



36 the global CO<sub>2</sub>-consumption rate can be expected if identified highly active areas are affected by  
37 changes in the overall spatial patterns of the hydrological cycle due to ongoing global climate change.  
38 Specifically if comparing the Last Glacial Maximum with present conditions it is probable that also the  
39 global carbon cycle has been affected by those changes. It is expected that results will contribute to  
40 improve global carbon and global circulation models.

41

42 Keywords: chemical weathering, CO<sub>2</sub>, silicate, carbonate, global model, lithology

43

#### 44 **Introduction**

45 Chemical weathering of silicate rocks is - on geological time scales - one of the most important  
46 processes regulating the level of atmospheric CO<sub>2</sub> (Kempe, 1979; Grassl et al., 1984; Kempe and  
47 Degens, 1985; Lenton and Britton, 2006). It is thus essential to distinguish proportions of the two most  
48 important lithological groups, i.e., carbonates and silicates, and evaluate their global CO<sub>2</sub>-consumption  
49 due to chemical weathering. Consumption of atmospheric and biogenic soil CO<sub>2</sub> by weathering is  
50 estimated to 258 to 288 Mt C a<sup>-1</sup> at present days; results obtained using either two end-member  
51 lithologies (granitoids and carbonates) (Gaillardet *et al.*, 1999) or six lithological classes (Amiotte-  
52 Suchet et al., 2003). Accordingly, global silicate weathering proportions are 49 and 60%, respectively.  
53 It is suggested that basalt weathering alone accounts for as much as 30 to 35 % of CO<sub>2</sub>-consumption  
54 by silicate weathering (Gaillardet *et al.*, 1999; Dessert *et al.*, 2003). This high proportion implies a high  
55 significance of basalt weathering for the long-term global carbon cycle.

56 Chemical weathering releases preferentially Ca, Mg, Na and K that are - to a large proportion -  
57 balanced by bicarbonate (DIC, dissolved inorganic carbon) derived from atmospheric and/or soil CO<sub>2</sub>  
58 (Figure 1). Because carbonate dissolution is not a geologic long-term sink (since carbonate  
59 precipitation in the oceans returns the consumed CO<sub>2</sub> relatively rapid) accurate understanding of  
60 silicate to carbonate weathering proportion and its spatial distribution is essential, when discussing  
61 CO<sub>2</sub> as a climate factor (Lenton and Britton, 2006). Climate models apply, in general, a silicate to  
62 carbonate proportion for estimating the potential long-term sink of CO<sub>2</sub> due to chemical weathering  
63 (c.f. Berner and Kothavala, 2001; Munhoven, 2002; Kohler *et al.*, 2005; Lenton and Britton, 2006;  
64 Lerman *et al.*, 2007).

65 Global CO<sub>2</sub>-consumption rates by chemical weathering are generally estimated by two different  
66 approaches: (i) the reverse methodology and (ii) forward modeling.

67 The first approach uses river chemical data to recalculate rock weathering products (Garrels and  
68 Mackenzie, 1967; Meybeck, 1987; Gaillardet *et al.*, 1999) under the assumption that weathering  
69 products are characterized by specific geochemical end-members representing lithologies (e.g.  
70 carbonate and granitoids). This method does not allow for a spatial resolution of CO<sub>2</sub>-consumption  
71 beyond the resolution of the catchment areas of applied river sampling locations. In addition, only for  
72 the applied river catchments data are available (in general major world rivers).

73 Method (ii) extracts functional relations between rock weathering rates of specific lithological classes  
74 (derived from mono-lithological or multi-lithological catchments) and 'major controlling factors' (Bluth  
75 and Kump, 1994; Amiotte-Suchet *et al.*, 2003; Hartmann *et al.*, 2009; Hartmann, 2009). Applying this  
76 method it was shown that lithology and runoff are the dominating factors controlling CO<sub>2</sub>-consumption  
77 rates and the resulting bicarbonate fluvial export to coastal zones (Bluth and Kump, 1994; Amiotte-  
78 Suchet *et al.*, 2003; Hartmann, 2009). Other factors like relief or land cover were estimated to be less  
79 important, if the regional or global scale is the target for application of forward models (compare:  
80 Drever and Zobrist, 1992; Drever, 1994; Gislason *et al.*, 1996; Brady *et al.*, 1999; Navarre-Sitchler and  
81 Thyne, 2007; Hartmann, 2009). A temperature dependence in global models calibrated by measured  
82 data was only implemented for basalt weathering, as sufficient data from various climatic provinces  
83 exist (Dessert *et al.*, 2003). This can be attributed to the observation that the combination of runoff and  
84 lithology represents to a significant proportion other factors identified to be important on a plot or local  
85 scale, thus diluting their effects. This holds specifically for relief and land cover in some regions  
86 (Hartmann *et al.*, 2009; Hartmann, 2009). In addition, basalts contain silicate minerals with higher  
87 dissolution rates under comparable natural conditions if compared to other lithological classes. This  
88 observation may be the cause why only for the mafic to intermediate volcanic lithological classes a  
89 significant temperature dependence on CO<sub>2</sub>-consumption has been identified using field data (c.f.  
90 Hartmann, 2009; Gislason *et al.*, 2009). As such, with the exception of temperature for basalt, other  
91 factors than lithology and runoff were not implemented in global CO<sub>2</sub>-consumption studies which are  
92 based on training data from a homogeneous data base (Bluth and Kump, 1994; Gibbs *et al.*, 1999;  
93 Amiotte-Suchet *et al.*, 2003). Globally or regionally applied forward models distinguished five or six  
94 lithological classes (sands/sandstone, shales, shield rocks or granites, carbonate rocks, acid  
95 volcanics, and basalts) (Bluth and Kump, 1994; Gibbs *et al.*, 1999; Amiotte-Suchet *et al.*, 2003).  
96 However, it has not been analysed if these lithological classes do adequately represent the large  
97 variety of geochemical or mineralogical properties (specifically for siliciclastic sediments) and their

98 diagenetic history (e.g., consolidated versus unconsolidated sediments) (Dürr *et al.*, 2005). In addition,  
99 it has been suggested that about half of the global CO<sub>2</sub> sequestration due to chemical weathering  
100 occurs in warm and high runoff regions (Ludwig *et al.*, 1998), predominantly in so called hyperactive  
101 regions (with weathering rates 5-10 times the world average) and hotspots (> 10 times the world  
102 average) (Meybeck *et al.*, 2006). Such regions were not included in previous forward model  
103 calibrations; instead Central European (France) or predominantly North-American data were used  
104 (Bluth and Kump, 1994; Amiotte-Suchet *et al.*, 2003). Previous global studies used lithological maps  
105 with a spatial resolution of 1 and 2° (Gibbs *et al.*, 1999; Munhoven, 2002; Amiotte-Suchet *et al.*, 2003).  
106 Because variation of CO<sub>2</sub>-consumption rates between lithological classes is high (for given runoff  
107 conditions), it remains uncertain if highly active regions are spatially resolved appropriately by 1° to 2°  
108 grid data. A recent literature and map review improved the global lithological data base (Dürr *et al.*,  
109 2005). It was suggested that at least 15 lithological classes should be distinguished for global  
110 chemical weathering studies due to differences in mineral composition, sedimentary properties and  
111 diagenetic history of sediments (Table 1). The resulting high-resolution (if compared to previous  
112 attempts) global lithological map recognizes these lithological characteristics. That map is used in this  
113 study to apply a new CO<sub>2</sub>-consumption model, based on the forward methodology (Bluth and Kump,  
114 1994; Amiotte-Suchet *et al.*, 2003) and trained with data of 382 Japanese catchments (Hartmann,  
115 2009). Applied hydrochemical data were corrected for atmospheric deposition and represent river  
116 catchments from warm to temperate climates, including regions with high runoff (>3000 mm a<sup>-1</sup>);  
117 details are provided in Hartmann (2009). The applied data set allows calibration of a model for regions  
118 that have high CO<sub>2</sub>-consumption rates. The model is applied globally on a 1 km<sup>2</sup> grid lithological map  
119 based on the vectorized map after Dürr *et al.* (2005). This high spatial resolution allows analysis of the  
120 contribution of hotspots and hyperactive areas to the global CO<sub>2</sub> consumption by chemical weathering  
121 as well as mobilized bicarbonate counterbalanced by cations derived from weathering processes or  
122 atmospheric deposition. Contribution of carbonates from 'non carbonate' sedimentary rocks or vein  
123 calcite in acid plutonics or metamorphics is attributed to in the model approach.

124

## 125 **Data and methodology**

126

### 127 **Applied data**

128 To achieve a new model recognizing the new lithological classification scheme, river chemical data  
129 were taken from a data base of Japanese rivers (Harashima *et al.*, 2006) based on the work of  
130 Kobayashi (1960) (c.f. Hartmann, 2009). Each sampling location covers a full seasonal cycle  
131 (bimonthly or monthly). From this data set, 382 sampling locations, only insignificantly influenced by  
132 anthropogenic or hydrothermal activity (compare: Hartmann, 2006; Hartmann *et al.*, 2009), were  
133 chosen. Bicarbonate fluxes were calculated by using mean concentrations and runoff (Fekete *et al.*,  
134 2002). Data were corrected for chloride normalized atmospheric deposition based on data from more  
135 than 150 monitoring stations (Kunimatsu *et al.*, 2008; c.f. Hartmann *et al.*, 2009; Hartmann, 2009).  
136 Seasalt ratio correction was omitted, because of significant proportions of non-seasalt Ca, S and K  
137 (Seto *et al.*, 2004; Hartmann *et al.*, 2008). Because weathering-derived major cation equivalents  
138 exceed alkalinity, HCO<sub>3</sub> (represented by alkalinity) has been chosen as the representative measure for  
139 CO<sub>2</sub>-consumption for each catchment.

140

#### 141 **Bicarbonate flux model**

142 Parameters for the herein presented model are calibrated using a newly developed high resolution  
143 lithological map of Japan that was derived from the detailed digital geological map of the Japanese  
144 Archipelago (Geological Survey of Japan, 2003; Hartmann *et al.*, 2009; Hartmann, 2009) applying the  
145 lithological class definitions of the global lithological map, introduced by Dürr *et al.* (2005). As nearly all  
146 catchments include multiple lithological classes, a multi-lithological regression was applied for  
147 retrieving bicarbonate flux rates using a linear equation type (c.f. Hartmann *et al.*, 2009):

$$148 \quad F(\text{Alk}) = L_1 b_1 q + L_2 b_2 q + \dots + L_n b_n q$$

149 F(Alk) represents the bicarbonate flux due to weathering processes (t C km<sup>-2</sup> a<sup>-1</sup>), L<sub>x</sub> is the areal  
150 proportion of each lithological class x for each catchment, and q represents the average runoff in mm  
151 a<sup>-1</sup>. b<sub>L</sub> are parameters derived from regression analysis using the Levenberg-Marquardt estimation  
152 technique, implemented in the statistical software package Statistica 8.0 (Statsoft).

153 b<sub>x</sub>-parameters for each lithological class and the model itself were significant on the p-level of 0.0001.

154 Thus the model was identified as being stable. The model was evaluated reviewing residuals, which  
155 were found to be normally distributed. The sum of modelled bicarbonate fluxes from all applied  
156 catchments is within a range of 5% of all observed fluxes. This is a good value if compared to previous  
157 approaches (Amiotte-Suchet and Probst, 1993b; Bluth and Kump, 1994; Ludwig *et al.*, 1998).

158 For calculation of carbonate contribution to bicarbonate fluxes from non-carbonate sedimentary rocks,  
159 a Ca/Na normalization technique has been applied (Hartmann, 2009). This procedure is necessary  
160 because the lithological classes siliciclastic sedimentary rocks (SS), mixed sedimentary rocks (SM),  
161 acidic plutonics (PA) and metamorphics (MT) can contain significant amounts of carbonates or  
162 secondary/trace calcite, contributing to the bicarbonate flux.

163

#### 164 **Application to the global scale**

165 CO<sub>2</sub>-consumption rates in t C km<sup>-2</sup> a<sup>-1</sup> are estimated, enhancing previous approaches (compare: Gibbs  
166 et al., 1999; Amiotte-Suchet et al., 2003) by applying the estimated parameters b<sub>L</sub> for bicarbonate  
167 fluxes and a correction factor a<sub>L</sub> for the carbonate contribution based on the linear bicarbonate model :

$$168 \quad F(\text{CO}_2\text{-consumption})_L = b_L a_L q$$

169 with b<sub>L</sub> being the calibration parameter for the lithological class L, q denotes annual runoff in mm a<sup>-1</sup>,  
170 and a<sub>L</sub> corrects for the contribution of carbonates to bicarbonate fluxes for the lithological class L. The  
171 parameter a<sub>L</sub> addresses the proportion of silicate and carbonate weathering derived  
172 alkalinity/bicarbonate. CO<sub>2</sub>-consumption calculation recognizes that half of the bicarbonate fluxes from  
173 carbonate weathering represent lithogenic carbon (Figure 1). Derived equations were applied globally  
174 and 'spatially explicit', using the new global lithological map (Dürr et al., 2005) transformed from vector  
175 to raster mode with 1 km grid-size, combined with calibrated global runoff data (Fekete et al., 2002).  
176 No model equations could be calculated for the lithological classes carbonate sedimentary rocks (SC),  
177 basic plutonics (PB), complex lithology (CL), loess (LO) and Precambrian shields (PR), as their  
178 proportions to the total area of Japan are insignificant (with respect to the lithological map of Japan).

179 Due to the definition of named lithological classes (Dürr et al., 2005) and based on regional studies on  
180 chemical weathering covering large and medium-sized basins in South America, North America, Asia  
181 and Europe (Meybeck, 1986; Bluth and Kump, 1994; Boeglin et al., 1997; Huh et al., 1998; Galy and  
182 France-Lanord, 1999; Mortatti and Probst, 2003; Amiotte-Suchet et al., 2003; Hren et al., 2007) the  
183 equations for these classes are substituted by flux equations from other lithological classes, providing  
184 a first estimate:

$$185 \quad \text{PR} = \text{PA} \text{ (PA: acidic plutonics)}$$

$$186 \quad \text{PB} = \text{VB} \text{ (VB: basic volcanics)}$$

$$187 \quad \text{CL} = (\text{SM} + \text{SS} + \text{MT})/3 \text{ (composition was chosen based on literature review (Dürr et al., 2005);}$$

$$188 \quad \text{SM: mixed sedimentary rocks, SS: siliciclastic sedimentary rocks, MT: metamorphics)}$$

189 LO = 0.2 SS + 0.2 SC (assuming an average 60 % SiO<sub>2</sub> content in loess)  
190 SC = 0.019032 \* q (global equation established in previous works (c.f. Amiotte-Suchet and  
191 Probst, 1993a; Ludwig et al., 1998; Amiotte-Suchet et al., 2003)  
192 Carbonate rock weathering bicarbonate fluxes are assumed to be double as high as CO<sub>2</sub> consumed.  
193 This was recognized in the application of the model for sedimentary classes using the correction factor  
194 'a<sub>L</sub>'. No CO<sub>2</sub>-consumption is assigned to classes IG (glaciated areas), EP (evaporites) and DS (dune  
195 sands with the assumed composition: pure SiO<sub>2</sub> rocks). The model suggests for the lithological class  
196 alluvial deposits (AD) very high bicarbonate fluxes if compared to averages of other regions (Ganges-  
197 Brahmaputra, Amazon, Garonne, Congo, a.o.). The above named literature review revealed that  
198 globally AD bicarbonate fluxes should be in the range of the lithological class SU for Japanese  
199 settings (Meybeck, 1986; Bluth and Kump, 1994; Boeglin et al., 1997; Huh et al., 1998; Galy and  
200 France-Lanord, 1999; Mortatti and Probst, 2003; Amiotte-Suchet et al., 2003; Hren et al., 2007). In  
201 comparison to larger basins in other regions are alluvial sediments in Japanese catchments relatively  
202 unweathered (c.f. Imai et al., 2004). This observation is attributed to the transport history of minerals,  
203 which underwent less weathering cycles in the steep, small Japanese catchments. Thus the equation  
204 for SU was assigned globally to AD for not overestimating the global contribution of AD. Exorheic and  
205 endorheic areas are distinguished using the data set provided by the group of Vörösmarty in New  
206 Hamsphire (Dürr *et al.*, 2005).

207

## 208 **Results and discussion of results**

209

210 The resulting high-resolution forward model yields a total CO<sub>2</sub>-consumption rate of 237 Mt C a<sup>-1</sup> for  
211 exorheic areas (Table 1), similar to previous studies (Table 2) (Gaillardet et al., 1999; Amiotte-Suchet  
212 et al., 2003). The contribution of endorheic areas amounts to only 3.7 Mt C a<sup>-1</sup> (Figure 2). The global  
213 exorheic average rate accounts to ~ 2 t C km<sup>-2</sup> a<sup>-1</sup>. Differences between global average CO<sub>2</sub>-  
214 consumption rates per lithological class (Table 1) can be explained by the applied equations in  
215 dependence from runoff (Figure 3) and the spatial correlation between lithological classes and runoff  
216 (Figure 4).

217 Carbonate sedimentary rocks (SC), e.g., are less abundant in areas with high runoff if compared to  
218 other lithological classes like basic volcanics (VB) or complex lithology (CL) (Figure 4c). The observed  
219 differences in the exposure to runoff affect the global estimate and thus the silicate to carbonate CO<sub>2</sub>-

220 consumption ratio (compare Figure 4 with Figure 5), because the carbonate CO<sub>2</sub>-consumption rates  
221 are at least a magnitude above those of the average silicate rates (Figure 3). Note, in addition to  
222 carbonate sedimentary rocks (SC) some lithological classes hold high CO<sub>2</sub>-consumption rates  
223 because of significant abundance of carbonates (e.g. SM, MT, or CL).  
224 Among other sedimentary classes than SC does the global mean CO<sub>2</sub>-consumption rates vary  
225 significantly, specifically between consolidated (SS, SM and CL; CL is assumed to be composed by  
226 2/3 of sediments) and unconsolidated sediments (SU, AD, LO) (Table 1). Unconsolidated sediments,  
227 comprising mostly continental plains (Dürr *et al.*, 2005), contribute ~ 15.5 % to CO<sub>2</sub>-consumption, but  
228 have the lowest CO<sub>2</sub>-consumption rates (0.6 to 1.3 t C km<sup>-2</sup> a<sup>-1</sup>). Siliciclastic sedimentary rocks (SS)  
229 are characterized by values (1.2 t C km<sup>-2</sup> a<sup>-1</sup>) which are not significantly different from unconsolidated  
230 sediments. However, the average rate for mixed sediments (SM) is about double of siliciclastic  
231 sedimentary rocks, which is in accordance to the applied equations (Figure 3) and is attributed to the  
232 assumed high contribution from carbonates. The highest average CO<sub>2</sub>-consumption rate for  
233 'sedimentary classes', apart from carbonate sedimentary rocks (SC), is calculated for the class  
234 "complex lithology" (3.1 t C km<sup>-2</sup> a<sup>-1</sup>), which is typically located in mountain belts (Dürr *et al.*, 2005) that  
235 often have elevated runoff (c.f. Viviroli *et al.*, 2007). This is confirmed in Figure 4.  
236 Crystalline, non-sedimentary, lithological classes (without volcanics) are characterized on average by  
237 values slightly below the global mean (1.9 t C km<sup>-2</sup> a<sup>-1</sup>), and volcanics, specifically due to basic and  
238 intermediate volcanics (VB), show values clearly above global mean (3.0 t C km<sup>-2</sup> a<sup>-1</sup>).  
239 Results show that differences in mineral composition and diagenesis state have a profound influence  
240 on the estimation of the spatial distribution of global CO<sub>2</sub>-uptake by chemical weathering (Table 1 & 2,  
241 Figure 2, 3 and 5), specifically if consolidated and unconsolidated sediments are distinguished. With  
242 respect to assumed changing global runoff patterns, differences in CO<sub>2</sub>-consumption rates between  
243 lithological classes (under comparable runoff conditions) are relevant for global CO<sub>2</sub>-consumption due  
244 to their distribution in different climates (Figure 3 & 4).

245

#### 246 **CO<sub>2</sub>-consumption from carbonate weathering**

247 The contribution of carbonates to CO<sub>2</sub>-consumption from silicate dominated classes SS, SM, MT and  
248 PA is 13%, 53%, 46% and 16%, respectively. These proportions were identified from the training data  
249 set representing catchments on the Japanese Archipelago, but may be different if further regional data  
250 would be recognized for model calibration. Applied on the global scale this model reveals that about

251 12.6% of the carbonate CO<sub>2</sub>-consumption can be attributed to silicate dominated lithological classes.  
252 Specifically carbonate contribution from silicate dominated sediments SS and SM is important (Table1  
253 and Table 2, last column). This result underlines the importance of recognizing carbonates in  
254 sediments other than SC as well as secondary/trace calcite in crystalline rocks. Previous regional and  
255 global approaches aggregated sediments to shale or sandstone lithological classes without  
256 recognizing carbonate contribution (Bluth and Kump, 1994; Amiotte-Suchet et al., 2003). Results  
257 (Table 2) suggest that the global contribution of carbonate sedimentary rocks (SC) has been  
258 overestimated previously (40.1% of the CO<sub>2</sub>-consumption compared to 24.4% in this study). This is  
259 supported by applying the previously established global equation for carbonate sedimentary rock  
260 weathering (Amiotte-Suchet et al., 2003) to the new lithological map and the global runoff data. Thus  
261 globally calculated CO<sub>2</sub>-consumption of weathering from the lithological class carbonate sedimentary  
262 rock (SC) is 58 Mt C a<sup>-1</sup>. That is 34% lower than has been calculated previously, applying the  
263 lithological map and the GEM-CO<sub>2</sub> model of Amiotte-Suchet et al., but the same runoff data as has  
264 been applied here (Munhoven, 2002) (Table 2). The 17% difference in carbonate sedimentary rock  
265 area (SC) in both applied lithological maps, 13.4% (Amiotte-Suchet et al., 2003) to 11.2% (Dürr et al.,  
266 2005), does not counterbalance this result. It is concluded that differences in the spatial correlation  
267 between lithology and runoff account for this observation, specifically since a new lithological map with  
268 increased resolution has been applied.

269 The resulting silicate/carbonate ratio after Munhoven (2002) is nearly the same (60:40) as has been  
270 calculated by Amiotte-Suchet et al. (2003), but the CO<sub>2</sub>-consumption rate decreased to 133.2 10<sup>6</sup> t C  
271 a<sup>-1</sup> for silicates and 88.6 10<sup>6</sup> t C a<sup>-1</sup> for carbonates. Latter value for global carbonate rock CO<sub>2</sub>-  
272 consumption is nearly the same as has been calculated for the total carbonate CO<sub>2</sub>-consumption in  
273 this study. Note, the contribution of non-carbonate rock (SC) lithological classes to carbonate CO<sub>2</sub>-  
274 consumption was not considered in the study of Amiotte-Suchet et al. (2003) and Munhoven (2002),  
275 but the problem has been noticed. Recognizing carbonate weathering in other lithological classes than  
276 SC the carbonate proportion of the total exorheic, global CO<sub>2</sub>-consumption rate is 37% (Table 2). The  
277 model applied in this study has been calibrated using the same runoff data as have been applied  
278 globally. Other models had been calibrated by instantly measured discharge data and then the derived  
279 model has been applied to different data sets.

280 The carbonate proportion on total weathering CO<sub>2</sub>-consumption (51.4%) in the referenced reverse  
281 model of Gaillardet et al. (1999) is also high if compared with results here (Table 2). This is probably

282 caused by the application of only two end-member compositions (i.e., granitoid and carbonate rocks)  
283 for distinction between silicate and carbonate weathering on the global scale (Gaillardet *et al.*, 1999;  
284 Dessert *et al.*, 2003). Note, results of the reverse methodology are sensitive to the chosen end-  
285 member chemical composition. Basalts, for example, are characterized by a different end-member  
286 composition than granitoids. Thus including basalt or other lithological classes as additional end-  
287 members would result into a lower proportion of carbonate weathering to global CO<sub>2</sub>-consumption  
288 using the reverse model approach (compare: Gaillardet *et al.*, 1999; Dessert *et al.*, 2003).

289

### 290 **The significance of basalt weathering**

291 The contribution of basalt to global silicate weathering is estimated here to 16.5% (Table 1). However,  
292 based on the established global basalt CO<sub>2</sub>-consumption model (Dessert *et al.*, 2003), it was  
293 suggested that the contribution of basalts to global CO<sub>2</sub>-consumption by silicate weathering is 30% to  
294 35 %. In this case the lower silicate CO<sub>2</sub>-consumption proportion on the global CO<sub>2</sub>-consumption after  
295 Gaillardet *et al.* (1999) has been used for calculation. Note, the areal proportion of basalt is about 6%  
296 of the total exorheic land area. For warm climates (>18°C), the global basalt weathering model of  
297 Dessert *et al.* (2003) yields about double the CO<sub>2</sub>-consumption rates as the model applied here.  
298 However, that global basalt model was established in a study focusing on the lithology basalt solely,  
299 applying regionally averaged flux values for distinguished provinces. For evaluation, this model has  
300 been applied alternatively to the new geodata used in this study (lithology and runoff). In result, global  
301 CO<sub>2</sub>-consumption increases by 19.6 Mt C a<sup>-1</sup> and silicate weathering proportion increases from 63.0%  
302 to 65.6%, while the contribution of basalt weathering to global CO<sub>2</sub>-consumption of silicates is found to  
303 be 25.5% (Table 1, last column). However, results from the Lesser Antilles suggest that for some  
304 areas the global basalt weathering equation overestimates CO<sub>2</sub>-consumption in tropical climates if  
305 thick soil layers are present (Rad *et al.*, 2006). Note that basalt areas are over proportionally located in  
306 high runoff areas (Figure 4).

307

### 308 **The contribution of highly active weathering regions**

309 The graph describing the relationship between consumed CO<sub>2</sub> and land area reveals that 9.1% of the  
310 exorheic land area account for 50% of consumed CO<sub>2</sub> (Figure 6). The contribution of hotspots and  
311 hyperactive areas to the exorheic CO<sub>2</sub>-consumption is 28.2% while these regions represent only 3.4%  
312 of the exorheic land area. Changes in controlling factors (here runoff) can impact the global CO<sub>2</sub>-

313 consumption rate largely even if only a small areal proportion is affected. The graph describing areal-  
314 proportion versus bicarbonate fluxes (DIC: atmospheric plus lithogenic bicarbonate) resulting from  
315 chemical weathering follows a similar shape as the CO<sub>2</sub>-consumption-graph (Figure 6), and the  
316 additional lithogenic C from carbonates causes a steeper curve. It can be assumed that the general  
317 shape of the graph changes not much in case temperature or other factors would be included in an  
318 enhanced model because lithology and runoff are the dominant controlling factors (compare  
319 'Introduction'-section). Because carbonate sedimentary rocks (SC) are located currently under  
320 average in low runoff regions (Figure 4c) and carbonate CO<sub>2</sub>-consumptions rates in dependence of  
321 runoff are by far the highest, shifts in the spatial correlations between SC and runoff may have  
322 significant impacts on the calculated global CO<sub>2</sub>-consumption rate.

323

#### 324 **Discussion addressing Earth System Models**

325

326 Weathering-derived bicarbonate fluxes to the coastal zone are an important part of the global C-cycle  
327 and impact the evolution of climate on geological time scales. This has been shown by studies using  
328 box-models (e.g., Berner, 2006; Arvidson et al., 2006). Results from this study indicate that previously  
329 applied global CO<sub>2</sub>-consumption models emphasizing a spatial resolution of typically 1° to 2° for  
330 lithology (and recognizing only 5 or 6 lithological classes) may not resolve the contribution of identified  
331 regions responsible for most of global CO<sub>2</sub>-consumption. But especially in those regions variability of  
332 hydrological parameters due to climate changes has a pronounced impact on the CO<sub>2</sub>-consumption  
333 rates. Note, until now no spatially explicit weathering model module was incorporated into a spatially  
334 explicit Global Circulation Model (GCM). Typical GCMs, excluding box models, use spatially explicit  
335 functions for matter transfer between applied reservoirs with a geodata resolution of 2° to 3.75°.  
336 Results from this study suggest that to integrate high-resolution global weathering models into such  
337 GCMs demands a calibration of weathering functions and applied lithology for upscaling effects to  
338 address the small, highly active, areas being responsible for the majority of weathering derived fluxes.  
339 Presented CO<sub>2</sub>-consumption models focus on the uptake of CO<sub>2</sub> by chemical weathering and  
340 subsequent transport of bicarbonate into the fluvial systems. It remains unknown if all bicarbonate  
341 fluxes reach the coastal zones as suggested by some studies reporting losses of inorganic carbon in  
342 lakes (e.g., Einsele et al., 2001). In case this process impacts the budgets significantly GCMs should  
343 address this process.

344

345 **Relevance for glacial-interglacial cycle research**

346 Glacial-interglacial changes of continental CO<sub>2</sub>-consumption rates have already been studied by  
347 Ludwig *et al.* (1998), Jones *et al.* (2002) and Munhoven (2002). Besides a few estimates of glacial-to-  
348 interglacial variations of weathering related atmospheric CO<sub>2</sub>-consumption and river bicarbonate  
349 (HCO<sub>3</sub><sup>-</sup>) fluxes obtained by inversion of marine signals (e.g., Munhoven and Francois, 1996), most  
350 CO<sub>2</sub>-consumption estimates were derived from empirical forward weathering models comparable to  
351 this study in its design, like GKWM (Gibbs *et al.*, 1999), as extended by Munhoven (2002) (used by  
352 Jones *et al.*, 2002; Tranter *et al.*, 2002; Munhoven, 2002), and GEM-CO2 (Amiotte-Suchet and Probst,  
353 1995) (used by Ludwig *et al.*, 1998; Aumont *et al.*, 2001; Munhoven, 2002).

354 However, fully coupled Earth System Models were not applied in these studies. Instead runoff data  
355 derived from GCM's were applied to calculate differences in CO<sub>2</sub>-consumption between present time  
356 and the Last Glacial Maximum (LGM). Specifically, the identified relevance of hotspots and  
357 hyperactive areas was not analyzed, emphasizing the possible significance of changes in the spatial  
358 correlation between runoff and lithology for such regions. Results presented here indicate that the  
359 carbonate contribution from sediments other than "carbonate sedimentary rocks" (SC) are important to  
360 notice. Uncertainty may have been introduced in studies on glacial-interglacial variation of CO<sub>2</sub>-  
361 consumption, because of their disregard of carbonate contribution from non-carbonate rock lithological  
362 classes.

363 Besides the applied lithological classes and their resolution, further dilution of results in previous  
364 studies may be expected from the extrapolated lithology on shelf regions for the LGM. Until now, no  
365 detailed lithological map for these regions exists for application in such studies. Another shortcoming  
366 is that changes of the potentially important controlling factor temperature are not recognized (c.f.  
367 Lerman *et al.*, 2007). In this study, temperature could not be established as a dominant controlling  
368 factor, probably due to the properties of the applied training catchments and because it was found that  
369 temperature information is partly represented by the applied runoff data (see for further discussion:  
370 Hartmann, 2009). However, considering the temperature differences between the LGM and today this  
371 factor may be of importance. Also, possible effects of changes in land cover (note: runoff is impacted  
372 by land cover) as well as differences in the distribution of loess (containing carbonates in general)  
373 since the LGM are not considered until now.

374 Besides the land-ocean bicarbonate fluxes, weathering derived silica fluxes to the ocean are important  
375 for the global carbon cycles (compare: Levitus et al., 1993; Ragueneau et al., 2002; Buesseler et al.,  
376 2007; Harashima, 2007; Street-Perrott and Barker, 2008). Because silica land-ocean fluxes are  
377 assumed to be controlled predominantly by lithology and runoff (Bluth and Kump, 1994; Hartmann et  
378 al., 2009), it can be hypothesized that for the LGM conditions dissolved silica fluxes to the coastal  
379 zone have been different from present days, as well. This is implied by the runoff scenarios used for  
380 LGM weathering studies (Munhoven, 2002). However, it remains currently unknown how such  
381 differences may have impacted the coastal and oceanic biological pump and thus the global carbon  
382 cycle and possibly atmospheric CO<sub>2</sub>. In case the listed shortcomings are included in a new evaluation  
383 of the potential influence of chemical weathering on the carbon cycle for the LGM conditions, different  
384 results will probably be obtained.

385

## 386 **Conclusions**

387

388 For the first time, differences in sediment composition beyond the three classes carbonates, shales  
389 and sandstones are recognized using a new high-resolution model for global CO<sub>2</sub>-consumption by  
390 chemical weathering. It is calibrated with data mainly from Japan and evaluated with regional  
391 literature. However, future models should be calibrated region by region, incorporating local to regional  
392 data on geochemical composition for distinguished lithological classes, as well as weathering and  
393 diagenetic history, specifically for sediment classes (comparison of CO<sub>2</sub>-consumption models for the  
394 regions North America, France and Japan is provided in Hartmann, 2009). Contribution of  
395 metamorphics and acidic plutonics to carbonate CO<sub>2</sub>-consumption was not recognized in previous  
396 studies focusing on the global scale while applying forward CO<sub>2</sub>-consumption prediction models.  
397 Recognition of carbonate contribution from metamorphics and acidic plutonics contributes only to a  
398 small proportion of the global CO<sub>2</sub>-consumption budget according to the model presented here.  
399 However this picture may change if significantly increased carbonate contribution is identified for other  
400 regions than used for calibrating the here used model (c.f. Jacobson et al., 2003). For crystalline rocks  
401 enhancements of weathering models might be expected by including information on age and  
402 weathering history to lithological data bases (c.f. White and Brantley, 2003; Riebe *et al.*, 2004).  
403 Because CO<sub>2</sub>-consumption is linked to the combination of runoff (and thus climate) and lithology,  
404 future global dynamic carbon models need to recognize changes in the spatial correlation between

405 runoff and lithology. The contribution of only a small proportion of exorheic land (9%) to half of CO<sub>2</sub>-  
406 consumption indicates that global chemical weathering is highly sensitive to changing controlling  
407 factors (i.e. at least runoff, and temperature in case of basalt). Earth system models emphasizing a  
408 spatial resolution of typically 2 to 3.75° may not resolve the contribution of identified small regions  
409 responsible for most of global CO<sub>2</sub>-consumption and their variability due to changes in climate.  
410 However, many of the highly active CO<sub>2</sub>-consumption areas are spatially correlated. Thus, global  
411 weathering modules integrated in to global circulation models should be calibrated for scaling effects  
412 to produce a robust and representative CO<sub>2</sub>-consumption estimation for the full range of applied  
413 climate conditions.

414

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576 **Table 1:** Global estimates of CO<sub>2</sub>-consumption for each of the 15 lithological classes<sup>a),b)c)</sup>.

lithology	CO <sub>2</sub> -consumption, this study (exorheic land area), model not modified				Application of global basalt weathering equation of Dessert et al. (2003)	Silicate CO <sub>2</sub> -consumption, model not modified	Silicate CO <sub>2</sub> -consumption, application of global basalt weathering law of Dessert et al. (2003)
	global mean	global sum	relative flux of total	relative area of total	relative flux of total	relative flux of total	relative flux of total
	t C km <sup>2</sup> a <sup>-1</sup>	10 <sup>6</sup> t C a <sup>-1</sup>	%	%	%	%	%
glaciated areas (excluding Antarctica) (IG)	-	-	-	(1.14)	-	-	-
<b>carbonate rocks (SC)</b>	<b>4.35</b>	<b>57.74</b>	<b>24.39</b>	<b>11.17</b>	<b>22.67</b>	-	-
<b>sediments (SC excluded)</b>							
loess (LO)	0.56	1.79	0.76	2.71	0.70	0.22	0.20
Quaternary evaporites (EP)	-	-	-	(0.04)	-	-	-
dune sediments (DS)	-	-	-	(1.25)	-	-	-
semi- to unconsolidated sediments (SU)	1.12	12.66	5.35	14.89	4.97	8.49	7.58
alluvial deposits (AD)	1.25	22.19	9.38	16.61	8.72	14.89	13.29
siliciclastic sedimentary rocks (SS)	1.24	24.50	10.35	9.53	9.62	14.30	12.76
mixed sedimentary rocks (SM)	2.40	21.26	8.98	7.47	8.35	6.71	5.98
complex lithology (CL)	3.09	18.43	7.79	5.02	7.24	7.10	6.34
<b>average/sum sediments (SC excluded)</b>	<b>1.47</b>	<b>100.84</b>	<b>42.61</b>	<b>56.24</b>	<b>39.60</b>	<b>51.71</b>	<b>46.15</b>
<b>crystalline rocks</b>							
basement rocks (Precambrian shields) (PR)	1.98	29.23	12.35	12.43	11.48	19.61	17.50
metamorphics (MT)	1.74	8.97	3.79	4.33	3.52	3.25	2.90
plutonics, acid (PA)	1.65	14.38	6.08	7.33	5.65	8.30	7.40
plutonics, basic (PB)	3.81	0.98	0.41	0.22	0.38	0.66	0.58
<b>average/sum crystalline rocks (without volcanics)</b>	<b>1.85</b>	<b>53.55</b>	<b>22.63</b>	<b>24.30</b>	<b>21.03</b>	<b>31.81</b>	<b>28.39</b>
volcanics, acid (VA)	1.34	1.52	0.64	0.95	0.60	1.02	0.91
volcanics, basic (VB)	3.21	23.03	9.73	6.04	16.10	15.45	24.55
<b>average/sum volcanics</b>	<b>2.95</b>	<b>24.55</b>	<b>10.37</b>	<b>7.00</b>	<b>16.70</b>	<b>16.47</b>	<b>25.46</b>
<b>total average/sum</b>	<b>1.99</b>	<b>236.7</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>

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- a) Area weighted mean values of specific CO<sub>2</sub>-consumption, total CO<sub>2</sub>-consumption, relative proportion of total global CO<sub>2</sub>-consumption, and relative area proportion for each lithological class (without IG).  
b) The fifth column presents relative proportions on global CO<sub>2</sub>-consumption by chemical weathering if the global model equation for basalts is applied. Global and basalt weathering CO<sub>2</sub>-consumption increases by 19.6 10<sup>6</sup> t C a<sup>-1</sup> if compared to the unchanged model is applied. In result basalt weathering proportion of silicate weathering increases from 16.5 to 25.5% (last two columns).  
c) The total land area applied accounts for 135 10<sup>6</sup> km<sup>2</sup>, while exorheic land area holds 121 10<sup>6</sup> km<sup>2</sup>.

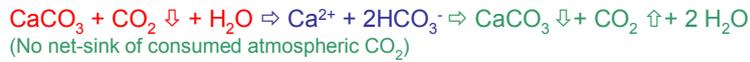
585 **Table 2:** Comparison of estimated global CO<sub>2</sub>-consumption presented in previous studies (Gaillardet et al., 1999; Amiotte-Suchet et al., 2003) with results from this study<sup>a)b)</sup>. The last column assumes that the calculated CO<sub>2</sub>-consumption from acidic plutonics and metamorphic rocks is entirely from silicate weathering<sup>c)</sup>.

	Gaillardet et al. (1999)		Amiotte-Suchet et al. (2003) <sup>1)2)</sup>		Munhoven (2002)		This study		This study		This study	
	reverse model; large rivers; fixed end-member compositions		GEM-CO2 model; runoff data of Korzoun et al. (1977); lithological map Amiotte-Suchet & Probst (1995)		GEM-CO2 model, GRDC runoff data (Fekete et al., 2002), lithological map Amiotte-Suchet & Probst (1995)		Original set up		Basalt weathering law of Dessert et al. (2003) applied		No carbonate contribution from plutonic and metamorphic rocks assumed	
	10 <sup>6</sup> t C a <sup>-1</sup>	%	10 <sup>6</sup> t C a <sup>-1</sup>	%	10 <sup>6</sup> t C a <sup>-1</sup>	%	10 <sup>6</sup> t C a <sup>-1</sup>	%	10 <sup>6</sup> t C a <sup>-1</sup>	%	10 <sup>6</sup> t C a <sup>-1</sup>	%
silicates	140	48.6	154	59.9	133.2	60.3	149	63.0	167	65.6	155	65.6
carbonates	148	51.4	104	40.1	87.6	39.7	88	37.0	88	34.4	81	34.4
flux total	288		258		220.8		237		255		237	

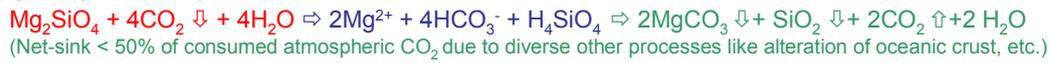
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- a) Carbonate proportions on total CO<sub>2</sub>-consumption from lithological classes SS, SM, MT and PA are applied as explained in the text.  
b) The difference in the work of Amiotte-Suchet et al. (2003) and Munhoven (2002) is the applied runoff data. The global runoff of Korzoun et al. (1977) is about 19% higher than the global runoff calculated by Fekete et al. (2002). However, the global CO<sub>2</sub>-consumption after Amiotte-Suchet et al. is 17.3% and 8.8% higher than calculated by Munhoven (2002) and in this study with the original set up, respectively.  
c) The last column shows that globally the carbonate CO<sub>2</sub>-consumption from lithological classes MT and PA are not highly important based on the results of the applied model (compare with column three).

598 **Figure 1:** Simplified, typical chemical weathering mineral reactions (educts → ions in dissolution → possible precipitation  
599 reactions in the ocean). The oceanic Na concentration is affected by diverse processes like reverse weathering or evaporite  
600 precipitation. Because of this is Na-silicate weathering not representing a 100 % atmospheric CO<sub>2</sub> sink, on geological time  
601 scales. Similar can be found for Mg-silicates.  
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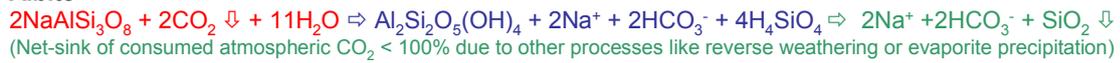
#### Carbonate



#### Olivine



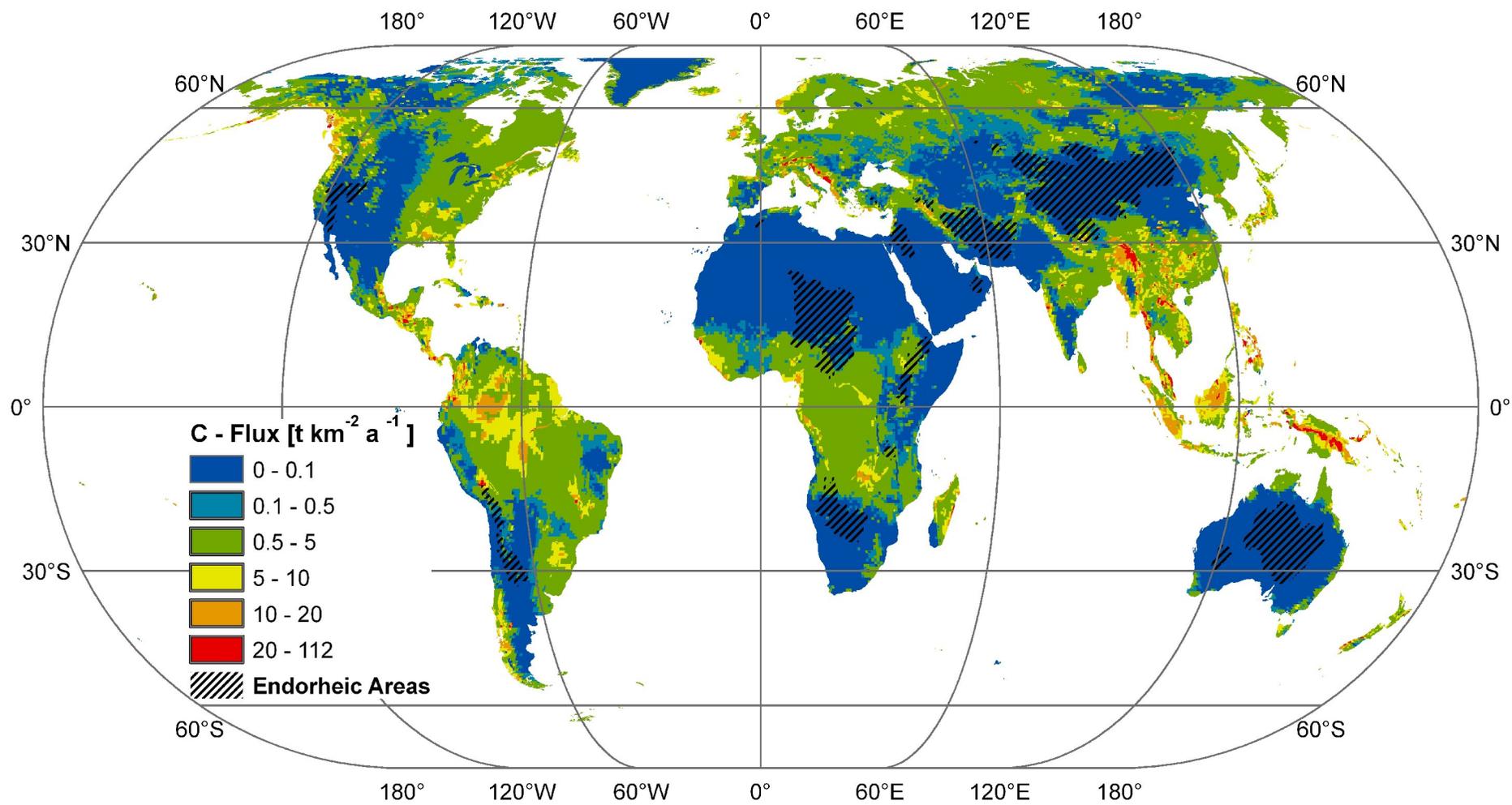
#### Albite



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605 **Figure 2:** Global distribution of CO<sub>2</sub>-consumption by chemical weathering. Note the global average for exorheic areas is ~2 t C km<sup>-2</sup> a<sup>-1</sup>.

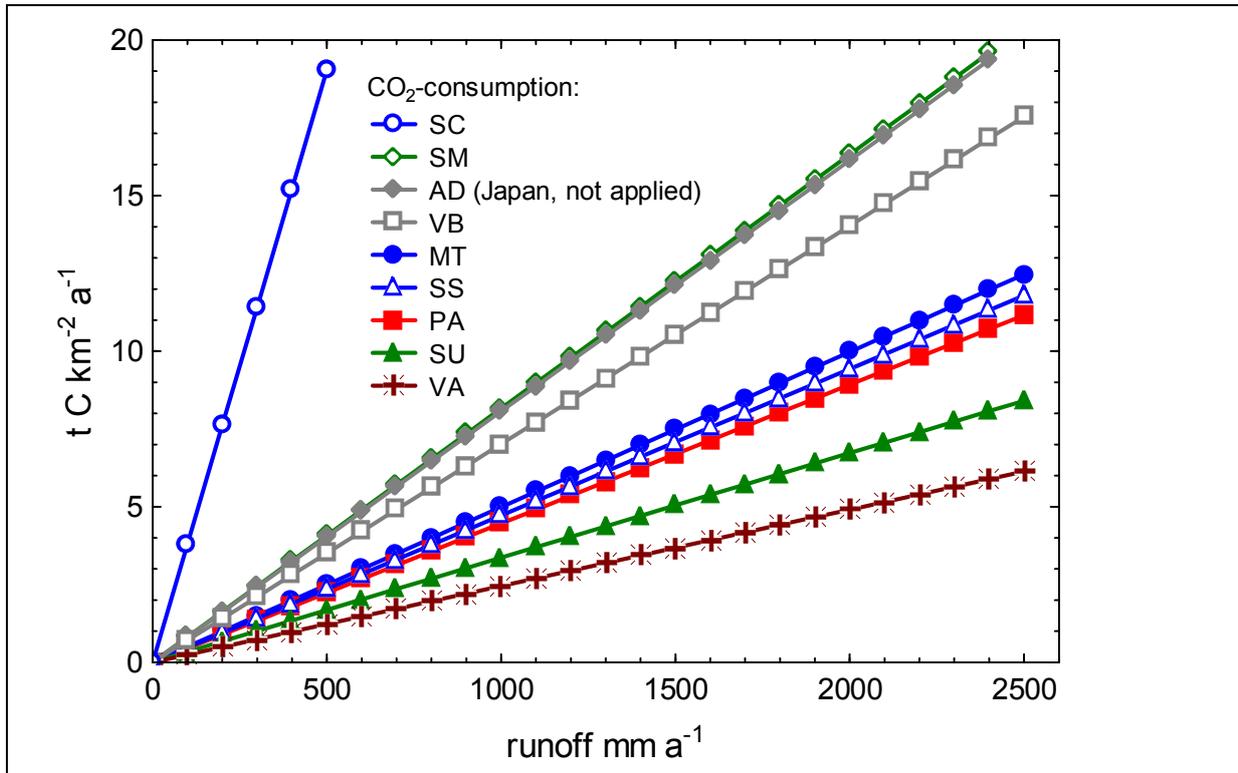
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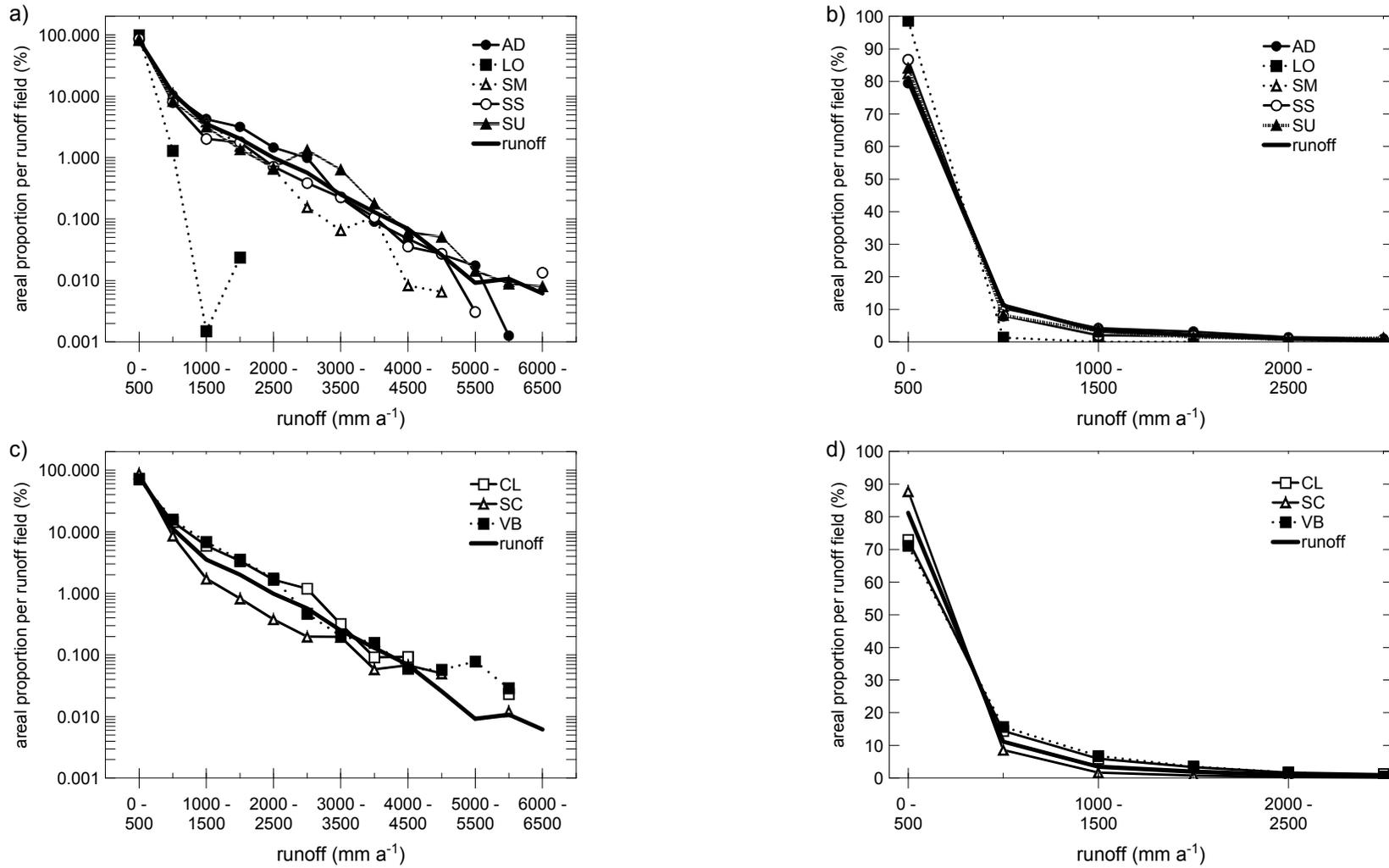
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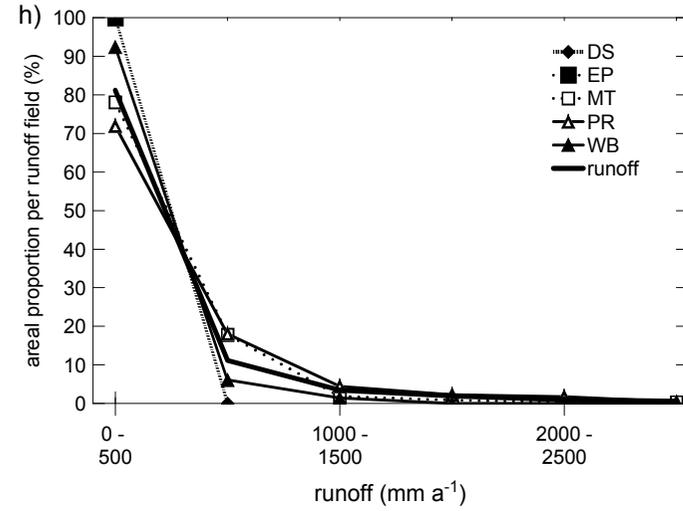
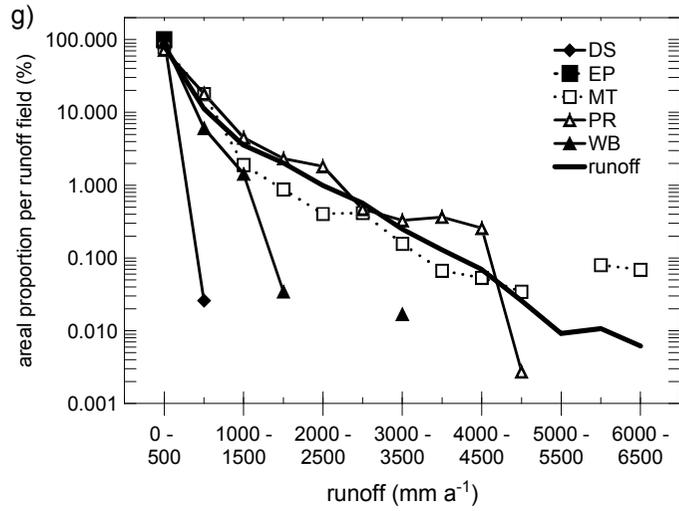
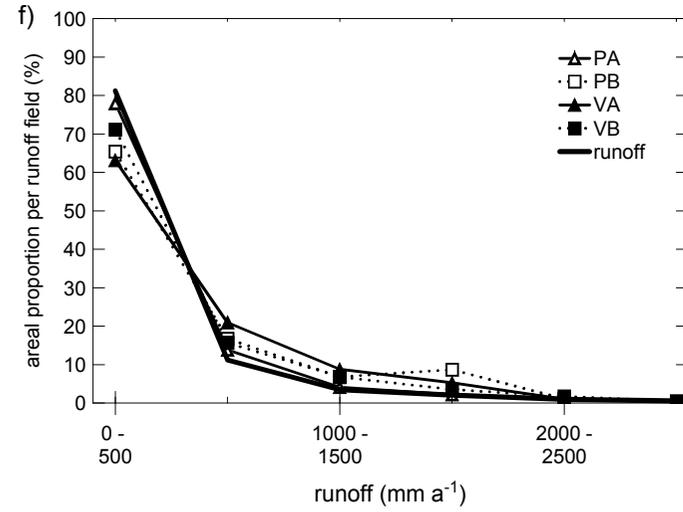
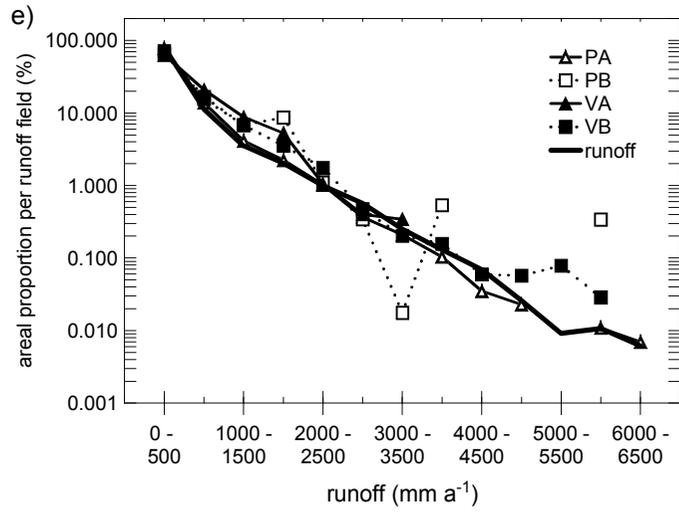
609 Figure 3: CO<sub>2</sub>-consumption in dependence of runoff for selected lithological classes. Abbreviations are  
 610 explained in Table 1. The contribution of carbonates to CO<sub>2</sub>-consumption from silicate dominated  
 611 classes SS, SM, MT and PA is 13%, 53%, 46% and 16%, respectively.  
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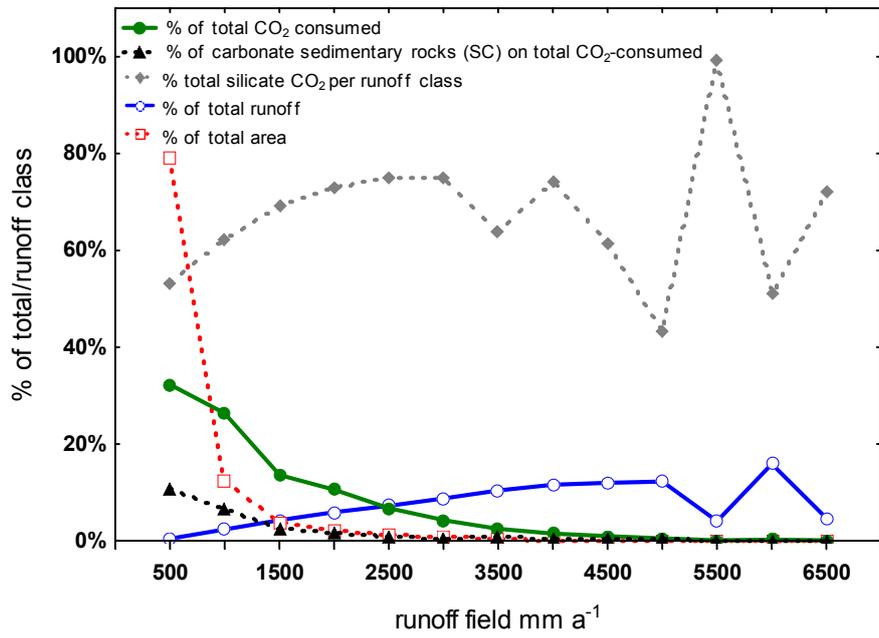
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Figure 4: Aerial proportion per runoff field for each lithological class. Runoff classes were calculated in steps with ranges of  $500 \text{ mm a}^{-1}$ . Abbreviations are explained in Table 1. For comparison runoff distribution and the abundance of water bodies (WB) is provided.



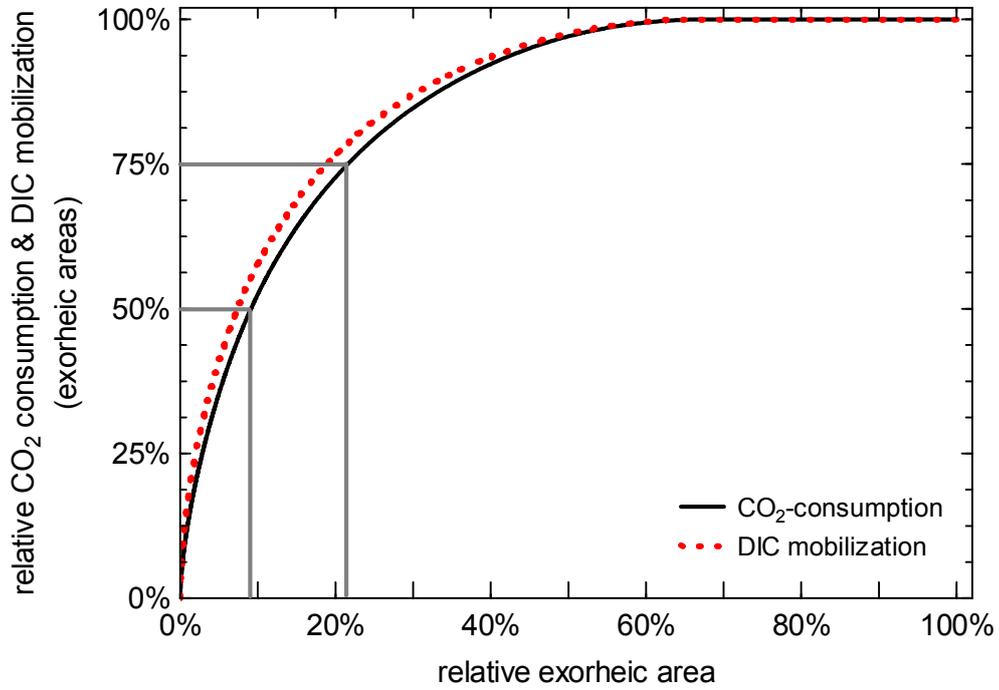


617 **Figure 5:** Proportions of distinguished runoff classes (in 500 mm steps) on total CO<sub>2</sub>-consumption, CO<sub>2</sub>-consumption of  
 618 carbonate sedimentary rocks, of silicates per runoff class, total runoff and total exorheic land area,  
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**Figure 6:** Relative proportion of exorheic CO<sub>2</sub>-consumption and bicarbonate (DIC) transport into the aquatic system due to chemical weathering compared to the relative exorheic land area. Hotspots (10 times world average) and hyperactive areas (> 5 times world average) are responsible for 8.6 and 19.6% of CO<sub>2</sub>-consumption, while representing only 0.51 and 2.9% of the exorheic land area, respectively.



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