou-Gustafson et al. (2018) compared
133 the output of A2M with directly determined XRPD mineralogies at two sites, applying A2M in two different ways.
134 In the first case the information on available minerals in the model input was obtained from direct XRPD mineral
135 identifications and information on mineral stoichiometry from direct microprobe analysis of the minerals at the
136 specific site (hereafter denoted "site-specific"). In the second case the mineral stoichiometry and mineral identity
137 were both assumed based on an expert assessment of the probable mineralogy at the regional scale as given by
138 Warfvinge and Sverdrup (1995), hereafter denoted "regional". Casetou-Gustafson et al. (2018) concluded that
139 using A2M in combination with regional input data yielded results with large deviations from directly (XRPD)
140 measured quantitative mineralogy, particularly for two of the major minerals, K-feldspar and dioctahedral mica.
141 When site-specific mineralogical input data was used, measured and modeled quantitative mineralogy showed a
142 better correspondence for most minerals. For a specific mineral and a specific site, however, the bias in
143 determination of quantitative mineralogy might be significant depending on the accuracy of input data to A2M,
144 i.e. total geochemistry and/or mineral stoichiometry (Casetou-Gustafson et al., 2018). ~~Potential~~ ~~Errors~~ like these
145 in mineralogical input data might be assumed to affect the calculated weathering for different base cations
146 significantly.

147 In the present study, we used the different mineralogical data from Casetou-Gustafson et al. (2018) to model
148 weathering rates of soils with the PROFILE model. Rates calculated based on measured mineral abundances using
149 quantitative XRPD in combination with measured mineral elemental compositions are taken as ‘reference’
150 weathering rates to which other rates are compared. Samples for this study were collected from podzolised till
151 soils from 8 soil profiles at two forest sites in northern and southern Sweden, respectively.

152 The primary objective of this study was to describe and quantify the effect of differences in mineralogy input on
153 PROFILE weathering rates, leaving all other input parameters of the PROFILE model constant to isolate the effects
154 of variation in input of mineral stoichiometry and abundance. A first specific aim was to determine the
155 uncertainties in weathering rates caused by uncertainties in normative quantitative mineralogy. This was
156 approached by comparing PROFILE runs using modeled mineralogies based on the presence of minerals of a
157 specific site or a larger geographic region (i.e. site-specific and regional mineralogy) with PROFILE runs using
158 the directly measured mineralogy. The latter was assumed to represent the ‘true’ mineralogy at each site. ~~This~~
159 comparison of PROFILE weathering rates, based on XRPD versus A2M mineralogy, was done using 1000 random

160 solutions per sample from the entire multidimensional A2M [mineralogical](#) solution space. In the following,
161 weathering rates calculated by PROFILE based on XRPD and A2M mineralogies are denoted W_{XRPD} and W_{A2M} ,
162 respectively.

163 A second specific aim was to investigate how the over- or underestimation of W_{A2M} in relation to W_{XRPD} mirrors
164 the over- or underestimation of mineral contents estimated with A2M.

165 The following hypotheses were made:

166 (1) PROFILE weathering rates obtained with [normative quantitative mineralogy calculated based on](#) site-specific
167 mineralogical [information about mineral identity and mineral stoichiometry, data](#) are more similar to the reference
168 weathering rates than PROFILE runs obtained with [normative quantitative mineralogy calculated based on](#)
169 [regional information only, respectively, regional mineralogical input data](#)

170 (2) Over- and underestimations of weathering rates of different base cations by the PROFILE model can be
171 explained by over- ~~and~~ underestimations of mineral contents of a few specific minerals.

172

173 2. Materials and methods

174 2.1 Study sites

175 Two experimental forest sites, Asa in southern, and Flakaliden in northern Sweden, were used for the study (Table
176 1). Both sites have Norway spruce (*Picea abies* (L.) Karst) stands of uniform age, but differ in climate. Flakaliden
177 is located in the boreal zone with long cold winters, whereas Asa is located in the hemiboreal zone. The soils have
178 similar texture (Sandy loamy till), soil types (Spodosols) and moisture conditions. According to the geographical
179 distribution of mineralogy types in Sweden the sites belong to different regions (Warfvinge and Sverdrup, 1995).
180 The experiments, which started in 1986, aimed at investigating the effects of optimized water and nutrient supply
181 on tree growth and carbon cycling in Norway spruce forests (Linder 1995, Albaugh et al. 2009). The sites are
182 incorporated in the Swedish Infrastructure for Ecosystem Science (SITES).

183 2.2 Soil sampling and stoniness determination

184 Soil sampling was performed in October 2013 and March 2014 in the border zone of four plots each of the sites.
185 Plots selected for sampling were untreated control plots (K1 and K4 at Asa, 10B and 14B at Flakaliden) and
186 fertilized 'F' plots (F3, F4 at Asa, 15A, 11B at Flakaliden). A rotary drill was used in order to extract one intact
187 soil core per plot (17 cm inner diameter) except for plot K4, F3 and F4 at the Asa site. A 1 x 1m soil pit was
188 excavated at each of the three latter plots due to inaccessible terrain for forest machinery. The maximum mineral
189 soil depth varied between 70–90 cm in Flakaliden and 90–100 cm in Asa.

190

191 The volume of stones and boulders was determined with the penetration method by Viro (1952), and by applying
192 penetration data to the functions by Stendahl et al. (2009). A metal rod was penetrated at 16 points per plot into
193 the soil until the underground was not possible to penetrate any further, or to the depth 30 cm. There was a higher

194 average stoniness at Flakaliden than Asa (39 vol-% compared to 29 vol-% in Asa) that could partially explain the
195 lower maximum sampling depth at Flakaliden.

196 **2.3 Sample preparation**

197 Soils samples for chemical analyses were taken at 10 cm depth intervals in the mineral soil. Prior to analysis all
198 soil samples were dried at 30–40 °C and sieved at 2 mm mesh. Soil chemical analyses were performed on the fine
199 earth fraction (< 2mm).

200 **2.4 Analysis of geochemistry, total carbon and soil texture**

201 Total carbon was determined using a LECO elemental analyzer according to ISO 10694. Analysis of total
202 geochemical composition, conducted by ALS Scandinavia AB, was made by inductively coupled plasma
203 spectrometry (ICP-MS). Prior to analyses, the samples were ignited at 1000° C to oxidize organic matter and
204 grinded with an agate mortar. Particle size distribution was analyzed by wet sieving and sedimentation (Pipette
205 method) in accordance with ISO 11277. More details about the analytical procedure was given by Casetou-
206 Gustafson et al. (2018).

207 **2.5 Determination of quantitative mineralogy**

208 A detailed description of methods used to quantify mineralogy of the samples [wasere](#) given by Casetou et al.
209 (2018); and [these](#) are described in brief below.

210 **2.5.1 Measured mineralogy**

211 Quantitative soil mineralogy was determined with the X-ray powder diffraction technique, XRPD (M_{XRPD}) (Hillier
212 1999, 2003) ([Table S1a-b](#)). Preparation of samples for determination of XRPD patterns was made from spraying
213 ~~and~~ drying slurries of micronized soil samples (<2 mm) in ethanol. Quantitative mineralogical analysis of the
214 diffraction data was performed using a full pattern fitting approach (Omotoso et al., 2006). In the fitting process,
215 the measured diffraction pattern is modelled as a weighted sum of previously recorded and carefully verified
216 standard reference patterns of the prior identified mineral components. The chemical composition of the various
217 minerals present in the soils was determined by electron microprobe analysis (EMPA) ([Table S6](#)).

218 **2.5.2 Calculated mineralogy**

219 The A2M program (Posch and Kurz, 2007) was used to calculate quantitative mineralogical composition (M_{A2M})
220 from geochemical data. Based on a set of pre-determined data on mineral identity and stoichiometry, the model
221 outcome is a range of equally possible mineralogical compositions. The multidimensional structure of this
222 normative mineralogy model is a consequence of the number of minerals being larger than the number of analysed
223 elements, where a specific element can often be contained in several different minerals. A system of linear
224 equations is used to construct an M-N dimensional solution space (Dimension M= Number of minerals, Dimension
225 N=number of oxides). In this study we used one thousand solutions to cover the range of possible quantitative
226 mineralogies that may occur at a specific site.

227

228 A2M was used to calculate 1000 quantitative mineralogies each for two different sets of mineral identity and
229 element stoichiometry, $M_{A2M-reg}$ (regional) and $M_{A2M-site}$ (site-specific). Regional mineralogy refers to the mineral
230 identity and stoichiometry for the four major mineralogical provinces in Sweden [as](#) suggested by Warfvinge and
231 Sverdrup (1995), of which Asa and Flakaliden belong to different regions ([Table S5](#)). Site-specific mineralogy
232 refers to the measured mineral identity and stoichiometry determined by the XRPD and electron microprobe
233 analyses of the two sites ([Table S6](#)) (Casetou-Gustafson et al., 2018).

234 **2.6. Estimation of weathering rates with PROFILE**

235 **2.6.1 PROFILE model description**

236 The biogeochemical PROFILE model can be used to study the steady state weathering (i.e. stoichiometric mineral
237 dissolution) of soil profiles, as weathering is known to be primarily determined by the physical soil properties at
238 the interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, thus, for each soil
239 layer, parameters are specified based on field measurements and estimation methods (Warfvinge and Sverdrup,
240 1995). Furthermore, isotropic, well mixed soil solution conditions are assumed to prevail in each layer as well as
241 surface limited dissolution in line with early views by Aagard and Helgeson (1982) and Cou and Wollast (1985)
242 (Sverdrup, 1996). Based on these major assumptions, PROFILE calculates chemical weathering rates from a series
243 of kinetic reactions that are described by laboratory determined dissolution rate coefficients and soil solution
244 equilibria (i.e. transition state theory) (Sverdrup and Warfvinge, 1993). The PROFILE version (September 2018)
245 that was used in this study is coded to produce information on the weathering contribution of specific minerals,
246 which allowed us to test our second hypothesis. This version is based on the weathering rates of 15 minerals. Of
247 these, apatite, pyroxene, illite, dolomite and calcite were not found at the two study sites according to XRPD data
248 (Table S1).

249 **2.6.2 PROFILE parameter estimation**

250 The only parameter that was changed between different PROFILE runs was the quantitative mineralogy for each
251 soil layer, as described above. Hence, PROFILE estimated weathering rates (W) based on measured mineralogy
252 (W_{XRPD}), and the two versions of A2M calculated mineralogy, regional ($W_{A2M-reg}$), and site-specific ($W_{A2M-site}$). In
253 the regional mineralogy, plagioclase is assumed to occur as pure anorthite and pure albite for simplification as has
254 been used in previous studies (Stendahl et al., 2013; Zanchi et al., 2014). This simplification was done in order to
255 avoid having a number of minerals containing different amount of Ca and Na, as a result of plagioclase forming a
256 continuous solid solution series, since it would not affect the weathering rates.

257
258 The physical soil layer specific parameters, that were kept constant between different profile runs, were exposed
259 mineral surface area, stoniness, soil bulk density and soil moisture (Table 2). Exposed mineral surface area was
260 estimated from soil bulk density and texture analyses in combination with an algorithm specified in Warfvinge
261 and Sverdrup (1995) [and critically discussed in Hodson et al. \(1998\)](#). The volumetric field soil water content in
262 Flakaliden and Asa was estimated to be $0.25 \text{ m}^3 \text{ m}^{-3}$ according to the moisture classification scheme described in
263 Warfvinge and Sverdrup (1995). It was used to describe the volumetric water content for each soil pit.

264

265 Another group of parameters kept constant was chemical soil layer specific parameters. Aluminum solubility
266 coefficient needed for solution equilibrium reactions, defined as $\log\{Al^{3+}\}+3pH$, was estimated applying a
267 function developed from previously published data (Simonsson and Berggren, 1998) on our own total carbon and
268 oxalate extractable aluminum measurements. The function is based on the finding that the Al solubility in the
269 upper B-horizon of Podzols is closely related to the molar ratio of aluminum to carbon in pyrophosphate extracts,
270 and that below the threshold value of 0.1, Al solubility increases with the Al_p/C_p ratio (Simonsson and Berggren,
271 1998). Thus, a function was developed for application to our own measurements of Al_{ox} and C_{tot} based on the
272 assumption that it is possible to use the Al_{ox}/C_{tot} ratio instead of the Al_p/C_p ratio. Data on soil solution DOC were
273 available from lysimeters installed at 50 cm depth for plot K4 and K1 in Asa and 10B and 14B in Flakaliden, and
274 these values were also applied to soil depths below 50 cm (H. Grip, unpublished data). The E-horizon (0 –10 cm
275 at Flakaliden) and A-horizon (0 –10 cm at Asa) were characterized by higher DOC values based on previous
276 findings –(Fröberg et al., 2013) and the classification scheme of DOC in Warfvinge and Sverdrup (1995). Partial
277 CO_2 pressure values in the soil were taken from the default estimate of Warfvinge and Sverdrup (1995).

278
279 Other site-specific parameters that were kept constant between PROFILE runs were evapotranspiration,
280 temperature, atmospheric deposition, precipitation, runoff and nutrient uptake. Temperature is one of the important
281 factors that regulate the weathering rate, and for steady-state calculations in PROFILE the mean annual
282 temperature is used. Kronnäs et al. (2019) demonstrates how weathering rates varies between seasons, due to e.g.
283 variations in temperature. Precipitation is used in PROFILE to calculate vertical water flow through the soil profile.
284 The main effect of precipitation on weathering rates is its impact on soil moisture, but in PROFILE soil moisture
285 is not internally modeled, but given as input. An estimate of the average evaporation per site was derived from
286 annual averages of precipitation and runoff data using a general water balance equation. Deposition data from two
287 sites of the Swedish ICP Integrated Monitoring catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden)
288 (Löfgren et al., 2011) were used to calculate the total deposition. The canopy budget method of Staelens et al.
289 (2008) was applied as in Zetterberg et al. (2014) for Ca^{2+} , Mg^{2+} , K^+ , Na^+ . The canopy budget model is commonly
290 used for elements that are prone to canopy leaching (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-}) or canopy uptake (NH_4^+ , NO_3^-)
291 and calculates the total deposition (TD) as the sum of dry deposition (DD) and wet deposition (WD). Wet
292 deposition was estimated based on the contribution of dry deposition to bulk deposition, both for base cations and
293 anions, using dry deposition factors from Karlsson et al. (2012, 2013). Base cation and nitrogen accumulation rate
294 in above-ground tree biomass (i.e. bark, stemwood, living and dead branches, needles) was estimated as the
295 average accumulation rate over a 100 years rotation length in Flakaliden compared to a 73 years rotation length in
296 Asa. These calculations were based on Heureka simulations using the StandWise application (Wikström et al.,
297 2011) for biomass estimates in combination with measured nutrient concentrations in above- ground biomass (S.
298 Linder unpubl. data).

299 2.7 A definition of significant discrepancies between W_{A2M} and W_{XRPD}

300 A consequence of the mathematical structure of the A2M program is that the final solution space of possible
301 quantitative mineralogies ~~in the end~~ produces an uncertainty range of weathering estimates, but in a different sense
302 than the uncertainty caused by e.g. uncertainties in chemical analyses, because all mineralogies produced within
303 this range are equally likely. Thus, here we define a significant discrepancy between W_{XRPD} and W_{A2M} to occur

304 when the former is outside the range of the latter, as illustrated in Fig. 1a. The opposite case is a non-significant
 305 discrepancy, when the weathering rates based on XRPD are contained in the weathering range based on A2M
 306 (Figure 1b).

307
 308 The uncertainty range of W_{A2M} can potentially be reduced by reducing uncertainties in analyses of soil
 309 geochemistry but most particularly by definitions of available minerals and their stoichiometry. Furthermore, some
 310 discrepancies between W_{XRPD} and W_{A2M} might also arise due to limitations of the XRPD method, particularly
 311 when minerals occur near or below the detection limit.

312 2.8 Statistical analyses

313 In order to quantify the effect of mineralogy on PROFILE weathering rates two statistical measures were used to
 314 describe the discrepancies between W_{XRPD} and W_{A2M} . Firstly, root mean square errors (RMSE) of the differences
 315 between W_{XRPD} and the arithmetic mean of weathering rates based on regional and site-specific mineralogy, i.e.,
 316 $W_{A2M-reg}$ and $W_{A2M-site}$, were calculated:

$$317 \quad RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (W_{XRPD_i} - W_{A2M_i})^2} \quad RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (W_{XRPD}_i - W_{A2M})^2}$$

318 Eq. (1)

319 RMSE's were calculated individually for each element, soil layer and soil profile for two data sets. An RMSE
 320 expressing the error of the aggregated, total weathering rates in the 0–50 cm soil horizon was calculated to test our
 321 first hypothesis (RMSE of total weathering). In addition, an RMSE expressing the errors originating from
 322 discrepancies between W_{XRPD} and W_{A2M} for individual minerals was also calculated (RMSE of weathering by
 323 mineral). In the latter case, sums of RMSE's by mineral were calculated for each element and soil profile by
 324 analogy with the summing up of weathering rates for the whole 0–50 cm soil profile.

325
 326 Secondly, relative discrepancies (i.e. average percentage of over- or underestimation of W_{A2M} compared to
 327 W_{XRPD}) were calculated as the absolute discrepancy divided by the measured value.

$$328$$

$$329$$

$$330$$

$$331 \quad \text{Relative error} = \left(\frac{W_{A2M_i} - W_{XRPD_i}}{W_{XRPD_i}} \right) * 100 \quad \text{Relative error} = \left(\frac{(W_{A2M})_i - W_{XRPD}_i}{W_{XRPD}_i} \right) * 100$$

332 Eq. (2)

333
 334 Relative errors were calculated for each site by comparing the average sum of W_{A2M} in the upper mineral soil (0–
 335 50 cm) with the sum of W_{XRPD} in the upper mineral soil.

336 Statistical plotting of results was performed using R (version 3.3.0) (R Core Team, 2016) and Excel 2016.

337 3. Results

338 3.1 Weathering rates based on XRPD mineralogy

339 Weathering estimates with PROFILE are hereafter presented as the sum of weathering rates in the 0–50 cm soil
340 horizon, since this soil depth is commonly used in weathering rate studies. Information on individual, and deeper
341 soil layers (50-100 cm) is given in Table S2.

342
343 Weathering rates of the base cations based on quantitative XRPD mineralogy (W_{XRPD}), i.e. the reference
344 weathering rates, were ranked in the same order at both sites, i.e., with $\text{Na} > \text{Ca} > \text{K} > \text{Mg}$ (Table S2). On average,
345 weathering rates of Na, Ca, K and Mg at Asa were 17.7, 8.4, 5.6 and 3.6 $\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$, respectively.
346 Corresponding figures for Flakaliden were of similar magnitude, i.e., 14.8, 9.8, 5.7 and 5.6 $\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$. The
347 variation in weathering rates between soil profiles was smaller at Asa than at Flakaliden, as the standard deviation
348 in relation to the means for different elements ranged between 0.2-2.3 at Asa, and 2.0 –5.7 at Flakaliden (Table
349 S2).

350

351 3.2 Comparison between weathering rates based on XRPD and A2M mineralogy

352 At Flakaliden, $W_{\text{A2M-site}}$ was generally in closer agreement with W_{XRPD} than $W_{\text{A2M-reg}}$ (Fig. 2b), in line with the first
353 hypothesis. The discrepancies between W_{XRPD} and W_{A2M} were small and non-significant for Mg regardless of the
354 mineralogy input used in A2M, although the estimated discrepancies were reduced when site-specific mineralogy
355 was used. The use of regional mineralogy in A2M underestimated K release rates compared to W_{XRPD} , and the
356 discrepancy was significant. Using site-specific mineralogy resulted in smaller and non-significant discrepancy
357 for K release rates. A similar response to different mineralogies was revealed for Ca, although the result varied
358 more among soil profiles. In contrast to K and Ca, the release of Na was overestimated by both $W_{\text{A2M-site}}$ and $W_{\text{A2M-}}$
359 reg compared to W_{XRPD} . The discrepancies were significant regardless of the mineralogy input used in A2M,
360 although using site-specific mineralogy slightly reduced the discrepancy. The generally closer agreement between
361 $W_{\text{A2M-site}}$ and W_{XRPD} than $W_{\text{A2M-reg}}$ at Flakaliden was also indicated by the lower RMSEs of total weathering for all
362 base cations when site-specific mineralogy was used (Fig. 3a). Relative RMSE were below 20 % for $W_{\text{A2M-reg}}$, but
363 below 10 % for $W_{\text{A2M-site}}$. However, RMSE for Na was only slightly smaller for $W_{\text{A2M-site}}$ than $W_{\text{A2M-reg}}$ (16 % for
364 $W_{\text{A2M-site}}$).

365

366 PROFILE weathering rates for Asa revealed a different pattern compared to Flakaliden, and the results for Ca, Mg
367 and K were contradictory to hypothesis one. $W_{\text{A2M-reg}}$ was in close agreement with W_{XRPD} for K, Ca and Mg, and
368 the small discrepancies were non-significant (Fig. 2a). However, $W_{\text{A2M-reg}}$ for Na was consistently overestimated
369 compared to W_{XRPD} and the discrepancies were significant. Using site-specific mineralogy improved the fit
370 between W_{XRPD} and W_{A2M} for Na, but had rather the opposite effect on the other base cations at this site. For K,
371 Ca and Mg, $W_{\text{A2M-site}}$ overestimated weathering rates, and resulted in significant discrepancies, and larger RMSE,
372 whereas the discrepancies for Na were reduced and non-significant (Fig. 3a). At Asa, the highest relative RMSEs
373 of total weathering occurred for Ca and Mg with $W_{\text{A2M-site}}$ (> 30 %) (Fig. 3a). Large standard deviations were due
374 to a single soil profile, F4. The better consistency with $W_{\text{A2M-reg}}$ was indicated by RMSE below 10 % for Ca and

375 Mg, and that RMSE for Mg was half of the error with $W_{A2M-site}$. Only for Na, RMSE was lower for $W_{A2M-site}$ than
376 with $W_{A2M-reg}$.

377
378 A complementary illustration of the relationships between weathering rates based on XRPD and A2M is shown in
379 Fig. 4 and provided as Tables S3 and S4, which includes all data from individual soil layers 0–50 cm. A general
380 picture is that $W_{A2M-site}$ was less dispersed along the 1:1-line than $W_{A2M-reg}$, in particular for Flakaliden. On the
381 other hand, for weathering rates in the lower range ($< 5 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) site-specific mineralogy tended to generate
382 both over- and underestimated weathering rates. In most soil profiles, deviations from the 1:1-line were frequent
383 in soil layers below 20 cm. For Na under- and overestimations occurred in the whole range of weathering
384 estimates,

385 3.3 Mineral-specific contribution to weathering rates

386 In spite of its intermediate dissolution rate plagioclase was, due to its abundance, the most important Na-bearing
387 mineral determined in this study (Table 3 and Fig. 5). Plagioclase is a variable group of minerals with different
388 stoichiometric proportions of Ca and Na, from the purely sodic albite on the one hand to the purely calcic anorthite
389 on the other hand (Table S5) as well as with intermediate compositions (Table S6). For simplicity, they will be
390 referred to in this study as sodic and calcic plagioclase. Based on the same quantitative mineralogy (i.e. same
391 elemental compositions and identity of minerals), W_{XRPD} and $W_{A2M-site}$ gave strong weight to both calcic and sodic
392 plagioclase in estimating Na release rates, but $W_{A2M-site}$ gave stronger weight to calcic versus sodic plagioclase at
393 Asa, and vice-versa at Flakaliden (Fig. 5). In spite of these differences, the resultant release rates of Na according
394 to $W_{A2M-site}$ and W_{XRPD} were rather similar (Fig. 5).

395
396 Total Na release rates of $W_{A2M-reg}$ compared to W_{XRPD} were moderately overestimated. The relative RMSE of
397 weathering by specific Na-containing minerals were of more similar magnitude for Na at Flakaliden compared to
398 Asa (Fig. 3b). However, the standard deviations of RMSE were relatively large at Flakaliden, due to large RMSE
399 for albite in one specific soil profile (11B) (Table S7). Contrary to relative RMSE of total weathering, the relative
400 RMSE of weathering by specific minerals was lower for Na at Asa with regional than site-specific mineralogy.

401
402 According to W_{XRPD} , calcic plagioclase weathering was the most important source to Ca release at Flakaliden, and
403 the second most important source at Asa after epidote (Fig. 5). As for Na, $W_{A2M-site}$ gave stronger weight to calcic
404 plagioclase than W_{XRPD} at Asa. It was the other way around for $W_{A2M-site}$ at Flakaliden and the regional mineralogy
405 (i.e. W_{XRPD} gave stronger weight to calcic plagioclase than $W_{A2M-site}$). Another important Ca source in weathering
406 estimates based on A2M was apatite. This mineral was not detected in the XRPD analyses; but was included in
407 both A2M mineralogies as a necessary means to allocate measured total phosphorus content to a specific mineral
408 (Casetou-Gustafson et al. 2018).

409
410 Similar to Na, relative RMSE of weathering by Ca-containing minerals were several magnitudes larger than RMSE
411 of the total weathering of Ca. In other words, although an overall similar weathering rates might be generated by
412 the PROFILE model based on different quantitative mineralogies, the underlying modelled contributions from
413 different minerals can be markedly different. At Flakaliden, the mean relative RMSE by specific minerals were

414 larger for regional than site-specific mineralogy at Flakaliden (Fig. 3b). However, the difference was not
415 significant since the standard deviations were high, probably due to larger RMSE for Ca-bearing minerals in soil
416 profile 11B (Table S7).

417
418 A general picture of the mineral contribution to Mg release is that W_{XRPD} placed most weight to amphibole whereas
419 in W_{A2M} Mg release was more equally distributed among other minerals, notably hydrobiotite, trioctahedral mica
420 and vermiculite. At Asa, and to an even larger extent at Flakaliden, Mg release by A2M mineralogies was
421 determined by a higher contribution of minerals with high dissolution rates (Fig. 5 and Table 3) (i.e. In $W_{A2M-site}$,
422 hydrobiotite and trioctahedral mica; In $W_{A2M-reg}$, muscovite and vermiculite at Asa and biotite and illite at
423 Flakaliden). At Asa, less weight was given to amphibole by $W_{A2M-site}$ compared to W_{XRPD} . At Flakaliden, the W_{A2M-}
424 $site$ was close W_{XRPD} in spite of the very different allocations of weathering rates to different minerals. The
425 underestimation of Mg release by $W_{A2M-reg}$ was largely explained by the lower weight given to amphibole in both
426 A2M scenarios (Fig. 5). However, A2M gave larger weight to other minerals. The sums of RMSEs of weathering
427 from specific Mg-bearing minerals were much larger for regional than site-specific mineralogy at Flakaliden and
428 reached a maximum value of 156 %. A contributing factor were generally larger RMSE for the mineral
429 contribution of amphibole to Mg weathering and the fact that pyroxene contributed to the RMSEs of the total
430 weathering of Mg. Furthermore, a large standard deviation for the sum of RMSE of specific minerals (Fig. 3b)
431 was caused by soil profile 11B where more weight was placed on amphibole and biotite in contributing to Mg
432 weathering (Table S7). The two A2M mineralogies resulted in the same RMSEs for Mg-bearing minerals at Asa
433 (Fig. 3b).

434
435 Potassium release rates were largely dominated by K-Feldspar weathering in both W_{XRPD} and $W_{A2M-site}$. However,
436 K release by $W_{A2M-reg}$ (Fig. 5) were largely determined by micas at both sites. Together with Mg, these elements
437 had also the lowest weathering rates, indicating that differences between $W_{A2M-reg}$ and W_{XRPD} in relative terms were
438 not correlated with the magnitude of weathering. Unlike the other base cations, relative RMSE of K-bearing
439 minerals were lower at both sites when site-specific mineralogy was used instead of regional (Fig. 3b), and the
440 mineral specific RMSEs were also of similar magnitude as the RMSE of the total weathering (Fig.3a). $W_{A2M-site}$ of
441 K (Fig. 3b), were not several magnitudes larger than RMSE of the total weathering (Fig. 3a). The largest relative
442 RMSEs of K-containing minerals were reached by $W_{A2M-reg}$ at Flakaliden in soil profile 11B, indicated by the high
443 standard deviation.

444 4. Discussion

445 4.1 General range of weathering rates in relation to expectations from other sensitivity studies, and the 446 range of discrepancies between W_{XRPD} and W_{A2M}

447 To our knowledge, the present study is the first to have examined the sensitivity of the PROFILE model on real
448 case study differences of directly measured mineralogy versus indirectly determined normative mineralogy.
449 However, a few systematic studies have been made previously to test the influence of mineralogy inputs, amongst
450 other input parameters, to PROFILE weathering rates. Jönsson et al. (1995) concluded that uncertainty in
451 quantitative mineralogy could account for a variation from the best weathering estimate of about 20 %, and that
452 variations in soil physical and chemical parameters could be more important. The sensitivity analysis of Jönsson

453 et al. (1995) was made by a Monte Carlo simulation where mineralogical inputs were varied by $\pm 20\%$ of abundant
454 minerals, and up to $\pm 100\%$ of minor minerals. Shortly after, Hodson et al. (1996) examined the sensitivity of the
455 PROFILE model with respect to the sensitivity of weathering of specific minerals and concluded that large
456 uncertainties ~~in particular especially~~ in soil mineralogy, moisture, bulk density, temperature and surface area
457 determinations will have a larger effect on weathering rates than was reported by Jönsson et al. (1995).

458 Compared with the sensitivity analyses by Jönsson et al. (1995), the range of uncertainty in dominating mineral
459 inputs used in the present study was of similar order of magnitude. For this study we used the XRPD measured
460 (M_{XRPD}) and A2M estimated mineralogies (M_{A2M}) determined by Casetou-Gustafson et al. (2018). For example,
461 they concluded that $M_{\text{A2M-reg}}$ produced a low relative RMSE of total plagioclase (7 – 11 %) but higher relative
462 RMSE for less abundant minerals, such as dioctahedral mica (90 – 106 %). They also showed that when regional
463 mineral identity and assumed stoichiometry was replaced by site-specific mineralogy ($M_{\text{A2M-site}}$), the bias in
464 quantitative mineralogy was reduced.

465 Thus, given this bias in quantitative mineralogy input to PROFILE, discrepancies of W_{A2M} from W_{XRPD} at our
466 study sites should have been on the order of 20 % or less, and site-specific mineralogy inputs should produce
467 weathering rates with ~~lower~~ discrepancies than regional mineralogy. The result of this study was in agreement
468 with this expectation for all elements at Flakaliden but only for Na at Asa. The different quantitative mineralogies
469 resulted in discrepancies between W_{A2M} and W_{XRPD} that differed with site (Fig. 3a, 5).

470 **4.2 Is $W_{\text{A2M-site}}$ more consistent than $W_{\text{A2M-reg}}$?**

471 Our first hypothesis, that using site-specific mineralogy in the PROFILE model compared to regional mineralogy,
472 should result in weathering rates closer to XRPD-based mineralogy, and thus be more consistent, was generally
473 supported for Flakaliden, but only for Na at Asa. This result was revealed from both the occurrence of significant
474 discrepancies as well as the RMSE of the total weathering rates. Thus, the results did not support our first
475 hypothesis in a consistent way. The possible reasons for this outcome are discussed below, based on the analysis
476 of how different minerals contributed to the overall weathering rates.

477 **4.3 How are discrepancies between W_{A2M} and W_{XRPD} correlated to bias in determinations of quantitative** 478 **mineralogy**

479 The version of the PROFILE model used in this study allowed a close examination of the per element weathering
480 rate contributions obtained from different minerals that provide some insight into the causes to the total W_{A2M}
481 discrepancies.

482 **4.3.1 Sodium release rates**

483 A biased determination of mineralogy may not necessarily result in a corresponding bias of PROFILE weathering
484 estimates if the discrepancies are cancelling each other out, and if dissolution rates of the different minerals are
485 rather similar. This was probably the case for Na. At both study sites and for both W_{XRPD} and W_{A2M} , Na release
486 rates were largest for plagioclase minerals. The Na release from $W_{\text{A2M-site}}$ and $W_{\text{A2M-reg}}$ were close to W_{XRPD} at both
487 study sites (i.e. all weathering rates were in the range of 17-19 $\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) ~~in spite of that nonetheless~~ $W_{\text{A2M-}}$
488 $_{\text{site}}$ placed more weight to calcic plagioclase and $W_{\text{A2M-reg}}$ more weight to albitic plagioclase (Fig.5). Contrary to

489 our second hypothesis, the relatively high precision in total release rates (i.e.<10%; Fig. 3a) of Na was not
490 correlated to the actual low precision in mineral contribution to the total Na release rates (i.e. >30 %; Fig. 3b). The
491 latter can be explained by the fact that in PROFILE all types of plagioclase have the same dissolution rate
492 coefficients (Table 3). Due to this, and in combination with the fact that plagioclase type minerals are a major
493 source for Na, the mineralogical uncertainty in estimating Na release rates with PROFILE was relatively low in
494 this study (i.e. <20 %). In context, however, we note that it is generally accepted that under natural conditions
495 different plagioclase minerals weather at different rates, (Allen and Hajek, 1989, Blum and Stillings, 1995).

496 4.3.2 Calcium release rates

497 According to W_{XRPD} and W_{A2M} , a key mineral for Ca release rates was calcic plagioclase at Flakaliden and epidote
498 at Asa. In line with our second hypothesis, the overestimation of calcic plagioclase in $M_{\text{A2M-site}}$ at Asa at the expense
499 of epidote and amphibole (Casetou-Gustafson et al., 2018) was directly reflected in the significant discrepancy
500 and overestimated weathering rates of Ca by $W_{\text{A2M-site}}$ compared to W_{XRPD} (Fig. 5, and 1a). This discrepancy was
501 due to differences between $W_{\text{A2M-site}}$ and W_{XRPD} in the mineral stoichiometry of calcic plagioclases, and not in
502 geochemistry, as the same geochemical analyses were also used for $W_{\text{A2M-reg}}$.

503
504 At Flakaliden, A2M based on site-specific mineralogy overestimated epidote at the expense of amphibole
505 (Casetou-Gustafson et al., 2018), leading to an underestimation of Ca weathering rates from amphibole compared
506 to epidote (Fig. 5). On the other hand, at Asa, it was the regional mineralogy input to A2M that resulted in
507 overestimated amounts of epidote at the expense of dioctahedral vermiculite and amphibole, and this bias was
508 directly reflected in the underestimated release of Ca from amphibole in $W_{\text{A2M-reg}}$. Conversely, the relatively small
509 and non-significant discrepancies of Ca release by $W_{\text{A2M-site}}$ at Flakaliden and by $W_{\text{A2M-reg}}$ at Asa did not depend
510 on a high precision in estimating the contribution from different minerals, since the precision was actually low. In
511 these cases, the good fits seem to be simply coincidental. Owing to differences in dissolution rates, Ca-bearing
512 minerals tend to compensate each other in terms of the total weathering rate that is calculated. This compensatory
513 effect is perhaps the reason why by coincidence, both $W_{\text{A2M-reg}}$ and $W_{\text{A2M-site}}$ discrepancies for Ca diverge in
514 different directions at Asa compared to Flakaliden.

515
516 Another source of uncertainty associated with the release of Ca is the role of minerals with high dissolution rates
517 that occur in low abundance, for example apatite, ~~and~~ pyroxene and calcite. Apatite was included in M_{A2M} , but if
518 present in the soils studied was below the detection limit of 1 wt.% in the XRPD analyses as were pyroxene and
519 calcite (Casetou-Gustafson et al., 2018). Additionally, ~~the~~ assumption made in the A2M calculations that all P
520 determined in the geochemical analyses is allocated to apatite will likely overestimate the abundance of this
521 mineral since soil P can also occur bound to Fe and Al oxides and soil organic matter in acidic mineral soils (Weil
522 and Brady, 2016). The relatively high abundance occurrence of paracrystalline Fe-oxyhydroxide and Al-containing
523 allophane and imogolite at Flakaliden indicates that this could be the case, at least at Flakaliden.

524
525 Regarding pyroxene, XRPD might also have failed to detect and quantify pyroxene due to their low abundancies
526 at Flakaliden (Casetou-Gustafson et al., 2018). Analytical limitations of XRPD would thus imply that W_{XRPD} of
527 Ca might be underestimated at Flakaliden and Asa. However, in the absence of XRPD detection it is also possible

528 that $M_{A2M-reg}$ overestimated the pyroxene contents at Flakaliden. Thus, apatite and pyroxene added relatively large
529 uncertainties to the weathering estimates of Ca at Flakaliden due to the fact that they have a low abundance in
530 combination with very high dissolution rates. In terms of other reactive trace mineral phases, White et al. (1996,
531 2017) has highlighted the importance of small amounts of calcite in intact granitoid rocks and its significance for
532 Ca found in watershed studies. They also noted that in laboratory leaching experiments on the rocks they studied,
533 reactive calcite became exhausted after just 1.5 years. Given the trace concentrations involved and the high
534 solubility of calcite it is doubtful that calcite is or has been of any long-lived significance in the soil profiles
535 studied, even though they are derived largely from rocks of granitic composition. However, Although, the results
536 of White et al. (1996, 2017) do suggest indicate that calcite present in the in-situ granitoid rocks underlying the
537 soils probably will may well contribute to Ca export from the catchment. Additionally Furthermore, the
538 overestimation of the slowly weatherable mineral illite by $M_{A2M-reg}$ (Casetou-Gustafson et al., 2018) resulted in an
539 underestimation of Ca release by $W_{A2M-reg}$ at Flakaliden, since less Ca was allocated to the more weatherable
540 minerals. Although, it should also be noted parenthetically that Ca can only occur as an exchangeable cation in
541 illite, it is not an element that occurs as part of the illite crystal structure, such that the 'illite' composition used in
542 PROFILE may is in need of some revision.

543 4.3.3 Magnesium release rates

544 At both study sites, a large number of Mg-containing minerals contributed to the release of Mg, but amphibole
545 was the predominant mineral according to W_{XRPD} and $W_{A2M-site}$. The only significant discrepancy in Mg release
546 rates was revealed for $W_{A2M-site}$ at Asa, which resulted in an overestimation by 41 %. This overestimation was an
547 effect of underestimated contribution from amphibole in combination with overestimated contributions from
548 hydrobiotite and trioctahedral mica. This result for Asa supported our second hypothesis. At Flakaliden, $W_{A2M-site}$
549 produced the same shift in the contribution of Mg by minerals, but the net effect was a very small and non-
550 significant discrepancy to W_{XRPD} . As was noted for Ca, the different outcomes of using site-specific mineralogies
551 at Asa and Flakaliden has no systematic underlying pattern.

552 Using PROFILE based on regional mineralogy resulted in surprisingly low and non-significant discrepancies in
553 Mg release rate, despite both the qualitative and quantitative mineralogies being very different from XRPD,
554 particularly at Flakaliden. For example, both pyroxene and illite were included in $M_{A2M-reg}$, but not in M_{XRPD} . Thus,
555 at Flakaliden, the overestimation of illite in $M_{A2M-reg}$ caused an underestimation of Mg release rates comparable to
556 the underestimation of Ca release rates.

557 4.3.4 Potassium release rates

558 Weathering of K-feldspar was the most important source of K release by PROFILE regardless of the different
559 types of mineralogy input. Casetou-Gustafson et al. (2018) showed a strong negative correlation between $M_{A2M-reg}$
560 and M_{XRPD} for two of the major K-bearing minerals observed at both study sites, i.e., illite (or dioctahedral mica,
561 muscovite) and K-feldspar. Contrary to our second hypothesis, the results of the present study demonstrate that
562 over- or underestimation of $W_{A2M-reg}$ compared to W_{XRPD} cannot be explained by significant negative correlation of
563 illite and K-feldspar in $M_{A2M-reg}$. However, this is likely related to the fact that illite and K-feldspar have the lowest
564 and also quite similar dissolution rates among minerals included in PROFILE (i.e. the highest dissolution
565 coefficients, Table 3). Although very different inputs in relation to K bearing minerals produced very similar

566 outputs, we note that this appears contradictory to differences in the behaviour of K-feldspars and K-micas as
567 sources of K via weathering to plants as reviewed for example by Thompson and Ukrainczyk (2002). [Additionally](#)
568 [we note that Hodson et al. \(1997\) compared reaction rate constants for different minerals from Sverdrup et al.](#)
569 [\(1990\) with their own calculations and the discrepancies were relatively large for some minerals, e.g. muscovite.](#)

570 5. Concluding remarks

- 571 • Based on comparing the full solution span of normative mineralogy from the A2M program to measured
572 reference mineralogy from XRPD overall similar weathering rates were generated by the different
573 mineralogical inputs to the PROFILE model. However, the underlying contributions from different
574 minerals to the overall rates differed markedly. Although the similarity of overall rates lends some support
575 to the use of normative mineralogy as input to weathering models, the details of the comparison reveal
576 potential short-comings and room for improvements in the use of normative mineralogies.
- 577 • Compared with regional mineralogy, weathering rates based on site-specific mineralogy were more
578 comparable to the reference rates generated from XRPD mineralogy, in line with hypothesis 1, at one of
579 the study sites (Flakaliden), but not at the other (Asa). Thus, although intuitively the more detailed site
580 specific quantitative mineralogy data might be expected to give more comparable results, this is not
581 supported by this study.
- 582 • For Ca and Mg the differences between weathering rates based on different mineralogies could be
583 explained by differences in the content ([modelled or actual](#)) of some specific Ca- and Mg-bearing
584 minerals, e.g. amphibole, apatite, pyroxene, [calcite](#) and illite. Improving [certainty in relation to the](#)
585 [precision in the content and](#) presence versus absence of some of these minerals [and if present accurate](#)
586 [quantification at low levels](#) would reduce weathering [rate calculation](#) uncertainties.
- 587 • High uncertainties in mineralogy, due for example to different A2M assumptions, had surprisingly low
588 effect on the weathering from Na- and K-bearing minerals. This can be explained by the fact that the
589 weathering rate constants for the minerals involved, e.g. the plagioclase feldspars and K-feldspar and
590 dioctahedral micas, are similar in PROFILE such that they compensate each other in the overall
591 weathering rate outputs for these elements, a situation that is unlikely to reflect reality.
- 592 • For more in-depth analysis of the uncertainties in weathering rates caused by mineralogy, the rate
593 coefficients of minerals should be revisited and their uncertainties assessed. A revision of rate constants
594 could lead to results more in line with hypothesis 1.

595 596 6. Authors contribution

597 Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment, PROFILE
598 model analyses, interpretation and writing. C. Akselsson: study design, PROFILE model development,
599 interpretation and writing. B.A. Olsson: study design, interpretation and writing. S. Hillier: interpretation and
600 writing.

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755 **Table 1.** Characteristics of the study sites.

Site	Asa	Flakaliden
Coordinates ^a	57° 08' N; 14° 45' E	64° 07' N; 19° 27' E
Elevation (m a.s.l.) ^a	225-250	310-320
Mean annual precipitation (mm) ^b	688	523
Mean annual air temperature (°C) ^b	5.5	1.2
Bedrock ^c	Acidic intrusive rock	Quartz-feldspar-rich sedimentary rock
Soil texture ^d	Sandy loam	Sandy loam
Type of quaternary deposit ^d	Sandy loamy till	Sandy loamy till
Soil moisture regime (Soil taxonomy) ^e	Udic	Udic
Soil type (USDA soil taxonomy) ^e	Spodosols	Spodosols
Region/province ^f	3	1

^a Bergh et al. 2005

^b Long-term averages of annual precipitation and temperature data (1961-1990) from nearest SMHI meteorological stations (Asa: Berg; Flakaliden: Kulbäcksliden)

^c SGU bedrock map (1:50000)

^d Soil texture based on own particle size distribution analysis by wet sieving according to ISO 11277

^e USDA Soil Conservation service, 2014

^f Warfvinge and Sverdrup (1995)

756

757 **Table 2.** PROFILE parameter description.

Parameter	Description	Unit	Source
Temperature	Site	°C	Measurements from nearby SMHI stations
Precipitation	Site	m yr	Measurements from nearby SMHI stations
Total deposition	Site	mmol _c m ⁻² yr ⁻¹	Measurements of open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites
BC net uptake	Site	mmol _c m ⁻² yr ⁻¹	Previously measured data from Asa and Flakaliden: Element concentration in biomass from Linder (unpublished data). Biomass data from Heureka simulations.
N net uptake	Site	mmol _c m ⁻² yr ⁻¹	Previously measured data from Asa and Flakaliden: Element concentration in biomass from Linder (unpublished data). Biomass data from Heureka simulations.
BC in litterfall	Site	mmol _c m ⁻² yr ⁻¹	Literature data for element concentrations from Hellsten et al. 2013
N in litterfall	Site	mmol _c m ⁻² yr ⁻¹	Literature data for element concentrations from Hellsten et al. 2013
Evapofraction	Site	Fraction	Own measurements and measurements from nearby Swedish Integrated Monitoring Sites
Mineral surface area	Soil	m ² m ⁻³	Own measurements used together with Eq. 5.13 in Warfvinge and Sverdrup (1995)
Soil bulk density	Soil	kg m ⁻³	Own measurements
Soil moisture	Soil	m ³ m ⁻³	Based on paragraph 5.9.5 in Warfvinge and Sverdrup (1995)
Mineral composition	Soil	Weight fraction	Own measurements
Dissolved organic carbon	Soil	mg l ⁻¹	Previously measured data from Asa and Flakaliden: Measurements for B-horizon from Harald Grip and previously measured data from Fröberg et al. 2013
Aluminium solubility coefficient	Soil	kmol m ⁻³	Own measurements for total organic carbon and oxalate extractable aluminium together with function developed from previously published data (Simonsson and Berggren, 1998)
Soil solution CO ₂ partial pressure	Soil	atm.	Base on paragraph 5.10.2 in Warfvinge and Sverdrup (1995)

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760 **Table 3** Mineral dissolution rate coefficients ($\text{kmol}_c \text{ m}^{-2} \text{ s}^{-1}$) used in PROFILE for the reactions with H^+ , H_2O ,
 761 CO_2 and organic ligands (R^-) (Warfvinge and Sverdrup, 1995).

Mineral	pKH	pKH ₂ O	pKCO ₂	pKR
Pyroxene	12.3	17.5	15.8	14.4
Apatite	12.8	15.8	15.8	19.5
Hornblende	13.3	16.3	15.9	14.4
Epidote	14	17.2	16.2	14.4
Plagioclase	14.6	16.8	15.9	14.7
K-Feldspar	14.7	17.2	16.8	15
Biotite	14.8	16.7	15.8	14.8
Chlorite	14.8	17	16.2	15
Vermiculite	14.8	17.2	16.2	15.2
Muscovite and Illite	15.2	17.5	16.5	15.3

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779 **Figure captions**

780 **Figure 1.** The first scenario for describing the effect of mineralogy on weathering rates in the upper mineral soil
781 for a specific soil profile (a) happens when the PROFILE weathering rate based on XRPD (reference weathering
782 rates) is not contained in the weathering range produced using PROFILE in combination with the full A2M
783 solution space. There are two possible explanations of why a significant discrepancy introduces an uncertainty
784 range, i.e. (1) due to uncertainties related to the mineralogical A2M input and (2) due to uncertainties related to
785 the limitation of the XRPD method itself (i.e. detection limit). The second scenario (b) occurs when the reference
786 weathering rate is contained in the full A2M weathering span. In this case we speak of ‘non-significant
787 discrepancies’.

788 **Figure 2.** Comparison of PROFILE weathering rates of base cations ($\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) at Asa (a) and Flakaliden
789 (b) sites in the 0–50 cm horizon based on XRPD mineralogy (vertical dashed lines) with PROFILE weathering
790 rates based on one thousand random regional A2M mineralogies versus one thousand random site-specific A2M
791 mineralogies. Data presented are from four different soil profiles per site. Regional graph for soil profile 10B at
792 Flakaliden is missing since A2M did not calculate 1000 solutions for soil layer 20-30, due to “Non-positive
793 solution”.

794 **Figure 3.** Root-mean square error (RMSE) of average PROFILE weathering rates ($\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) of one
795 thousand A2M mineralogies per soil layer, compared to weathering rates based on XRPD mineralogy per soil
796 layer. Comparisons are based on the total weathering per element (A) and on the sum of mineral contributions to
797 total weathering per element (B). RMSE describes the prediction accuracy for a single soil layer.

798 **Figure 4.** Comparison of PROFILE weathering rates based on XRPD mineralogy ($\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) with
799 PROFILE weathering rates based on regional A2M mineralogy (upper figures) versus site-specific mineralogy
800 (lower figures). Each data point represents a mean of one thousand PROFILE weathering rates for a specific soil
801 depth of one of 4 soil profiles per site.

802 **Figure 5.** Comparison of sums of PROFILE base cation weathering rates for different minerals in the upper
803 mineral soil (0-50 cm) based on XRPD mineralogy and the average PROFILE base cation weathering rate (i.e.
804 based on one thousands input A2M mineralogies per mineral) according to the two normative mineralogical
805 methods and for each study site (i.e. Asa site-sepcific, Flakaliden site-specific, Asa regional, Flakaliden
806 regional). For W_{A2M} , relative error (% of W_{XRPD} estimate) are given at the end of each bar to illustrate the
807 average deviation of W_{A2M} and W_{XRPD} in the upper mineral soil. *=significant discrepancy as defined in section
808 2.7. Vrm1=Trioctahedral vermiculite; Vrm2=Diocahdreal vermiculite. Information on chemical compositions of
809 minerals are given in Table S5 and S6.

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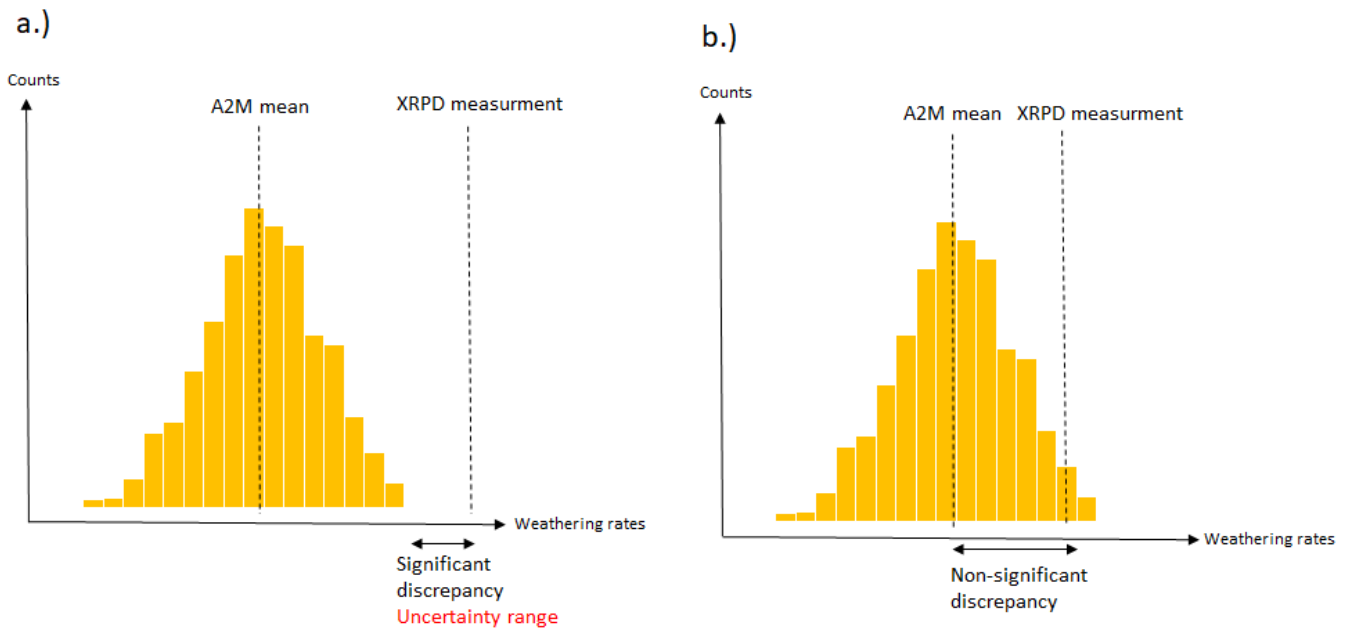
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821 Figure 1a,b

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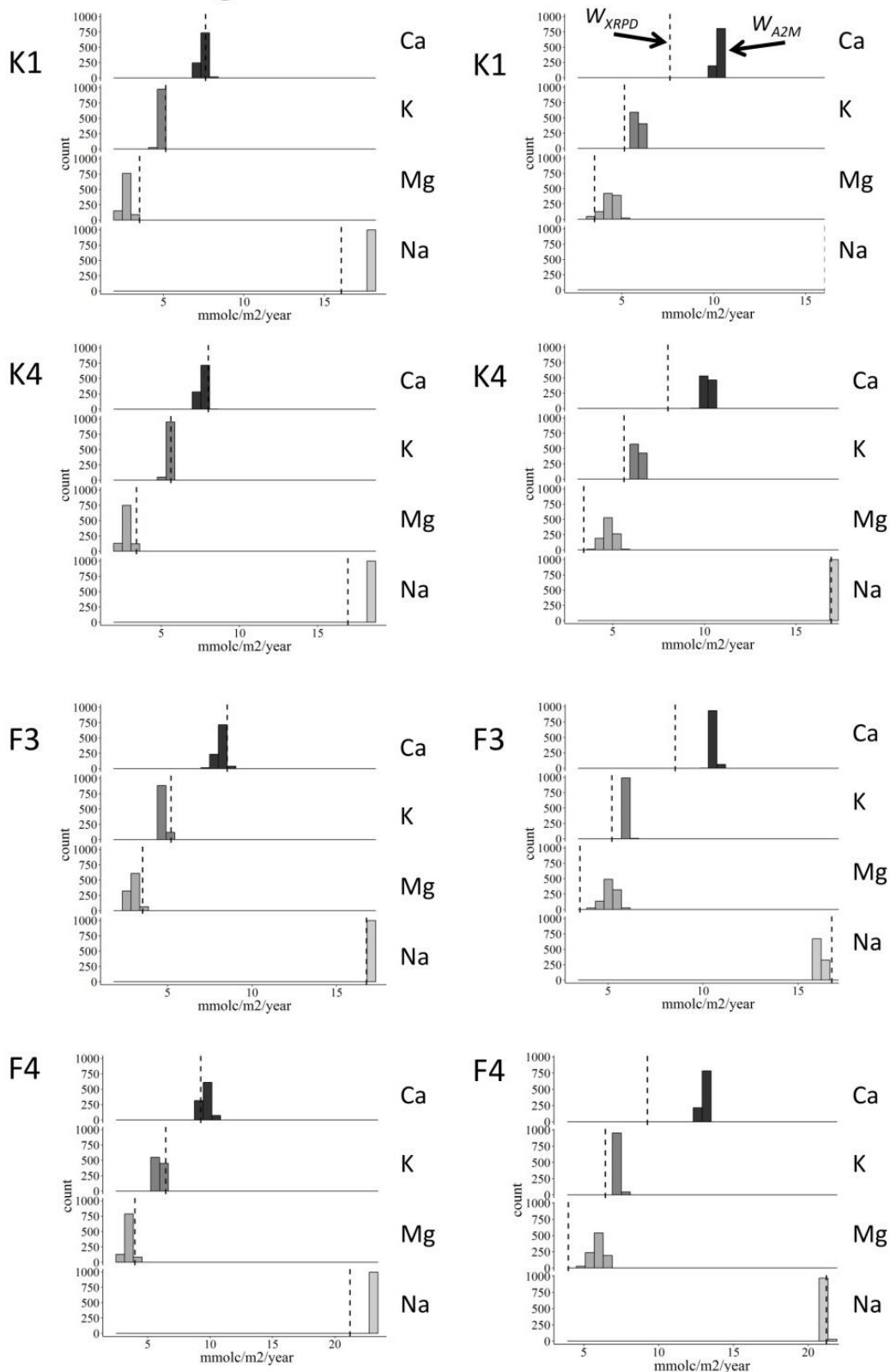
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a.

Asa

Regional

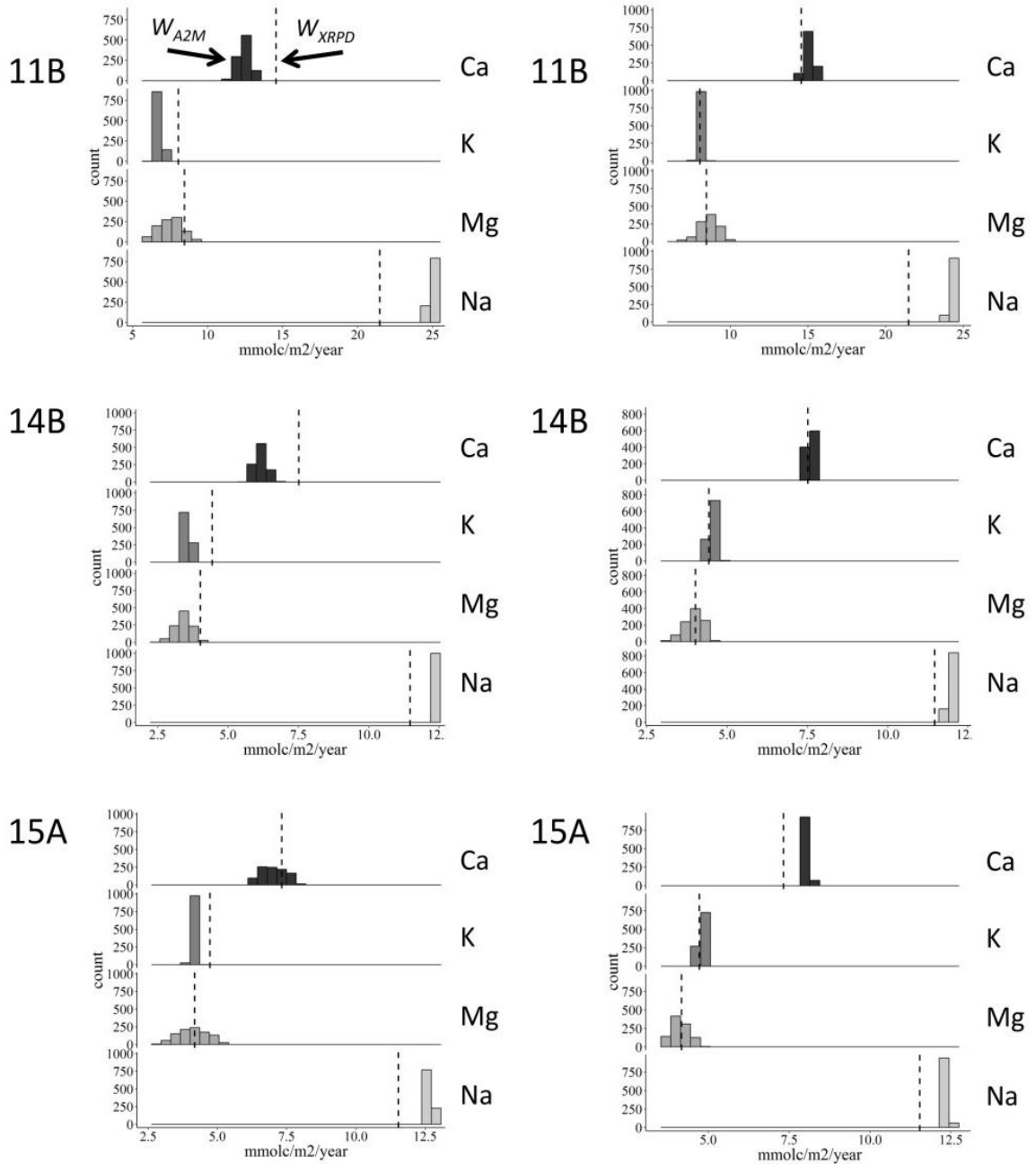
Site-specific



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838 Figure 2a

b. Flakaliden **Regional** **Site-specific**



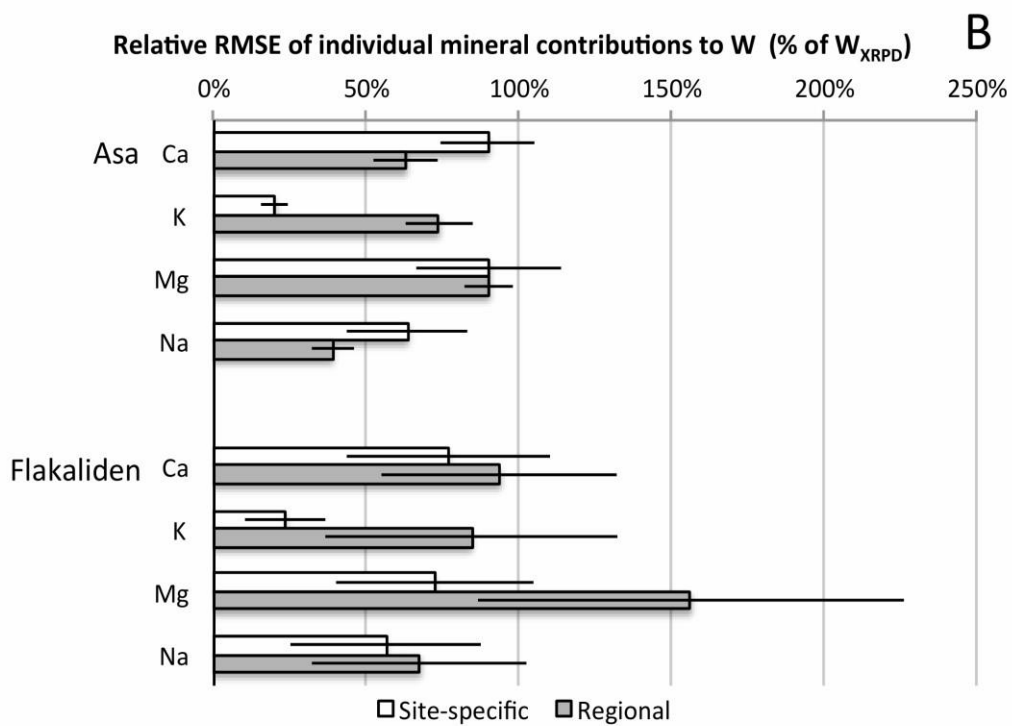
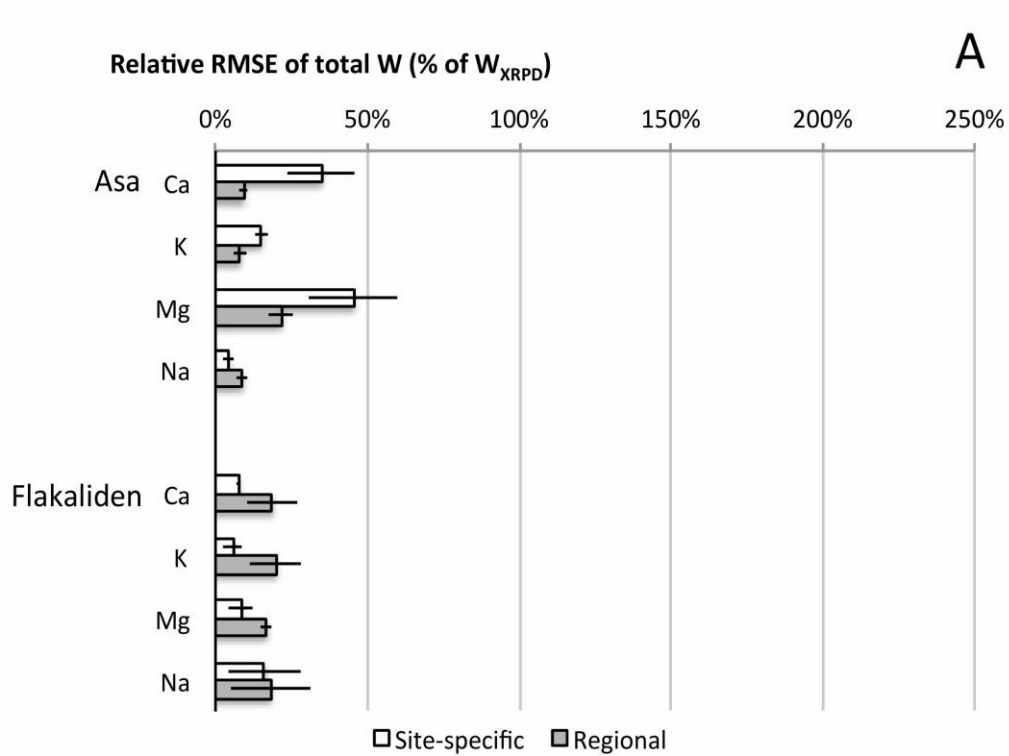
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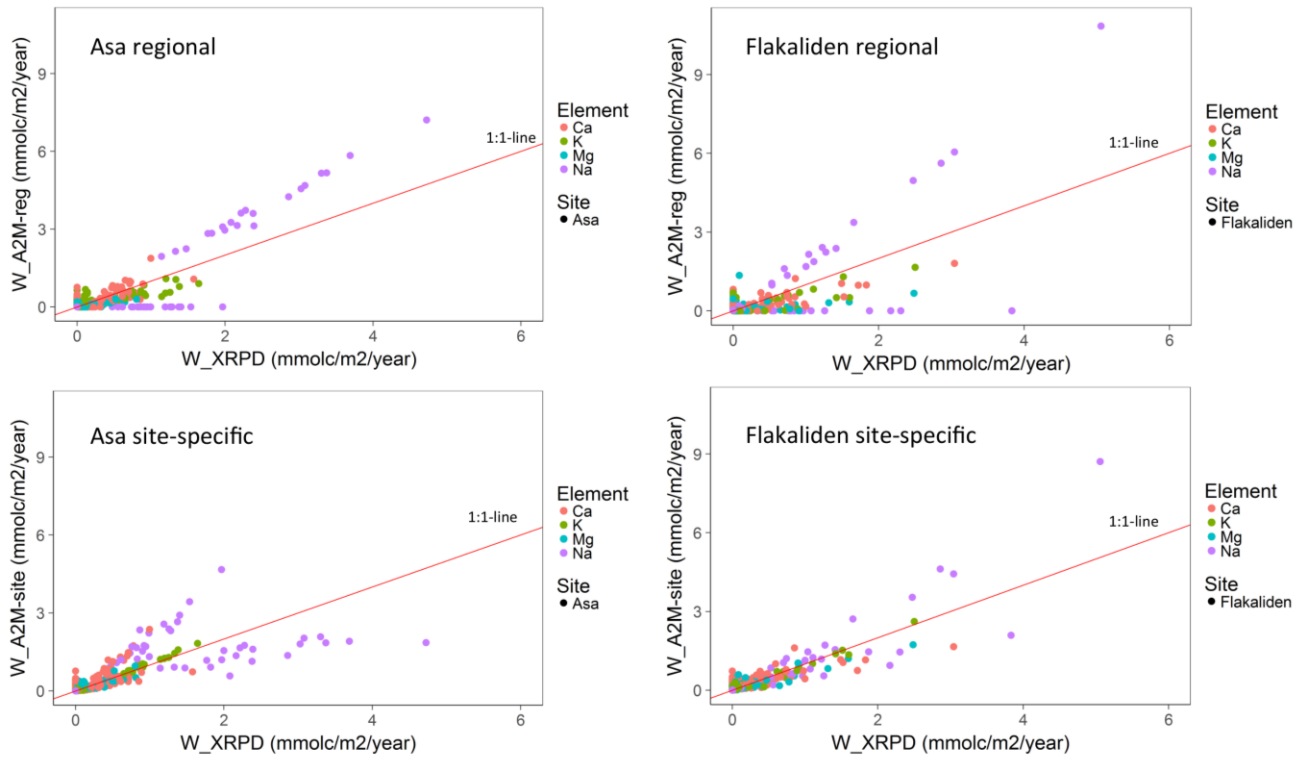
846 Figure 3, A, B

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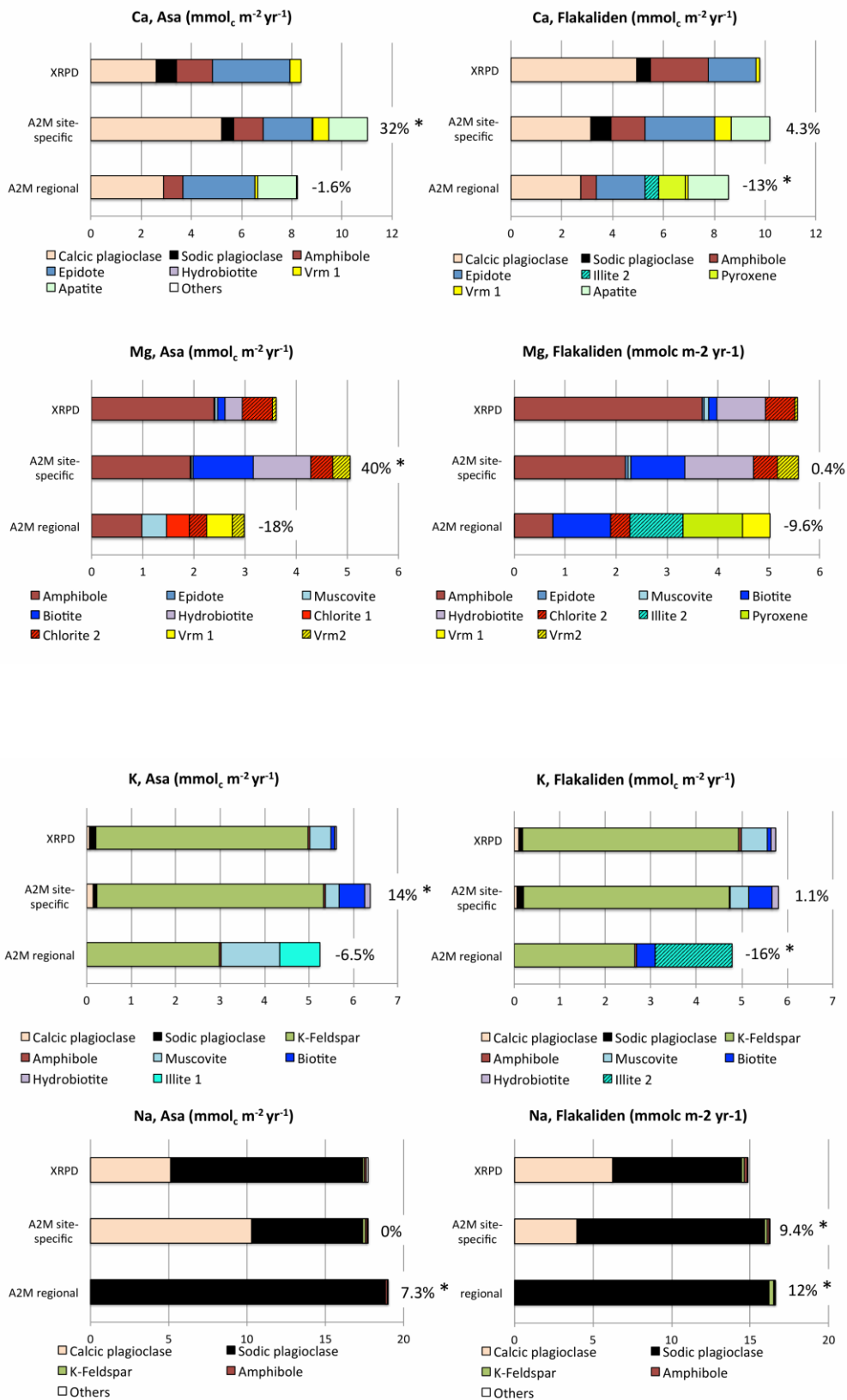


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852 Figure 4

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Figure 5

858 Resubmission letter

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860 Dear Prof. Andersson,

861

862 Thank you for providing the reviews and for your editorial comments on our manuscript and the
863 opportunity to submit a revised version. Your suggestions (marked in grey color) were:

864

865 1) Clarification and simplification of the abstract

866 2) Clarify hypothesis 1

867 3) Discussion of the possible role of calcite or other reactive trace phases on weathering fluxes.

868 4) With regard to point 4 in RC 2, please describe the relationship between mean annual
869 precipitation and temperature (used in the model) and the range in these values (which may
870 actually be the more relevant drivers of weathering)

871 5) Briefly explain how PROFILE works

872 6) Improve presentation of Figure 5

873 Please explain your decisions with regard to all major comments of the reviewers.

874

875 Non-public comments to the Author:

876 There are other sources than the White paper that consider the role of highly reactive phases on
877 weathering fluxes. Two that spring to mind are: Anderson et al., 2000, GCA (my own work, sorry--
878 not intending to just congratulate myself!), and Jacobson et al., 2002, GCA (Vol. 66, No. 1, pp. 13-
879 27, 2002)

880

881 We have carefully read through all the comments and have critically discussed possible changes. We
882 hope that you will find all major points sufficiently addressed and that the manuscript is acceptable to
883 you in revised form.

884

885 In terms of changes we have focused mainly on your suggestions:

886

887 Details of the changes are as follows in the manuscript with track and changes:

888

889 1. Abstract (Lines 18-43): We have reduced the length of the abstract by removing text about the
890 detailed use of A2M. We also introduced new sentences in the beginning of the abstract, which should
891 give the background of the study. Further, we have tried to clarify hypothesis one in the abstract.

892

893 2. Introduction (Lines 96-99): We have included a better short description of the PROFILE model in line
894 with point 5 of your suggestions.

895

896 3. Introduction (Lines 166-169): We have attempted to clarify hypothesis one in line with point 2 of
897 your suggestions.

898

899 4. Material and Methods (Lines 280-285): In line with point 4 of your suggestions, we have included a
900 point about the use of average annual temperature and precipitation data in PROFILE.

901

902 5. Discussion (Lines 517, 530-537, 584): We have introduced a discussion about the possible role of
903 calcite on weathering fluxes and added White et al. (1996) and White et al. (2017) to the reference list
904 (Lines 730-734).

905

906 6. Figure 5: The presentation is improved.

907

908 Additional changes:

909

910

911 We have by mistake not been consistent in abbreviating journal names and in the handling of DOIs and
912 have corrected for this in the reference list where required.

913

914 We also remade equation 1 and 2, because there was a bracket too much and an *i* lacking (Line 317 and
915 331).

916 Concerning our decisions with respect to all major comments of the reviewers:

917

918 -Anonymous **referee 1**:

919 1: We have now cited the Hodson et al. (1997) publication in the introduction (Lines 109-110) and
920 included it in the reference list (Lines 664-665): With regard to mineralogy, Hodson et al. (1997)
921 referred mainly to errors in input data, and input data varies between different model runs, depending
922 on the user.

923 2. In line with the editor suggestion, we have tried to clarify hypothesis 1 (Lines 166-169).

924 3. We have included Table S1a, S1b and S6 in section 2.5.1 and Table S5 in section 2.5.2 (Lines 212,
925 217, 233, 231).

926 4. We have included the Hodson et al. (1998) publication in the material and method section (Line 261)
927 and hence in the reference list (Lines 660-661)).

928 5. In line with the editor suggestion, we have introduced a discussion about calcite (Lines 517, 530-537,
929 584).

930 6. With regard to the suggestion of referencing Hodson et al. (1997) in the concluding remarks, we have included
931 their criticism about the reaction rate coefficients in the last sentences of the discussion (Lines 568-569) and
932 added a reference to the reference list (Lines 713-714).

933

934 **-Referee 2 (Paul Schröder):**

935

936 1: In line with the editor suggestion in point 4, we have given a better explanation of the use of annual
937 temperature and precipitation data in PROFILE (Lines 280-285).

938

939 In addition to the revised manuscript we have also provided a version with tracked changes, so that
940 the revisions are clearly visible. We have also been carefully through the whole text and made some
941 additional minor revisions which we believe aid clarity. We hope you will find our revised manuscript
942 acceptable for publication in Geoderma and look forward to hearing from you in due course.

943

944 On behalf of all authors, yours sincerely,

945

946 Sophie Casetou-Gustafson,

947

948 Corresponding author

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950