Supplementary material: MATERIALS AND METHODS

CONTENTS:

S1.1 Model description:

To identify the factors controlling chemical weathering of carbonates and to quantify their effect in given environments, we used an updated version of the WITCH box-model (Goddéris et al. 2006; Roelandt et al. 2010; Goddéris et al. 2010). WITCH simulates the time evolution of the chemical composition of belowground waters and vertical drainage. In its original design, WITCH includes the mathematical description of the dissolution/precipitation of mineral phases in the various horizons of the weathering profile, from the surface down to the impervious bedrock. Laboratory kinetic laws derived from the transition state theory (Eyring 1935) are used to describe the interaction between water and minerals.

Here, the code has been adapted to the specific conditions of the studied area. The main improvement of the WITCH model is the computation of a budget equation for carbon, accounting for both diffusion and ventilation. The only lithology considered in the simulations is the carbonate rock lithology, assumed to be 100% calcitic according to the mineralogical analysis at the El Llano de los Juanes site. Calcite dissolution/precipitation rate F_{cal} (mol m^{-2} s^{-1}) is described kinetically by the following equation (Goddéris et al. 2010):

$$F_{cal} = \left(k_H^{cal} \cdot a_H + \frac{k_o}{1 \cdot 10^{-5} + a_{CO3}} \right) \cdot \left(1 - \Omega_{cal}\right) \qquad \textit{(Eq. S1)}$$

where k_H^{cal} equals $10^{-0.659}$ mol m^{-2} s^{-1} and k_o 10^{-11} mol m^{-2} s^{-1} at 25°C (Wollast 1990). The activation energies for rate constants are respectively set to 8.5 kJ mol^{-1} and 30 kJ mol^{-1} (Alkattan et al. 1998; Pokrovsky et al. 2009). a_H and a_{CO3} stand for the activity of aqueous protons and carbonate ion respectively, and Ω_{cal} is the solution saturation state with respect to calcite. Dissolution or precipitation occurs when reactions depart from equilibrium (Goddéris et al. 2006) (e.g. when Ω_{cal} is respectively lower or greater than 1). The dependence on temperature of calcite solubility product is given by (Drever 1997):

$$K_{cal} = 10^{-8.48} \exp\left[-\frac{9610}{R} \cdot \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \qquad \textit{(Eq.S2)}$$

where R is the gas constant and T the temperature in Kelvin.
The mass balance is solved for each water reservoir (corresponding to a given soil and weathering profile layer) for every time step. The outputs of these budget equations - carbon content, dissolved calcium, and total alkalinity in each modeled layer - are injected at each time step into the speciation module that calculates the complete carbonate speciation accounting for the environmental conditions (such as the fluctuating temperature and water volumetric content).

We designed the model simulations to accord with the conditions of the Mediterranean study area (see below S1.2: Site description and geological context). The weathering profile was prescribed as a ten layer structure with a total thickness of 100 m, the two upper layers having soil properties (porosity 0.59 m^3m^{-3} -measured on site- and thickness 15 cm each) and the others layers having bedrock properties (porosity of 0.03 m^3m^{-3} -measured on site- and thickness resp. 4 m, 4 m, 4 m, 10 m, 10 m, 10 m, 10 m and 47.7 m with increasing depth). Half hourly meteorological data (see below: S1.3 Measurements) from 2009 were used to force the model, these include: the soil water content (which defines the volumetric size of each reservoir and the fraction of the total reactive mineral surface that is available for weathering), rainfall, soil temperature and inputs of CO_2 from biological production. The latter was estimated by means of a Q_{10} function using the nighttime CO_2 fluxes from eddy covariance measurements during biologically active periods when geochemical fluxes were negligible. This production was prescribed only in the two upper layers (soil) and was assumed to be zero during the drought period, during which all plants are senescent and CO_2 efflux was typically zero in the absence of high turbulence. The measured daytime effluxes in this season could therefore not be attributed to respiration, making this the appropriate period to study ventilation.

To account for the effect of ventilation on the weathering rates, we introduced an equation in the WITCH model to account for the CO2 efflux due to ventilation (F_{Vent}):

$$F_{Vent} = k\ .u_*.\Delta[CO_2]\ .I_r\ .u_{*\theta} \qquad \textit{(Eq.S3)}$$

Where u_* is the friction velocity, a parameter strongly controlling ventilation as can be seen in Figure S1 (Supplementary Materials: Figure S1). $\Delta[CO_2]$ is the difference in CO_2 concentration between the layer where ventilation occurs and the atmosphere. Ventilation ceases if soil CO_2 concentrations are depleted. I_r is the solar radiation deduced from measurements of PPFD (photosynthetic photon flux density). It accounts for surface heating, which induces mass transport through convective flows. k is a constant accounting for the site specific texture of belowground system. The more fractioned it is and the more caves occur in it, the higher the value of k. Ventilation is promoted in highly fractioned Karst systems such as our study area. $u_{*\theta}$ is a threshold depending on the ratio between the amplitude of atmospheric turbulence and the amount of water in the soil $\left(\frac{u*}{VWC}\right)$, and on the maximum water content for enabling ventilation (VWC_{Vmax}). In these simulations we allowed ventilation only when $u_{*\theta} > 2$ (VWC expressed in m^3m^{-3} and u_* in $m.s^{-1}$) and $VWC_{Vmax} \leq 0.1$. By adjusting this equation to meet the observed fluxes, we achieved a realistic estimate for the amount of CO_2 that is extracted from the soil by ventilation. In this simulation, we prescribed ventilation to occur only in the upper 30 cm of the surface. We emphasize the fact that this ventilation equation (Eq. S3) has not been validated and therefore cannot be easily extrapolated to other areas. Estimations for k and $u_{*\theta}$ are site-specific. In spite of this, the equation functions well enough for the purpose of this study, which is to evaluate the effect of extracting CO_2 from the soil on carbonate weathering rates.

S1.2 Site description and geological context:

The Sierra de Gádor is a mountain range in the South East of Spain (province of Almería) which reaches 2246 meters above sea level (Li et al. 2007, 2008). The Sierra consists of an up to 1000 meter thick series of Triassic carbonate rocks (limestone and dolomite) that are highly permeable and fractured. The carbonates are intercalated with calcoschists of low permeability and underlain by impermeable metapelites of Permian age (Pulido-Bosch et al. 2000; Contreras et al. 2008). The Sierra de Gádor is part of the Betic Cordillera, the westernmost alpine mountain belt in Europe. It was collisionally generated during convergence between African and Iberian plates in Tertiary times. The Betic Cordillera is composed of rocks ranging from Paleozoic or even Precambrian age up to present day. Two main tectonic domains can be distinguished in the Betic Cordilera: the External Zones, located to the west and north of the Granada Basin, where Mesozoic and Tertiary carbonate rocks are very abundant (limestones and dolomites) and the Internal Zones, located to the south and east of the Granada Basin, which are composed mainly of siliceous rocks (e.g. mica schists, phyllites, quartzites) and carbonates rocks as limestones and dolomites. Calcareous accumulations are very common in the area and are formed by leaching of carbonates from red soils (pedogenic) or during later diagenesis. Karst landforms are widely represented in the calcareous areas of the Betic Cordillera, with good examples of specific karst formations, such as dolines, karren and caves. The Sierra de Gádor is an uplifted zone located to the south-east of the Sierra Nevada, the area where the most noticeable vertical movements in the Betic Internal Zones has occurred, and is separated from it by the narrow Alpujarra Corridor (Sanz de Galdeano and Alfaro 2004). The karstic landscape of the Sierra de Gádor is characterized by a mosaic of rock outcrops, bare soil and vegetation patches.

The study site “El Llano de los Juanes”, with an elevation of about 1660 m above sea level is a relatively flat shrub-land area corresponding to a well developed karstic plateau (Serrano-Ortiz et al. 2007). The carbonate rocks here are mainly dark limestone, with 98% calcite (X-ray diffraction analysis) (Were et al. 2010). The site is characterized by a semiarid montane Mediterranean climate, with a mean annual temperature of 12 °C and mean annual precipitation of ca. 475 mm, falling mostly during autumn and winter, and by a very dry season in summer (Serrano-Ortiz et al. 2007; Kowalski et al. 2008). Thickness of the soil overlaying the bedrock ranges from 0 to 0.5 m. The vegetation, so called “Macchia” or “Matorral”, at this study site is sparse and only around 0.5 m in height, but nonetheless biodiverse. The two most predominant species are *Festuca scariosa* (Lag.) Hackel (19.0 % ground cover) and *Genista pumila* (Vierh) ssp. *pumila* (11.5 % ground cover) Other common species are *Hormathophylla spinosa* (L.) P. Küpfer, *Thymus serpylloides* Bory, *Phlomis lychnitis* L., *Lavandula lanata* Boiss, *Salvia lavandulifolia* Vahl., and *Eryngium campestre* L.

S1.3 Measurements:

In 2009, the fluxes of CO_2 and H_2O were estimated from 10 Hz eddy covariance measurements at 2.5 m height. The extent of fetch, i.e. the distance upwind over the homogeneous surface, is several hundreds of meters from the tower in every direction. An open-path infrared gas analyzer (*Li-Cor 7500*, Lincoln, NE, USA) measured densities of CO_2 and H_2O; it was calibrated monthly using an N_2 standard for zero and a 500.1 µmol(CO_2) mol^{-1} gas standard as a span. Wind speed and sonic temperature were measured by a three-axis sonic anemometer (*CSAT-3, Campbell Scientific*, Logan, UT, USA).

A thermohygrometer (*HMP 35C, CSI*, USA) at 1.5 m above the surface was used to measure air temperature and humidity. Soil water content (SWC) was measured by three water content reflectometers (*CS615, CSI*) at 4 cm depth. Soil temperature was determined as the mean of two pairs of thermocouples (TCAV, CSI) at 2 cm and 6 cm. Rainfall was measured by a tipping bucket (0.2 mm) rain gauge (model *785 M, Davis Instruments Corp.*, Hayward, CA, USA). Fluxes of incident and reflected photons in photosynthetic wavelengths, measured by two quantum sensors (*Li-190, Li-Cor*, Lincoln, NE, USA) at 1.5 m over a representative ground surface were used to determine F_p (photosynthetically active photon flux density).
The measurement system centers on a datalogger (*CR3000, CSI*) that calculated and stored means, variances and co-variances of 10 Hz data every 30 min. Eddy fluxes calculated from density fluctuations (Webb et al. 1980) and coordinate rotations (McMillen 1988) were carried out in post-processing. Measurements of nighttime CO_2 fluxes with friction velocity lower than 0.2 m s^{-1} were eliminated from the analysis to avoid possible underestimation due to low turbulence (Serrano-Ortiz et al. 2009). For further details see Serrano-Ortiz et al. (Serrano-Ortiz et al. 2009).

Deep CO_2 molar fraction was measured in a borehole (7 m depth and 0.1 m diameter) through the bedrock outcropping using a GMP-343 (*Vaisala, Inc., Finland*). These measurements were made every 30s and stored as 5 min averages in a datalogger (*CR23X,CSI*).

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