



Impact of low denudation rates on soil chemical weathering intensity: A multiproxy approach



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ARTICLE INFO

Article history:

Received 18 August 2016

Received in revised form 24 February 2017

Accepted 4 March 2017

Available online 8 March 2017

Keywords:

Chemical weathering
Soil weathering intensity
Low denudation rates
Semi-arid environment
Betic cordillera
Silicon isotopes

ABSTRACT

Quantifying the influence of denudation, i.e., physical erosion and chemical weathering, on soil weathering intensity is an important component for a comprehensive understanding of element biogeochemical cycles. The relation between the weathering intensity and the denudation rate is not clear and requires further investigation in a variety of climatic and erosional settings. Here, in the Betic Cordillera (southern Spain), we assess the soil chemical weathering intensity with a multiproxy approach combining different indicators of chemical weathering of the soil: the Total Reserve in Bases (TRB), the content in Fe-oxides, the quartz and clay content, the soil cation exchange capacity (CEC), and the silicon (Si) isotope composition of the clay-sized fraction. Our multiproxy approach demonstrates that in this semi-arid environment at low denudation rates, an increasing denudation rate decreases the soil weathering intensity, whereas Si mobility remains limited. Our results converge with previous conclusions based on chemical mass balance methods in the same geological setting. Mass balance methods, and particularly Chemical Depletion Fractions (CDF), are based on the immobility of a refractory element (commonly zirconium, Zr) relative to major cations in soils. Interestingly, our study suggests that a weathering index such as the TRB may provide a useful complement to assess soil chemical weathering intensity in eroding landscapes where the application of chemical mass balances may be hampered by potential Zr mobility in the soil or by heterogeneity of Zr concentrations in the bedrock.

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1. Introduction

The Critical Zone is the uppermost part of Earth surface where chemical, biological, physical and geological processes interact to support life (National Research Council, 2001; Brantley et al., 2007). Soil cover influences the interactions occurring within this upper layer and it can be thought of as a feed-through reactor, with a thickness controlled by the balance between the removal of material by denudation processes, i.e., the total loss of material from soils by both physical and chemical processes, and the advance of the weathering front down to the bedrock (e.g., Heimsath et al., 1997; Anderson et al., 2007). We can therefore expect denudation and weathering processes to be closely linked. Understanding the relationship between denudation and weathering

processes is of great importance, as they control soil physical and chemical properties. Moreover, weathering processes have important implications for the global carbon cycle and the climate through the consumption of atmospheric CO₂ by silicate weathering (review in Goudie and Viles, 2012).

The relationship between denudation and weathering is traditionally studied through mass-balance calculations using the chemical depletion fraction (CDF, dimensionless) that represents the enrichment or depletion of an immobile element within the soil column relative to the parent material (e.g., Riebe et al., 2004). The relation between the weathering intensity (CDF) and the denudation rate is not clear.

Previous work has tackled this relation (e.g., global compilations in Dixon and von Blanckenburg, 2012 and in Ferrier et al., 2016) but the conclusions remain diverse and highlight a controversy. While some studies have shown a negative relation between CDF and denudation rate (e.g., Dixon et al., 2012), others show no specific pattern (e.g., Riebe et al., 2004; Dixon et al., 2009). Thus, more work across all climatic and erosional settings is needed to resolve the controversy.

The CDF estimations are commonly based on zirconium, which is considered to be conservative in the soil. There are number of studies

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that have successfully used the CDF based on Zr concentrations to constrain the chemical weathering intensity (e.g., Riebe et al., 2004; Dixon et al., 2009; Dixon et al., 2012; Ferrier et al., 2012; Schoonejans et al., 2016a). In certain environments, such as shown by Kurtz et al. (2000) for volcanic soils in Hawaii, Zr mobility can increase with rainfall, leading to potential underestimation of weathering losses (Hill et al., 2000; Hodson, 2002). As such, other conservative elements (e.g. Hf, Ti, Nb) have been used as an alternative (Kurtz et al., 2000; Little and Lee, 2010). In some areas, the heterogeneity in immobile element concentrations in the parent material might add uncertainty to the mass balance estimates (Ferrier et al., 2012).

Soil weathering indexes may provide complementary methods to constrain the relationship between denudation and weathering. Chemical weathering indexes such as the Chemical Index of Alteration (CIA) or the Weathering Index of Parker (WIP) have been applied in the past to study the relationship between weathering and soil production (Burke et al., 2007; Larsen et al., 2014).

Here, we test a multiproxy approach to derive soil weathering indexes in a semi-arid region where the mass balance approach based on CDF was successfully applied, the Spanish Betic Cordillera (Schoonejans et al., 2016a). The existence of a good correlation between our approach and CDF estimates would generate complementary information to quantify chemical weathering intensity in specific environments where the use of CDF might be prevented (i.e., mobility of the reference elements and/or heterogeneity in the parent material). Our approach combines physico-chemical soil properties, mineralogy and isotope geochemistry to derive soil weathering indexes and estimate the soil weathering intensity. Five weathering indexes classically used in soil science are considered (the Total Reserve in Bases, TRB; Herbillon, 1986), the amount of Fe-oxides, the amount of quartz, the clay content (fraction <2 μm), the cation exchange capacity) and combined with the silicon (Si) isotope composition of the clay-sized fraction.

The Si isotope composition of the clay-sized fraction can be used as a weathering index as Si isotopes respond to soil chemical weathering and clay formation (Ziegler et al., 2005a; Ziegler et al., 2005b; Georg et al., 2007; Opfergelt et al., 2009, 2010, 2011, 2012; Bern et al., 2010; Pogge von Strandmann et al., 2012; Cornéls et al., 2014). The application of Si isotopes to assessing the response of chemical weathering to physical denudation has been suggested previously (Georg et al., 2007; Opfergelt and Delmelle, 2012) although no publications have explored this application of Si isotopes so far.

2. Environmental setting

The study site is located in the Betic Cordillera in Southeast Spain, Almería province, the southernmost extreme of the European Alpine belt. The cordillera is subdivided in the External and Internal Zones. This study focuses on the eastern part of the Internal Zone (Fig. 1). Three catchments with comparable lithology and catchment size have been selected along a gradient of denudation rates (Bellin et al., 2014): from north-west to south-east, in the Sierra de las Estancias (EST), Sierra de los Filabres (FIL-1) and Sierra Cabrera (CAB). The FIL-1 and CAB catchments belong to the Nevado-Filábride geological complex, whereas the EST catchment is part of the Alpujarride complex. Both complexes underwent similar metamorphic evolutions at different geological times (López et al., 2001). According to Junta de Andalucía (2004) the main lithology of these catchments is mica schist with a local occurrence of quartzite and phyllite. In-situ produced ^{10}Be denudation rates for the eastern Betic Cordillera (Vanacker et al., 2014) range from 34 ± 24 mm/kyr for Sierra de las Estancias ($n = 5$), 54 ± 25 mm/kyr for Sierra de los Filabres ($n = 8$) to 164 ± 74 mm/kyr for Sierra Cabrera ($n = 3$). The spatial pattern and magnitude of ^{10}Be based denudation rates are consistent with tectonic uplift constrained by Braga et al. (2003) and Masana et al. (2005) based on marine deposits and trenching observations (Table 1, Bellin et al., 2014).

Average annual precipitation ranges from 275 mm/yr in CAB to 425 mm/yr in EST, while mean annual temperature ranges from 17 °C in CAB to 12 °C in EST (García, 2009). Evapotranspiration varies between 900 mm/yr for CAB and 794 mm/yr for EST (Junta de Andalucía, 2008). Following the UNEP's aridity index (ratio evapotranspiration/rainfall; Barrow, 1992) the study sites are characterized by a semi-arid climate (Table 1). In the three catchments, the dominant vegetation type is Mediterranean shrub characterized by a sclerophyllous and thorny vegetation (locally known as *matorral*), with some remnants of *Quercus* trees at higher altitudes (Bellin et al., 2011; Table 2).

In each catchment (or its close vicinity), two profiles were sampled on exposed ridgetops to avoid the complexities of soil-forming processes associated with lateral transport of chemical fluids and soil particles along slope. The sampling sites have similar slope gradients, between 14 and 28°. The sampling sites were selected avoiding locations with clear anthropogenic disturbances such as quarrying or terracing activities. These soil profiles present no evidences of strong anthropogenic perturbations (Schoonejans et al., 2016a).

3. Materials and methods

3.1. Sampling and pre-treatments

Soil description and sampling was conducted in September 2013, as part of a larger sampling campaign described in Schoonejans et al. (2016a) and Schoonejans et al. (2016b). The soil profiles were sampled in the Sierra de las Estancias, Sierra de los Filabres and Cabrera (Table 1). The soil thickness was evaluated: EST-A is the deepest soil (47 cm) and EST-B, CAB and FIL-1 (both A and B) have similar soil depth (20–30 cm). The CAB and FIL-1 soil profiles are characterized by only one horizon, while EST soils have two horizons.

Soil samples were air-dried and sieved through a 2 mm size mesh. The <2 mm fraction was analysed for the total element content, cation exchange capacity (CEC), and Fe content following selective extractions. The soil mineralogy, particle size distribution, pH and Si isotopic composition of the clay fraction (<2 μm) were determined on a set of samples selected as representative from the top and bottom horizons (eight samples in total: EST-A-U1, EST-A-U3, EST-B-U1, EST-B-U3, FIL-1-A-U1, FIL-1-B-U1, CAB-A-U2, CAB-B-U2).

Bedrock samples were collected below the soil-bedrock boundary, right under the soil profile. The weathering rinds of rock samples were removed via sawing in order to measure the most unweathered parent material. The bedrock samples were analysed for their total element content, mineralogy and Si isotopic composition.

3.2. Physico-chemical characterization of soils

The selected samples were characterized for their particle size distribution; we applied the USDA Textural Soil Classification (1987). The sand fraction (50 μm –2 mm) was recovered after dispersion of the fine earth fraction with an ultrasonic disperser (Branson Sonifier 250) and wet sieving. The separation of silt (2 μm –50 μm) and clay fractions (<2 μm) was achieved by dispersion with Na^+ -resin (Rouiller et al., 1972) and followed by 24 h cycles of decantation according to the Stokes law. The separated sand-sized and clay-sized fractions were then characterized for their mineralogy and Si isotopic composition.

The cation exchange capacity (CEC) of the soil was measured following standard procedures (Page et al., 1982) through soil saturation with ammonium acetate and posterior desorption and quantification of the ammonia retained on the negative charges of soil, originating from both organic matter and clay minerals.

The soil pH in DI-water was measured on the set of selected samples (Section 3.1) using a ratio of 25 mL of water for 5 g of soil.

The total carbon content (C_T) in soils was measured using a Vario Max dry combustion CN analyser instrument (Elementar Analysensysteme GmbH, Germany; uncertainty 0.1%). The inorganic

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