RESEARCH ARTICLE

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Controls on Physical and Chemical Denudation in a Mixed Carbonate-Siliciclastic Orogen

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Key Points:

- Quantify chemical weathering and physical erosion fluxes for a mixed-lithology mountain range
- Physical erosion dominates the denudation signal and carbonate weathering dominates the weathering signal
- Up to 90% of chemically weathered Ca^{2+} is precipitated as solid secondary carbonate that becomes part of the physical denudation flux

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Mixed siliciclastic-carbonate active orogens are common on Earth's surface, yet most studies have focused on erosion and weathering in silicate-rich landscapes. Relative to purely siliciclastic landscapes, the response of erosion and weathering to uplift may differ in mixed-lithology regions. However, our knowledge of weathering and erosion in mixed carbonate-silicate lithologies is limited and, thus, so is our understanding of the mechanistic coupling between uplift, weathering, and the carbon cycle. Here, we partition denudation fluxes into erosion and weathering fluxes of carbonates and silicates in the Northern Apennines—a mixed carbonate-siliciclastic active orogen—using dissolved solutes, the carbonate sand fraction, and existing ^{10}Be denudation rates. Erosion generally dominates total denudation fluxes relative to weathering by an order of magnitude. Carbonate and silicate contributions to erosion vary between lithologic units, but weathering fluxes are systematically dominated by carbonates. Silicate weathering may be kinetically limited, whereas carbonate weathering may be limited by acid supply. Carbonate re-precipitation estimated by comparing ion ratios (Sr, Ca, Na) from rivers and bedrock suggests that up to 90% of dissolved Ca^{2+} is lost from carbonate-rich catchments. Corresponding $[\text{Ca}^{2+}]$ estimates for the weathering zone are high, likely driven by high soil CO_2 partial pressures ($p\text{CO}_2$); however, re-equilibration with atmospheric $p\text{CO}_2$ in rivers converts solutes back into grains that become part of the physical denudation flux. Weathering limits in this landscape therefore differ between the subsurface weathering zone and riverine exports, and our findings suggest that carbon cycle models may overestimate the sensitivity to erosion of solute exports (Ca^{2+} and HCO_3^-) derived from carbonate weathering.

Plain Language Summary Erosion moves sediment across the surface and controls how natural resources (e.g., sand and gravel) are generated. Conversely, the dissolution of rock in water (weathering) is the source for nutrients and carbon transported in rivers. Understanding how total surface lowering (denudation) is divided into weathering and erosion is important for establishing the link between mountain-building processes and the generation of sediments and dissolved material. Existing studies on denudation in mountainous ranges have primarily focused on landscapes comprised of silicate rocks. However, many mountain ranges are characterized by mixed silicate-carbonate rocks, and the processes that influence denudation of these landscapes may differ relative to silicate-rich landscapes. In this study, we separate measurements of denudation into erosion and weathering for the Northern Apennine Mountains of Italy, a mixed-lithology mountain range. Similar to silicate-rich landscapes, erosion is the dominant process here. Carbonate weathering dominates the total weathering signal, and rock type is an important control on the amount of eroded carbonate delivered to river channels. Most rivers are oversaturated in carbonate, therefore limiting the amount that can be dissolved in rivers. This has resulted in the transformation of dissolved material back into carbonate rock that is once again available to be eroded.

1. Introduction

Tectonically active orogens are responsible for the majority of sediments and solutes delivered annually to the world's oceans (Larsen et al., 2014; Milliman & Farnsworth, 2011). Fresh rock uplifted in mountain ranges is broken down by chemical weathering and physical erosion, thereby creating solutes, soils, and sediments. Driven by topographic gradients, runoff then transports these sediments and solutes to the surrounding floodplains and to the ocean. This process is so fundamental to the cycling of rocks, nutrients, and carbon on Earth that changes in the activity or spatial distribution of active orogens is frequently invoked to

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explain a variety of phenomenon observed throughout Earth's history. For example, periods of icehouse and greenhouse climates have been attributed to tectonic activity, because the uplift and erosion of rock generates fresh mineral surfaces that become available for silicate weathering, thereby modulating atmospheric CO₂ concentrations (Berner & Raiswell, 1983; Caves Rugenstein et al., 2019; Goddris et al., 2017; Raymo & Ruddiman, 1992).

The interplay between physical erosion and chemical weathering and its impact on the geological carbon cycle is fundamentally controlled by the type of lithology that is exposed and eroded. Previous studies on denudation fluxes in orogenic landscapes have focused on settings with silicate-rich bedrock (e.g., Brandon & Vance, 1992; Carretier et al., 2015; Codilean et al., 2018; Emberson et al., 2017; Granger et al., 1996; Jacobson & Blum, 2003; Jacobson et al., 2003; Kirchner et al., 2001; Matmon et al., 2003; Moore et al., 2013; Portenga & Bierman, 2011). In these landscapes, physical erosion fluxes typically dominate the denudation signal by an order of magnitude relative to chemical weathering fluxes (Jacobson & Blum, 2003; Riebe et al., 2001; West et al., 2005). Silicate weathering fluxes are thought to increase with increasing denudation rates up to a limit, at which point the sluggish kinetics of silicate dissolution lag behind the exposure of fresh mineral surfaces (Gabet & Mudd, 2009; West et al., 2005). However, many active orogens today are underlain not by pure silicate bedrock, but by either carbonate rock or interbedded siliciclastic and carbonate sedimentary rocks. The partitioning of denudation into physical erosion and chemical weathering in these lithologies may be fundamentally different than the partitioning in silicate-rich terranes. For example, the dissolution kinetics of carbonates are more than three orders of magnitude faster than for silicates (Stallard & Edmond, 1987), and weathering fluxes are globally dominated by carbonate weathering (Gaillardet et al., 1999). Even in places where carbonate constitutes a minor component of the bedrock, carbonate weathering is frequently the dominant source of cations (Calmels et al., 2007; Hilton & West, 2020; Jacobson & Blum, 2003; Sarin et al., 1989; Torres et al., 2016). Importantly, carbonate and silicate weathering produce different nutrients and soils (Ott, 2020) and differ in their impact on the carbon cycle. Whereas silicate weathering is a carbon sink on timescales longer than the calcium-compensation time in the ocean, carbonate weathering is either carbon-neutral, or it is a carbon source where dissolution occurs via sulfuric acid (Calmels et al., 2007).

Existing weathering models based on silicate-rich settings are typically parameterized as mineral supply limited for lower denudation rates, where weathering and erosion are coupled, and kinetically limited at faster denudation rates, where weathering and erosion are decoupled (West et al., 2005). In contrast, because of more rapid kinetics, carbonate weathering is unlikely to be kinetically limited and, instead, is either limited by the supply of fresh minerals or by the availability of acid (primarily carbonic acid) that can dissolve carbonate rock (Bufe et al., 2021; Calmels et al., 2011; Gaillardet et al., 2018; Romero-Mujalli et al., 2018). The supply of acid is controlled by a number of factors, including temperature, atmospheric CO₂ partial pressures ($p\text{CO}_2$), the efficiency of soil respiration that supplies CO₂ for carbonic acid to the bedrock, and the oxidation of sulfates that creates sulfuric acid. Both the total CO₂ available for weathering and the temperature control the saturation of the solution with respect to calcite (Drake & Wigley, 1975). Thus, for undersaturated fluids, carbonate weathering may be strongly coupled with erosion, whereas it becomes decoupled from erosion and coupled to acid availability once saturation is achieved. As a consequence, the mechanisms that control how denudation is partitioned in a dominantly carbonate orogen may differ substantially from those that control denudation partitioning in silicate orogens (Gaillardet et al., 2018; Ott et al., 2019).

Young orogens in particular often expose marine sedimentary sequences that can host significant volumes of carbonate, either as massive carbonate terranes or interbedded with siliciclastic sedimentary rocks. For example, the entire Alpine-Zagros-Himalayan orogenic complex has a common genesis during the Mesozoic, when carbonate platforms covered a large area of the Tethys Ocean. These carbonates have been subsequently uplifted during the ongoing closure of the Tethys Ocean in the Cenozoic (Dercourt & Vrielynck, 1993; Philip et al., 1996). Yet, because such ranges are poorly represented in existing studies, we lack the ability to understand how uplift of such ranges may impact biogeochemical cycling and sediment budgets. Indeed, cooling during the Cenozoic is frequently attributed to the uplift of mountains, but if the majority of active ranges in the Cenozoic are composed of carbonate-rich bedrock, the mechanistic coupling between mountain uplift and cooling—and subsequent impacts on the carbon cycle—may require revision.

Figure 1. (a) Overview map with locations of sampled sediment and water (white circles) and discharge stations (yellow triangles). White polygons illustrate sampled catchment areas for sediment and water samples, and numbers correspond to catchment names given in tables. (b) Geologic map of the Northern Apennines. The Ligurian Unit is divided into the Internal Ligurian Unit (IntL; dark green) and the External Ligurian Unit (ExtL; light green). Limestone-precipitating springs (blue dots; Cantonati et al., 2016; Segadelli & de Nardo, 2018) and catchment boundaries (black outlines) are illustrated. Gray areas are not mapped, and white area represents the Ligurian Sea.

In this study, we investigate the partitioning of physical and chemical denudation between carbonates and silicates in a carbonate-rich orogen, the Northern Apennines (Figure 1). To this end, we use existing ^{10}Be catchment-averaged denudation rates (Cyr & Granger, 2008; Cyr et al., 2014; Erlanger, 2020; Wittmann et al., 2016), riverine dissolved solutes, and the fraction of carbonate sand in river sediment in 18 individual catchments draining the Northern Apennines. The results from this study reveal four key characteristics of denudation partitioning in mixed-lithology active orogens: (a) physical erosion dominates the total denudation flux in the Northern Apennines, and the relative contribution of carbonates and silicates to the physical erosion flux appears to be lithologically controlled, (b) denudation fluxes are decoupled from both silicate and carbonate weathering, likely due to kinetic limitations on silicate weathering and acid-supply limits on carbonate weath-

ering, (c) the carbonate weathering flux is greater than the silicate weathering flux, and (d) in carbonate-rich catchments, up to 90% of dissolved Ca^{2+} ions are precipitated as secondary calcite, an important process that converts chemically mobilized solutes back into solid grains that can once again be transported physically.

2. Setting

2.1. Geology

The Northern Apennines form part of the Alpine orogenic belt and were uplifted and sub-aerially exposed by $\sim 4\text{--}5$ Ma (e.g., Balestrieri et al., 2003; Fellin et al., 2007; Le Pichon et al., 1971). This mountain range is a type example for the initial stages of orogenesis, characterized by an intact sedimentary cover of mixed siliciclastic-carbonate lithologies, with little to no metamorphic rocks and a relatively low average elevation (400 m). Lithologies exposed in the Northern Apennines are dominated by marine sedimentary sequences deposited as turbidites (Tertiary Foredeep units) (Figures S1a and S1b), which are divided into the Macigno, Cervarola, and Marnoso Arenacea Units (Figure 1b). Overlying these deposits are remnants of the Ligurian Tethys Ocean (Ligurian Unit), comprised of pelagic successions and turbidites (Vai & Martini, 2001). The Ligurian Unit is subdivided into (a) the External Ligurian Unit (ExtL) (Figure S1e), which consists of continuous units of carbonaceous and siliciclastic turbidites, and broken units of clayey shales with embedded limestone/sandstone clasts; and (b) the Internal Ligurian (IntL) Unit (Figures S1d and S1f), which consists of pelagic limestones, sandstones, and minor ophiolites (Molli, 2008; Ricci Lucchi, 1986). Overlying the ExtL, mixed siliciclastic and carbonate deposits formed in perched basins from the mid-Eocene to the Pliocene, collectively called the Epiligurian Unit (Figure S1c).

Carbonate in these bedrock units exists within a range of grain sizes. In the Marnoso Arenacea Unit, sand-sized grains of carbonate are present within the sandstone bodies, and carbonate is also present in the marls and in the cement (e.g., Fontana et al., 1986). Due to burial by the overlying Ligurian Unit, the Macigno and Cervarola Units have experienced strong compaction during the evolution of the Northern Apennines, and are devoid of carbonate cement. In these units, carbonate is thus only present in veins and as sand-sized grains within the sandstones. In the ExtL, carbonates are visible as gravel-sized clasts, which are relicts from original limestone beds (Simoni et al., 2013). At the mouth of the Reno River (No. 18, Figure 1a), these gravel clasts are still visible within the exposed stratigraphy of the Holocene fan, as well as sand-sized carbonate grains that account for $<10\%$ of grain point counts (Simoni et al., 2013). In the IntL, carbonates are found within occasional limestone beds embedded in shale units (Figure S1d), or as minor crystalline calcite (mm-scale) in tectonic/hydrothermal veins at the top of the oceanic basement in ophiolite deposits (Figure S1f).

We refer to the northeast flank of the mountain range as the Adriatic side, where all rivers drain into the Po Plain and ultimately to the Adriatic Sea, and refer to the southwest flank as the Ligurian side, where rivers drain into the Ligurian Sea (Figure 1a). On the Adriatic side, limestone-precipitating springs (LPS) have been mapped primarily in the Tertiary Foredeep and Epiligurian units (Figure 1b) and are associated either with perched, isolated aquifers formed from slope-gravitational movements, or with aquifers formed along fault planes (Cantonati et al., 2016). Other LPS have been observed in the Ligurian Units and are also associated with gravitational processes (i.e., landslides) that are a common occurrence in these lithologies (Carlini et al., 2016; Segadelli et al., 2017).

2.2. Climate

The climate in the Northern Apennines is characterized as Mediterranean, with average temperatures of $\sim 10^\circ\text{C}$. Average January temperatures on both sides of the mountain range are 0°C , but reach up to 10°C on the Ligurian coastlines, compared with a more spatially consistent July average of $15\text{--}20^\circ\text{C}$ (Brunetti et al., 2014). Precipitation primarily falls as snow or winter rain, with a maximum (300–800 mm) during the months of September through February, and a minimum (150–300 mm) during the months of June through August (Crespi et al., 2018). During the fall, winter, and spring, precipitation is approximately a factor of 2 higher on the Ligurian side and in the highest elevations on the Adriatic side, relative to the middle and lower reaches of catchments on the Adriatic side (Crespi et al., 2018). During the summer months (June, July, and August), seasonal precipitation is similar across the divide (250–350 mm) in the Northern Apennines (Crespi et al., 2018).

Maximum river discharge occurs during the months of November to March. Average annual runoff (discharge divided by upstream catchment area) compiled for each studied catchment over the last five available years varies from ~ 0.3 to 2.2 m/yr (Table 1). Runoff and denudation typically illustrate a positive correlation (Summerfield & Hulton, 1994), although catchment-averaged denudation fluxes and runoff from the Northern Apennines appear to be negatively correlated (Figure S1).

3. Materials and Methods

3.1. Sediment Sampling and Analysis

We sampled sediment from active channels and overbank deposits during two sampling seasons in March and July of 2018. These two months broadly correspond to the times of yearly maximum and minimum runoff, respectively, and were chosen to bracket as much as possible the yearly range of streamflow conditions. Sampling sites (Figure 1a) were chosen near locations with existing constraints on catchment-averaged denudation rates (Erlanger, 2020).

We decanted floating organic material (e.g., leaves and wood) from each sample, and sieved the sample to obtain the 250 – 500 μm fraction. We used grain sizes within the range of the ^{10}Be denudation rates (125 – 700 μm), in order to avoid potential grain size bias when comparing silicate and carbonate weathering and erosion fluxes. We weighed ~ 50 g of sand (or the available mass) and treated it with concentrated (36%) HCl. The remaining mass was rinsed, dried, and weighed. The difference between the original and final mass was assumed to represent the percent carbonate within the sand-sized fraction.

3.2. Catchment-Averaged Denudation Rates

Detrital, catchment-averaged denudation rates derived from ^{10}Be concentrations were compiled from catchments around the Northern Apennines (Cyr & Granger, 2008; Cyr et al., 2014; Erlanger, 2020; Wittmann et al., 2016). Because these samples were collected over different years and assume different cosmogenic nuclide scaling schemes to calculate denudation rates, we use the denudation rates given in Erlanger (2020), which includes rates from other studies (Cyr & Granger, 2008; Cyr et al., 2014; Wittmann et al., 2016) that were recalculated using the method of Lupker et al. (2012). All denudation rates were then converted to fluxes using a quartz density of 2.65 g/cm³.

3.3. Water Chemistry

3.3.1. Sample Collection and Measurements

We collected water samples from the Northern Apennines over the course of four sampling campaigns (May 2017, July 2017, March 2018, and July 2018) in order to quantify chemical weathering and physical erosion fluxes. For each sample location, we collected three 30 mL bottles of river water and filtered the water through 0.22 μm nylon VWR filters. We measured alkalinity in the field (maximum 24 h after collection) for most samples using either end-point or Gran titration techniques with a Hach digital titrator.

We acidified cation samples with laboratory-grade HCl to a pH of 2 or lower, and kept all samples cool and away from light until analysis. We analyzed cation concentrations of water samples on a Thermo-Fischer Element XR sector-field inductively coupled-plasma mass spectrometer. We then calculated concentrations from the measured intensities, using a single-point calibration compared with an in-house primary standard. In-house standards were calibrated with the Certified Reference Standards of DIONEX, and we used the National Research Council of Canada river standard SLRS-6 and NIST 1640 secondary multi-element standards to assess the accuracy and precision of these measurements. Standards solute concentrations agree with certified values to within 5%–10%, and 2σ uncertainties for replicate analyses of the standards were less than 7%. We analyzed anion concentrations and cation replicates on a Dionex DX-120 ion chromatography (IC) instrument, with an IonPac AS14, 4×250 mm column and an ASRIS-Ultra Suppressor with AutoSuppression. To prepare all eluents of NaCO_3 , we used deionized water (with a resistance greater than 18.2 M Ω) from a Milli-Q water unit. For all anions and cations, analytical uncertainties were below 5%.

Table 1
Denudation Fluxes, Physical Erosion Fluxes, and Chemical Weathering Fluxes

River number	River name	Sample number	Latitude	Longitude	Sampling date	D (t/km ² /yr)	W_{Total} (t/km ² /yr)	W_{Carb} (t/km ² /yr)	W_{Sil} (t/km ² /yr)	E_{Total} (t/km ² /yr)
2	Lima	1	43.999°	10.554°	15/07/2018	504 ± 58	178 ± 57	154.2 ± 56	24.2 ± 8.8	325 ± 81
4	Serchio	1	44.137°	10.374°	15/07/2018	511 ± 69	114 ± 38	105.0 ± 38	8.9 ± 3.2	398 ± 79
5	Magra	1	44.187°	9.926°	20/03/2018	572 ± 85	128 ± 41	106.9 ± 40	20.9 ± 7.9	445 ± 94
6	Vara	1	44.192°	9.858°	20/03/2018	278 ± 42	126 ± 30	105.8 ± 29	20.1 ± 5.6	152 ± 52
6	Vara	2	44.190°	9.858°	15/07/2018	278 ± 42	221 ± 54	191.2 ± 53	29.4 ± 8.2	58 ± 68
7	Entella	1	44.351°	9.362°	20/03/2018	286 ± 34	199 ± 36	173.9 ± 35	25.0 ± 5.1	87 ± 50
7	Entella	2	44.351°	9.362°	15/07/2018	286 ± 34	300 ± 49	227.5 ± 47	72.3 ± 14.7	−14 ± 60
8	Scrivia	1	44.719°	8.860°	18/03/2018	710 ± 126	104 ± 59	94.2 ± 59	10.2 ± 6.4	606 ± 139
10	Trebbia	1	44.908°	9.590°	22/03/2018	1,171 ± 594	143 ± 46	129.0 ± 46	13.6 ± 4.9	1,029 ± 595
10	Trebbia	2	44.909°	9.589°	15/07/2018	1,171 ± 594	142 ± 40	103.7 ± 37	37.9 ± 13.6	137 ± 595
11	Nure	1	44.828°	9.617°	15/07/2018	1,063 ± 193	166 ± 94	143.4 ± 93	22.7 ± 14.6	897 ± 215
11	Nure	1	44.882°	9.653°	21/03/2018	1,063 ± 193	193 ± 110	168.6 ± 109	24.2 ± 15.6	870 ± 223
12	Taro	1	44.698°	10.093°	21/03/2018	1,598 ± 326	163 ± 39	148.8 ± 39	14.4 ± 3.8	1,435 ± 328
12	Taro	2	44.697°	10.094°	15/07/2018	1,598 ± 326	161 ± 36	136.5 ± 36	24.8 ± 6.4	1,437 ± 328
13	Baganza	2	44.606°	10.123°	15/07/2018	726 ± 289	119 ± 35	94.3 ± 34	25.0 ± 9.1	607 ± 291
13	Baganza	1	44.605°	10.120°	21/03/2018	726 ± 289	163 ± 55	150.5 ± 55	12.8 ± 4.6	563 ± 294
14	Parma	1	44.569°	10.237°	15/07/2018	1,140 ± 201	168 ± 33	133.4 ± 32	34.9 ± 8.3	971 ± 204
15	Enza	1	44.627°	10.413°	15/07/2018	1,317 ± 329	187 ± 33	145.2 ± 32	41.9 ± 9.1	1,130 ± 330
17	Panaro	1	44.420°	10.925°	04/07/2017	790 ± 121	138 ± 26	114.0 ± 26	23.8 ± 5.3	652 ± 123
18	Reno	1	44.338°	11.213°	01/05/2017	1,540 ± 305	98 ± 30	83.8 ± 30	14.0 ± 4.9	1,442 ± 306
18	Reno	1	44.362°	11.257°	03/05/2017	2,226 ± 925	134 ± 37	99.3 ± 35	35.0 ± 12.4	2,092 ± 926
19	Senio	1	44.227°	11.632°	15/07/2018	1,269 ± 265	126 ± 42	90.9 ± 39	34.7 ± 15.0	1,144 ± 268
20	Lamone	1	44.065°	11.601°	15/07/2018	822 ± 94	148 ± 42	121.7 ± 41	25.9 ± 8.8	674 ± 103
21	Montone	1	44.121°	11.885°	15/07/2018	1,545 ± 295	71 ± 22	52.1 ± 21	18.7 ± 7.5	1,474 ± 296

D = Denudation flux (physical erosion + chemical weathering); W_{Total} = total weathering flux; W_{Carb} = carbonate weathering flux; W_{Sil} = silicate weathering flux; E_{Total} = total physical erosion flux; E_{Carb} = carbonate physical erosion flux; E_{Sil} = silicate physical erosion flux. $^{\text{§}}W_{\text{Total}}$ = total weathering flux (excluding CO₃ from carbonate weathering); $^{\text{§}}W_{\text{Carb}}$ = carbonate weathering flux (excluding CO₃ from carbonate weathering); $^{\text{§}}E_{\text{Total}}$ = total physical erosion flux (excluding CO₃ from carbonate weathering); ND = fluxes not determined for sample due to lack of carbonate sand measurements.

3.3.2. Water Solute Corrections

For some catchments, we collected a repeat sample from the same location during both the winter and summer season. Where appropriate, when we discuss results from one of the repeat measurements, we refer to an individual “sample.” When the collective set of sample(s) from a catchment are discussed, we refer to the “catchment.”

Solute concentrations (square brackets designate concentrations) were initially corrected to account for rainwater inputs. We additionally assess the saturation state of the samples with respect to calcite, because the widespread presence of travertine deposits and limestone-precipitating springs in the Northern Apennines (Figure 1b) (Cantonati et al., 2016; Segadelli & de Nardo, 2018) suggests that waters in many catchments may be oversaturated with respect to calcite.

We corrected our solute concentrations for rainwater inputs using the concentration of atmospheric Cl[−] as an index for atmospheric inputs to rivers. Globally, non-polluted rivers have atmospheric [Cl[−]] lower than 30 μmol/L (Gaillardet et al., 1999). The lowest measured [Cl[−]] across all samples is 64.6 μmol/L, which is consistent with measured [Cl[−]] from precipitation chemistry measurements in the Central Apennines (Vet

E_{Carb} (t/km ² /yr)	E_{Sil} (t/km ² /yr)	Annual runoff (m/yr)	$\frac{E_{\text{Total}}}{W_{\text{Total}}}$	$\frac{E_{\text{Carb}}}{E_{\text{Sil}}}$	${}^{\S}W_{\text{Total}}$ (t/km ² /yr)	${}^{\S}W_{\text{Carb}}$ (t/km ² /yr)	${}^{\S}E_{\text{Total}}$ (t/km ² /yr)	$\frac{{}^{\S}E_{\text{Total}}}{W_{\text{Total}}}$	$\frac{{}^{\S}W_{\text{Carb}}}{W_{\text{Sil}}}$
65 ± 81	260 ± 115	1.2 ± 0.4	1.8	0.3	165 ± 29	92.7 ± 25	121 ± 45	0.7	1.3
ND	ND	0.6 ± 0.2	3.5	ND	99 ± 21	57.0 ± 19	1,218 ± 329	12.3	1.4
110 ± 94	335 ± 133	0.9 ± 0.4	3.5	0.3	48 ± 25	38.3 ± 24	662 ± 101	13.6	3.8
28 ± 52	124 ± 73	1.5 ± 0.4	1.2	0.2	72 ± 23	45.8 ± 21	750 ± 97	10.5	1.8
11 ± 68	47 ± 97	1.5 ± 0.4	0.3	0.2	38 ± 13	19.4 ± 11	1,507 ± 296	39.5	1.0
15 ± 50	72 ± 70	2.2 ± 0.4	0.4	0.2	65 ± 19	43.8 ± 17	508 ± 87	7.8	2.1
−2 ± 60	−11 ± 85	2.2 ± 0.4	0.0	0.2	63 ± 14	42.5 ± 13	216 ± 28	3.4	2.1
343 ± 139	263 ± 197	0.6 ± 0.4	5.8	1.3	73 ± 24	60.1 ± 23	653 ± 289	9.0	4.7
618 ± 595	411 ± 842	0.8 ± 0.3	7.2	1.5	75 ± 21	39.8 ± 17	2,151 ± 904	28.7	1.1
82 ± 595	55 ± 841	0.8 ± 0.3	1.0	1.5	68 ± 26	32.9 ± 22	1,202 ± 239	17.8	0.9
601 ± 215	296 ± 304	0.8 ± 0.5	5.4	2.0	79 ± 23	41.2 ± 18	199 ± 20	2.5	1.1
583 ± 223	287 ± 315	0.8 ± 0.5	4.5	2.0	89 ± 47	65.2 ± 45	973 ± 199	10.9	2.7
910 ± 328	525 ± 464	0.8 ± 0.2	8.8	1.7	69 ± 15	44.9 ± 14	721 ± 106	10.5	1.9
911 ± 328	526 ± 464	0.8 ± 0.2	8.9	1.7	47 ± 14	33.4 ± 13	1,492 ± 291	31.5	2.4
467 ± 291	140 ± 412	0.7 ± 0.3	5.1	3.3	86 ± 26	61.6 ± 24	418 ± 64	4.87	2.5
433 ± 294	129 ± 416	0.7 ± 0.3	3.4	3.3	51 ± 16	42.3 ± 16	460 ± 53	9.0	4.8
693 ± 204	278 ± 289	1.0 ± 0.2	5.8	2.5	73 ± 18	58.5 ± 18	1,525 ± 308	20.9	4.1
677 ± 330	453 ± 467	1.0 ± 0.2	6.0	1.5	105 ± 26	75.4 ± 25	173 ± 16	1.7	2.6
248 ± 123	404 ± 175	0.8 ± 0.2	4.7	0.6	77 ± 41	54.5 ± 38	985 ± 198	12.8	2.4
516 ± 306	926 ± 433	0.7 ± 0.2	14.8	0.6	78 ± 19	53.0 ± 18	1,520 ± 307	19.5	2.1
749 ± 926	1,343 ± 1,309	0.7 ± 0.2	15.6	0.6	62 ± 19	36.8 ± 16	664 ± 289	10.8	1.5
289 ± 268	854 ± 379	0.5 ± 0.2	9.1	0.3	88 ± 19	52.8 ± 17	1,052 ± 182	12.0	1.5
142 ± 103	532 ± 146	0.7 ± 0.2	4.6	0.3	95 ± 17	69.9 ± 17	191 ± 39	2.0	2.8
625 ± 296	849 ± 419	0.3 ± 0.1	20.8	0.7	65 ± 20	51.4 ± 20	1,106 ± 573	17.0	3.8

et al., 2014), so we use this as our reference [Cl^-]. The high values in our river samples and in precipitation may result from a strong seawater contribution of Cl^- , due to the proximity of the Northern Apennines to the Ligurian and Adriatic Seas. We also performed this correction using elemental ratios from a local precipitation station in Central Italy, and find that it changes the corrections by a maximum of 3.3% (Table S1), illustrating that there is little difference between the two methods. We thus use the global seawater ratios for correcting our samples.

We corrected major dissolved species by subtracting a reference concentration for each ion from the measured concentration. For rainwater inputs, we calculated reference ion concentrations by dividing the stoichiometric ratios of global average seawater for Na/Cl, Ca/Cl, K/Cl, Mg/Cl, and SO_4^{2-} /Cl by our reference [Cl^-]. For sulfate, we assume that SO_4^{2-} /Cl ratios in rain are twice as high as in seawater, following Stallard and Edmond (1981).

3.3.3. Saturation Index

The saturation index (SI) of a solution is defined as (Langmuir, 1971):

$$SI = \log(IAP / K) \quad (1)$$

$$IAP = a_{Ca} \cdot a_{HCO_3^-} \cdot K_2 / 10^{-pH} \quad (2)$$

where IAP is the ionic activity product, K is the equilibrium constant for carbonate, a_{Ca} and $a_{HCO_3^-}$ are the activities of Ca^{2+} and HCO_3^- (Davies & Shedlovsky, 1964), and K_2 is the second dissociation constant of H_2CO_3 . Here, we assume that the concentrations of Ca^{2+} and HCO_3^- are equal to the activities.

3.4. Calculation of Fluxes

Denudation, weathering, and physical erosion fluxes were calculated for 25 samples from 18 catchments. We excluded samples from these calculations due to unavailable carbonate sand measurements (River No. 4); unavailable discharge data (River No. 9); unavailable denudation measurements (Cutigliano sample from River No. 2, and Castello di Sambuca sample from River No. 18); textile pollution (River No. 1), based on elevated Na^+ and SO_4^{2-} (Cortecci et al., 2002), for which we cannot confidently correct; or to “contamination” by evaporite weathering (Text S1), based on either mapped distributions of evaporites (Chiesi et al., 2010) or isotopic signatures of sulfate (Boschetti et al., 2005; Cortecci et al., 2008) in these catchments.

For silicate weathering, the contribution of major dissolved ions was calculated by summing the concentrations of the following species, expressed as major cations and silicon derived from silicate rocks (expressed in kg/m^3 or g/L):

$$TDS_{sil} = [Ca^{2+}]_{sil} + [Mg^{2+}]_{sil} + [Na^+]_{sil} + [K^+]_{sil} + [Si] \quad (3)$$

We refer to this quantity as “silicate dissolved solids” (TDS_{sil}). Because Ca^{2+} and Mg^{2+} can be derived from both carbonate and silicate weathering, we partitioned the concentrations based on molar ratios from a global compilation of streams draining pure silicate lithologies Ca_{sil}/Na (0.35) and Mg_{sil}/Na (0.24) (Gailardet et al., 1999). In the absence of local constraints, this global silicate endmember appears to be a fair approximation of the local endmember in the Northern Apennines (Figure S4), and we find no local lithological data that supports the use of a single endmember for the entire group of data.

We calculated the silicate chemical weathering flux ($t/km^2/yr$) using the following equation:

$$W_{sil} = \frac{Q_{riv} * TDS_{sil}}{A_{riv}} = \frac{Q_{riv}}{A_{riv}} * (M_{Na} * [Na^+]_{sil} + M_K * [K^+]_{sil} + M_{Mg} * [Mg^{2+}]_{sil} + M_{Ca} * [Ca^{2+}]_{sil} + M_{Si} * [Si]) \quad (4)$$

where M_x is the molar mass (g/mol) of element X , and Q_{riv}/A_{riv} is the runoff, expressed as the time-integrated water discharge (m^3/y) divided by the upstream drainage area (m^2). This mass flux assumes that the anion contribution to the dissolved load from silicate minerals is negligible.

For carbonate weathering, $[Ca^{2+}]_{carb}$ and $[Mg^{2+}]_{carb}$ are assumed to be the difference between the total concentrations and the silicate contribution. We define the “carbonate dissolved solids” (TDS_{carb}) as:

$$TDS_{carb} = [Ca^{2+}]_{carb} + [Mg^{2+}]_{carb} = ([Ca^{2+}]_{Total} + [Mg^{2+}]_{Total}) - ([Ca^{2+}]_{sil} + [Mg^{2+}]_{sil}) \quad (5)$$

In turn, we calculate a carbonate weathering mass flux that includes both cations (Mg^{2+} and Ca^{2+}) and anions (CO_3^{2-}) to compare with the total denudation mass flux from ^{10}Be erosion rates:

$$W_{carb} = \frac{Q_{riv} * TDS_{carb}}{A_{riv}} = \frac{Q_{riv}}{A_{riv}} * (M_{MgCO_3} * [Mg^{2+}]_{carb} + M_{CaCO_3} * [Ca^{2+}]_{carb}) \quad (6)$$

Here, we use ^{10}Be concentrations of river sands to infer the total denudation flux (D) in each catchment. Although ^{10}Be denudation rates record the exhumation of only the quartz grains, we assume that these rates reflect the lowering rate of all rocks over the entire catchment, and thereby apply to both siliciclastic and carbonate lithologies. This assumption is reasonable, because in the Northern Apennines, carbonates occur both interbedded with and as accessory minerals within siliciclastic lithologies (Figure S1), and no

Figure 2. Percent carbonate sand for each catchment. Numbers correspond to catchments in Table S1. The hatched pattern applies to River No. 4, for which data are unavailable. Light green color beneath the hatched pattern corresponds to River No. 3, which includes upstream tributaries in Rivers No. 2 and 4.

steep carbonate cliffs or large areas that drain exclusively quartz or carbonate lithologies are reported here (Bigi et al., 1983). The total denudation flux (D) is defined as the sum of the chemical weathering fluxes ($W_{\text{carb}} + W_{\text{sil}}$) and the physical erosion flux (E) (Equation 7). Therefore, we can infer the physical erosion flux from the denudation and chemical weathering fluxes:

$$E_{\text{total}} = D - (W_{\text{sil}} + W_{\text{carb}}) \quad (7)$$

To partition the physical erosion flux into carbonates and silicates, we use the percent carbonate sand determined for each river to obtain the carbonate erosion flux:

$$E_{\text{carb}} = E_{\text{total}} * \% \text{Sand}_{\text{carb}} \quad (8)$$

and:

$$E_{\text{sil}} = E_{\text{total}} - E_{\text{carb}} \quad (9)$$

From this method, we infer the ratio of carbonate and silicate physical erosion flux only for the sand sized fraction, and we acknowledge that the proportion of these minerals in the sand fraction may not map directly onto the proportion of carbonates and silicates in the total physical erosion flux across all grain sizes. We propagate uncertainties of all quantities from the analytical and reported uncertainties of the underlying measurements.

4. Results

4.1. Carbonate Sand

Catchment-wide percent carbonate sand varies from 17% to 76% (Figure 2, Table S2) and values observed here are consistent with point counts of lithic carbonate sand grains (Lc) observed in river or beach sands derived from these catchments (Garzanti et al., 1998, 2002) (Table S2). The carbonate content ranges from 17% to 18% for catchments draining the IntL (No. 6–7), from 20% to 28% for catchments draining the Macigno/Cervarola Unit (No. 1–3), from 21% to 42% for catchments draining the Marnoso Arenacea Unit

Figure 3. Catchment area that exposes the ExtL plotted against percent carbonate sand. River numbers are shown in parentheses.

Figure 4. Histogram of saturation index results. Undersaturated samples (blue) have values below zero, samples with values at zero (green) are at saturation, and oversaturated samples (orange) have values above zero. River No. 1 (hatched pattern) is affected by pollution from nearby textile industries (Cortecchi et al., 2002) and produced high ion concentrations that could not be attributed to natural sources.

Additionally, we distinguish between oversaturated samples (solid pattern) and undersaturated/saturated samples (“x” pattern).

For catchments draining the ExtL, we find that percent carbonate sand does not scale with denudation fluxes, but there is a strong correlation with non-ExtL catchments ($R^2 = 0.82$) (Figure 5a). In turn, denudation fluxes illustrate either a decoupling or weak coupling with TDS_{Carb} , TDS_{Sil} , and TDS_{Total} (Figures 5b–5d). However, we find a strong correlation, albeit with low significance ($p = 0.08$) due to the small sample size, between carbonate weathering and denudation fluxes in all undersaturated/saturated samples ($R^2 = 0.85$) (Figure 5d). Similarly, TDS_{Carb} and the percent carbonate sand are decoupled for oversaturated catchments (Figure 6) but illustrate a moderate correlation ($R^2 = 0.71$) for undersaturated samples, although the significance is again low ($p = 0.16$).

(No. 19–21), and from 60% to 76% for catchments draining the ExtL (No. 10–14). Sampled catchments that drain a mixture of units generally have carbonate sand percentages outside the range of those that exclusively drain one lithology (Figures 1 and 2). We also find a strong positive correlation ($R^2 = 0.82$) between the percent carbonate sand and the areal exposure of the ExtL within a catchment (Figure 3).

4.2. Solutes

Riverine samples from the Northern Apennines are slightly alkaline, with pH values ranging from 7.7 to 9.1, and major dissolved ion concentrations that are dominated by Ca^{2+} and HCO_3^- (Table S3). Most catchments have SI values greater than zero (Figure 4, Table S4), which indicates that the waters are oversaturated with respect to calcite. The lowest SI values (<0) reflect undersaturated conditions and are sourced exclusively from catchments on the Ligurian side of the drainage divide.

4.3. Erosion and Weathering Fluxes

Total denudation fluxes derived from ^{10}Be concentrations vary over an order of magnitude, from 278 to 2,226 t/km²/yr (Table 1). Total physical erosion fluxes (E_{Total}) range from 0 to 2,092 t/km²/yr. Partitioned into carbonate physical erosion (E_{Carb}) and silicate physical erosion (E_{Sil}), the ratio of E_{Carb}/E_{Sil} varies from 0.21 to 3.4, where 52% of samples have higher E_{Sil} fluxes than E_{Carb} fluxes (Table 1).

Total weathering fluxes (W_{Total}) vary from 71 to 300 t/km²/yr (Table 1). E_{Total}/W_{Total} is 6 on average, illustrating that physical erosion fluxes generally exceed chemical weathering fluxes by a factor of 6. Carbonate weathering fluxes ($W_{Carb} = 52\text{--}227$ t/km²/yr) are higher than the silicate weathering fluxes ($W_{Sil} = 9\text{--}72$ t/km²/yr). The ratio of W_{Carb}/W_{Sil} varies from 2.6 to 11.9 (average $W_{Carb}/W_{Sil} = 5.9$) demonstrating that carbonate weathering is dominant in all catchments and on average a factor of 5 higher than silicate weathering fluxes.

4.4. Partitioning Denudation Between Carbonates and Silicates

We compare denudation fluxes with total dissolved solids (TDS) as a proxy for chemical weathering, and with the percent carbonate sand as a proxy for carbonate physical erosion (Figure 5). In each figure, we plot the entire set of samples, but differentiate between catchments draining the ExtL (gray circles), defined as catchments where the ExtL constitutes at least 50% of the exposed lithologies, from all other units (cyan circles).

Figure 5. Denudation fluxes plotted against (a) percent carbonate sand, (b) TDS_{Total} , (c) TDS_{Sil} , and (d) TDS_{Carb} . ExtL Unit samples (gray circles) are differentiated from Other Units (cyan circles). Dashed lines illustrate linear regressions for each full data set with associated R^2 statistic and p -value. In (a) dotted line refers only to Other Unit samples, and numbers refer to catchments shown in Figure 1a. In (d) solid circles illustrate oversaturated samples; undersaturated/saturated samples are overlaid with a “x.” The dotted regression line refers only to undersaturated/saturated samples.

5. Discussion

In the following discussion, we investigate the mechanisms that control how denudation is partitioned between erosion and weathering and between carbonates and silicates, and we compare denudation and

weathering fluxes from the Northern Apennines with a global data compilation from silicate-rich landscapes. To discuss the limits on weathering, we use the terminology of Bufer et al. (2021), whereby: (a) a (mineral) supply limit refers to weathering limited by the supply of fresh minerals to the subsurface weathering zone (SWZ); (b) a kinetic limit refers to weathering limited by the kinetics of mineral dissolution, and (c) an acid limit refers to weathering limited by the availability of acid for mineral/rock dissolution.

In the Northern Apennines, physical erosion is the dominant denudational process, and ratios of E_{Carb}/E_{Sil} are variable, suggesting that both erosion of carbonates and silicates is important in this landscape (Table 1). However, we observe some important lithologic controls on carbonate erosion. In particular, the highest carbonate sand percentages (67%–76%) are found in catchments exclusively draining the ExtL (Figures 1b and 2). Percent carbonate sand and areal coverage by the ExtL illustrate a strong linear correlation (Figure 3), suggesting that the ExtL is the most important source of carbonate sand grains to river channels in the Northern Apennines. However, we find no obvious lithologic

Figure 6. Percent carbonate sand plotted against TDS_{Carb} . Linear regression, R^2 statistic, and p -value refer only to undersaturated/saturated samples.

control on the partitioning of chemical weathering and denudation (Figures 5b–5d). While our carbonate sand percentages are similar to detrital sand point counts measured in Garzanti et al. (1998, 2002), they are higher than point counts of carbonate sand from bedrock (Garzanti et al., 2002), suggesting that the fraction of carbonate sand we find in river sediment may have increased through (a) secondary precipitation of carbonate, and/or (b) comminution of larger, gravel-sized carbonate clasts into sand. Our results and observations indicate that both of these mechanisms likely occur in the Northern Apennines. Moreover, the distribution of carbonate in the Reno River (No. 18) does not appear to be equally partitioned between gravel and sand grains (Simoni et al., 2013). Because we do not have quantitative constraints on the grain size partitioning of carbonate and silicate from other catchments, the uncertainty of our estimate in the relative carbonate and silicate erosion fluxes remains unclear. However, the measured carbonate sand fraction in the ExtL (Figure 3) is consistent with a higher lithic carbonate (Lc) content measured in Ligurian bedrock near the study area, relative to the Lc content measured in the Tertiary Foredeep Units (Garzanti et al., 2002). We thus suggest that the regional variation of carbonate and silicate erosion is captured by our data.

Silicate and carbonate weathering fluxes (TDS $\times$ runoff) are uncorrelated with denudation, which could be explained by a negative relationship between denudation and runoff (Figure S2). Using annual runoff estimates could result in over- or under-estimating denudation fluxes (depending on seasonal discharge), although the low variability in solute concentrations between replicate samples collected during high flow conditions (winter) and low flow conditions (summer) (Table S3) is consistent with a low sensitivity of concentrations to discharge (termed chemostatic behavior). Chemostatic behavior has been observed in other, similarly sized rivers in the US and around the world (Godsey et al., 2009, 2019; Moon et al., 2014) and suggests that dilution is not a controlling factor on our solute concentrations.

Although we have only 1 or, at best 2, samples for each location, the magnitude of variability in solute concentrations (a factor of 2–3.5) that we observe is similar to the variability that others have observed in ^{10}Be denudation rates by sampling the same location during different seasons (Cyr et al., 2010). We also recognize that millennial-scale denudation fluxes derived from ^{10}Be concentrations, chemical weathering fluxes derived from river water chemistry, and runoff estimates reflect different timescales, and may limit our ability to compare both metrics, particularly for River No. 7, where we calculated a negative physical erosion flux (Table 1). To this end, we additionally compare millennial scale denudation fluxes with decadal-scale denudation fluxes derived from available suspended sediment yield data from Northern Apennine Rivers (Bartolini et al., 1996; Grauso et al., 2021) (Table S5). To convert the denudation rates from Bartolini et al. (1996) to a flux, we assume the same sediment density of 2.65 g/cm^3 used to convert the ^{10}Be denudation rates into fluxes. Accounting for the uncertainties in the millennial-scale denudation fluxes, the decadal-scale and millennial-scale denudation rates are less than a factor of 2 different for all rivers except River No. 12, although there is no clear pattern whereby denudation rates calculated with one method are consistently higher or lower than the other. This similarity between millennial-scale denudation fluxes and short-term denudation fluxes supports our use of ^{10}Be denudation fluxes with dissolved solute concentrations.

Consequently, we interpret the observed weak coupling or decoupling between weathering proxies and denudation fluxes as a reflection of weathering limits for both silicates and carbonates at erosion rates characteristic of the Northern Apennines or higher. A kinetic limit on silicate weathering rates has previously been suggested for denudation rates $>48 \text{ t/km}^2/\text{yr}$ (West et al., 2005). Based on the widespread oversaturation of sampled waters with respect to calcite, and the common occurrence of limestone precipitating springs, we suspect that carbonate weathering rates are most likely acid-limited. As long as acid availability does not increase with erosion rate, weathering rate and denudation should be decoupled, consistent with our observations. The decoupling between carbonate weathering and denudation fluxes for oversaturated samples, and possible strong correlation with undersaturated/saturated samples (Figure 5d), further support the hypothesis that the carbonate weathering rate is supply limited for a minority of samples (undersaturated/saturated samples) and acid-limited in most locations (oversaturated samples).

Figure 7. Northern Apennines denudation fluxes and total weathering fluxes derived from major cations and Si (i.e., excluding CO_3 from the carbonate weathering flux) plotted against a global data compilation. Triangles illustrate physical erosion fluxes derived from suspended sediment or average annual sediment fluxes, and circles illustrate denudation rates derived from cosmogenic nuclide data.

5.1. Global Comparison With Silicate-Rich Orogens

Relative to other silicate-rich orogens with similar denudation fluxes (e.g., Eastern Southern Alps of New Zealand, Colorado Rockies, Swiss Alps, and Andes Mountains), weathering fluxes (Text S2) are generally higher in the Northern Apennines (red circles; Figure 7).

We compare our fluxes in more detail with those from the Eastern Southern Alps of New Zealand (ESA), as both regions are in temperate climates, and weathering fluxes partitioned into carbonate and silicate components are also available for the Southern Alps (Jacobson & Blum, 2003). Note that for this comparison we use fluxes that exclude the contribution of anions (i.e., CO_3) from carbonate weathering for consistency with the other datasets (Table 1). Physical erosion fluxes from the ESA (140–1,700 $\text{t/km}^2/\text{yr}$) are similar to estimates from the Northern Apennines (121–2,151 $\text{t/km}^2/\text{yr}$). However, the ratio of physical erosion to total weathering ($E_{\text{Total}}/W_{\text{Total}}$) in the ESA ranges from 9 to 150, with an average of 64, reflecting weathering fluxes that are 1–2 orders of magnitude lower than physical erosion fluxes. Average ratios of erosion to weathering fluxes ($E_{\text{Total}}/W_{\text{Total}} = 13$) are lower in the Northern Apennines, reflecting the more important role of carbonate weathering in this setting. Carbonate weathering fluxes range from 8 to 100 $\text{t/km}^2/\text{yr}$ in the ESA, compared with the range of 19–93 $\text{t/km}^2/\text{yr}$ found in the Northern Apennines. Although the ESA are dominated by silicate-rich greywacke and schist lithologies with minor hydrothermal calcite veins, the ratio of carbonate to silicate weathering ($W_{\text{Carb}}/W_{\text{Sil}}$) is >1 for all except one sample, and has an average ratio of $W_{\text{Carb}}/W_{\text{Sil}} = 1.6$. In the Northern Apennines, average $W_{\text{Carb}}/W_{\text{Sil}} = 2.4$ —approximately a factor of 1.5 higher relative to the ESA—and we suggest that the difference in ratios between these two settings is due to lithologic differences. A lack of carbonate in stream sediments of the Southern Alps implies that carbonate weathering is likely supply limited. In contrast, in the majority of the Northern Apennines sample sites, exported solutes from carbonate weathering appear to be limited by acid availability, rather than mineral supply. The current weathering state (i.e., the exported flux to rivers) in the Northern Apennines is thus one that is generally decoupled from mineral supply and entirely controlled by the kinetics of silicate dissolution (which modulates silicate weathering) and acid availability (which modulates carbonate weathering).

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5.2. Limits on Weathering and Erosion in the Northern Apennines

5.2.1. Secondary Carbonate

Similar to carbonate-rich terranes globally (Romero-Mujalli et al., 2018), we observe that the vast majority of Northern Apennine waters are oversaturated with respect to calcite. When soil waters equilibrate at high $p\text{CO}_2$ in the subsurface and are discharged to streams, they begin to de-gas excess CO_2 to equilibrate with the lower atmospheric $p\text{CO}_2$. The resulting supersaturation of the waters with respect to the dissolved carbonates leads to the secondary precipitation of carbonate (Bickle et al., 2015). The abundance of limestone-precipitating springs (Figure 1b) suggests that subsurface waters in the Northern Apennines are typically (close to) saturation with respect to carbonate. Furthermore, we observe clear secondary grains in the Lamone River (No. 20) sand sample (Figure S6), suggesting that precipitation and erosion of secondary carbonates is a major process in the Northern Apennines. Cavazza et al. (1993) similarly observed that up to 35% of the sand fraction in the Senio River (No. 19) are such secondary carbonate “peloid” grains, comprised of organic material or quartz grains in the core and coated by a carbonate crust (see their Figure 4). Critically, secondary carbonate precipitation converts solutes back into rock that can be physically eroded—hence, it is a process that could further decouple the weathering processes within the weathering zone from the export of solutes by rivers from the orogen. By estimating the degree of secondary carbonate precipitation that occurred upstream of our sampling locations, we can infer the flux of initially weathered

Figure 8. (a–d) Ratios of Na/Ca plotted against Sr*1000/Ca for the primary lithologic units in the study area. Open circles and dashed regression lines represent bedrock data for each unit from Dinelli et al. (1999) for the (a) Macigno-Cervarola and (b) Marnoso Arenacea Units and from Bracciali et al. (2007) for the (c) IntL Unit and (d) ExtL Unit. Closed circles represent water samples from catchments analyzed in this study, categorized based on the dominant lithologic unit draining the catchment. Circles with an “x” through the center represent samples that were not corrected for secondary calcite precipitation.

material that has been subsequently converted back to solid grains and is no longer recorded in the flux of exported solutes in the river.

We estimate the proportion of secondary carbonate precipitation in each lithology, adopting the procedures of Bickle et al. (2015) (Text S3). We assume that secondary precipitation of calcite from supersaturated waters is responsible for the enrichment of Sr^{2+} in the remaining solution (Bickle et al., 2015; Emberson et al., 2018; Jacobson et al., 2002). The elemental composition of local bedrock is used to constrain the initial ratios of Sr/Ca and ultimately, an endmember mixing line. A line is regressed through solute samples whose catchment area drains only the local bedrock unit (Figure 8), and any deviation between the solute regression line and bedrock endmember mixing is interpreted to reflect secondary calcite precipitation.

Although some of our samples drain mixed lithologies, we chose to correct these samples for secondary precipitation using the bedrock mixing line that constitutes the dominant lithology in the catchment (Table S4). One exception is River No. 17, which has highly saturated waters ($\text{SI} = 0.9$). The ExtL covers 55% of the catchment area, yet the solute samples do not deviate from the ExtL mixing line. Based on the SI value and the presence of limestone precipitating springs in River No. 17 (Figure 1b), we are confident that secondary precipitation is occurring along this river, so we instead compared the solute samples to the Macigno-Cervarola bedrock mixing line (Table S4) because these are the other primary lithologies exposed in this catchment. We did not correct the $[\text{Ca}^{2+}]$ in undersaturated and saturated samples, because no secondary calcite precipitation is expected, which is consistent with the observation that the solute samples lie along their respective bedrock mixing lines.

Figure 9. Results from secondary calcite precipitation calculations, showing γ plotted against $\text{TDS}_{\text{Total}}^*$ for major dissolved ions and trace elements, calculated with the adjusted $[\text{Ca}^{2+}]$. Samples with an “x” were not corrected for secondary calcite precipitation.

We perform the correction for secondary precipitation over the entire concentration of Ca^{2+} , prior to partitioning the $[\text{Ca}^{2+}]$ into carbonate and silicate contributions to weathering. All quantities that include the inferred concentration of solutes lost to secondary precipitation are designated by an “*” (e.g., $\text{TDS}_{\text{Total}}^*$) and are referred to as weathering zone fluxes. A value of $\gamma = 1$ indicates that no secondary precipitation can be inferred from the chemical composition, and a value of $\gamma = 0$ corresponds to the (hypothetical) situation in which all calcium was lost to secondary calcite precipitation. Oversaturated samples have average γ values between 0.8 and 0.1, which indicates that between 20% and 90% of $[\text{Ca}^{2+}]$ was lost to secondary calcite precipitation (Figure 9). Catchments draining the ExtL illustrate the largest offset between the solute regression line and bedrock regression line (Figure 8d), which results in the greatest corrections to $[\text{Ca}^{2+}]$. For the Baganza River (No. 13) in particular, we recognize that the correction for secondary carbonate seems anomalously high, considering that carbonate grains observed under a microscope were mostly primary grains (Figure S6). However, we have excluded aragonite as a source of Sr^{2+} in the Northern Apennines and can find no other logical source other than secondary precipitation for the high Sr/Ca ratios measured in this catchment.

5.2.2. Weathering Zone Fluxes

Total weathering zone fluxes (W_{Total}^*) vary from 125 to 1,432 t/km²/yr (Table 2). The average ratio of total erosion fluxes to these weathering zone fluxes ($E_{\text{Total}}/W_{\text{Total}}^* = 1.3$) is a factor of ~ 4.5 lower than the average ratio for the exported fluxes ($E_{\text{Total}}/W_{\text{Total}} = 5.9$). Five samples have negative erosion rate fluxes, because the weathering zone flux exceeds the total denudation flux (Table 2). One reason for such a discrepancy could be that we underestimate the ^{10}Be denudation flux. Previous work has modeled the potential for ^{10}Be to underestimate total denudation fluxes where weathering constitutes a significant part of the total denudation. ^{10}Be records denudation rates across the upper 60 cm of soil and regolith (Riebe & Granger, 2013), whereas the SWZ may in fact be many meters deep (Uhlir et al., 2020). If weathering occurs at depths of greater than a few meters, it is capable of contributing to the overall denudation flux without affecting ^{10}Be . In turn, this may result in an overall underestimation of the denudation flux of up to 100% (Riebe & Granger, 2013).

We illustrate the results in terms of the weathering zone total TDS concentrations ($\text{TDS}_{\text{Total}}^*$) and weathering zone carbonate dissolved solids ($\text{TDS}_{\text{Carb}}^*$). Note that the estimated concentrations from silicate dissolved solids ($\text{TDS}_{\text{Sil}}^*$) are unaffected by the correction for secondary calcite precipitation. $\text{TDS}_{\text{Carb}}^*$ constitutes 70%–97% of $\text{TDS}_{\text{Total}}^*$, and both measures are decoupled from denudation fluxes when considering the entire data set (Figures 10a and 10b). Catchments draining the ExtL are characterized by the highest $\text{TDS}_{\text{Total}}^*$ values and are also decoupled from denudation. We also observe a moderate correlation between $\text{TDS}_{\text{Carb}}^*$ and the percent catchment area covered by the ExtL ($R^2 = 0.64$) (Figure 10c) and the percent carbonate sand ($R^2 = 0.66$) (Figure 10d).

Among these data, we observe a strong increase in $\text{TDS}_{\text{Carb}}^*$ with (a) increasing catchment area covered by the ExtL and (b) with increasing percent carbonate sand. These data suggest a strong lithologic control on carbonate weathering rates in the Northern Apennines, where the ExtL provides higher $\text{TDS}_{\text{Carb}}^*$ concentrations and percent carbonate sand relative to other units. Based on an abundance of primary carbonate in river sands (e.g., Baganza River, Figure S6), supersaturation of spring waters, and the absence of a correlation between denudation fluxes and $\text{TDS}_{\text{Total}}^*$ or $\text{TDS}_{\text{Carb}}^*$ (Figures 10a and 10b), acid availability seems to ultimately limit weathering in the SWZ. Nevertheless, the correlation between carbonate weathering and ExtL (Figure 10c) suggests that the underlying lithology may modulate weathering rates – perhaps because of differences in the acid availability.

The increase of $\text{TDS}_{\text{Carb}}^*$ with the fraction of the catchment covered by ExtL (Figure 10c) is further consistent with a parallel increase of the percent of carbonate grains (Figure 10d) because the relative carbonate content is highest in the ExtL (Figure 3). We suggest that this coupling of carbonate weathering flux and carbonate erosion flux is tied in large part to the secondary precipitation of carbonates that converts chem-

Table 2
Denudation Fluxes, Physical Erosion Fluxes, and Chemical Weathering Fluxes Adjusted for Precipitation of Secondary Carbonate

River number	River name	Latitude	Longitude	Sampling date	D (t/km ² /yr)	W_{Total}^* (t/km ² /yr)	W_{Carb}^* (t/km ² /yr)	W_{Sil}^* (t/km ² /yr)	E_{Total}^* (t/km ² /yr)	E_{Carb}^* (t/km ² /yr)	E_{Sil}^* (t/km ² /yr)	$\frac{E_{\text{Total}}^*}{W_{\text{Total}}^*}$
2	Lima	43.9993°	10.5538°	15/07/2018	503.5 ± 58.3	453.3 ± 158.0	429.0 ± 157.7	24.2 ± 8.8	50.2 ± 168.4	10.1 ± 168.4	40.2 ± 238.1	0.11
4	Serchio Filicaia	44.1374°	10.3741°	15/07/2018	511.5 ± 68.9	252.8 ± 88.5	243.9 ± 88.5	8.9 ± 3.2	258.7 ± 112.2	ND	ND	1.02
5	Magra	44.1869°	9.9256°	20/03/2018	572.4 ± 84.8	127.9 ± 41.2	106.9 ± 40.4	20.9 ± 7.9	444.5 ± 94.3	110.0 ± 94.3	334.5 ± 133.3	3.48
6	Vara	44.1897°	9.8578°	20/03/2018	278.3 ± 42.4	125.9 ± 29.9	105.8 ± 29.4	20.1 ± 5.6	152.4 ± 51.9	28.1 ± 51.9	124.3 ± 73.4	1.21
6	Vara	44.1919°	9.8584°	15/07/2018	278.3 ± 42.4	220.6 ± 53.7	191.2 ± 53.1	29.4 ± 8.2	57.7 ± 68.4	10.6 ± 68.4	47.0 ± 96.8	0.26
7	Entella	44.3509°	9.3619°	20/03/2018	286.2 ± 34.5	199.0 ± 35.8	173.9 ± 35.4	25.0 ± 5.1	87.2 ± 49.7	14.9 ± 49.7	72.3 ± 70.2	0.44
7	Entella	44.3513°	9.3618°	15/07/2018	286.2 ± 34.5	299.8 ± 48.8	227.5 ± 46.6	72.3 ± 14.7	-13.6 ± 59.8	-2.3 ± 59.8	-11.3 ± 84.5	-0.05
8	Scrivia	44.71943°	8.8602°	18/03/2018	710.2 ± 125.9	704.7 ± 436.1	694.5 ± 436.1	10.2 ± 6.4	5.5 ± 453.9	3.1 ± 453.9	2.4 ± 642.0	0.01
10	Trebbia	44.9081°	9.5897°	22/03/2018	1171.3 ± 593.6	762.9 ± 270.8	749.3 ± 270.8	13.6 ± 4.9	408.4 ± 652.5	245.2 ± 652.5	163.2 ± 922.7	0.54
10	Trebbia	44.90890°	9.5893°	15/07/2018	1171.3 ± 593.6	141.6 ± 39.6	103.7 ± 37.3	37.9 ± 13.6	136.7 ± 594.9	82.1 ± 594.9	54.6 ± 841.3	0.97
11	Nure	44.82832°	9.6173°	15/07/2018	1062.7 ± 193.5	841.6 ± 530.9	818.9 ± 530.7	22.7 ± 14.6	221.1 ± 565.0	148.1 ± 565.0	73.0 ± 799.1	0.26
11	Nure	44.8816°	9.6532°	21/03/2018	1062.7 ± 193.5	1302.8 ± 828.2	1278.6 ± 828.1	24.2 ± 15.6	-240.1 ± 850.5	-160.9 ± 850.5	-79.2 ± 1202.8	-0.18
12	Taro	44.6976°	10.0934°	21/03/2018	1598.0 ± 326.0	1000.3 ± 260.3	985.9 ± 260.3	14.4 ± 3.8	597.6 ± 417.2	378.9 ± 417.2	218.7 ± 590.0	0.60
12	Taro	44.6975°	10.0936°	15/07/2018	1598.0 ± 326.0	814.0 ± 211.0	789.3 ± 210.9	24.8 ± 6.4	783.9 ± 388.3	497.0 ± 388.3	286.9 ± 549.1	0.96
13	Baganza	44.6045°	10.1202°	15/07/2018	726.1 ± 288.9	1165.5 ± 420.2	1140.5 ± 420.1	25.0 ± 9.1	-439.4 ± 509.9	-338.3 ± 509.9	-101.1 ± 721.1	-0.38
13	Baganza	44.6061°	10.1226°	21/03/2018	726.1 ± 288.9	1432.4 ± 520.1	1419.6 ± 520.1	12.8 ± 4.6	-706.3 ± 594.9	-543.8 ± 594.9	-162.4 ± 841.3	-0.49
14	Parma	44.5688°	10.23709°	15/07/2018	1139.5 ± 201.4	1345.9 ± 323.0	1311.0 ± 322.9	34.9 ± 8.3	-206.4 ± 380.7	-147.3 ± 380.7	-59.0 ± 538.4	-0.15
15	Enza	44.6267°	10.4133°	15/07/2018	1317.1 ± 328.6	1108.2 ± 245.9	1066.3 ± 245.7	41.9 ± 9.1	208.8 ± 410.4	125.1 ± 410.4	83.8 ± 580.4	0.19
17	Panaro	44.41981°	10.9245°	15/07/2018	789.7 ± 120.6	391.3 ± 87.2	367.5 ± 87.1	23.8 ± 5.3	398.4 ± 148.8	151.6 ± 148.8	246.8 ± 210.5	1.02
18	Reno	44.3380°	11.2125°	01/05/2017	1539.7 ± 304.8	168.0 ± 55.4	154.0 ± 55.2	14.0 ± 4.9	1371.7 ± 309.8	491.1 ± 309.8	880.5 ± 438.1	8.16
18	Reno	44.3622°	11.2573°	03/05/2017	2226.0 ± 924.9	371.2 ± 121.3	336.2 ± 120.7	35.0 ± 12.4	1854.8 ± 932.8	664.1 ± 932.8	1190.7 ± 1319.1	5.00
19	Senio	44.2266°	11.6324°	15/07/2018	1269.4 ± 265.0	349.0 ± 137.5	314.4 ± 136.7	34.7 ± 15.0	920.3 ± 298.6	232.8 ± 298.6	687.5 ± 422.2	2.64
20	Lamone	44.0651°	11.6009°	15/07/2018	821.5 ± 94.1	514.3 ± 166.9	488.5 ± 166.7	25.9 ± 8.8	307.2 ± 191.6	64.7 ± 191.6	242.5 ± 271.0	0.60
21	Montone	44.1210°	11.8853°	15/07/2018	1545.0 ± 295.5	269.8 ± 101.0	251.1 ± 100.7	18.7 ± 7.5	1275.1 ± 312.3	540.6 ± 312.3	734.6 ± 441.6	4.73

D = Denudation flux (physical erosion + chemical weathering); W_{Total}^* = total weathering zone flux; W_{Carb}^* = carbonate weathering zone flux; W_{Sil}^* = silicate weathering zone flux; E_{Total}^* = total physical erosion flux; E_{Carb}^* = carbonate physical erosion flux; E_{Sil}^* = silicate physical erosion flux.

Figure 10. Denudation fluxes plotted against (a) TDS_{Total}^* and (b) TDS_{Carb}^* . Linear regressions in (a) and (b) apply only to oversaturated Other Units samples. (c and d) TDS_{Carb}^* plotted against (c) percent catchment area covered by the ExtL and (d) percent carbonate sand. Linear regression (dashed line), R^2 statistic, and p -value are for the entire data set. For all panels, samples draining the ExtL are distinguished from samples draining Other Units. No correction to TDS_{Total} or TDS_{Carb} was made for samples overlaid with an “x.”

ical fluxes back into a physical flux. To estimate this effect, we quantify the flux of calcium initially weathered from carbonate that has been converted back to solid grains (i.e., the secondary calcium erosion flux) for each catchment, by assuming that the difference between $[Ca^{2+*}]$ and $[Ca^{2+}]$ represents re-precipitation of calcium carbonate (Table 3). The solid calcium fluxes vary from 0 to 494 t/km²/yr, and represent 0%–68% of the total denudation flux (Table 3), with median and average values of 14% and 18%, respectively. Moreover, the fraction of carbonate sand grains across the study area correlates well with the fraction of secondary calcium in the total denudation flux (Figure S7). These data suggest that the variation of carbonate physical erosion can be closely tied to the chemical dissolution and re-precipitation of carbonate. If we calculate the flux of secondary calcium carbonate (i.e., $CaCO_3$) instead of secondary calcium, we find that the inferred flux of sediments exceeds the total denudation fluxes (estimated with ¹⁰Be) for some rivers (Table 3, Figure S7), suggesting that we are either overestimating secondary carbonate precipitation or underestimating the total denudation flux.

Thus far, we have assumed that carbonic acid is the primary weathering agent in the Northern Apennines. Sulfuric acid sourced from the oxidation of sulfide minerals is an important additional source of acidity in a number of mountain ranges (Bufe et al., 2021; Calmels et al., 2007; Emberson et al., 2016; Torres et al., 2016) and a source of dissolved sulfate (SO_4^{2-}). The production of sulfuric acid has been observed in a number of caves in northern and central Italy, and has been associated with sulfate reduction of Triassic gypsum/anhydrite deposits (Angeli et al., 2019). This sulfuric acid could surface either through connections between karst springs and river channels (Chiesi et al., 2010) or by faulting (Angeli et al., 2019). Further, minor pyrite in sedimentary units could be a source of sulfuric acid (Cortecchi et al., 2008). Quantifying the contribution of sulfuric acid to weathering in the northern Apennines would require constraining evaporite

Table 3
Secondary Calcium Fluxes and Comparison With Total Denudation Fluxes

River number	River name	Sample	Latitude	Longitude	Sampling date	[Ca ²⁺] lost to secondary precipitation (μmol/L)	Solid flux of calcium (t/km ² /yr)	Percent of total denudation flux	Solid flux of CaCO ₃ (t/km ² /yr)	Percent of total denudation flux
2	Lima	2	43.9993°	10.5538°	15/07/2018	2172.8 ± 196.3	107.0 ± 40.0	21	267.2 ± 100.0	140
4	Serchio Filicaia	1	44.1374°	10.3741°	15/07/2018	2372.8 ± 236.3	54.1 ± 20.1	11	135.0 ± 50.2	170
5	Magra	1	44.1869°	9.9256°	20/03/2018	0	0	0	0	0
6	Vara	1	44.1897°	9.8578°	20/03/2018	0	0	0	0	0
6	Vara	2	44.1919°	9.8584°	15/07/2018	0	0	0	0	68
7	Entella	1	44.3509°	9.3619°	20/03/2018	0	0	0	0	43
7	Entella	2	44.3513°	9.3618°	15/07/2018	0	0	0	0	53
8	Scrivia	1	44.71943°	8.8602°	18/03/2018	9986.6 ± 611.8	233.7 ± 146.9	33	583.5 ± 366.8	0
10	Trebbia	1	44.9081°	9.5897°	22/03/2018	7306.3 ± 482.5	241.5 ± 87.7	21	603.0 ± 219.1	13
10	Trebbia	2	44.90890°	9.5893°	15/07/2018	0	0	0	0	62
11	Nure	0	44.82832°	9.6173°	15/07/2018	8414.6 ± 602.1	262.9 ± 170.7	25	656.6 ± 426.3	102
11	Nure	1	44.8816°	9.6532°	21/03/2018	13827.0 ± 871.7	432.0 ± 280.1	41	1078.9 ± 699.6	31
12	Taro	1	44.6976°	10.0934°	21/03/2018	9643.1 ± 568.7	325.8 ± 86.6	20	813.7 ± 216.4	100
12	Taro	2	44.6975°	10.0936°	15/07/2018	7519.4 ± 587.0	254.1 ± 68.8	16	634.5 ± 171.8	4
13	Baganza	0	44.6045°	10.1202°	15/07/2018	14284.9 ± 1075.7	407.2 ± 150.5	56	1016.9 ± 375.8	10
13	Baganza	5	44.6061°	10.1226°	21/03/2018	17328.8 ± 1119.9	494.0 ± 181.5	68	1233.6 ± 453.4	82
14	Parma	1	44.5688°	10.23709°	15/07/2018	11314.6 ± 820.2	458.4 ± 113.9	40	1144.7 ± 284.3	17
15	Enza	1	44.6267°	10.4133°	15/07/2018	9202.0 ± 837.4	358.5 ± 84.2	27	895.3 ± 210.4	26
17	Panaro	1	44.41981°	10.9245°	04/07/2017	3141.1 ± 364.0	98.7 ± 24.8	12	246.4 ± 61.9	51
18	Reno	5	44.3380°	11.2125°	01/05/2017	1017.6 ± 133.6	27.3 ± 10.3	2	68.3 ± 25.8	40
18	Reno	12	44.3622°	11.2573°	03/05/2017	3432.3 ± 299.1	92.2 ± 33.6	4	230.3 ± 83.9	51
19	Senio	1	44.2266°	11.6324°	15/07/2018	4129.2 ± 338.9	87.0 ± 38.2	7	217.2 ± 95.3	0
20	Lamone	2	44.0651°	11.6009°	15/07/2018	5307.0 ± 347.9	142.8 ± 49.1	17	356.5 ± 122.6	0
21	Montone	1	44.1210°	11.8853°	15/07/2018	5962.5 ± 396.5	77.4 ± 31.2	5	193.4 ± 78.0	0

contributions to sulfate using sulfur isotopes. Because [SO₄²⁻] are, for the most part, more than an order of magnitude lower than TDS_{carb}* (Figure 11b), sulfuric acid cannot be the dominant control on carbonate weathering in the Northern Apennines, although the moderate correlation between dissolved sulfate and TDS_{carb}* in non-ExtL catchments suggests a potential contribution of sulfuric acid to carbonate weathering in these catchments.

5.2.3. Carbonate Weathering and Precipitation Pathways in the Northern Apennines

Here, we summarize the preceding discussion in the context of (1) where carbonate weathering and secondary precipitation occur in the landscape, and (2) the limits on carbonate weathering across the landscape (Figure 12). The SWZ is composed of mixed carbonate-siliciclastic bedrock and the overlying sediment and soil. Here, for simplicity, we illustrate only the pathways for carbonate sediments in this landscape. Solute compositions in soil waters correspond to the concentrations adjusted for secondary precipitation—the SWZ conditions. In the SWZ, plant and microbial respiration (white arrows) produce soil CO₂, which interacts with soil water to form carbonic acid (Romero-Mujalli et al., 2018). High pCO₂ in the soil water (full conical flask symbols) allows a relatively large volume of carbonate to be dissolved in the SWZ, although, based on the presence of primary calcite grains, it is still insufficient to dissolve the abundant supply of carbonate in Northern Apennine rivers (Figures 10b–10d).

Figure 11. (a) Runoff plotted against $\text{TDS}_{\text{Carb}}^*$ and (b) $[\text{SO}_4^{2-}]$ plotted against $\text{TDS}_{\text{Carb}}^*$. Linear regressions refer to samples from Other Units (all cyan circles).

The dissolution of carbonate rock produces HCO_3^- and Ca^{2+} ions, which are discharged to rivers (blue arrows). Here, CO_2 -charged soil water equilibrates with atmospheric $p\text{CO}_2$ by degassing excess CO_2 (black gradient arrows). This loss of acidity and subsequent pH increase leads to supersaturation of the water with respect to carbonate. Carbonate is thus re-precipitated in the river channel (dashed gray arrows), particularly along steep sections of the river channel with highly turbulent flow (e.g., waterfalls or catch dams). As a result, the river sediments in the channel are a mix of primary carbonate grains (gray sediment in river channel) and secondary carbonate grains (white sediment in river channel). Given the large initial weathering fluxes and secondary carbonate erosion fluxes that we calculate, it may even be that much of the secondary carbonate precipitation occurs within the SWZ, which is supported by the presence of pedogenic carbonate observed in older soils developed on terrace deposits in the Reno River (No. 18) (Eppes

Figure 12. Schematic of weathering pathways in the Northern Apennines, illustrating the locations of carbonate weathering and re-precipitation processes in the subsurface and at the surface, respectively. E/W numbers refer to calculated ratios of erosion to weathering at different points on the landscape, dependent upon the degree to which carbonate has been re-precipitated between initial dissolution and export from the mountain front.

et al., 2008). This precipitation would presumably occur before entering the river channel, and imply that there are large dissolution and re-precipitation fluxes within the SWZ. Such fluxes would concentrate Sr/Ca in soil waters and imply that the SWZ has far more dynamic dissolution and re-precipitation fluxes than previously suspected for carbonate-rich landscapes.

The initial dissolution and subsequent re-precipitation of carbonate grains results in a decoupling between the limits on the dissolved carbonate flux in soil waters and in river waters. In the SWZ, carbonate weathering is most likely limited by the $p\text{CO}_2$ of soils. Comparing the ExtL and other units, differences in acid availability may reflect differences in temperature (Gaillardet et al., 2018), primary porosity (Brook et al., 1983), agricultural practices (Raich & Schlesinger, 1992), or vegetation (Calmels et al., 2014). We also cannot entirely exclude dilution as a control on carbonate weathering in non-ExtL units, although the SI values for our rivers suggest dilution is not a control on riverine ion fluxes. The magnitude and importance of weathering within the SWZ is further illustrated by the ratio of erosion to weathering fluxes ($E/W = 1.3$), as reflected in the weathering zones fluxes.

Once solutes are discharged to streams, the total export of $[\text{Ca}^{2+}]$ becomes limited by acid availability in the stream, due to equilibration with atmospheric $p\text{CO}_2$. Thus, the export of $[\text{Ca}^{2+}]$ becomes decoupled from the processes in the SWZ and will instead be limited by rates of in-stream CO_2 degassing and secondary precipitation of carbonate, with the ultimate limit being set by the $p\text{CO}_2$ in the atmosphere and the quantity of organic matter re-mineralized in river water. The grains and travertine deposits that are newly formed by secondary carbonate once again join the physical denudation flux and the export of sediment from mountains. Additional dissolution may occur downstream in floodplains when undersaturated floodplain waters interact with oversaturated mountain streams. Samples collected from mountain streams will reflect the erosion to weathering ratios ($E/W = 6$) of our exported fluxes. We surmise that upstream reaches of the river could have lower ratios in between those calculated for the SWZ ($E/W = 1$) and for exported river fluxes, whereas, at the orogen front, E/W ratios will be even higher, given the importance of secondary carbonate physical erosion in this landscape. Thus, the processes of secondary precipitation and dissolution provide a bridge between physical and chemical erosion of carbonate rock that has to be considered in order to quantify the coupling between mountain uplift and denudation.

5.3. Geologic Carbon Cycle Implications

Our findings provide a more detailed look at how carbonate weathering occurs across an erosion-rate gradient in such mixed lithology ranges. Though carbonate weathering has no direct, long-term influence on the inventory of carbon in the ocean-atmosphere system, carbonate weathering does supply phosphorus to the ocean (Hartmann et al., 2014) and can further influence the long-term carbon isotope composition of oceanic DIC (Shields & Mills, 2017). Previous workers who have modeled carbonate weathering and its impact on the geological carbon cycle have largely assumed that carbonate weathering scales with erosion (Caves Rugenstein et al., 2019; Lenton et al., 2018; Shields & Mills, 2017). In contrast, our data suggest that the export of carbonate-derived solutes (such as Ca^{2+} and HCO_3^-) from mixed-lithology mountain ranges is not correlated with erosion and is decoupled from dissolution fluxes in the SWZ. While SWZ fluxes are partly controlled by the supply of material (i.e., uplift), the export of these solutes to the ocean is instead limited by the acid-carrying capacity of the streams and rivers that drain mountains. Such acid-carrying capacity is likely to be influenced by a range of other factors partly independent of uplift, including roughness of the terrain, climate and therefore productivity of the local vegetation, and possibly even by the atmospheric $p\text{CO}_2$. As a consequence, geological carbon cycle models that scale carbonate weathering with uplift and erosion may further be overestimating the degree to which weathering of carbonate contributes Ca^{2+} and HCO_3^- to the ocean, and therefore the degree to which carbonate weathering can independently modify the carbon isotope signature of seawater (cf Shields & Mills, 2017). Interestingly, sulfuric-acid mediated carbonate weathering works to short-circuit the acid limitation in streams, thereby more tightly coupling carbonate weathering to SWZ conditions and possibly explaining why some datasets of carbonate weathering do show a pronounced coupling between carbonate weathering and erosion (cf Bufe et al., 2021).

6. Conclusions

In this study, we partition denudation fluxes into physical erosion and chemical weathering fluxes for both carbonates and silicates, in an orogenic setting with mixed siliciclastic-carbonate lithologies. Physical erosion dominates the denudation fluxes, and the proportion of carbonate and silicate in the physical erosion flux is apparently controlled, to first order, by the composition of the bedrock. In contrast, carbonate weathering fluxes dominate the total weathering signal irrespective of the lithology, although the exposure of the External Ligurian Unit in catchments appears to systematically raise carbonate weathering in the SWZ.

Relative to other orogens, the ratio of erosion to total weathering (E/W) is smaller in the Northern Apennines, due to generally higher total weathering fluxes. In the Northern Apennines, carbonate weathering represents an important component of the total weathering flux, and secondary calcite precipitation is ubiquitous. This process converts dissolved riverine solutes back into solid carbonate, and we estimate that 20%–90% of $[Ca^{2+}]$ is lost to precipitation of secondary calcite.

We conclude that the controls on carbonate weathering vary across the landscape. In the SWZ, carbonate weathering appears to be limited by the partial pressure of CO_2 in soils, but the discharge of waters to rivers and the equilibration with atmospheric pCO_2 fundamentally alter this limit. In rivers, the concentration of dissolved carbonates becomes limited instead by the rates of CO_2 degassing and secondary carbonate precipitation. As a consequence, the exported volume of solutes from mountain catchments becomes, at least in part, decoupled from subsurface weathering-zone processes.

The results from this study advance our understanding of denudational processes in a young mountain range that typifies the initial stages of orogenesis. We have shown that understanding the weathering and erosional processes of carbonate in an acid-limited landscape requires quantifying both the primary processes responsible for carbonate erosion and weathering, as well as the secondary processes responsible for the re-precipitation of carbonates and re-introduction of physical carbonate into the river channels. Finally, our results suggest that geological carbon cycle models that scale carbonate weathering with uplift and erosion may further be overestimating the contribution of Ca^{2+} and HCO_3^- to the ocean due to erosion-driven carbonate weathering.

Conflict of Interest

The authors declare no conflicts of interest with respect to the results of this paper.

Data Availability Statement

Water chemistry measurements and other supporting material to this manuscript can be found in the supporting material. The ^{10}Be catchment-averaged denudation rate data (Erlanger, 2020) that support the findings of this study are openly available in the ETH Zürich Research Collection “Erosion and weathering of the Northern Apennines with implications for the tectonic and kinematics of the orogen” at <https://doi.org/10.3929/ethz-b-000393261>.

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