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Comparison of field and laboratory weathering rates in carbonate rocks from an Eastern Mediterranean drainage basin

Yael Levenson [a], Uri Ryb [b], Simon Emmanuel [a,*]

[a] Institute of Earth Sciences, The Hebrew University, Jerusalem 91904, Israel
[b] California Institute of Technology, 1200E California Blvd, Pasadena, CA 91125, United States

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ABSTRACT

The rates of carbonate rock weathering affect the global carbon cycle over timescales of hundreds to thousands of years. While field measurements show that the rate of carbonate denudation increases with rainfall, significant variability exists. To determine whether the mineralogical composition of the rocks causes this variability, we compare published long-term field denudation rates determined from cosmogenic isotopes (^{36}Cl) with the weathering rates measured in laboratory experiments conducted on the same rock samples. The samples were collected from natural-rock outcrops across the Soreq drainage basin (Israel) that experience similar mean annual precipitation, but exhibit long-term denudation rates that vary from 6 mm ky^{-1} to 20 mm ky^{-1}. In laboratory experiments, we found that the laboratory rates also varied, decreasing as the ratio of dolomite to calcite increased. However, no correlation was evident between the long-term denudation rates and mineral composition, suggesting that the variability in field rates was not controlled by the kinetics of dissolution. Other factors, such as rain intensity, biological activity, and mechanical erosion are likely to control the variability in the rates by inhibiting or accelerating the weathering of carbonate surfaces in natural settings.

1. Introduction

Climate is affected by atmospheric CO_2 levels (Berner et al., 1983; IPCC, 2014), and numerous studies have attempted to quantify the various sources and sinks of carbon at both local and global scales (Falkowski, 2000; Gaillardet et al., 1999; Kuhlbusch and Crutzen, 1995; Tans et al., 1990). On geological time scales, the chemical weathering of silicate rocks is considered to be a major sink of atmospheric CO_2. However, carbonate rocks, such as limestone and dolostone that cover a significant portion of the Earth's surface (~15%, Ford and Williams, 2013), are extremely reactive, and may affect atmospheric carbon on much shorter decadal to millennial scales (Liu et al., 2011; Szramek et al., 2007; Zhang, 2011).

For rocks containing calcite and dolomite, dissolution consumes CO_2 according to the reactions:

$$\overset{calcite}{CaCO_3} + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (1)$$

$$\overset{dolomite}{(Ca,Mg)CO_3} + CO_2 + H_2O \leftrightarrow \frac{1}{2}Ca^{2+} + \frac{1}{2}Mg^{2+} + 2HCO_3^- \quad (2)$$

The overall reaction is limited by both the partial pressure of CO_2 and the availability of water. When meteoric water reaches thermodynamic equilibrium with carbonate minerals, the potential rate of weathering can be expressed mathematically as (White, 1984):

$$D_{max} = \frac{100}{\rho}\left(\frac{K_c K_1 K_{CO_2}}{4K_2}\right)^{\frac{1}{3}} P_{CO_2}^{\frac{1}{3}}(P - E), \quad (3)$$

where D_{max} is the maximal chemical weathering rate for the system (expressed in mm ky^{-1}), ρ is rock density, P_{CO_2} is the partial pressure of CO_2 (atm), K_c, K_1, K_2, K_{CO_2} are the thermodynamical constants (see Ford and Williams, 2013), P is precipitation (mm y^{-1}), and E is evapotranspiration (mm y^{-1}). For a given temperature and atmospheric partial CO_2 pressure, the relation between the maximal chemical weathering rate and the effective precipitation (i.e., P–E) is linear. When calcite dissolution in the field is transport limited, this calculated rate should reflect the regional rate of chemical weathering (i.e., the dissolution of rocks and minerals). However, rates at the outcrop scale could also be influenced by kinetic effects (Ryb et al., 2014b) and should be affected by physical weathering too.

To determine the actual rates of weathering in the field, a number of different approaches have been taken (Ford and Williams, 2013; Gabrovšek, 2009). Indirect methods are commonly based

* Corresponding author.
E-mail address: swemmanuel@gmail.com (S. Emmanuel).

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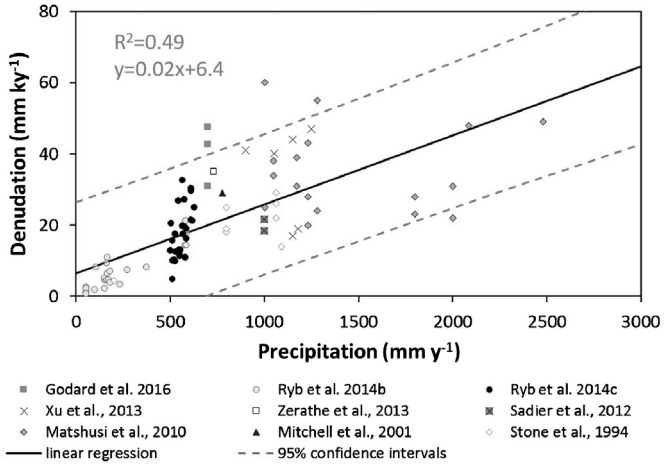

Fig. 1. Denudation rates (calculated from ^{36}Cl data) as a function of present day mean annual precipitation. The solid line represents the linear best fit and the dashed lines represent the upper and lower limit of 95% confidence. The data were compiled from carbonate terrains in Israel (Mitchell et al., 2001; Ryb et al., 2014b, 2014c), Australia (Stone et al., 1994), Japan (Matsushi et al., 2010), China (Xu et al., 2013), and France (Godard et al., 2016; Sadier et al., 2012; Zerathe et al., 2013). The data do not include bedrock sites from steep-slopes. All the denudation rates calculated from the sites studied by Ryb et al. (2014b, 2014c) were recalculated with the Cronus 2.0 calculator (Marrero et al., 2016a) using the pathway-specific production rates determined by Marrero et al. (2016b) and the time-dependent Lifton–Sato–Dunai (LSD) scaling scheme (Lifton et al., 2014). All the other rates appearing in this figure were taken directly from each source. Some of the variability between studies may be due to differences in scaling and production rates used in the calculations. Tables S-3 and S-4 in the supplementary material provides the full dataset used for this figure. A similar plot (Fig. S-3) in which the data from Ryb et al. (2014b, 2014c) is scaled according to the scheme by Stone (2000) is provided in the supplementary material.

on the solute load of springs and rivers (Gaillardet et al., 1999; Gunn, 1981; Ryb et al., 2014c; Szramek et al., 2007) or weight loss measurements of rock tablets exposed to weathering (Krklec et al., 2013; Plan, 2005; Zhang, 2011). Surface lowering can also be measured directly by using micro-erosion meters (Allred, 2004; Cucchi et al., 2006) or by measuring the topography of eroded rocks relative to a datum (Emmanuel and Levenson, 2014).

Measurements of cosmogenic ^{36}Cl in carbonate rocks have also been used to calculate denudation rates (i.e. the rate at which the Earth-surface is lowered, this include chemical and physical weathering) over timescales of 10^3–10^5 yr (Godard et al., 2016; Matsushi et al., 2010; Mitchell et al., 2001; Ryb et al., 2014b, 2014c; Sadier et al., 2012; Stone et al., 1994; Xu et al., 2013; Zerathe et al., 2013). The rates calculated using this technique reflect the weathering rates of exposed bedrock at the outcrop scale, with rates ranging from 0.9 mm ky^{-1} in hyper-arid climates to 60 mm ky^{-1} in subarctic environments. On average, cosmogenically derived denudation rates appear to increase with increasing mean annual precipitation (Ryb et al., 2014b), although there is significant variability (Fig. 1).

The high variability in weathering rates (normalized root-mean-square deviation of 48%) may be due to a number of factors. The estimated uncertainty in the rates calculated using the ^{36}Cl method is thought to be <15% (Ryb et al., 2014b, 2014c), suggesting that physical, biological, and chemical mechanisms contribute significantly to the overall variability. Matsushi et al. (2010) suggested that differences in temperature, which determines both the kinetics of mineral dissolution and mechanical weathering, may increase the variability of weathering rates. Spatial variation in biological activity too can affect weathering rates by controlling the concentrations of the organic acids and P_{CO_2} in soils (Berner, 1997; Danin, 1983). However, one factor that has not yet been fully explored is the effect of carbonate mineralogy on rock denudation rates.

Table 1
Properties of rock samples. Sample names are the same as those used in the study by Ryb et al. (2014c) that examined the same samples. Additional data are given in Ryb et al. (2014c) and Table S-1 of the supplementary material.

Sample	Calcite (%)[a]	Dolomite (%)[a]	Mg/Ca[b]	MAP (mm)[c]
UB1	1.9	98.1	0.989	525
UB19	11.5	88.5	0.760	528
UB21	27.6	72.4	0.534	546
UB17	35.4	64.6	0.452	525
UB13	88.9	11.1	0.077	550
UB11	88.9	11.1	0.085	553
UB9	92.8	7.2	0.058	549
UB7	100	0	0.011	546
UB15	100	0	0.005	522
SQ13	100	0	0.014	512

[a] Percentage in the rock by weight from XRD data. The average difference between duplicates taken from the same outcrop was 6%.
[b] Molar ratio in the rock from ICP-MS data.
[c] Present-day mean annual precipitation (MAP) in the sampling site based on Israel Meteorological Survey database for the years 1980–2010 (ims.data.gov.il).

In this study, we determine how the proportions of calcite and dolomite in carbonate rocks affect the weathering rates in laboratory experiments. We compare these rates to the long-term field denudation rates calculated for the same rock samples, and explore the relation between the lab and field rates. Finally, we discuss the mechanisms controlling the weathering rates in rocks with mixed mineralogy, and discuss the way other factors contribute to the observed variability in natural denudation rates.

2. Methods

2.1. Sites and samples

All sampling sites in the study are naturally exposed rock outcrops of Upper-Cretaceous marine carbonates located in the Soreq drainage basin in Israel (see location map in the supplementary material: Fig. S-1). The climate in this area is Mediterranean with mean annual temperatures in the range of 18–20 °C. Rainfall is generally limited to the wintertime (December to early March) during which the mean temperature is 14–16 °C. Rainfall events are intermittent (on average 53 days of rainfall per year) and each rain event lasts several days at most.

We selected ten sites with similar mean annual precipitation in the range 512–553 mm y^{-1} (Table 1) to minimize the contribution of differences in rainfall to the variability in the weathering rates. The samples in the present study were collected from the exact outcrops that were studied with cosmogenic isotopes (within a distance of 50 cm) in earlier work by Ryb et al. (2014c). A detailed description of the rock outcrops and their environmental settings are listed in the supplementary material (Table S-1). The mineralogical composition of the samples was determined using X-ray diffraction (XRD D8 Advance) and found to contain calcite and dolomite with different proportions (Table 1).

2.2. Long-term field denudation rates from ^{36}Cl data

In the earlier work by Ryb et al. (2014c), the Cl isotope ratios in the rock samples were measured at the accelerator mass spectrometer (AMS) facility in Centre de Recherche et d'Enseignement de Géosciences de l'Environnement (CEREGE), Aix en Provence, France. Although the isotopic ratios and denudation rates were originally published in Ryb et al. (2014c), since the publication of that dataset, a more reliable method to calculate denudation rates