Auxiliary material: MATERIALS AND METHODS

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A1.1 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):

$$F_{cal} = \left(k_H^{cal} \cdot a_H + \frac{k_o}{1 \cdot 10^{-5} + a_{CO3}} \right) \cdot \left(1 - \Omega_{cal}\right) \qquad \textit{(Eq.A1)}$$

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):

$$K_{cal} = 10^{-8.48} \exp\left[-\frac{9610}{R} \cdot \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \qquad \textit{(Eq.A2)}$$

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).

A1.2 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.

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