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Ultramafic weathering in tropical volcanic arcs: Geochemistry and inverse modeling of rivers draining the Zambales Ophiolite Complex (ZOC), Philippines

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Abstract

Mafic and ultramafic rocks are highly susceptible to silicate weathering, a key negative feedback which modulates atmospheric CO₂ over geological timescales. The tectonic exposure of these reactive lithologies, such as the Neogene uplift of the volcanic islands in maritime Southeast Asia, has been hypothesized to enhance this global feedback and contribute to long-term global cooling. However, the extent of its contribution is not clearly expressed in marine radiogenic strontium isotopic records. Evaluating this hypothesis motivates improving constraints on solute fluxes across the geologically complex region to refine interpretations of geochemical proxies for weathering. This work characterizes the silicate weathering process in the Zambales Ophiolite Complex (ZOC), Philippines using an updated geochemical dataset of major ions (Ca²⁺, Mg²⁺, Na⁺, Cl⁻) and ⁸⁷Sr/⁸⁶Sr, combining published data with new measurements of water, soil, and rocks collected from three sampling campaigns covering wet and dry seasons across 25 catchments. We employ inversion modeling to partition river geochemistry, explicitly accounting for lithological

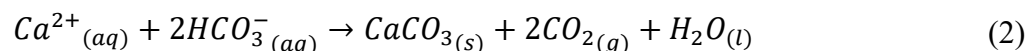
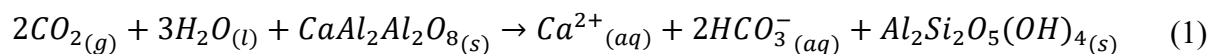
complexity and incorporating $^{87}\text{Sr}/^{86}\text{Sr}$ data and clay formation as a solute sink. Sensitivity analysis shows that the incorporation of these constraints substantially influences the calculated contributions of sources to the overall weathering flux. This approach yields a long-term silicate weathering-derived CO_2 consumption of $2.15 \times 10^6 \text{ mol CO}_2 \text{ km}^{-2} \text{ yr}^{-1} \pm 25.77\% (1\sigma)$ in the ZOC, significantly higher than global average. While adopting a more conservative framework returned an estimate lower than previous studies, it reinforces the disproportionately high area-normalized weathering fluxes from the ZOC. Principal component analysis additionally shows association between CO_2 consumption and watershed features related to topography and runoff. Combining our calculations with published data, we estimate that SEA, despite occupying <2% of the Earth's continental surface, accounts for approximately 7.6% of the global silicate weathering budget. This regional CO_2 consumption per unit area corresponds to approximately four times the global continental average. Further, several altered ultramafic samples exhibit higher $^{87}\text{Sr}/^{86}\text{Sr}$ values than expected for mantle-derived material, a signature also expressed in a subset of river water samples. Compiling published data for mafic and ultramafic rocks across the region also show a considerable range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.702-0.709). These findings highlight the importance of incorporating the geochemical variability of mafic and ultramafic bedrocks in inversion models to estimate weathering fluxes and motivates further work on investigating its influence on marine isotopic records to better understand the role of SEA in the evolution of the global carbon cycle.

Keywords

Silicate weathering, geochemical inversion, Southeast Asia, river geochemistry, CO_2 consumption

1. Introduction

The regulation of atmospheric CO₂ over geological timescales has been primarily attributed to the chemical weathering of silicates, which balances the CO₂ released from solid Earth degassing and stabilizes climate through negative feedbacks within the Earth's surface (Berner et al., 1983; Berner & Caldeira, 1997; Lovelock & Whitfield, 1982; Walker et al., 1981). This process involves the drawdown of CO₂ via the dissolution of silicate rocks, transforming carbon into bicarbonate (HCO₃⁻), the dominant form of alkalinity in natural water systems. Bicarbonate ions are subsequently transported to the ocean through river systems, where it precipitates as primarily Ca- and Mg-carbonate minerals that are ultimately buried in marine sediments (Eqs. 1 and 2).



The concept of these reactions as a climate-regulating mechanism was first proposed by Ebelmen (1845) and later formalized by Urey (1952). Since then, this process has served as a fundamental component in many modern geological carbon cycle models (e.g., Berner, 1994; Berner and Kothavala, 2001; Godd  ris et al., 2008; Li and Elderfield, 2013; Mills et al., 2014, 2019; Lenton et al., 2018; Zhang and Planavsky, 2019; Park et al., 2020; Kukla et al., 2023).

While ongoing research continues to explore other substantial carbon fluxes, giving rise to an expanding view of the geological carbon cycle beyond the simplified balance between weathering and degassing (e.g., Torres et al., 2014, 2017; Hilton and West, 2020; Murray and Jagoutz, 2024; Mu  oz et al., 2024, 2026), accurately constraining modern silicate weathering rates remains a challenge. Global CO₂ consumption from silicate weathering is estimated to range from 11.7 to 12.6 x 10¹² mol C/yr (Meybeck, 1987; Gaillardet et al., 1999; Hartmann et al., 2009; Moon

et al., 2014). These estimates were calculated by partitioning silicate weathering-derived Ca^{2+} and Mg^{2+} fluxes from the geochemical matrix of major global rivers, and in the case of Hartmann et al. (2009), determined by a forward model that uses surface lithology and runoff as inputs. However, estimates based on large watersheds integrate geochemical signals from a wide range of lithologies and climate types, obscuring the individual impact of factors such as rock type, topography, and hydrological regimes (Gaillardet et al., 1999; Moon et al., 2014).

The mafic and ultramafic lithologies that characterize volcanic arcs and oceanic islands have been suggested to disproportionately contribute to global silicate weathering (Dessert et al., 2003; Gaillardet et al., 1999, 2011; Hartmann et al., 2009; Schopka et al., 2011; Moon et al., 2014). Despite occupying <5% of the continental surface area (Dupré et al., 2003), tropical oceanic islands and volcanic arcs are estimated to account for 25–35% of the annual global CO_2 consumption associated with silicate weathering (Dessert et al., 2003; Gaillardet et al., 1999, 2011; Hartmann et al., 2009; Moon et al., 2014). This large contribution is attributed to a combination of steep topography, high precipitation and temperature, and highly reactive lithologies (Bluth and Kump, 1994; Dessert et al., 2003; Gaillardet et al., 2011; Ibarra et al., 2016).

However, substantial uncertainties remain in quantifying solute fluxes; in river geochemical approaches, uncertainties stem partly from the accurate partitioning of solutes generated by silicate weathering from those contributed by carbonate weathering and other physical processes (Moon et al., 2014; Hagedorn and Whittier, 2015; Torres et al., 2017). Geochemical observations remain sparse, particularly on the isotopic signature of rivers that drain mafic and ultramafic areas (Gaillardet et al., 2011; Hartmann et al., 2009). This is despite the wide use of isotopes such as strontium (Bain and Bacon, 1994; Bataille and Bowen, 2012; Su et al., 2021; Luo et al., 2024) and lithium (Pistiner and Henderson, 2003; Wimpenny et al., 2010; Kang

et al., 2022; Ramos et al., 2025) to trace solute sources, investigate secondary mineral precipitation, and assess weathering intensity across different geological settings.

The impact of these highly reactive landscapes on the evolution of Earth's climate through the coupled effects of tectonics and weathering has been a subject of continued active discussion (Li and Elderfield, 2013; Molnar and Cronin, 2015; Jagoutz et al., 2016; Ibarra et al., 2016; Zhang and Planavsky, 2019; Macdonald et al., 2019; Park et al., 2020; Rugenstein et al., 2021; Bayon et al., 2023; Martin et al., 2023; Chiang et al., 2024; Clift et al., 2024). Within this context, it has been hypothesized that the uplift of the mafic and ultramafic Southeast Asian (SEA) islands during the mid-Miocene substantially enhanced global silicate weathering (Park et al., 2020; Bayon et al., 2023; Chiang et al., 2024; Liu et al., 2026), driving the cooling trend observed in ocean proxy records from ~15 million years ago (Zachos et al., 2001, 2008; Herbert et al., 2016). However, seawater records derived from sediments demonstrate an increasing trend in the long-term strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and osmium ($^{187}\text{Os}/^{188}\text{Os}$) isotope ratios during the same period (DePaolo, 1986; Farrell et al., 1995; Peucker-Ehrenbrink and Ravizza, 2000; McArthur et al., 2001, 2025; Matsumoto et al., 2026), contrary to the decreasing trend that would be expected with an enhanced riverine delivery of unradiogenic mafic and ultramafic sediments from the emergence of SEA (Rugenstein et al., 2021; Zhang & Planavsky, 2019). Many carbon cycle models utilize silicate weathering estimates derived from modern geochemical data, under the assumption that the mechanisms of chemical weathering can be extrapolated from the present to the past (e.g. Jagoutz et al., 2016; Li and Elderfield, 2013; Park et al., 2020; Zhang & Planavsky, 2019). Therefore, constraining modern silicate weathering fluxes from mafic and ultramafic regions is necessary to gain a more accurate understanding of the contributions of these areas to the evolution of the geological carbon cycle.

Motivated by the potential long-term carbon cycle and paleoclimate implications of SEA weathering during the mid-Miocene, the objective of this work is to estimate the dissolved solute export and silicate weathering rates in the Zambales Ophiolite Complex (ZOC), Philippines, one of the best-studied ophiolite exposures in the region. We build upon the work of Schopka, et al. (2011) by presenting a geochemical analysis of an updated riverine solute dataset and applying an inversion model constrained by bulk rock geochemical data to produce improved estimates of silicate weathering-derived solute fluxes. We then examine the broader implications of these findings and their potential contribution to refining estimates of riverine inputs to the marine isotopic budget.

2. Study area

The Philippines, located in Southeast Asia, is an active silicate weathering hotspot based on mineralogical analyses of clay-sized sediments (Liu et al., 2009) and high river solute loads across the archipelago (Asio and Jahn, 2007; Goldsmith, 2009; Schopka et al., 2011; Sangalang et al., 2025). Schopka, et al. (2011) estimated that rivers draining ophiolitic and volcanic bedrocks across the island export $3.89 \pm 0.21 \times 10^6$ mol CO₂/km²/yr from silicate weathering, with rivers from Zambales and Angat ophiolites contributing $3.58 \pm 0.23 \times 10^6$ mol CO₂/km²/yr and those draining volcanic catchments contributing $5.99 \pm 0.64 \times 10^6$ mol CO₂/km²/yr. These rates are approximately 6 to 10 times higher than the global area-normalized average for basaltic landscapes (Dessert et al., 2003; Schopka et al., 2011).

Located on the western seaboard of Luzon (Figure 1a), the Zambales Ophiolite Complex is among the best-exposed and most extensively characterized ophiolite sequences in the region (e.g. Hawkins and Evans, 1983; Yumul and Dimalanta, 1997; Queaño et al., 2017). It spans the

entire Zambales mountain range, running 160 km from north to south and reaching up to 40 km at its widest point (Queaño et al., 2017).

2.1 Geologic setting and history

Detailed geological and petrological characterization of the ZOC, as published in the modern literature, dates back to studies in the early 1980s (Evans, 1983; Hawkins & Evans, 1983; Schweller et al., 1983; Schweller & Karig, 1982), following earlier overviews focused on its chromite deposits (Rossman, 1970; Stoll, 1958). This section provides a brief overview of the geology of ZOC; readers are referred to more recent syntheses for detailed discussions of its geology and emplacement history (Dimalanta et al., 2015; Queaño et al., 2017; Yumul & Dimalanta, 1997; Yumul et al., 2020).

Broadly, the ophiolite complex is comprised of fertile harzburgites and lherzolites, transitional dunite layers, a layered sequence of ultramafic (e.g., clinopyroxenite, wehrlite, websterite) and mafic (e.g., gabbro-norite, norite) cumulates, and basalt underlain by diabasic dikes (Rossman et al., 1989; Yumul, 2004). The complex is divided into three massifs: Masinloc (the northernmost and largest), Cabangan, and San Antonio (Hawkins & Evans, 1983; Geary et al., 1989; Yumul Jr, 1989). The Masinloc Massif is composed of two geochemically distinct blocks, namely Coto and Acoje, which resemble island arc tholeiite characteristics and typical back-arc basin compositions, respectively (Hawkins & Evans, 1983; Rossman et al., 1989). Geochemically, the Cabangan Massif is more akin to the Coto block, while San Antonio is more similar to the Acoje block. The southward displacement of the San Antonio massif from the rest of the Acoje block has been associated with strike-slip faulting (Yumul & Dimalanta, 1997).

Initial studies assigned the ophiolite complex an Eocene age (Fuller et al., 1989; Encarnación et al., 1993), with later dating of cherts in the Acoje block estimated a Late Jurassic to Early Cretaceous age (Queaño et al., 2017). Based on the overlying sedimentary sequences, exposure and presumably active weathering began in the late Oligocene to early Miocene, with final emergence between the Pliocene and Pleistocene (Schweller et al., 1983; Rossman et al., 1989; Queaño et al., 2017). Presently, tectonic activity in the western Philippines is greatly affected by the convergence of the Sundaland block and the Philippine Sea Plate (Queaño et al., 2020; Rangin et al., 1999).

Relatively few studies have characterized the sedimentary lithologies overlying the ZOC, with the most comprehensive mapping focused on its eastern and western sectors (Schweller et al., 1983; Queaño et al., 2017). These studies document heterogeneous sequences of siliciclastic, carbonate, and volcanoclastic rocks containing varying proportions of lithic fragments from the underlying ophiolite. Notable units include the Aksitero Formation, which comprises tuffaceous pelagic limestones interbedded with volcanoclastic turbidites (Schweller et al., 1983), and the western Cabaluan and younger Santa Cruz formations, which similarly contain carbonate and siliciclastic lithologies (Queaño et al., 2017). These sequences provide additional lithologic heterogeneity to the watersheds and represent additional sources of dissolved chemical species.

Mining activities operate in the northern part of the Zambales mountain range, which hosts some of the largest nickel laterite deposits in the Philippines (Mines and Geosciences Bureau, 2020). Recent work by Domingo et al. (2021, 2023) and Aquino et al. (2019, 2022) described the lithology, mineralogy, and sediment production associated with mining activities in the municipality of Santa Cruz (SC, Fig. 1b). Intensive weathering of the ultramafic landscape has resulted in the formation of iron and nickel oxide-rich deposits that overlay a predominantly

harzburgite bedrock with sporadic dunite lenses (Aquino et al., 2019, 2022). In addition, limestone formations have been reported within the Pamalabawan (PMB) River subcatchments, which are less affected by mining activities than the Santa Cruz catchments (Domingo et al., 2021).

2.1. Climatic setting

The study area is classified under Philippine Climate Type I, which is characterized by distinct wet (November to April) and dry (May to October) seasons (Coronas, 1920; Tolentino et al., 2016; Ibarra et al., 2021; Sekhon et al., 2022). Annual rainfall in the Zambales province is 3,551.7 mm, with monthly means ranging from 5.3 mm (January) to 929.1 mm (August) (PAGASA, 2020). The ZOC receives most of its annual precipitation from the southwest Asian monsoon (locally “*habagat*”, represented by arrows in Fig. 1a) that typically prevails from June to October (Wang et al., 2001).

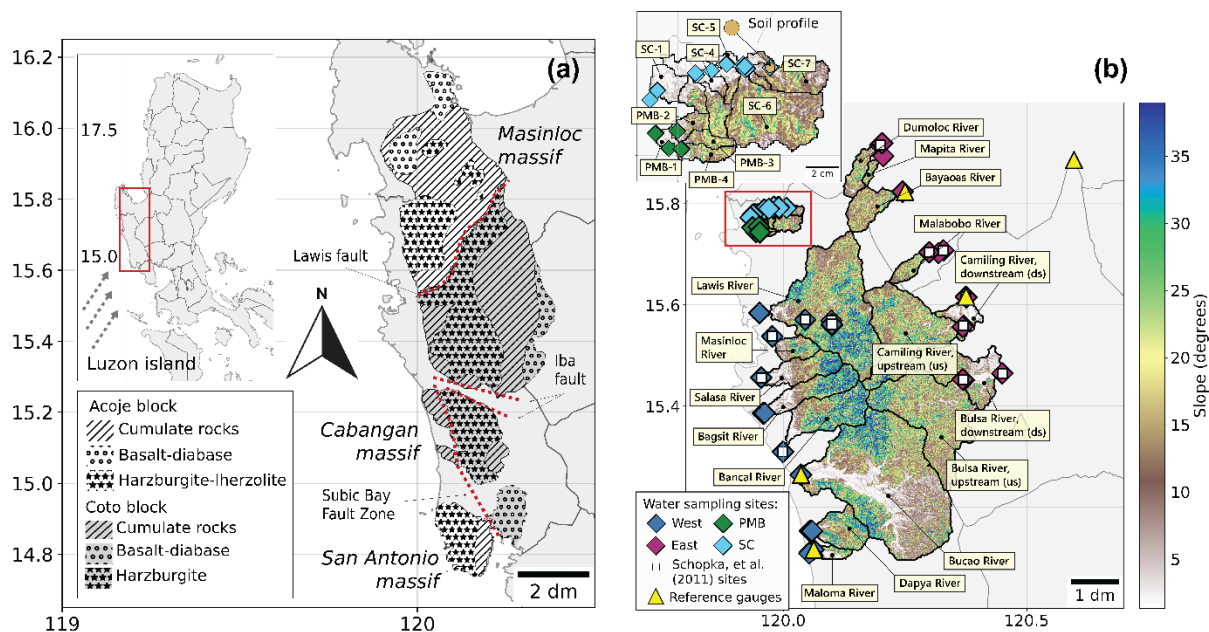


Figure 1. (a) Lithological map of the Zambales Ophiolite Complex. Inset map shows the Luzon Island. The Zambales Ophiolite Complex (red box) is located in the western seaboard of Luzon. Arrows illustrate the prevailing direction of the Southwest Monsoon. Figure modified from Yumul

et al. (1998), Dimalanta et al. (2015), and Queaño et al. (2017). (b) Stream sampling sites subgrouped into: (1) West, (2) East, (3) Pamalabawan River (PMB), and (4) Santa Cruz River (SC). Triangles mark the location of the gauges where discharge data were extracted. Inset map shows the SC and PMB watersheds (red box in), as well as site where soil samples were taken.

3. Methods

3.1 Field sampling and data

Sampling campaigns were conducted in December 2022 (dry period) and August 2023 and 2024 (wet periods) to supplement published geochemical data (Domingo et al., 2023; Schopka et al., 2011). River water samples were collected from 27 catchments (Figure 1a) during all three sampling periods, whereas most rock and river sediments were collected during August 2023 and 2024 field campaigns. Stream samples were collected from fast-flowing sections and filtered on-site through 0.45 μm PTFE and PES membrane filters and stored in acid-washed polyethylene (HDPE) bottles for cation and $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, and in glass bottles for anion analysis. Additionally, samples for cation analysis were acidified with 7N ultrapure HNO_3 to prevent oxide precipitation. A minimum of approximately 50 mL sample was collected for each parameter and kept refrigerated until analysis. Many of the sites in the larger catchments (Fig. 1a) build on the work of Schopka et al. (2011), while the smaller catchments (PMB and SC, Fig. 1b) are based on the study by Domingo et al. (2021, 2023).

Additionally, approximately 500 grams of soil was collected from an exposed soil profile near the SC catchments. A total of 22 rock samples were taken from 16 locations, with the selection primarily focused on obtaining representative lithologies for felsic, mafic, ultramafic, and carbonate rocks. Visual inspection of the hand samples was consistent with the field classifications,

including green serpentized ultramafic rocks from the mantle sequence, coarse-grained gabbroic rocks from the cumulate sequence, fine-grained basaltic to diabasic rocks from the crustal sequence, and calcite-rich limestones (Table S2). In contrast, the felsic samples (assigned as the high-Na silicate endmember, Section 4.2.1), exhibited greater lithological diversity, ranging from metamorphic rocks to light-colored igneous lithologies. Table 1 provides a summary of the river catchments sampled and their relevant statistics, while Fig. S1 and Table S2 show the locations and descriptions of the rock sample collection and other supplementary information used in this study.

3.2 Laboratory

3.2.1 Major ions and trace elements

Dissolved major cation concentrations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) in stream samples, together with all elemental concentrations in the bulk rock and soil samples, were determined using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) at the Environmental Geochemistry Facility (EGF), Brown University. Dissolved Sr^{2+} and Al^{3+} concentrations were measured using a Thermo Scientific iCAP RQ Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Brown University, while dissolved major anions were analyzed by Ion-Exchange High-Performance Liquid Chromatography (IEX-HPLC) at the EGF and the University of Massachusetts Amherst. Solid samples were prepared following methods adopted from Murray et al., (2000), involving fusion with lithium metaborate (LiBO_2) flux to produce a homogenous glass bead, which was subsequently dissolved in 10% HNO_3 and measured on separate analytical days via ICP-OES

3.2.2 Radiogenic strontium isotope ratios

Prior to strontium isotope ratio determination, rock samples were powdered to $<60\ \mu\text{m}$ grain size and treated with a 1:3 solution of 14M HNO_3 and 28M HF. This was followed by sequential acid digestions with concentrated HNO_3 , HCl, and aqua regia to remove fluorides formed from the initial HF treatment. Samples were dried down in between acid treatment steps; all acid digestions were conducted overnight on a hotplate set to 145°C .

Afterwards, aliquots ($<0.1\ \text{mL}$) of the dissolved rock and stream samples containing 200 ng Sr were evaporated to dryness. The specific aliquot volumes for each sample were determined based on trace metal concentrations analyzed via ICP-MS. Following reconstitution in 3N ultrapure HNO_3 , samples were subjected to chromatographic separation using Sr-selective resin packed micro-columns (Eichrom Sr-Spec). All sample preparations for isotope analysis were done in acid-washed teflon beakers at the Trace Metals Laboratory at Brown University.

Following separation, the eluted samples were analyzed for their $^{87}\text{Sr}/^{86}\text{Sr}$ isotope signature using a Thermo Scientific Neptune Plus Multicollector ICP-MS (Mallick et al., 2023). Samples were introduced to the instrument via an Apex Isotope Ratio (IR) system at an uptake rate of approximately $100\ \mu\text{L}\ \text{min}^{-1}$, with the analysis utilizing H sampler and H skimmer cones. Correction for instrumental mass fractionation used an $^{88}\text{Sr}/^{86}\text{Sr}$ value of 0.1194, with the final data reported relative to the $^{87}\text{Sr}/^{86}\text{Sr}$ of the SRM987 standard (0.71024 ± 0.00001) distributed by the National Institute of Standards and Technology. All isotope ratio measurements were conducted at the Mass Spectrometer Analytical Facility at Brown University (Mallick et al., 2023; Muñoz et al., 2024; Butler et al., 2025).

River	Sample IDs	Catchment area (km ²)	Estimated* annual discharge (m ³ /yr)	Relief** (m)	Mean slope (degrees)	Forest cover (%)**	Barren land cover (%)	Anthropogen ic land cover (%)**	Agricultural land cover (%)**	Open vegetation cover (%)**
<i>Eastern catchments (East)</i>										
Bayaoas River	ZAM-22-06, ZAM-23-06, ZAM-24-06 PH-07-34,	63.84	4.56×10^7	418.46	15.61	29.66	0.07	0.00	0.03	76.81
Bulsa River, ds	ZAM-22-01, ZAM-23-01, ZAM-24-01 PH-08-62,	144.36	2.06×10^8	334.57	12.92	14.52	0.83	1.62	22.48	66.82
Bulsa River, us	ZAM-22-02, ZAM-23-02, ZAM-24-02 PH-08-61,	296.61	4.83×10^8	529.41	17.28	44.96	0.43	0.15	1.76	59.54
Camiling River, ds	ZAM-22-04, ZAM-23-04, ZAM-24-04 PH-07-35,	41.82	3.98×10^7	99.83	5.25	4.33	2.14	5.91	69.52	24.74
Camiling River, us	ZAM-22-03, ZAM-23-03, ZAM-24-03 ZAM-22-29,	257.07	2.71×10^8	774.28	17.88	60.88	0.57	0.13	1.48	43.58
Dapya River	ZAM-23-26, ZAM-24-25 PH-07-37,	77.79	1.47×10^8	415.25	19.64	40.62	0.59	0.55	1.24	64.14
Dumoloc River	ZAM-22-07, ZAM-23-08, ZAM-24-08 PH-07-36, PH-	38.13	2.67×10^7	334.2	14.59	1.63	0.22	0.57	4.66	99.08
Malabobo River	07-39, PH-07- 40, ZAM-22-05, ZAM-23-05, ZAM-24-05 ZAM-22-08,	26.3	2.15×10^7	802.69	16.01	88.40	0.00	0.09	0.61	18.16
Mapita River	ZAM-23-07, ZAM-24-26	11.27	7.84×10^6	285.05	15.6	0.00	0.52	0.00	0.17	104.87

Pamalabawan catchments (PMB)

PMB-1	ZAM-22-09, ZAM-23-09, ZAM-24-13	1.18	1.31×10^6	19.65	2.93	0.00	0.00	1.10	58.64	48.66
PMB-2	ZAM-22-10, ZAM-23-10, ZAM-24-12	3.09	3.35×10^6	93.39	9.62	18.20	0.23	0.00	8.95	81.01
PMB-3	ZAM-22-13, ZAM-23-12, ZAM-24-11	2.57	2.79×10^6	231.35	14.97	15.29	8.56	0.00	0.00	84.54
PMB-4	ZAM-22-11, ZAM-23-13, ZAM-24-09	3.42	3.74×10^6	172.28	12.41	33.57	6.00	0.00	0.67	68.13

Santa Cruz mining catchments (SC)

SC-1	ZAM-22-15, ZAM-23-19, ZAM-24-18	3.96	2.89×10^6	14.04	2.66	0.00	0.00	2.94	66.98	36.33
SC-4	ZAM-22-22, ZAM-23-18, ZAM-24-17	2.04	1.49×10^6	25.98	3.76	0.00	0.00	0.00	73.44	33.48
SC-5	ZAM-22-20, ZAM-23-17	24	2.92×10^6	54.93	5.97	0.00	4.04	0.54	8.58	14.92
SC-6	ZAM-22-17, ZAM-23-15, ZAM-24-15	21.72	1.60×10^7	289.38	13.99	14.83	25.26	0.00	0.00	68.30
SC-7	ZAM-22-16, ZAM-23-16, ZAM-24-16	8.09	5.89×10^6	219.46	11.67	0.60	24.59	0.00	0.00	83.23

Western catchments (West)

Bagsit River	ZAM-22-26, ZAM-23-23, ZAM-24-22	89.35	1.83×10^8	641.85	18.25	52.27	1.75	0.19	8.57	44.66
Bancal River	PH-08-03, ZAM-22-27, ZAM-23-24, ZAM-24-23	128.65	2.63×10^8	655.77	21.88	49.61	0.72	0.03	3.53	52.78
Bucao River	ZAM-22-28, ZAM-23-25, ZAM-24-24	650.85	1.33×10^9	405.13	14.47	16.91	12.16	0.18	2.16	71.72

Lawis River	PH-07-04, PH-07-33, PH-08-05, PH-08-06, PH-08-07, ZAM-22-23, ZAM-23-20, ZAM-24-19	410.16	4.91×10^8	676.12	19.98	72.59	1.34	0.01	0.67	32.79
Maloma River	ZAM-22-30, ZAM-23-27, ZAM-24-26	17.16	3.09×10^7	108.96	12.5	7.19	6.33	0.75	21.94	68.54
Masinloc River	PH-07-05, PH-08-08, ZAM-22-24, ZAM-23-21, ZAM-24-20	40.12	6.12×10^7	461.9	16.2	59.68	0.00	0.00	1.61	46.04
Salasa River	PH-08-04, ZAM-22-25, ZAM-23-22, ZAM-24-21	79.75	1.59×10^8	534.73	15.29	62.85	0.35	0.42	13.99	29.59

**Estimated from nearby gauges via the drainage area ratio method (Hirsch, 1979). See Sections 3.3 and 3.4.2.*

***Land cover data calculated from geospatial data obtained from National Mapping and Resource Information Authority (NAMRIA). See Section 3.3.*

Forest cover = Open + closed forest

Anthropogenic land cover = Built up + fishpond

Agricultural land cover = Annual + perennial crops

Open vegetation cover = Grassland + brush/shrubs

3.2.3 Mineralogy

Mineralogical compositions of rock, soil, and sediment samples were characterized via X-ray diffraction (XRD) using a Rigaku MiniFlex benchtop X-ray diffractometer at Brown University. Samples were powdered to $<40\text{ }\mu\text{m}$ grain size and were analyzed using Cu K α radiation ($\lambda = 1.54059\text{ }\text{\AA}$) operated at 40 kV and 15 mA over a scanning range of $3\text{--}90^\circ 2\theta$, with a step width of 0.01° and scan speed of $0.50^\circ\text{ min}^{-1}$. The resulting diffraction patterns were then processed using the SmartLab Studio II software. Peak signals were identified by fitting reference patterns from the International Centre for Diffraction Data (ICDD) 2024 PDF-2 database (Kabekkodu et al., 2024).

3.3 Geospatial and hydrological data

Sampled catchments were delineated using the 30-m resolution Terra Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) Global Digital Elevation Model (GDEM v3; ASTGTM) (Earth Science Data Systems, 2025). Land cover data (Table 1) was extracted from the geospatial dataset distributed by the National Mapping and Resource Information Authority (NAMRIA) obtained through Geoportal Philippines (<https://geoportal.gov.ph/>). Hydrological information was estimated using publicly available gauge data obtained from the Streamflow Management System maintained by the Philippines' Department of Public Works and Highways (DPWH; <https://apps.dpwh.gov.ph/>), which has been used in previous studies by Tolentino et al. (2016), Ibarra et al. (2021), Sekhon et al. (2022), and Hoey et al. (2025). Given the limited availability of active gauges in the study area, annual and seasonal discharge for the catchments were estimated via the drainage area ratio method (Hirsch, 1979), utilizing long-term (1983 – 2020) records from six nearby gauged rivers (Table S1).

3.4 Principal Component Analysis

Principal Component Analysis (PCA) was used as a dimensionality reduction technique in two aspects of this work. First, PCA was applied to the bulk geochemical data of the rock samples to identify distinct lithological classes as geochemical inversion endmembers (Section 3.5.1.2). Second, PCA was applied to watershed characteristics (Table 1) to identify the environmental factors associated with variations in calculated silicate-derived CO₂ fluxes

3.5 Geochemical mixing model and flux calculations

3.5.1 MEANDIR overview

The partitioning of solute data from each catchment was performed using the Mixing Elements and Dissolved Isotopes in Rivers (MEANDIR), developed by Kemeny and Torres (2021). The MEANDIR algorithm builds on the inversion methods implemented by Négrel et al. (1993) for river geochemical data and later utilized by Gaillardet et al. (1999) and subsequent studies (Mortatti and Probst, 2003; Wu et al., 2005; Tripathy and Singh, 2010). It provides a flexible inversion framework that allows users to identify source and sink endmembers and define constraints on solution convergence. MEANDIR uses Monte Carlo methods to determine uncertainty and arrive at a distribution of fractional contributions from each endmember, with each iteration solved via a cost-function, minimizing the relative error for each solute reconstruction (Kemeny and Torres, 2021). This inversion algorithm was deemed suitable for this work as it allows for defining secondary silicate phase formation and lithological sources without the need for full mineral identification (Kemeny and Torres, 2021; Cole et al., 2022; Muñoz et al., 2024). A more detailed description of the algorithm is provided in Kemeny and Torres (2021).

336 3.5.1.1. Inversion equations

337 Mass balance equations used in geochemical inversions describe the total concentration of
338 dissolved elements as the sum of the contributions from a set of distinct endmembers, typically
339 reported in molar units (Négrel et al., 1993; Kemeny and Torres, 2021). This approach effectively
340 assumes that all major ions participate in the weathering reactions. Equation 1 represents the mass
341 balance of the major ions, whereas Equation 2 incorporates $^{87}\text{Sr}/^{86}\text{Sr}$:

$$\left(\frac{X_i}{\Sigma^+}\right)_{river} = \sum_{j=1}^n f_j \left(\frac{X_i}{\Sigma^+}\right)_j \quad (3)$$

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{river} \left(\frac{[\text{Sr}^{2+}]}{\Sigma^+}\right)_{river} = \sum_{j=1}^n f_j \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_j \left(\frac{[\text{Sr}^{2+}]}{\Sigma^+}\right)_j \quad (4)$$

342 where X_i/Σ^+ is the normalized molar concentration of an element (i) measured in a river water
343 sample (*river*) or is prescribed for a specific endmember (j), f_j is the fractional contribution of
344 endmember j , which may represent a source ($f_j > 0$) or a sink ($f_j < 0$), and n is the number of the
345 defined endmembers.

346 In this work, we adopt the normalization scheme described in Kemeny and Torres (2021)
347 where elemental concentrations are normalized to the unit sum concentration of $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$,
348 and $[\text{Na}^+]$, expressed in μM and represented by Σ^+ . In contrast to normalizing only by $[\text{Na}^+]$ (Négrel
349 et al., 1993; Gaillardet et al., 1999), using the sum of the major cations derived from the weathering
350 reactions allow carbonate, which has close to zero $[\text{Na}^+]$, to be represented stoichiometrically in
351 the inversion. Although this approach does not introduce new information into the inversion, it
352 allows all endmembers to be better represented in the mass balance calculations (cf. Kemeny and
353 Torres, 2021).

354

3.5.1.2. Endmember parametrization and assumptions

Users of MEANDIR define a set of *a priori* distributions of chemical molar ratios for each endmember that represent the major sources and sinks of dissolved riverine solutes. Broadly, the endmembers in this work are defined by mineral weathering and precipitation, both of which represent solute sources, and clay formation as a solute sink mechanism. These choices were based on prior geological work in the study area and geochemical studies that employed similar partitioning approaches (Schopka et al., 2011; Frondini et al., 2019; Kemeny and Torres, 2021; Cole et al., 2022; Harrington et al., 2024; Muñoz et al., 2024). The identification and chemical ratios of the lithological sources were informed by the geochemical and mineralogical analysis of the rocks obtained from field sampling. Additionally, literature data were used to constrain the chemical parameters of the precipitation and clay formation endmembers. A more detailed discussion of the endmember definitions used in the analysis is provided in Section 4.2.1.

The solutes utilized in this work are Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , Si, Sr^{2+} , and $^{87}\text{Sr}/^{86}\text{Sr}$. The major ions (Ca^{2+} , Mg^{2+} , Na^+) were chosen as they are among the main cations released during the dissolution of various rock types, with Na^+ being an important constraint for carbonate minerals where it exists in low concentrations (Négrel et al., 1993; Gaillardet et al., 1999). We excluded K^+ despite its abundance in feldspars as its dissolved concentration is heavily influenced by vegetation (Chaudhuri et al., 2007). However, we included dissolved Si as an additional parameter despite potential biological cycling (Derry et al., 2005) because of its incorporation in clays and demonstrated control on both the rates of primary silicate mineral dissolution and secondary mineral precipitation (Schott et al., 2009; Maher et al., 2009).

Previous geological characterization of the ZOC indicates the dominance of ultramafic and mafic lithologies, with overlying sedimentary and carbonate units (Dimalanta et al., 2015; Queaño

et al., 2017; Yumul & Dimalanta, 1997; Yumul et al., 2020). Accordingly, we assumed that evaporite dissolution is a negligible solute source and that all Cl^- is derived from atmospheric deposition or sea spray, which are represented by the precipitation endmember in our inversion framework. Although sulfide minerals, including those associated with nickel, have been reported in the literature (Rossman, 1970; Abrajano et al., 1989; Yumul and Dimalanta, 1997), their occurrence appears to be localized and does not substantially influence river chemistry based on the measured basic pH and relatively low $[\text{SO}_4^{3-}]$ values of our samples (Table 1). We therefore excluded pyrite oxidation as an additional endmember despite its importance in the geological carbon cycle (Torres et al., 2014; Kemeny et al., 2021). Consequently, we did not include SO_4^{3-} data in the inversions because we assume it is primarily derived from atmospheric deposition and not representative of a lithological endmember.

3.5.1.3 Inversion scenarios and solution parameters

Three inversion scenarios were constructed to estimate the fractional contributions of each endmember to the dissolved geochemistry of the river samples and evaluate the sensitivity of the inversion framework (Table 2). Consequently, samples without $[\text{Sr}^{2+}]$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data were not utilized in the scenarios that require them. We also excluded samples whose total charge equivalents for Cl^- and SO_4^{3-} exceed those of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ (PH-08-03, PH-08-08, ZAM-22-15, ZAM-23-24; Table 3). This charge imbalance likely reflects significant marine or anthropogenic inputs that could obscure lithological signals, although analytical artifacts cannot be ruled out.

Initially, each inversion scenario was solved for up to 200,000 simulations, from which 400 successful realizations were retained for analysis. Initial test runs indicated that this number was sufficient to produce stable and representative results. We defined a successful simulation

when the reconstructed geochemistry of each sample was within 85% to 115% of the observed concentration for each solute, and within ± 0.002 of the reported $^{87}\text{Sr}/^{86}\text{Sr}$ (Cole et al., 2022; Muñoz et al., 2024). Five samples (ZAM-23-19, ZAM-23-20, ZAM-23-21, ZAM-24-18, ZAM-24-23) initially yielded fewer than 200 successful simulations for the full geochemical scenario and were therefore ran for a maximum 2.5×10^6 simulations. The increased number of simulations eventually yielded 400 successful realizations. One sample (ZAM-23-25) did not yield any successful result across all inversion scenarios, regardless of the number of simulations conducted. Given the lack of a feasible solution, this sample was omitted from the calculation of solute fluxes.

To maintain the internal consistency of the mass balance calculations, a representative solute was assigned to each endmember. The representative solute was chosen as the one expected to receive the largest contribution from a corresponding endmember (e.g., Ca^{2+} for the carbonate endmember). The median values obtained from each inversion scenario were used to represent the resulting distributions, with the 25th and 75th percentiles taken as the inversion error for each estimated fractional contribution. The output fractions (median, 25th and 75th percentiles) and input scenario parameters to MEANDIR are provided as separate files in an online repository (Custado, 2026).

Table 2. Inversion scenarios tested. Endmember definitions are discussed in Section 4.2.

Inversion scenario	Purpose	Chemical species and endmembers
Full scenario	Partition endmember contributions	Full suite of chemical species and endmembers
Alternate scenario 1*	Test sensitivity to clay endmember	All chemical species excluding Si; all endmembers excluding clay
Alternate scenario 2	Test sensitivity to $^{87}\text{Sr}/^{86}\text{Sr}$	Full suite of endmembers; all chemical species excluding Sr^{2+} and $^{87}\text{Sr}/^{86}\text{Sr}$

*Solving for mass balance that includes Si without a sink mechanism was computationally intensive and yielded very few successful simulations for many of the samples.

420 3.5.1.4 Inversion-constrained mixing fractions

421 The calculated f values from Eq. 3 were subsequently used to calculate the proportion of
422 the observed solute concentration derived from the identified source endmembers, as well as the
423 fraction of the gross modeled solute input that was taken up by clay formation. In inversion
424 scenarios that include clay formation, which represents the sink mechanism, mass balance
425 calculations will allow the sum of raw f coefficients corresponding to source endmembers to be
426 greater than one. The excess is then offset by the negative f value calculated for the clay
427 endmember (f_{clay}):

$$\sum f_{j+} + f_{clay} = 1 \quad (5)$$

428
429 where j^+ represents the source endmembers, whose corresponding f coefficients are positive, while
430 f_{clay} is negative.

431 Therefore, to facilitate comparison across seasons and watersheds, the f value for each
432 source endmember were normalized to the sum of all positive f coefficients ($\sum f_{j+}$) such that:

$$\sum f_{j+, \text{ normalized}} = 1 \quad (6)$$

433
434 where $f_{j+, \text{ normalized}}$ is equal to $f_{j+} / \sum f_{j+}$.

435 Meanwhile, the raw f_{clay} coefficient was normalized by the same positive sum to represent
436 the fraction of gross modeled solutes from the source endmembers that are removed by clay
437 formation. This normalization is represented by the following equation (Cole et al., 2022):

$$f_{clay, \text{ normalized}} = -\frac{f_{clay}}{\sum f_{j+}} = -\frac{f_{clay}}{1 - f_{clay}} \quad (7)$$

where f_{clay} is a negative value. The leading negative sign ensures that the normalized f_{clay} is expressed as a positive quantity, representing the fraction of the gross modeled solute input incorporated into secondary mineral phases.

However, it should be noted that these normalization schemes implicitly assume complete reconstruction of the observed solute concentrations. In this analysis, successful inversion results were defined as mass balance calculations that reproduced between 85% and 115% of the observed solute concentrations. Therefore, the normalized f coefficients should be interpreted as approximate mixing fractions, with the inversion error represented by the 25th and 75th percentile f values of the successful simulations (Cole *et al.*, 2022; Kemeny and Torres, 2021; Muñoz *et al.*, 2024).

3.4.2 Discharge estimation and flux calculations

Fig. 2 shows the climatological monthly mean discharge from the six actively gauged rivers used as reference catchments (1983-2020, Table S1). Discharge estimates for each study catchment were based on the three nearest reference gauges, weighed according to their distance from the study catchment. Because records from the reference gauges are discontinuous and may not overlap, some daily estimates are based on fewer than three reference gauges. Daily discharge at each reference gauge were converted to specific discharge values and were combined using discharge-based weights prior to scaling to the drainage area of the study catchment (Hirsch, 1979). Afterwards, the daily estimates were resampled to monthly values by taking the median discharge for each month to reduce the influence of extreme discharge events, therefore are more

representative of long-term, baseline values. Climatological monthly and seasonal mean discharge fluxes were then calculated following the Type I climate classification of the study area, with the wet season defined from May to October and the dry season from November to April. Annual solute fluxes were calculated as the discharge-weighted averages of the solute data available for each season. The estimated Ca^{2+} and Mg^{2+} fluxes were converted stoichiometrically to long-term CO_2 sequestration rates using Equations 1 and 2. This calculation assumes that carbonic acid is the dominant source of protons driving silicate weathering and that contributions from other acids (e.g., sulfuric acid) are negligible.

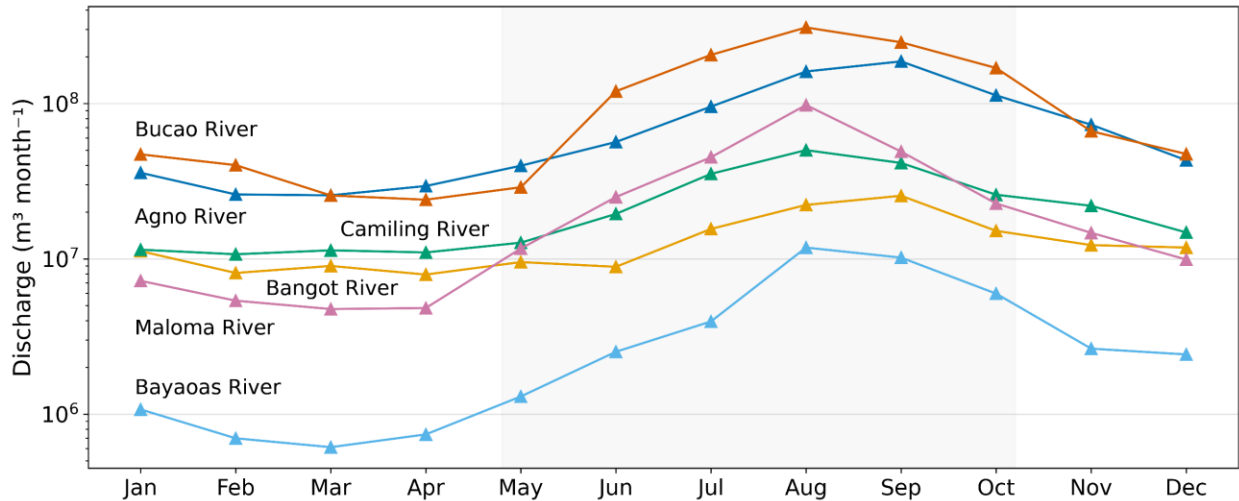


Figure 2. Monthly climatological mean discharge values of the six reference gauges, in m^3/month (1983-2020, Table S1). Shaded area corresponds to the assigned wet season (May to October).

3.4.3 Uncertainties

We adopt the scheme utilized by Schopka et al. (2011) to quantify the uncertainty in the flux calculations, propagating the coefficient of variations (CVs) of the chemical measurements for each solute ($[X]$), annual stream discharge (Q), and watershed area (A). The CVs for the chemical measurements and stream discharge were calculated from the reported data, whereas watershed area uncertainty was assigned following Schopka et al. (2011), who adopted the

476 watershed area CVs reported by Oksanen and Sarjakoski (2005): 24% for watersheds <2 km², 16%
 477 for watersheds between 2 and 22 km², and 3% for watersheds >22 km².

478 The following three equations were used to estimate the uncertainty of different fluxes
 479 calculated using the inversion-constrained fractions for a single catchment (*i*). First, equation 8
 480 estimates the uncertainty of the partitioned solute fluxes (F_c , Eq. 8) attributed to inversion-
 481 constrained endmembers for each catchment. Equation 9 was then used to propagate uncertainty
 482 for fluxes obtained by summing multiple independent components (F_{sum}), such as combined
 483 endmember fluxes (e.g., total silicate-derived fluxes from the ultramafic, low-Na silicate, and
 484 basaltic endmembers) or combined solute fluxes (e.g., the sum of Ca, Mg, and Na fluxes). Here,
 485 $F_{j,i}$ is the *j*-th component flux being summed (either an endmember-specific or solute-specific flux)
 486 for catchment *i*. Equation 10 estimates uncertainties for area-normalized fluxes (F_a) from either
 487 partitioned or summed fluxes.

$$CV_{F_c,i} = \sqrt{CV_{[X]}^2 + CV_{Q_i}^2} \quad (8)$$

$$CV_{F_{sum},i} = \frac{\sqrt{\sum_{n=1}^j (CV_{F_{j,i}} \times F_{j,i})^2}}{\sum_{n=1}^j F_{j,i}} \quad (9)$$

$$CV_{F_a,i} = \sqrt{CV_{F_i}^2 + CV_{A_i}^2} \quad (10)$$

488
 489 Finally, the uncertainties of the aggregated total solute flux (F_t , Eq. 11) and area-
 490 normalized flux (Eq. 12) for the entire ZOC were estimated as the discharge- and area-weighted
 491 CVs, respectively, following Schopka et al. (2011):

$$CV_{F_t,ZOC} = \sqrt{\frac{\sum_{n=1}^i [CV_{F_i}^2 \times Q_i]}{\sum_{n=1}^i Q_i}} \quad (11)$$

$$CV_{Fa,ZOC} = \sqrt{\frac{\sum_{n=1}^i [CV_{Fa,i}^2 \times A_i]}{\sum_{n=1}^i A_i}} \quad (12)$$

492

493

494 3.5 Principal Component Analysis

495 Principal Component Analysis (PCA) was used as a dimensionality reduction technique in
 496 two aspects of this work. First, PCA was applied to the bulk geochemical data of the rock samples
 497 to identify distinct lithological classes as geochemical inversion endmembers (Fig. 5). Second,
 498 PCA was applied to watershed characteristics (Table 1) to identify the environmental factors
 499 associated with variations in calculated silicate-derived CO₂ fluxes.

500
501

Table 3. Summary of chemical parameters for each sample used in the inversion. Data for samples with IDs beginning with ‘PH’ were reported by Schopka et al. (2011). Cation concentrations, except for Sr^{2+} and Al^{3+} , were determined using ICP-OES, whereas Sr^{2+} and Al^{3+} were based on ICP-MS.

Sample ID	Date	Seas	Lat	Lon	Grp	°C	TDS (ppm)	pH	Ca^{2+} (μM)	Mg^{2+} (μM)	Na^{+} (μM)	K^{+} (μM)	Si (μM)	Al^{3+} (nM)	Sr^{2+} (nM)	Cl ⁻ (μM)	SO_4^{3-} (μM)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr} \pm (2\sigma)$
PH-07-04	1/13/2007	Dry	15.569	120.099	West	23.2	146	8.31	94	769	62	2	434	-	-	30	23	-	-
PH-07-05	1/13/2007	Dry	15.538	119.977	West	29.9	236	7.65	277	999	114	6	614	-	911	39	44	0.70802	0.00008
PH-07-33	1/29/2007	Dry	15.569	120.099	West	23.2	154	8.69	63	833	55	2	390	-	137	39	31	0.70383	0.00012
PH-07-34	2/1/2007	Dry	15.452	120.370	East	27.5	237	8.60	500	612	358	10	632	-	600	41	118	0.70433	0.00008
PH-07-35	2/2/2007	Dry	15.559	120.370	East	23.0	249	8.20	460	842	213	5	603	-	423	33	51	0.70394	0.00008
PH-07-36	2/2/2007	Dry	15.708	120.329	East	24.6	253	8.30	546	792	203	7	552	-	467	40	57	0.70381	0.00012
PH-07-37	2/2/2007	Dry	15.916	120.199	East	29.9	332	7.80	698	1,000	294	5	885	-	469	50	73	0.70433	0.00008
PH-07-39	3/5/2007	Dry	15.704	120.300	East	-	267	8.40	589	837	206	4	605	-	464	29	43	0.70383	0.00012
PH-07-40	3/5/2007	Dry	15.704	120.300	East	-	267	8.56	581	842	191	3	614	-	462	23	43	0.70377	0.00012
PH-08-03	1/24/2008	Dry	15.310	119.999	West	30.6	7,390	7.87	2,457	14,062	98199	3276	555	-	19,792	136,752	7,126	0.70904	0.00010
PH-08-04	1/24/2008	Dry	15.456	119.955	West	28.7	198	7.68	222	804	911	36	465	-	-	2,318	158	-	-
PH-08-05	1/25/2008	Dry	15.560	120.100	West	23.3	150	8.10	100	708	61	-	415	-	-	36	28	-	-
PH-08-06	1/25/2008	Dry	15.562	120.100	West	23.6	163	8.13	44	850	51	-	421	-	61	41	33	0.70488	0.00012
PH-08-07	1/25/2008	Dry	15.571	120.045	West	24.9	255	8.03	53	1,291	55	-	729	-	72	38	32	0.70527	0.00012
PH-08-08	1/25/2008	Dry	15.538	119.977	West	32.1	1,234	7.76	648	2,885	13874	482	625	-	3,586	20,185	1,092	0.7089	0.00015
PH-08-61	2/9/2008	Dry	15.616	120.375	East	27.7	279	8.61	488	933	222	7	612	-	-	91	81	-	-
PH-08-62	2/9/2008	Dry	15.465	120.450	East	29.7	262	8.40	486	696	308	13	712	-	-	71	128	-	-
ZAM-22-01	12/17/2022	Dry	15.465	120.450	East	25.4	143	8.38	481	580	327	25	527	-	-	57	81	0.70442	0.00002
ZAM-22-02	12/17/2022	Dry	15.452	120.371	East	26.3	135	8.04	457	572	298	21	562	1,106	498	36	79	0.70434	0.00001
ZAM-22-03	12/17/2022	Dry	15.559	120.370	East	27.4	155	7.90	435	836	215	22	471	342	421	53	55	-	nan
ZAM-22-04	12/17/2022	Dry	15.615	120.376	East	28.8	177	7.83	511	894	258	21	453	2,308	748	95	67	0.70402	0.00002
ZAM-22-05	12/17/2022	Dry	15.704	120.300	East	30.6	160	8.09	560	739	247	18	531	686	1,411	48	37	0.70392	0.00002
ZAM-22-06	12/17/2022	Dry	15.823	120.245	East	32.6	170	8.22	603	793	216	18	746	278	393	66	35	0.70411	0.00002
ZAM-22-07	12/17/2022	Dry	15.918	120.202	East	32.8	198	7.94	756	809	390	21	769	66	608	62	56	0.70442	0.00002
ZAM-22-08	12/17/2022	Dry	15.895	120.205	East	32.3	200	8.05	761	841	298	17	853	468	590	36	64	0.70423	0.00002
ZAM-22-09	12/18/2022	Dry	15.753	119.937	PMB	26.7	302	8.36	815	1,766	165	21	597	435	2,771	102	93	0.70866	0.00001
ZAM-22-10	12/18/2022	Dry	15.754	119.950	PMB	25.9	345	8.32	1,059	1,925	142	19	738	3,737	5,962	83	93	0.70868	0.00001
ZAM-22-11	12/18/2022	Dry	15.743	119.952	PMB	26.6	318	8.73	1,002	1,783	125	27	471	1,601	2,942	98	68	0.70872	0.00001

ZAM-22-12	12/18/2022	Dry	15.744	119.952	PMB	26.4	314	8.52	985	1,797	113	16	560	1,527	2,477	91	62	-	nan
ZAM-22-13	12/18/2022	Dry	15.744	119.952	PMB	25.9	313	9.26	984	1,790	110	16	664	4,013	2,049	93	63	0.70866	0.00001
ZAM-22-15	12/18/2022	Dry	15.779	119.937	SC	29.0	300	8.31	841	3,933	25,145	515	547	13,617	6,427	36,811	1,783	0.70899	0.00001
ZAM-22-16	12/18/2022	Dry	15.791	119.993	SC	30.0	160	8.05	61	1,284	262	19	475	1,242	147	264	29	0.70696	0.00001
ZAM-22-17	12/18/2022	Dry	15.791	119.991	SC	32.3	190	8.61	59	1,662	115	16	547	83	164	104	28	-	nan
ZAM-22-19	12/18/2022	Dry	15.794	119.990	SC	32.1	184	8.54	59	1,570	158	17	524	-	161	157	28	-	nan
ZAM-22-20	12/18/2022	Dry	15.794	119.980	SC	32.1	204	8.53	98	1,661	174	19	605	38	198	111	36	-	nan
ZAM-22-22	12/18/2022	Dry	15.787	119.961	SC	31.1	210	8.44	167	1,648	174	22	575	-	220	110	46	-	nan
ZAM-22-23	12/19/2022	Dry	15.584	119.951	West	25.9	142	8.41	234	996	121	17	488	507	161	52	30	0.70500	0.00002
ZAM-22-24	12/19/2022	Dry	15.538	119.978	West	27.1	144	8.14	227	684	358	141	421	194	1,038	95	53	0.70805	0.00002
ZAM-22-25	12/19/2022	Dry	15.456	119.955	West	28.4	297	7.96	268	1,024	1,505	46	418	6	937	2,322	132	0.70793	0.00001
ZAM-22-26	12/19/2022	Dry	15.386	119.961	West	29.3	140	7.82	161	1,034	126	20	448	5,413	400	59	32	0.70686	0.00001
ZAM-22-27	12/19/2022	Dry	15.309	120.000	West	30.6	6,008	7.36	8,297	42,814	57,167	7,409	3,910	7,187	14,371	90,944	4,302	0.70896	0.00002
ZAM-22-28	12/19/2022	Dry	15.265	120.037	West	31.1	217	7.67	828	851	1,024	87	773	823	2,081	477	1,073	0.70442	0.00001
ZAM-22-29	12/19/2022	Dry	15.154	120.054	West	31.0	752	7.57	335	1,739	6,029	152	674	30,677	79,872	6,875	456	-	nan
ZAM-22-30	12/19/2022	Dry	15.116	120.062	West	32.5	144	7.91	281	860	305	42	761	-	592	92	76	0.70455	0.00001
ZAM-23-01	8/22/2023	Wet	15.465	120.450	East	27.9	88	8.28	459	518	394	30	717	n.d.	2,583	84	n.d.	-	nan
ZAM-23-02	8/22/2023	Wet	15.452	120.369	East	27.5	85	8.53	447	529	355	23	749	8,248	447	57	n.d.	0.70438	0.00001
ZAM-23-03	8/22/2023	Wet	15.559	120.370	East	27.4	83	8.43	380	643	218	18	632	2,057	265	56	n.d.	-	nan
ZAM-23-04	8/22/2023	Wet	15.615	120.376	East	28.4	89	8.49	397	666	225	19	618	588	327	83	n.d.	0.70442	0.00001
ZAM-23-05	8/22/2023	Wet	15.703	120.319	East	28.0	78	8.41	409	526	196	15	601	637	303	58	64	0.70382	0.00001
ZAM-23-06	8/22/2023	Wet	15.824	120.245	East	29.9	104	8.74	574	711	228	16	920	981	338	83	21	0.70411	0.00001
ZAM-23-07	8/22/2023	Wet	15.894	120.205	East	30.7	130	8.39	763	797	346	16	1,061	1,135	534	79	15	0.70418	0.00002
ZAM-23-08	8/22/2023	Wet	15.920	120.204	East	29.7	123	8.34	658	853	313	21	974	8,770	391	111	0.9	0.70441	0.00001
ZAM-23-09	8/23/2023	Wet	15.753	119.936	PMB	27.4	223	8.15	910	1,664	200	20	764	-	2,560	174	0.3	0.70867	0.00001
ZAM-23-10	8/23/2023	Wet	15.754	119.950	PMB	27.1	244	8.25	1,005	1,798	178	28	941	-	2,719	166	3.6	0.70868	0.00001
ZAM-23-11	8/23/2023	Wet	15.744	119.952	PMB	27.5	226	8.36	888	1,613	169	14	628	-	2,552	168	n.d.	-	nan
ZAM-23-12	8/23/2023	Wet	15.744	119.952	PMB	27.1	219	8.45	745	1,840	152	15	956	-	542	158	0.8	0.70859	0.00001
ZAM-23-13	8/23/2023	Wet	15.744	119.952	PMB	27.9	227	8.39	1,084	1,622	176	15	590	-	2,605	133	n.d.	0.70870	0.00001
ZAM-23-14	8/23/2023	Wet	15.794	119.990	SC	33.5	140	8.53	51	1,485	136	15	753	n.d.	132	59	1.9	-	nan
ZAM-23-15	8/23/2023	Wet	15.793	119.991	SC	32.6	139	8.58	48	1,487	132	14	758	-	-	42	0.9	-	nan
ZAM-23-16	8/23/2023	Wet	15.791	119.992	SC	32.3	127	8.53	50	1,283	187	14	657	43	125	20	0.2	0.70627	0.00001

ZAM-23-17	8/23/2023	Wet	15.794	119.980	SC	34.4	144	8.56	62	1,501	165	18	753	-	150	28	0.2	0.70578	0.00001
ZAM-23-18	8/23/2023	Wet	15.789	119.961	SC	33.9	148	8.37	111	1,606	183	19	792	13,775	199	12	0.2	0.70572	0.00001
ZAM-23-19	8/23/2023	Wet	15.778	119.937	SC	30.5	473	8.17	322	1,955	5,692	55	572	11,254	1,339	108	n.d.	0.70879	0.00001
ZAM-23-20	8/24/2023	Wet	15.584	119.951	West	26.6	99	8.27	204	839	152	15	618	192	177	775	n.d.	0.70476	0.00001
ZAM-23-21	8/24/2023	Wet	15.538	119.977	West	26.9	83	8.66	185	643	161	15	524	-	525	745	n.d.	0.70691	
ZAM-23-22	8/24/2023	Wet	15.456	119.955	West	26.3	72	7.89	183	501	194	18	403	-	366	85	47	0.70726	0.00001
ZAM-23-23	8/24/2023	Wet	15.386	119.958	West	26.8	74	8.09	126	611	146	16	431	-	-	15	n.d.	0.70879	
ZAM-23-24	8/24/2023	Wet	15.309	120.000	West	27.7	545	7.90	265	1,448	7,688	25	95	-	1,678	33,102	n.d.	0.70842	
ZAM-23-25	8/24/2023	Wet	15.264	120.036	West	31.1	161	8.38	567	759	562	45	737	918	1,161	3,025	n.d.	0.70478	0.00001
ZAM-23-26	8/24/2023	Wet	15.154	120.055	West	28.9	93	8.11	144	705	88	15	513	296	261	217	n.d.	-	-
ZAM-23-27	8/24/2023	Wet	15.111	120.054	West	31.9	99	7.71	215	686	285	36	764	2,038	485	91	n.d.	0.70470	0.00001
ZAM-24-01	8/13/2024	Wet	15.465	120.450	East	27.0	95	8.06	392	519	295	15	663	695	439	38	28	0.70447	0.00001
ZAM-24-02	8/13/2024	Wet	15.453	120.368	East	26.3	89	8.19	354	500	264	10	640	330	378	34	28	0.70441	0.00001
ZAM-24-03	8/13/2024	Wet	15.557	120.368	East	27.6	99	8.54	352	704	169	7	566	3,411	297	31	21	0.70422	0.00001
ZAM-24-04	8/13/2024	Wet	15.616	120.375	East	28.7	106	8.63	366	739	159	11	552	1,847	322	42	19	0.70461	0.00001
ZAM-24-05	8/13/2024	Wet	15.704	120.300	East	29.0	96	8.40	439	633	126	4	568	191	300	41	10	0.70375	0.00001
ZAM-24-06	8/13/2024	Wet	15.824	120.245	East	32.2	140	8.46	581	911	194	5	923	590	359	43	9.4	0.70404	0.00001
ZAM-24-07	8/13/2024	Wet	15.894	120.205	East	33.5	160	8.38	765	897	263	4	1,053	407	506	45	38	0.70416	0.00001
ZAM-24-08	8/13/2024	Wet	15.919	120.203	East	31.0	178	8.04	712	1,003	272	19	942	3,140	452	66	31	0.70443	0.00001
ZAM-24-09	8/14/2024	Wet	15.743	119.952	PMB	30.6	170	7.94	743	2,441	100	1	667	401	1,854	59	41	0.70865	0.00001
ZAM-24-10	8/14/2024	Wet	15.744	119.952	PMB	29.9	243	7.77	660	2,256	86	3	803	265	1,490	68	51	0.70863	0.00001
ZAM-24-11	8/14/2024	Wet	15.744	119.952	PMB	29.3	235	7.68	616	2,219	76	3	937	226	1,018	76	57	0.70857	0.00001
ZAM-24-12	8/14/2024	Wet	15.754	119.950	PMB	29.2	265	7.65	939	2,256	112	8	995	353	1,948	39	55	0.70867	0.00001
ZAM-24-13	8/14/2024	Wet	15.753	119.936	PMB	31.3	259	7.58	863	2,096	129	9	769	394	2,072	88	98	0.70866	0.00001
ZAM-24-15	8/15/2024	Wet	15.793	119.992	SC	29.4	279	8.59	57	1,611	115	3	646	148	128	84	23	0.70618	0.00001
ZAM-24-16	8/15/2024	Wet	15.793	119.991	SC	29.7	288	8.71	48	1,713	57	3	730	139	123	51	13	0.70566	0.00003
ZAM-24-17	8/15/2024	Wet	15.790	119.971	SC	30.9	300	8.57	152	1,665	111	9	682	279	192	81	26	0.70539	0.00002
ZAM-24-18	8/15/2024	Wet	15.773	119.933	SC	30.4	1,042	7.81	767	3,831	24,247	537	546	4,816	4,690	10,814	854	0.70903	0.00001
ZAM-24-19	8/15/2024	Wet	15.584	119.951	West	29.2	190	8.55	184	947	68	3	573	1,179	145	69	8.4	0.70474	0.00001
ZAM-24-20	8/16/2024	Wet	15.538	119.977	West	26.4	170		201	787	83	5	520	141	465	44	16	0.70785	0.00001
ZAM-24-21	8/16/2024	Wet	15.456	119.955	West	25.6	139	8.11	178	584	113	4	392	119	230	89	12	0.70725	0.00001
ZAM-24-22	8/16/2024	Wet	15.386	119.961	West	26.5	149	8.20	120	731	51	2	423	1,155	200	25	n.d.	0.70698	0.00001

ZAM-24-23	8/16/2024	Wet	15.310	119.999	West		1,538	7.96	181	1,360	4,217	88	564	1,192	1,185	1,437	107	0.70845	0.00001
ZAM-24-24	8/16/2024	Wet	15.264	120.036	West	36.0	266	8.50	583	1,021	546	48	714	3,604	1,127	160	638	0.70460	0.00001
ZAM-24-25	8/16/2024	Wet	15.154	120.059	West	29.9	206	8.15	143	1,051	103	4	674	212	189	45	11	0.70441	0.00001
ZAM-24-26	8/16/2024	Wet	15.109	120.053	West	33.3	227	8.09	236	863	350	28	807	1,953	467	139	34	0.70513	0.00001
<i>Mean values</i>						°C	TDS (ppm)	pH	Ca ²⁺ (µM)	Mg ²⁺ (µM)	Na ⁺ (µM)	K ⁺ (µM)	Si (µM)	Al ³⁺ (nM)	Sr ²⁺ (nM)	Cl ⁻ (µM)	SO ₄ ³⁻ (µM)	⁸⁷ Sr/ ⁸⁶ Sr	
<i>East rivers – dry season</i>						28.5	218	8.21	557	789	265	14	633	750	581	52	67	0.70411	
<i>East rivers – wet season</i>						29.0	109	8.39	503	697	251	15	761	2,064	515	59	18	0.70424	
<i>PMB rivers – dry season</i>						26.3	318	8.64	835	1,688	117	13	674	2,263	3,240	105	62	0.70868	
<i>PMB rivers – wet season</i>						28.7	231	8.02	709	1,602	100	7	700	164	2,038	86	44	0.70865	
<i>SC rivers – dry season</i>						31.1	208	8.41	214	1,960	3,254	101	545	2,497	1,220	6,260	325	0.70798	
<i>SC rivers – wet season</i>						31.8	308	8.44	167	1,814	3,103	69	689	3,116	787	1,130	92	0.70660	
<i>West rivers – dry season</i>						28.0	1,045	7.95	858	4,306	10,589	689	738	5,601	8,858	15,317	866	0.70659	
<i>West rivers – wet season</i>						28.9	257	8.17	232	846	925	23	547	867	577	2,504	55	0.70634	

4. Results

This section summarizes the geochemical data measured from the samples. Throughout the text, cation ratios are expressed as the molar ratio of the specific cation with the sum of Ca^{2+} , Mg^{2+} , and Na^+ (Σ^+).

4.1 Geochemical analysis

4.1.1 River geochemistry

The geochemical parameters measured for all water samples are reported in Table 3, with the major cation concentrations prior to seawater correction illustrated in Fig. 3. The pH measurements indicate that the rivers draining the study area are basic, consistent with the initial data from Schopka et al. (2011), which they attribute to low temperature serpentinization reactions (Neal & Shand, 2002). Additionally, the ternary diagram indicates that the majority of samples, particularly from the SC sites, trend towards Mg^{2+} -dominated (>50%) compositions. However, a few samples from the West (Bancal and Masinloc) and SC (SC1) subgroups are more Na^+ -dominated during the dry season (blue and cyan markers, Fig. 3a).

The majority of rivers experience dilution during the wet season, as reflected in the mean ion concentrations listed in Table 3 and comparison of wet versus dry season from repeat sampling campaigns; however, the magnitude of this effect varies across subgroups and chemical species. On average, western rivers exhibit the largest decreases in ion concentrations relative to other subgroups, with most measured ions declining by approximately an order of magnitude, except for Ca^{2+} and dissolved Si. In contrast, only six chemical species show increases in concentration from the dry to wet season across all subgroups. The most pronounced increases occur in mean Al^{3+}

concentrations in the East (+175%) and SC (+24.8%) subgroups, as well as in dissolved Si in the SC subgroup (+26.3%).

Seasonality appears to have limited influence on the median values of the major cation ratios across all subgroups ($\text{Ca}^{2+}/\Sigma^{+}$, $\text{Mg}^{2+}/\Sigma^{+}$, and Na^{+}/Σ^{+} , Fig. 3b-d). However, seasonal changes in the data spread are evident, particularly in the West subgroup, which shows less variability during the wet season compared to the dry season. Consistent with the ternary diagram, a majority of the SC rivers have the most Mg^{2+} -dominated chemistry. The East subgroup shows the highest Ca^{2+} molar ratios and a narrower range of cation ratios, whereas rivers in the West show the greatest variability.

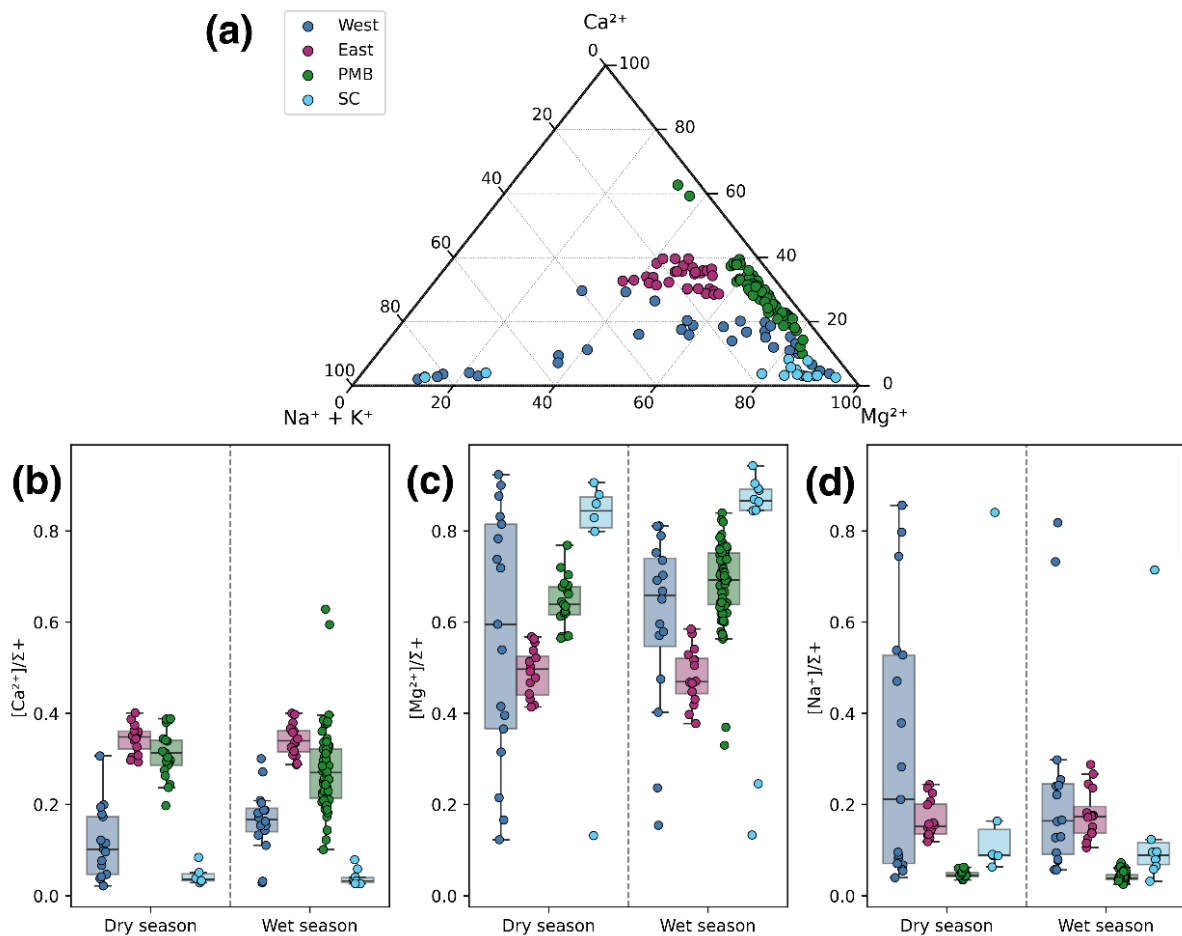


Figure 3. Summary figures of major cation data. (a) Ternary diagram of the major cation composition of the samples analyzed. (b-d) Box plots of the molar ratios for Ca^{2+} , Mg^{2+} , and Na^{+} , respectively relative to their total (Σ^{+}).

Geochemical modeling of river water saturation state with respect to secondary mineral phases indicates supersaturation with Mg-rich and Ca-rich phases (saturation index, $\text{SI} > 0$), as represented by saponite, and undersaturation ($\text{SI} < 0$) with amorphous SiO_2 (Fig. 4a-c). We interpret this pattern as the incorporation of dissolved Si into secondary mineral phases, with saponite saturation showing a clear dependence on pH (Fig. 4a-b). The activity diagram, shown in Fig. 4d, further suggests that dissolved silica and magnesium thermodynamically favor the formation of Mg-rich clay minerals, particularly saponite, and in some samples, chlorite (higher $a\text{Mg}^{2+}/a^2\text{H}^{+}$) and montmorillonite (lower $a\text{Mg}^{2+}/a^2\text{H}^{+}$) (Fig. 4d). However, the precise stability fields in Fig. 4c are highly sensitive to pH and Al^{3+} activity, as shown in Fig. S2 where these parameters are varied within the range of observed values.

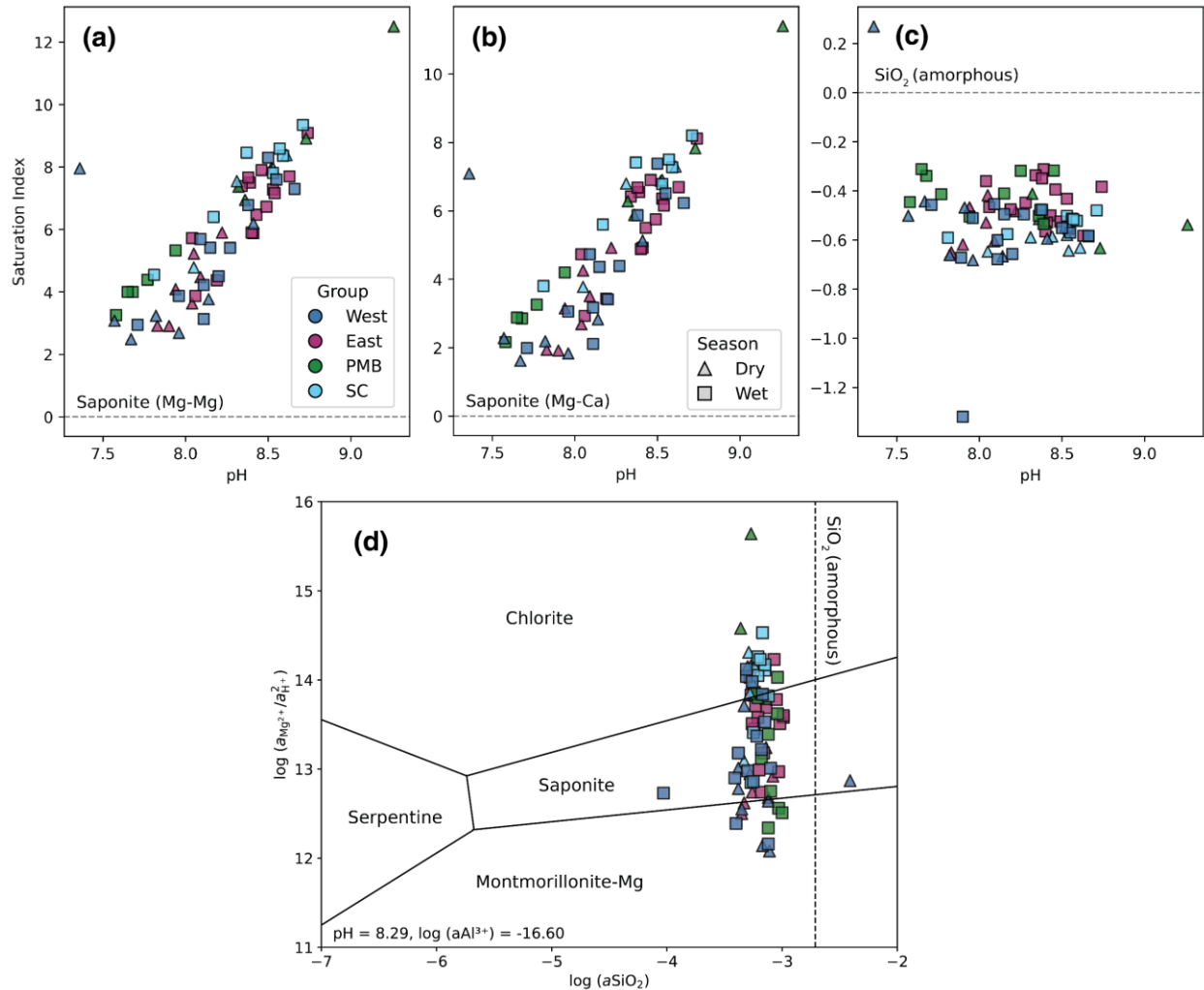


Figure 4. Mineral saturation diagrams for the samples, excluding data from Schopka et al. (2011) due to lack of available of Al³⁺ values. The calculated saturation indices of the samples with respect to saponite (a) with Mg²⁺ as the dominant interlayer cation and (b) with both Mg²⁺ and Ca²⁺ as interlayer cations, and (c) amorphous SiO₂ are plotted as a function of pH. The stability diagram (d) indicates which secondary phase are most thermodynamically stable based on the calculated activities of SiO₂ and Mg²⁺, plotted as log(aSiO₂) against log(aMg²⁺/a²H⁺). Saturation indices and ion activities were calculated using PHREEQC software, while mineral boundary lines were derived from the equilibrium reactions from the *core10.dat* database included with the software (Parkhurst & Appelo, 2013) at the median pH and log(aAl³⁺) values of the samples. The

representative minerals used were clinochlore-14A (chlorite), lizardite (serpentine), saponite-Mg-Mg (saponite), and montmorillonite-Mg. Fig. S2 shows stability diagrams at different pH and log ($a\text{Al}^{3+}$) to demonstrate sensitivity, including the negative correlation between pH and log ($a\text{Al}^{3+}$).

4.1.2. Bulk rock geochemistry

The bulk chemical compositions of the collected rock samples are reported in Table 4. Following the PCA of the molar cation ratios ($[\text{Ca}^{2+}]/\Sigma^+$, $[\text{Mg}^{2+}]/\Sigma^+$, $[\text{Na}^+]/\Sigma^+$, and $[\text{Sr}^{2+}]/\Sigma^+$) and $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 5), the rocks were classified into four subgroups: high-sodium silicates, low-sodium silicates, serpentinized ultramafics, and carbonates. These classifications were also verified by inspection of the hand samples in the field. This classification is further supported by XRD analysis of the powdered rock samples (Fig. S3). Based on the XRD spectra, the serpentinized ultramafic subgroup generally exhibits peaks attributable to lizardite and, in some samples, clinochlore (Fig. S3d). The low-sodium silicates are characterized by the presence of mafic minerals, primarily Mg-hornblende (Fig. S3c), whereas the high-sodium silicates exhibit strong quartz and albite peaks (Fig. S3b). Both carbonate rock samples display strong calcite peaks (Fig. S3a) as expected.

The first three principal components capture 87.3% of the variance in the cation and Sr isotope ratios of the rock samples, with the first component (PC-1) accounting for 50.4%. PC-1 primarily distinguishes the serpentinized ultramafics from the other subgroups, following the $[\text{Mg}^{2+}]/\Sigma^+$ and $^{87}\text{Sr}/^{86}\text{Sr}$ vectors which have an opposite direction relative to other chemical parameters. This indicates the distinct chemical signature of the ultramafic lithology in the study region. Meanwhile, the second principal component (PC-2) primarily captures the spread across the other silicate subgroups and carbonate, as distinguished by $[\text{Ca}^{2+}]/\Sigma^+$, $[\text{Na}^+]/\Sigma^+$, and $[\text{Sr}^{2+}]/\Sigma^+$. The low-Na silicates, primarily characterized by more distinct Mg-hornblende peaks in their XRD

spectra compared to the high-Na silicates, aggregate around the $[\text{Ca}^{2+}]/\Sigma^{+}$, presumably due to the more prominent presence of anorthite (Fig. S3c).

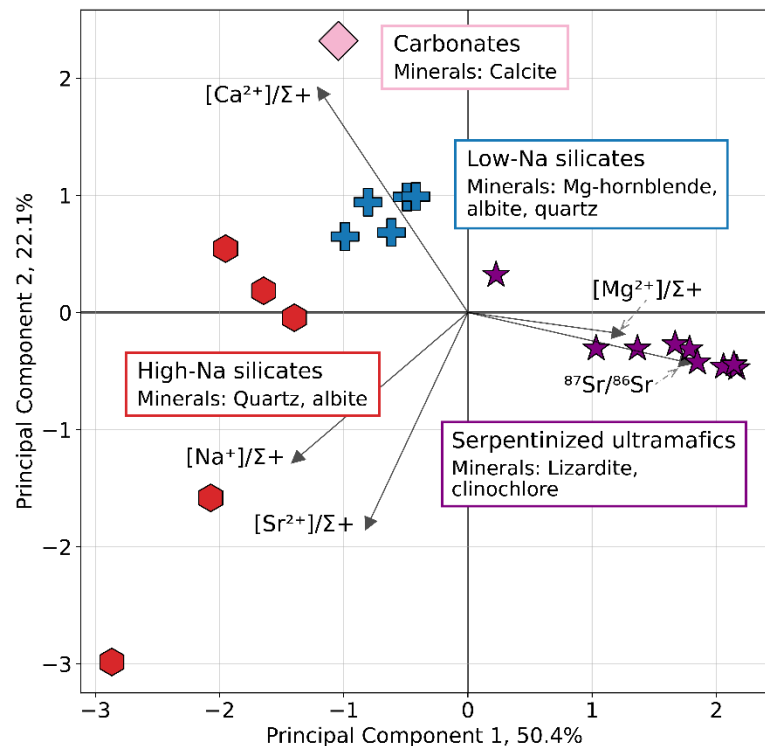


Figure 5. Principal component analysis of the normalized cation ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the rock samples. Labels indicate the most prominent mineral peaks in the XRD spectra in each subgroup (Fig. S3).

Plots of the bulk rock chemical compositions against wt. % SiO_2 (Fig. S4) reveal notable trends, particularly for MgO and SrO , both of which generally decrease with increasing SiO_2 in ultramafic samples. Additionally, Fe_2O_3 decreases with increasing SiO_2 in all rock samples, regardless of classification. Trends in the chemical composition of ultramafic rocks can be attributed to varying degrees of serpentinization, which alters the Mg and Fe composition of rocks through the hydration of Fe-Mg silicate minerals. This generally promotes the dissolution of these silicates, leading to an increase in the Fe and Mg oxides as SiO_2 decreases (Schwarzenbach et al., 2021; Davaasuren et al., 2024).

4.1.3. Sr isotope data

Cross-plots between the $^{87}\text{Sr}/^{86}\text{Sr}$, $[\text{Sr}^{2+}]/\Sigma^+$, $[\text{Ca}^{2+}]/\Sigma^+$, and $[\text{Mg}^{2+}]/\Sigma^+$ of all water samples indicate mixing between at least three geochemical sources (Fig. 6). Samples from eastern rivers consistently form a tight cluster across all panels in Fig. 6a-c, trending towards lower overall $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In contrast, the PMB subgroup generally exhibits higher Sr isotope ratios. Rivers in the West and SC subgroups show the greatest variability in the mixing space, indicating more heterogeneous geochemical sources (Fig. 7).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the rock samples broadly separate more radiogenic sources (higher ratios; serpentinized ultramafics and carbonates) from less radiogenic sources (lower ratio; low and high-Na silicates). This separation is best illustrated in Fig. 6a, which also shows the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values in the water samples span those of the rock samples. However, it should be noted that some serpentinized ultramafics also exhibit lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting variability in the extent of alteration of the ultramafic protolith. This is consistent with the observed spread in the linear relationship of Mg and Fe oxides with SiO_2 (Fig. S4b,h). Additionally, $[\text{Mg}^{2+}]/\Sigma^+$ further distinguishes rock types with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (carbonates and serpentinized ultramafics – low and high $[\text{Mg}^{2+}]/\Sigma^+$, respectively) and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (high-Na and low-Na silicates – low and high $[\text{Mg}^{2+}]/\Sigma^+$, respectively; Fig. 6b-c).

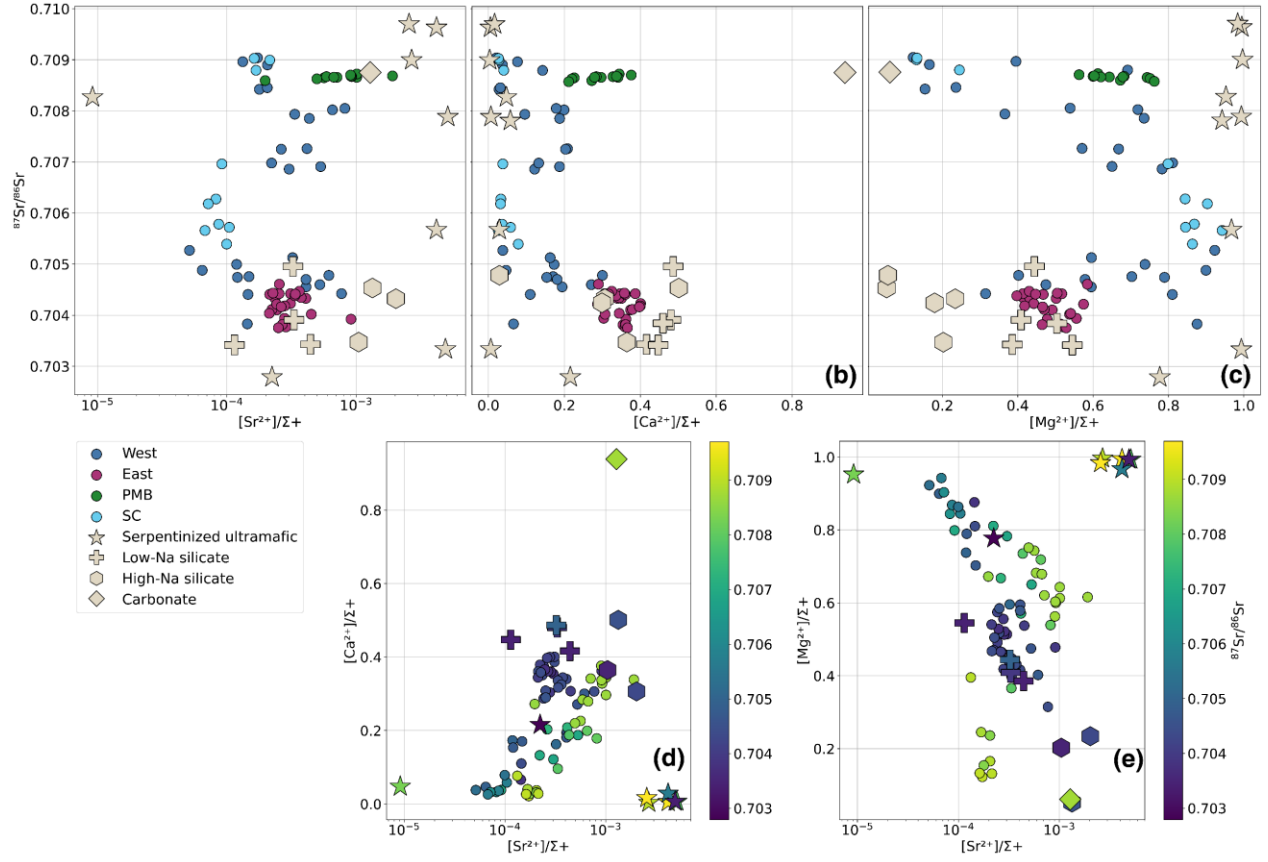


Figure 6. Cross-plots between river water and rock $^{87}\text{Sr}/^{86}\text{Sr}$, $[\text{Sr}^{2+}]/\Sigma^{+}$, $[\text{Ca}^{2+}]/\Sigma^{+}$, and $[\text{Mg}^{2+}]/\Sigma^{+}$ ratios. (a) $[\text{Sr}^{2+}]/\Sigma^{+}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$, (b) $[\text{Ca}^{2+}]/\Sigma^{+}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$, (c) $[\text{Mg}^{2+}]/\Sigma^{+}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$, (d) $[\text{Sr}^{2+}]/\Sigma^{+}$ vs. $[\text{Ca}^{2+}]/\Sigma^{+}$, and (e) $[\text{Sr}^{2+}]/\Sigma^{+}$ vs. $[\text{Mg}^{2+}]/\Sigma^{+}$. Note that the x-axis ($[\text{Sr}^{2+}]/\Sigma^{+}$) in (a), (d), and (e) are in log-scale. For additional reference, marine $^{87}\text{Sr}/^{86}\text{Sr}$ values estimated from microfossil and calcite records are 0.7091792 ± 0.0000021 for the modern ocean and 0.708792 ± 0.000001 at 15 Ma (Mokadem et al., 2015; McArthur et al., 2025).

Table 4. Bulk geochemistry of rock samples based on the ICP-OES analysis. Values are uncorrected for loss of ignition and are normalized to 100%.

Sample ID	Site	Class	SiO ₂ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	TiO ₂ (%)	Sr (ppm)	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr ± (2σ)
ZAM-23-13L	PMB4	Carbonate	0.96	94.34	4.40	-	-	0.03	-	0.03	1,038	0.70875	0.00001
ZAM-23-PMB	PMB3-PMB4 confluence	Carbonate	1.06	92.40	4.84	-	0.02	0.15	0.93	0.11	2,245	-	-
ZAM-24-11C ^a	PMB3	Carbonate	-	-	-	-	-	-	-	-	- ^b	0.70881	0.00002
ZAM-23-07	Dumloc River	High Na silicate	78.89	4.89	0.37	2.41	0.20	-	13.09	0.13	218	0.70453	0.00001
ZAM-23-23	Bagsit River	High Na silicate	56.03	7.95	3.18	5.22	0.36	10.15	16.07	0.99	400	0.70347	0.00001
ZAM-23-BM	Bucao River	High Na silicate	67.12	4.65	2.55	3.85	1.63	3.94	15.68	0.53	444	0.70432	0.00001
ZAM-24-04	Camiling River, ds	High Na silicate	75.45	0.48	0.66	8.37	0.26	0.28	14.24	0.25	- ^b	0.70478	0.00002
ZAM-24-24	Bucao River	High Na silicate	69.22	4.35	1.88	4.19	1.40	3.85	14.31	0.79	- ^b	0.70424	0.00001
ZAM-23-02	Bulsa River, us	Low Na silicate	52.95	13.31	8.14	1.69	0.04	5.98	17.29	0.57	129	0.70391	0.00001
ZAM-23-08	Bayaoas River	Low Na silicate	57.27	8.33	5.55	2.19	0.11	10.71	15.04	0.78	145	0.70343	0.00001
ZAM-23-22	Salasa River	Low Na silicate	53.09	12.91	8.47	1.01	0.08	7.17	16.77	0.48	142	0.70495	0.00001
ZAM-23-SC	SC6-SC7 confluence	Low Na silicate	52.36	14.62	12.80	0.14	-	6.77	13.16	0.15	62	0.70342	0.00002
ZAM-24-25L	Selbang River	Low Na silicate	52.07	15.11	11.90	0.66	0.19	2.61	17.18	0.28	- ^b	0.70384	0.00001
ZAM-24-14E	Soil profile	Serpentinized ultramafic	54.63	0.84	36.30	-	0.09	6.05	1.76	0.08	3,068	0.70970	0.00006
ZAM-24-14A	Soil profile	Serpentinized ultramafic	51.35	0.19	39.17	-	0.10	8.03	0.82	0.07	2,705	0.70900	0.00002
ZAM-23-10	PMB2	Serpentinized ultramafic	50.25	2.47	35.65	-	0.01	9.16	2.40	0.06	7	0.70827	0.00003
ZAM-23-20	Lawis River, ds	Serpentinized ultramafic	47.07	9.24	23.90	0.17	0.07	7.06	12.34	0.13	150	0.70279	0.00001
ZAM-24-14B	Soil profile	Serpentinized ultramafic	46.46	0.36	38.16	-	0.19	14.03	0.17	0.13	2,927	0.70788	0.00004
ZAM-24-16	SC7	Serpentinized ultramafic	43.02	1.91	46.35	0.15	0.19	5.86	1.84	0.16	3,516	0.70567	0.00001
ZAM-23-13D	PMB4	Serpentinized ultramafic	42.30	3.62	42.43	-	-	9.58	2.03	0.04	n.d.	0.70781	0.00003

ZAM-24-11NC	PMB3	Serpentinized ultramafic	40.17	0.37	48.30	-	0.20	7.59	2.69	0.16	3,721	0.70963	0.00002
ZAM-24-25D	Selbang River	Serpentinized ultramafic	32.75	0.46	50.92	0.01	0.24	10.69	4.08	0.21	3,837	0.70333	0.00001

^aInstrument detector saturated with respect to the Ca²⁺ signal. Given the absence of this data, percent composition of the other oxides was not calculated. This particular sample is calcite, as seen from its XRD spectra (Fig. S3a).

^bOutlier Sr²⁺ values below detection limit, not used in analysis.

622 4.2 Geochemical inversion analysis

623 4.2.1 Endmember definitions

624 Six endmembers were defined for the inversion analyses to represent lithological sources
625 and secondary mineral formation. Four endmembers were based on the classification of the rock
626 samples: (1) carbonates, (2) high-Na silicates, (3) low-Na silicates, and (4) serpentinized
627 ultramafic rocks. These endmembers we supplemented with (5) precipitation or sea-spray and (6)
628 clay formation, which serves as a solute sink. The inclusion of a sink mechanism was motivated
629 by the modeled saturation state of the river that shows a thermodynamic preference for the
630 precipitation of Mg-bearing secondary phases (Fig. 4). Cation exchange processes at the surface
631 of clay minerals can remove ions (Ca^{2+} , Mg^{2+} , Na^+ , Sr^{2+}) from the river matrix (Michaud et al.,
632 2016; Tipper et al., 2021), which would allow the inversion to solve for mass balance when
633 conservative mixing among source endmembers alone is insufficient to reproduce the observed
634 geochemistry of the samples (Kemeny and Torres, 2021). The distribution of chemical ratios for
635 each endmember is summarized in Table 5 and illustrated in Fig. 7.

636 Table 5. Chemical compositions of each endmember utilized in the inversion analysis. Uniform
637 distributions were implemented for all scenarios with the corresponding minimum and maximum
638 values.

		Carbonate	High-Na silicate	Low-Na silicate	Precipitation	Serpentinized ultramafic	Clay
$[\text{Ca}^{2+}]/\Sigma^+$	Min	0.751	0.023	0.333	0.261	0.003	0.346
$[\text{Ca}^{2+}]/\Sigma^+$	Max	1.000	0.602	0.584	0.623	0.259	1
$[\text{Mg}^{2+}]/\Sigma^+$	Min	0.049	0.042	0.309	0.063	0.622	0.099
$[\text{Mg}^{2+}]/\Sigma^+$	Max	0.073	0.281	0.654	0.184	1	0.668
$[\text{Na}^+]/\Sigma^+$	Min	0.000	0.346	0.006	0.280	0.000	0.009
$[\text{Na}^+]/\Sigma^+$	Max	0.000	1	0.238	0.664	0.009	0.266
$[\text{Cl}^-]/\Sigma^+$	Min	0.000	0.000	0.000	0.343	0.000	0.000
$[\text{Cl}^-]/\Sigma^+$	Max	0.000	0.000	0.000	1.000	0.000	0.000
$[\text{Si}]/\Sigma^+$	Min	0.007	1.918	1.183	0.000	0.343	1.224
$[\text{Si}]/\Sigma^+$	Max	0.011	9.054	3.204	0.000	1.232	3.089
$[\text{Sr}^{2+}]/\Sigma^+$	Min	0.001	0.001	0.000	0.000	0.000	0.000

$[\text{Sr}^{2+}]/\Sigma^{+}$	Max	0.002	0.002	0.001	0.023	0.006	0.003
$^{87}\text{Sr}/^{86}\text{Sr}$	Min	0.7080	0.7029	0.7029	0.7091	0.7022	<i>Source</i>
$^{87}\text{Sr}/^{86}\text{Sr}$	Max	0.7095	0.7049	0.7051	0.7093	0.7098	<i>Source</i>

The ranges of values from the bulk geochemistry of the rock samples were used to constrain the lithological endmembers. Similar to Muñoz et al. (2024), we expanded the ratios for these endmembers by $\pm 20\%$ to account for the uncertainty associated with the limited lithological sampling size. Monthly chemical data (2003–2021) from the Acid Deposition Monitoring Network in East Asia (Metro Manila station; 14.635833, 121.078611) were used as basis for the precipitation endmember (Network Center for EANET, 2024). The corresponding distributions of molar ratios were constrained within the average of the 25th and 75th percentile values from both the wet and dry seasons, as initial inversion runs using the minimum and maximum values produced a broader range than required. For $^{87}\text{Sr}/^{86}\text{Sr}$, we assigned a range of 0.7091–0.7093 based on the reported value of modern seawater (0.7091792 ± 0.0000021 ; Mokadem et al., 2015). Lastly, the chemical composition of the sink endmember was based on geochemical data reported by Liu et al. (2009) for clay-fraction separates ($< 2 \mu\text{m}$) from sediments collected in the Pampanga and Agno River systems in Luzon Island (Fig. S1). Following the methodology of Cole et al. (2022), we defined the $^{87}\text{Sr}/^{86}\text{Sr}$ to match the weighted average isotopic composition of the solute sources, assuming that Sr isotopes do not fractionate during secondary phase formation. This approach avoids introducing mathematical fractionation to the inversion (Cole et al., 2022).

4.2.2 Geochemical inversion results

Three inversion scenarios were constructed according to the descriptions provided in Table 2. Fig. 8 shows the solute partitioning for each river sampled using the full geochemical inversion model. Diagrams illustrating the sensitivity of the inversions to the constraints imposed by the clay endmember and Sr isotopic data are shown in Figs. S7 and S8.

4.2.2.1 Full geochemical inversion scenario: Major sources of solutes

The full inversion analysis revealed that the contributions of individual endmembers to dissolved river geochemistry differ among elements and vary across both catchments and seasons. Consistent with the Mg-rich composition of ultramafic minerals that extensively underlie the study area, weathering of the serpentinized ultramafic endmember contributes the most to the annual Mg^{2+} fluxes of 23 out of the 25 catchments studied (34.22% in SC-1 to 79.04% in Bagsit River, regardless of the season (Fig. 8b, right column). The particularly high ultramafic contributions observed in the SC and PMB catchments may also reflect the influenced of the exposed laterite deposits in the area, enhancing the weathering of the ultramafic minerals (Domingo et al., 2021, 2023; Aquino et al., 2019, 2022). Additionally, high-Na silicates are found to be the largest source of Na^+ in 20 catchments (36.10% in PMB-4 to 70.97% in Balsa River, ds; Fig. 8c, right column), consistent with the mineralogical characterization of this endmember as shown by the PCA of the bulk rock geochemistry (Fig. 5).

Carbonate weathering is a significant source of dissolved Ca^{2+} in many catchments, particularly in the PMB sites where substantial carbonate lithologies have been mapped (Domingo et al., 2021). This endmember represents the largest annual Ca^{2+} source in 14 catchments (42.65% in Bucao River to 62.20% in PMB-4; Fig. 8a, right column). However, the more substantial contribution of low-Na silicates to dissolved Ca^{2+} in 10 other catchments indicates that weathering of mafic lithologies also represents an important source of Ca^{2+} and associated alkalinity. This pattern is especially evident in the SC catchments and several of the larger watersheds, where the relatively modest contribution from annual carbonate weathering (18.97% in Lawis to 43.11% in Malabobo, Fig. 8a, right column) is matched or exceeded by contributions from low-Na silicates (39.26% in Lawis to 43.35% in Malabobo).

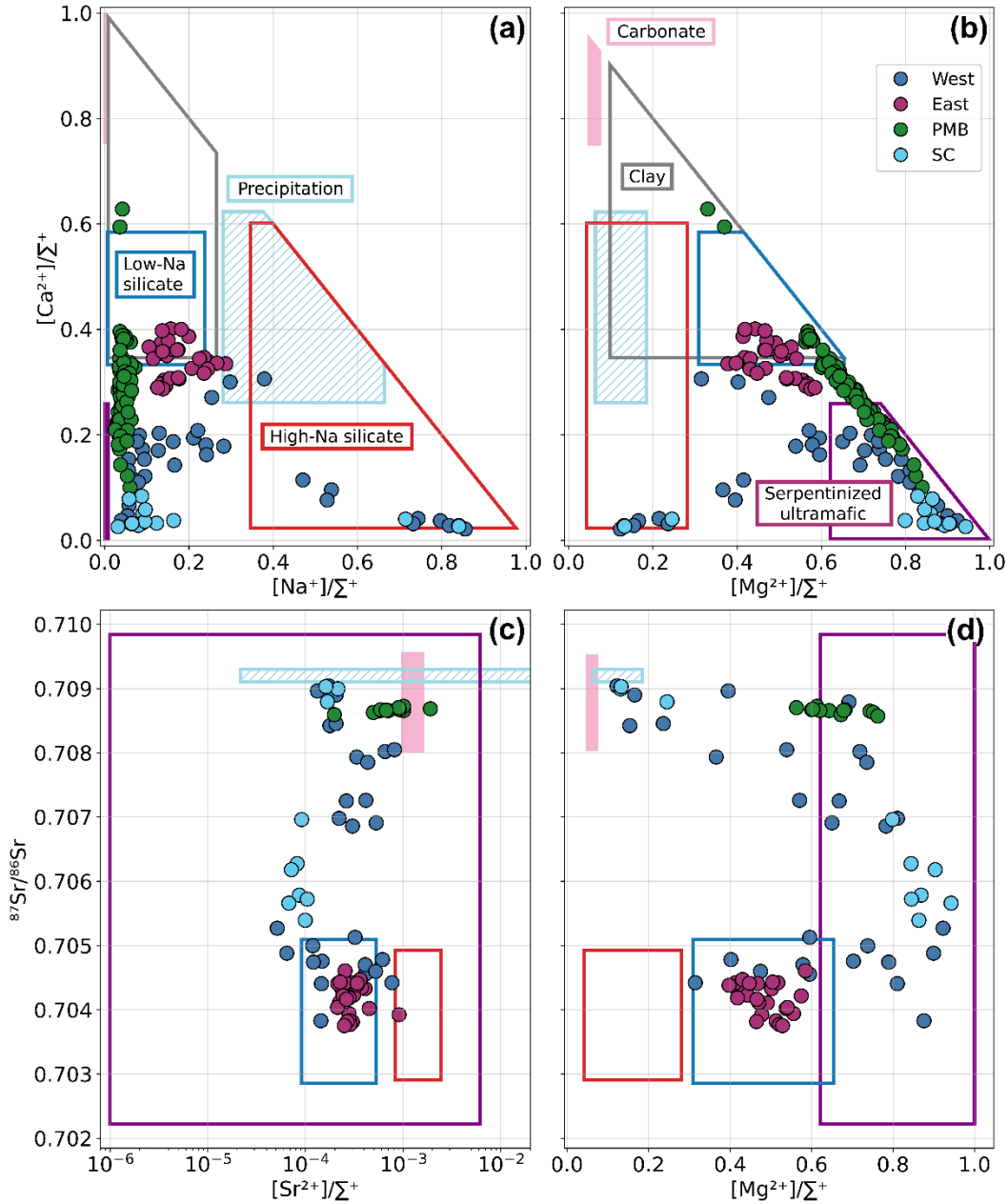


Figure 7. Measured elemental molar ratios of the river water samples plotted as (a) $[Na^+]/\Sigma^+$ vs. $[Ca^{2+}]/\Sigma^+$, (b) $[Mg^{2+}]/\Sigma^+$ vs. $[Ca^{2+}]/\Sigma^+$, (c) $[Sr^{2+}]/\Sigma^+$ vs. $^{87}Sr/^{86}Sr$, and (d) $[Mg^{2+}]/\Sigma^+$ vs. $^{87}Sr/^{86}Sr$. The plotted areas represent the range of endmember ratios as listed in Table 5, following the colored labels in (a) and (b). The polygons in (a) and (b) are truncated due to the compositional constraint imposed by the normalization variable ($\Sigma^+ = [Na^+] + [Ca^{2+}] + [Mg^{2+}]$), where any combination of $[Na^+]/\Sigma^+$, $[Ca^{2+}]/\Sigma^+$, and $[Mg^{2+}]/\Sigma^+$ values cannot have a sum exceeding one. Fig.

S5 shows similar plots that include $[\text{Ca}^{2+}]/\Sigma^+$ and $[\text{Mg}^{2+}]/\Sigma^+$ precipitation data plotted against $[\text{Cl}^-]/\Sigma^+$.

Seasonal comparisons reveal no consistent, systematic changes in the partitioned endmember contributions to the observed Ca^{2+} , Mg^{2+} , Na^+ , and Sr^{2+} concentrations across watersheds. Annual solute fluxes, however, are more strongly influenced by wet-season partitioning, as ~78% of the total volumetric discharge occurs during this period. Nonetheless, several catchments, particularly those in the West subgroup that drain into coastal areas, exhibit pronounced seasonal changes in their partitioned solute fractions (Fig. 8).

Precipitation fractions for Ca^{2+} and Na^+ in the Bancal and Salasa catchments show substantial decreases during the wet season, which are generally compensated by increased contributions from carbonate and high-Na silicate dissolution, respectively. This pattern is opposite to what is observed in the Masinloc and Lawis catchments (Figs. 8a, c) and may reflect differences in watershed characteristics that alter the relative importance of atmospheric inputs and mineral-water interactions during periods of elevated discharge. However, given the current limitation in the availability of detailed hydrological and geological data, resolving these differences would require further data collection. Nonetheless, previous studies have shown that lithology, in combination with runoff variability, can influence rates of solute production across different temporal scales through changes in mineral saturation states, flow paths, and fluid residence times (Maher, 2010; Maher and Chamberlain, 2014; Ibarra et al., 2016).

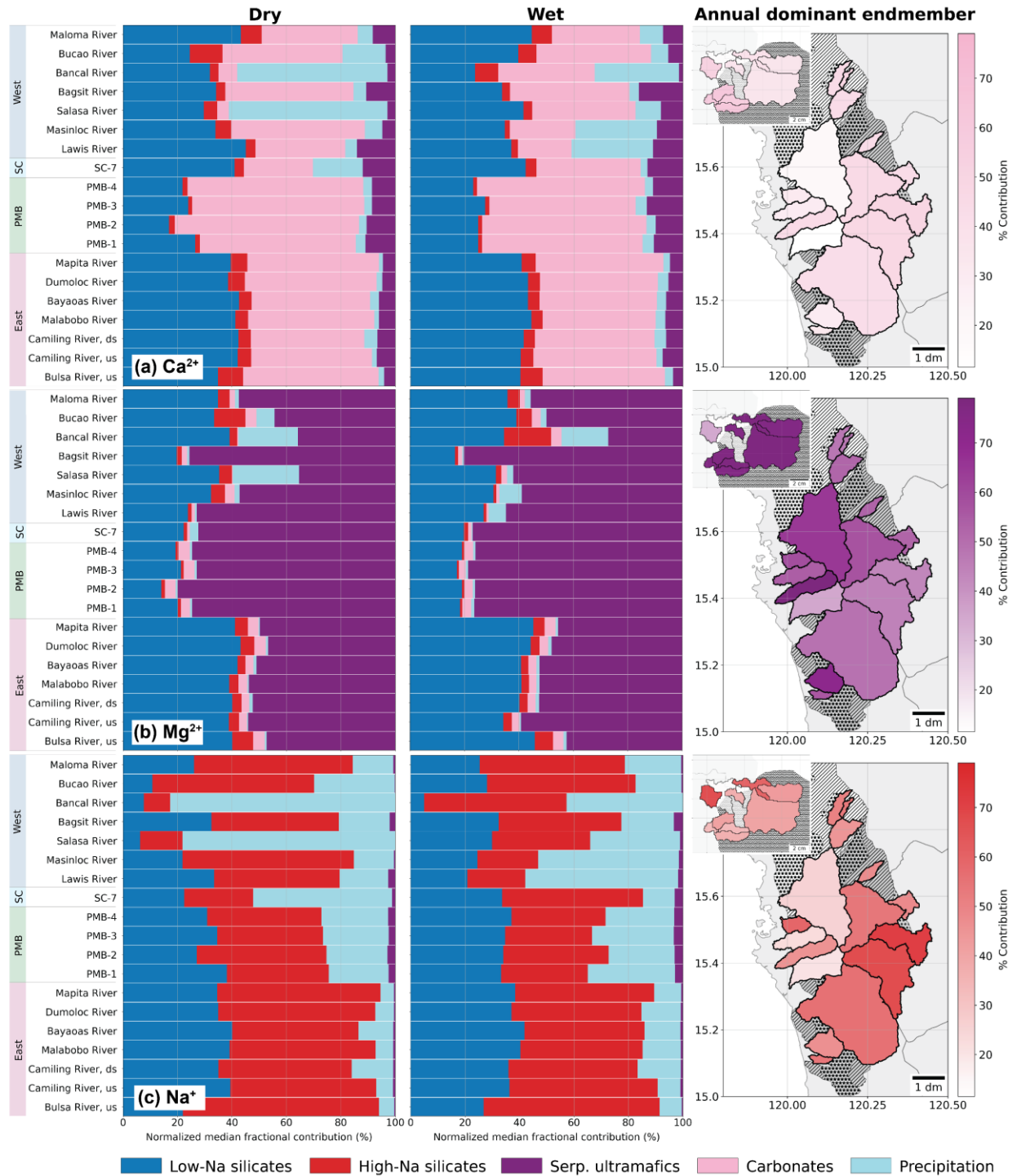


Figure 8. Inversion-constrained normalized median fractional contributions of the five source endmembers. Rows correspond to (a) Ca^{2+} , (b) Mg^{2+} , and (c) Na^+ . The left and middle columns show the mean normalized dry- and wet-season fractional contributions, respectively, for each catchment. Catchments are organized by geographic subgroup (top to bottom: West, SC, PMB,

and East). The rightmost column identifies the dominant annual endmember in each catchment, with shading indicating its normalized median contribution. Inset maps are the SC and PMB catchments. Fractional contributions are normalized to the sum of the inversion-constrained median source contributions, such that they sum to 100%, allowing comparison across catchments and seasons (Eq. 6). However, it should be noted that this normalization implicitly assumes 100% reconstruction of the observed solute concentrations, although successful inversion results were constrained to reconstruct 85% to 115% of the observed solute concentrations. Each panel shows the estimated fractions from samples collected during the dry (left) and wet (right) seasons. Not included are catchments with incomplete seasonal data: Bulsa River (downstream) lacks wet-season fractions, while Dapya River, SC-1, SC-4, SC-5, and SC-6 lack dry-season fractions. The cumulative distribution functions of the calculated fractions from the successful simulations are found in the supplement (Fig. S6).

Clay fractions suggest that secondary mineral phases primarily incorporate the dissolved Si generated by the weathering reactions, with Ca^{2+} , Mg^{2+} , and Na^+ being taken up variably across seasons and watersheds (Fig. 9). The modeled secondary mineral uptake across the rivers in the West subgroup appears to be the most variable; nonetheless, the consistent overlap between the wet- and dry-season boxplots across the majority of the rivers suggests that variations in the seasonal discharge and corresponding solute concentrations (i.e. the concentration-discharge relationships; cf. Ibarra et al., 2016) exert only a limited influence on the fraction of solutes removed by clay minerals in the ZOC.

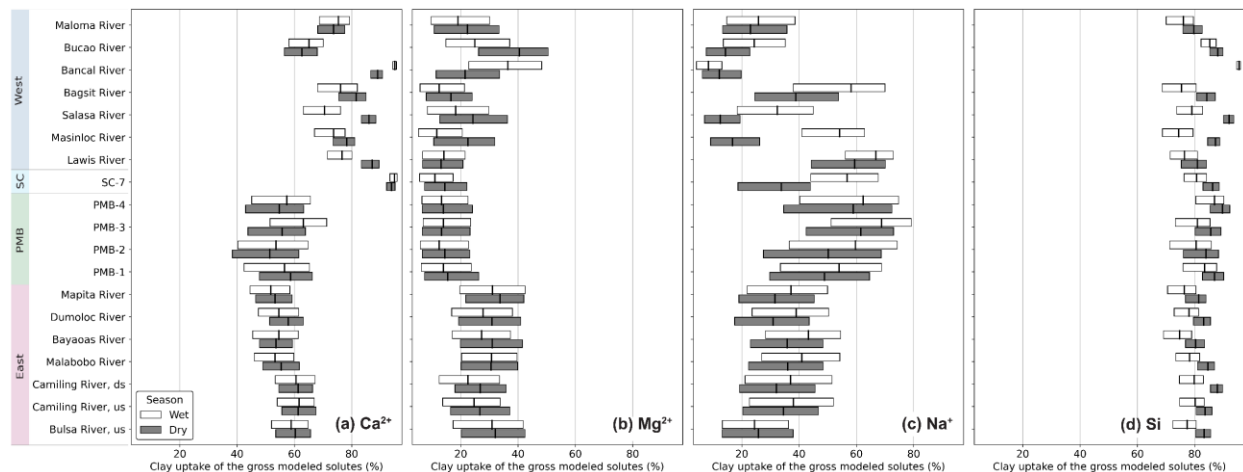


Figure 9. Median fractional solute uptake (%) of (a) Ca^{2+} , (b) Mg^{2+} , (c) Na^+ , and (d) dissolved Si estimated for each river per season. Length of each box is bound by the 25th and 75th percentile fractions, with the median denoted by the vertical line. Illustrated fractions are renormalized to reflect fraction of clay uptake relative to the gross modeled solute input (Eq. 7). However, it should be noted that this normalization implicitly assumes 100% reconstruction of the observed solute concentrations, although successful inversion results were constrained to reconstruct 85% to 115% of the observed solute concentrations. Not included are catchments with incomplete seasonal data: Bulsa River (downstream) lacks wet-season fractions, while Dapya River, SC-1, SC-4, and SC-6 lack dry season fractions.

4.2.2.2 Alternate inversion scenarios: Sensitivity tests

Figs. S7 and S8 demonstrate that the inclusion or exclusion of the sink endmember and Sr data constraints exerts variable influence on the partitioned solute contributions from each endmember. The sensitivity of the model to the clay endmember was initially done with dissolved Si data; however, solving for mass balance that includes Si without a sink mechanism was computationally intensive and yielded few, if any, successful simulations for many of the river samples. This result suggests that conservative mixing among source endmembers is insufficient

to reproduce the observed data and that the substantial removal of dissolved Si is required from the modeled solute input.

The major cations released from the weathering of serpentinized ultramafic rocks are particularly sensitive to these inversion constraints, with the partitioned Ca^{2+} and Mg^{2+} being generally higher in inversion scenarios with either the clay endmember (Fig. S7a-b) or Sr isotope data (Fig. S7e-f) excluded. In contrast, the inclusion of similar constraints shifted the low-Na silicate weathering-derived Ca^{2+} and Mg^{2+} and carbonate weathering- Ca^{2+} fractions toward higher values. Among the major cations, Na^+ appears to be comparatively the least responsive to variations in the inversion setup, as indicated by the consistency in the slope formed by the calculated endmember fractions across scenarios.

4.2.3 Inversion-constrained endmember $^{87}\text{Sr}/^{86}\text{Sr}$ values

Fig. 10 shows variability in the inversion-constrained $^{87}\text{Sr}/^{86}\text{Sr}$ values and the partitioned $[\text{Sr}^{2+}]$ across the studied catchments. The modeled $^{87}\text{Sr}/^{86}\text{Sr}$ values of the low-Na and high-Na silicate endmembers (~ 0.704), as well as those of the carbonate and precipitation endmembers (~ 0.709), were relatively consistent across catchments because their *a priori* distributions were tightly constrained by bulk-rock analyses and available data. However, the wide range of input $^{87}\text{Sr}/^{86}\text{Sr}$ values for the serpentinized ultramafic endmember enabled the inversion to distinguish catchments characterized by more radiogenic ultramafic signatures from those with less radiogenic isotopic compositions more similar to the other silicate endmembers.

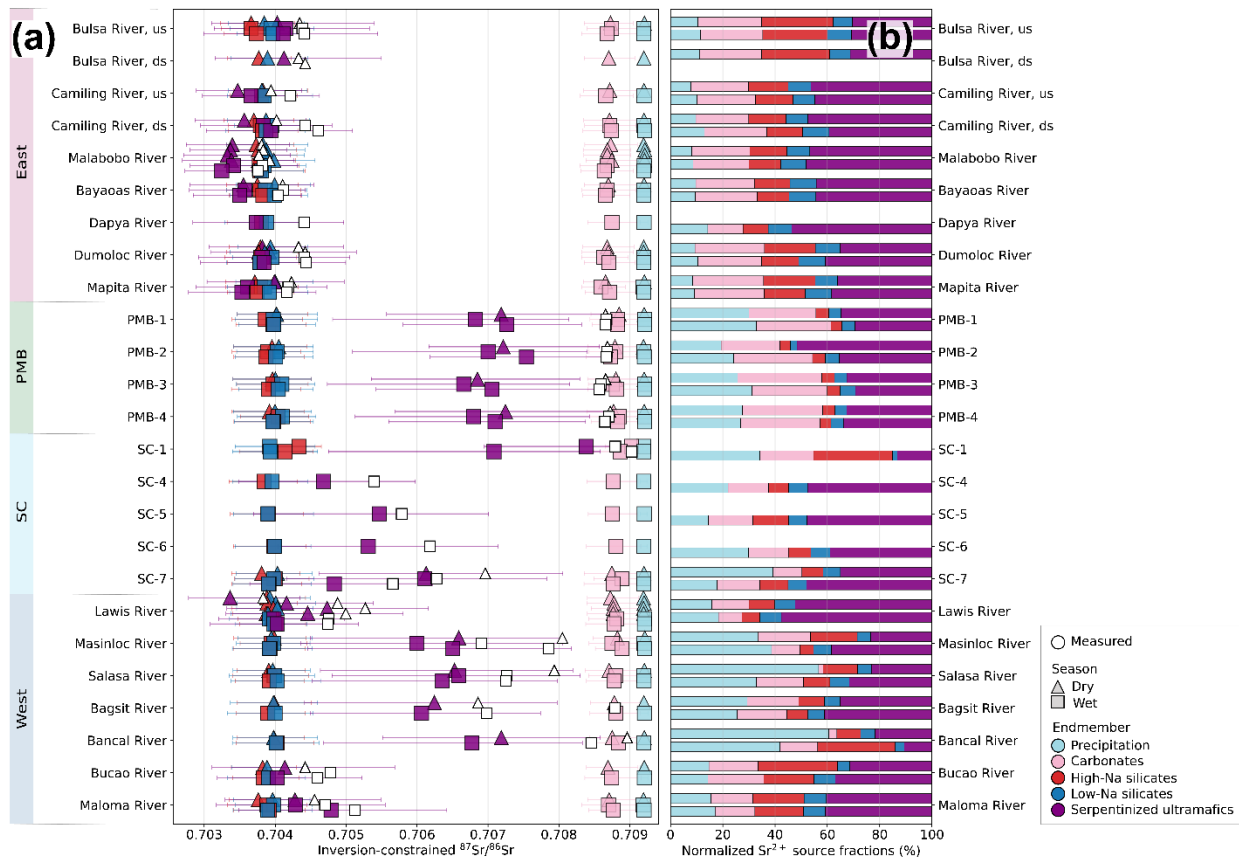


Figure 10. (a) Observed and inversion-constrained $^{87}\text{Sr}/^{86}\text{Sr}$ values for each sample from the studied catchments and (b) seasonal fractional contributions of the different source endmembers to the $[\text{Sr}^{2+}]$ concentration of the water samples. The fractions represent the median values from the inversion of the full geochemical model scenario. In (b), the upper bar for each catchment represents the mean inversion results for all available samples collected during the dry season, while the lower bar represents the wet season. Catchments with incomplete seasonal data include Bulsa River (downstream) which lacks wet-season fractions, and Dapya River, SC-1, SC-4, and SC-6, which lack dry-season fractions.

The analysis identifies the PMB sites consistently exhibit the highest median $^{87}\text{Sr}/^{86}\text{Sr}$ for the serpentized ultramafic endmember (~ 0.707), with the SC and several other catchments in the West subgroup having lower, but still elevated inversion-constrained ultramafic signatures

(~0.705-0.707) relative to the other silicate endmembers (~0.704). Comparison between the observed (white markers; Fig. 10a) and the inversion-constrained endmember values shows that PMB catchments have more similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to the relatively radiogenic signatures of the precipitation and carbonate endmembers. This pattern is consistent with the comparatively higher combined contributions of these endmembers (~60%) to $[\text{Sr}^{2+}]$ in most PMB catchments (Fig. 10b). In contrast, catchments in the SC and West subgroups with relatively elevated $^{87}\text{Sr}/^{86}\text{Sr}$, with the exception of Bancal River, appear to reflect a stronger influence from the silicate endmembers on the dissolved Sr^{2+} . However, the large uncertainties associated with the modeled isotopic ratios, particularly for the ultramafic endmember, suggest the need for additional lithological and geochemical constraints beyond those provided in this work.

4.3 CO_2 consumption rates and watershed characteristics

Table 6 summarizes the calculated area-normalized long-term CO_2 consumption of each study catchment, as well as the area-weighted regional averages, based on the partitioned dissolved $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$. Across all catchments, total area-normalized silicate-weathering derived CO_2 consumption ranges two orders of magnitude from 3.18×10^5 to 1.13×10^7 mol CO_2 km $^{-2}$ yr $^{-1}$. While carbonate dissolution does not contribute to long-term CO_2 consumption, comparable calculations (1 mol $\text{Ca}^{2+}/\text{Mg}^{2+}$: 1 mol CO_2) yield fluxes of 2.39×10^4 to 6.10×10^5 mol CO_2 km $^{-2}$ yr $^{-1}$. Uncertainties (Eqs. 8-12) are generally <40%; however, several catchments have higher uncertainties, particularly Bancal River, Masinloc River, and the carbonate-derived fluxes of Lawis River and PMB4.

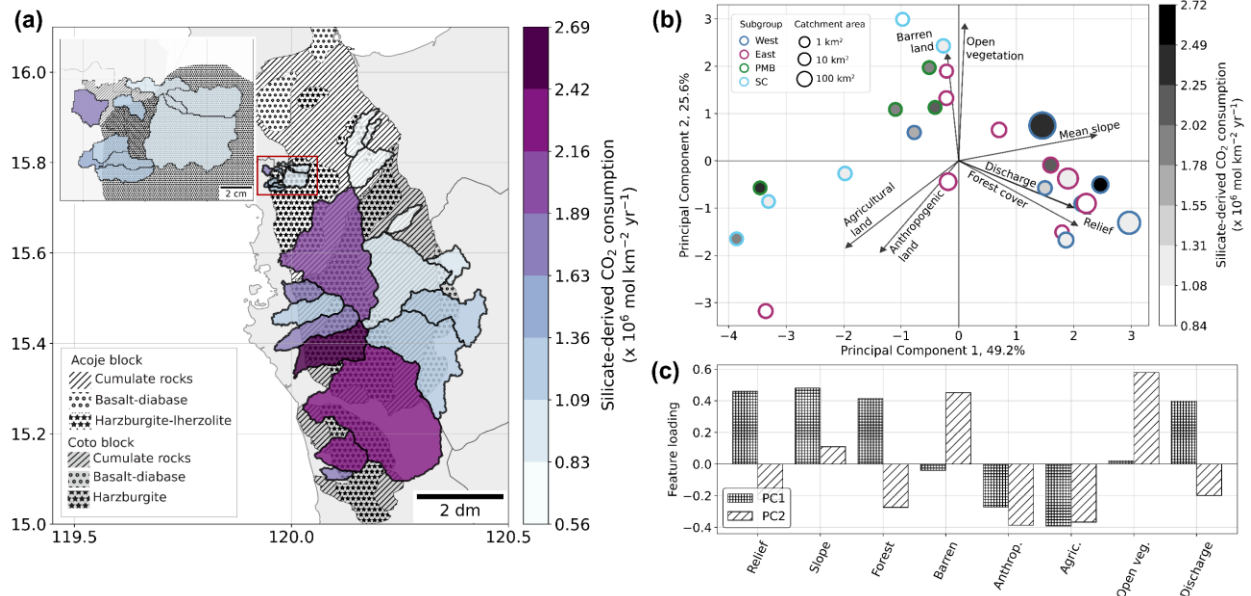


Figure 11. Comparison of the calculated area-normalized silicate weathering-derived CO₂ consumption (Table 6) with watershed features (Table 1). (a) CO₂ consumption per watershed overlain on the geologic map of ZOC. Inset map shows the SC and PMB watersheds (red box); (b) Principal component analysis of watershed features; (c) Cross-plot of PC1 and PC2 scores. Vectors in (b) represent the scaled factor loadings of each feature, while marker outline color, fill color, and size denote the geographical subgroup, calculated silicate-derived CO₂ consumption, and catchment area, respectively. (b) Factor loadings of each watershed feature on the first two principal components.

Comparing the area-weighted fluxes across the regional groupings, catchments in the West subgroup exhibit the highest area-weighted long-term CO₂ consumption, albeit with higher reported uncertainty (Fig. 11a, Table 6). Overall, we estimate that the Zambales Ophiolite Complex consumes 2.15×10^6 mol CO₂ km⁻² yr⁻¹ via silicate weathering, with an uncertainty of 25.77%. This total is mostly derived from the contributions of low-Na silicates (45.97%) and serpentinized ultramafics (47.30%), with minor contribution from high-Na silicates (6.74%).

Fig. 11b relates several features of each watershed to the modeled CO₂ consumption from the weathering of the silicate endmembers in principal component space, while Fig. 11c summarizes the loadings of each watershed feature on PC1 and PC2. The first two principal components from the PCA of watershed characteristics and estimated annual discharge account for 74.5% of the observed variance, with PC1 explaining 48.7% and PC2 explaining 25.8%.

Many of the catchments with the largest area and highest silicate-derived CO₂ fluxes cluster around the vectors that represent topographical features (slope and relief), discharge, and forest cover (Fig. 11b). These factors exhibit the most positive loadings on PC1, with anthropogenic and barren land covers showing more negative loadings (Fig. 11c), suggesting an opposing relationship among these two groups of features. Qualitatively, Fig. 11b-c shows that relief, slope, discharge, and forest coverage generally have a positive association on the magnitude of cation export derived from silicate weathering. Meanwhile, PC2 primarily distinguishes the contrasting relationships between barren land and open vegetation with agricultural and anthropogenic land cover. However, no clear relationship between PC2 and dissolved solute generation is evident in Fig. 11b.

833 Table 6. Annual area-normalized CO₂ consumption derived from seasonal discharge weighting of measured solute concentrations,
834 estimated discharge, and inversion-constrained median endmember fractions. Components of the total silicate weathering CO₂
835 consumption are given in fluxes and their % contribution. Uncertainty of the total silicate and carbonate CO₂ consumptions are given as
836 the coefficient of variation (CV), calculated using Equations 8-12.

	<i>High-Na silicate (mol CO₂ km⁻² yr⁻¹)</i>	<i>Contribution to silicate weathering (%)</i>	<i>Low-Na silicate (mol CO₂ km⁻² yr⁻¹)</i>	<i>Contribution to silicate weathering (%)</i>	<i>Serp. Ultramafic (mol CO₂ km⁻² yr⁻¹)</i>	<i>Contribution to silicate weathering (%)</i>	Total silicate (mol CO₂ km⁻² yr⁻¹)	CV (%)	Total carbonate (mol CO₂ km⁻² yr⁻¹)	CV (%)
Bayaoas River	3.37×10^4	4.35%	4.16×10^5	53.59%	3.26×10^5	42.06%	7.76×10^5	9.54	1.98×10^5	11.76
Bulsa River, ds	1.14×10^5	10.92%	5.67×10^5	54.48%	3.60×10^5	34.61%	1.04×10^6	6.75	3.48×10^5	12.15
Bulsa River, us	1.22×10^5	10.16%	6.57×10^5	54.69%	4.23×10^5	35.16%	1.20×10^6	9.32	3.56×10^5	14.46
Camiling River, ds	3.97×10^4	4.39%	4.58×10^5	50.62%	4.07×10^5	45.00%	9.06×10^5	11.02	1.92×10^5	17.23
Camiling River, us	4.50×10^4	4.71%	4.43×10^5	46.38%	4.67×10^5	48.91%	9.56×10^5	9.12	2.06×10^5	13.34
Dapya River	3.96×10^4	1.87%	6.63×10^5	31.35%	1.41×10^6	66.78%	2.12×10^6	33.50	1.21×10^5	46.88
Dumoloc River	4.66×10^4	5.37%	4.88×10^5	56.27%	3.33×10^5	38.36%	8.68×10^5	8.94	2.38×10^5	12.45
Malabobo River	3.13×10^4	4.46%	3.72×10^5	53.07%	2.98×10^5	42.47%	7.01×10^5	11.54	1.77×10^5	17.52
Mapita River	5.39×10^4	6.51%	4.76×10^5	57.49%	2.98×10^5	36.00%	8.28×10^5	17.42	2.74×10^5	19.45
PMB1	3.26×10^4	1.40%	6.29×10^5	26.96%	1.67×10^6	71.64%	2.33×10^6	27.11	6.35×10^5	27.28
PMB2	3.02×10^4	1.59%	4.90×10^5	25.82%	1.38×10^6	72.59%	1.90×10^6	24.20	5.72×10^5	31.65
PMB3	2.35×10^4	1.26%	4.71×10^5	25.21%	1.37×10^6	73.53%	1.87×10^6	21.91	4.07×10^5	43.16
PMB4	2.93×10^4	1.41%	5.62×10^5	26.98%	1.49×10^6	71.61%	2.08×10^6	24.24	6.40×10^5	85.16
SC1	4.86×10^5	25.80%	5.83×10^5	30.98%	8.13×10^5	43.22%	1.88×10^6	25.95	3.87×10^5	34.57
SC4	1.65×10^4	1.34%	2.91×10^5	23.58%	9.26×10^5	75.08%	1.23×10^6	18.20	5.16×10^4	23.13
SC5	2.33×10^4	2.06%	2.26×10^5	20.01%	8.82×10^5	77.94%	1.13×10^6	19.16	3.40×10^4	25.76
SC6	1.56×10^4	1.35%	2.37×10^5	20.50%	9.05×10^5	78.15%	1.16×10^6	18.88	2.75×10^4	18.95
SC7	1.83×10^4	1.74%	2.29×10^5	21.72%	8.07×10^5	76.55%	1.05×10^6	22.85	2.59×10^4	21.00
Bagsit River	2.83×10^4	1.75%	3.53×10^5	21.80%	1.24×10^6	76.45%	1.62×10^6	24.61	1.44×10^5	20.34
Bancal River	8.25×10^5	6.83%	6.18×10^6	51.20%	5.07×10^6	41.97%	1.21×10^7	81.32	4.51×10^5	100.29

Bucaos River	2.24×10^5	9.70%	1.14×10^6	49.46%	9.45×10^5	40.85%	2.31×10^6	12.35	6.09×10^5	24.67
Lawis River	1.89×10^4	1.70%	3.88×10^5	34.81%	7.08×10^5	63.50%	1.12×10^6	16.64	5.19×10^4	51.10
Maloma River	9.46×10^4	5.85%	6.94×10^5	42.93%	8.28×10^5	51.22%	1.62×10^6	20.09	1.65×10^5	24.10
Masinloc River	4.43×10^4	3.20%	5.33×10^5	38.43%	8.09×10^5	58.37%	1.39×10^6	52.10	1.38×10^5	55.01
Salasa River	4.66×10^4	3.64%	5.45×10^5	42.50%	6.91×10^5	53.87%	1.28×10^6	22.20	1.35×10^5	22.55
<i>Area-weighted fluxes</i>										
East	7.76×10^4	6.98%	5.45×10^5	48.99%	4.90×10^5	44.04%	1.11×10^6	13.01	2.67×10^5	18.83
PMB	2.85×10^4	1.42%	5.25×10^5	26.23%	1.45×10^6	72.35%	2.00×10^6	24.02	5.60×10^5	57.21
SC	5.02×10^4	4.24%	2.57×10^5	21.67%	8.77×10^5	74.09%	1.18×10^6	20.53	5.45×10^4	22.33
West	1.90×10^5	7.01%	1.28×10^6	46.99%	1.25×10^6	46.01%	2.72×10^6	29.98	3.58×10^5	45.80
Overall ZOC	1.42×10^5	6.94%	9.62×10^5	46.97%	9.44×10^5	46.09%	2.05×10^6	24.52%	3.16×10^5	37.25%

*CO₂ consumption flux: Derived from partitioned Ca + Mg (assuming 1 mol of each divalent cation sequesters 1 mol CO₂ long-term)

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5. Discussion

5.1 Secondary mineral formation as solute sink

Our sensitivity analysis shows that the inversion is sensitive to the inclusion of a solute sink, as demonstrated by the changes in source partitioning between inversion scenarios of major ions with and without the clay endmember (Figs. S7a-d). Most apparent is the overestimation of the fractional contribution of serpentinized ultramafics to Mg^{2+} in the no-sink scenario relative to the scenario with a solute sink. The full geochemical model further shows that this sink is not restricted to Mg^{2+} , but also removes substantial fractions of Ca^{2+} , Na^+ , and Si from the gross modeled solute influx (Fig. 9).

While conservative mixing between endmembers is sufficient to reconstruct the observed concentrations for the major cations (Ca^{2+} , Mg^{2+} , Na^+), inversion scenarios incorporating dissolved Si without a corresponding sink were unable to produce successful solutions, requiring the inclusion of a sink term to reproduce the observed river chemistry (Section 4.2.2.2). As seen from the inversion-constrained fractions from the full geochemical model, much of the modeled gross inflow of dissolved Si (~80%, Fig. 10d), regardless of season, is absorbed by the sink endmember. Additionally, inversion-constrained endmember ratios for the scenario without a sink tend to deviate from scenarios with sink, particularly for the high-Na silicate and serpentinized ultramafic endmember (Fig. S8). Together with the demonstrated oversaturation of the river samples with respect to Mg-rich secondary minerals and undersaturation with amorphous Si (Figs. 4a-c), these observations suggest ongoing solute exchanges with secondary mineral phases produced by incongruent weathering. Still, other processes such as biological uptake of dissolved Si may also contribute to the observed Si deficit and cannot be excluded based on the available data.

The clay-sized sediment fractions ($<2\ \mu\text{m}$) collected from catchments adjacent to the study area (the Agno and Pampanga River systems) and analyzed by Liu et al. (2009) are dominated by smectite (78–92%), with minor talc and clinochrysotile. A majority of these clay fractions are characterized by relatively higher MgO contents than CaO and Na₂O (Table 4 of Liu et al., 2009), consistent with the formation of Mg-rich smectites, such as saponite, as also suggested by the modeled saturation state of the water samples from this study (Fig. 4a-b). Smectites are highly reactive minerals owing to their permanent structural charge and expandable interlayers, which facilitate adsorption and cation exchange reactions (Sposito et al., 1999). Additionally, studies utilizing isotopic systems ($\delta^{26}\text{Mg}$, $\delta^{30}\text{Si}$, $\delta^7\text{Li}$) to investigate mafic and ultramafic weathering in both field (Ziegler et al., 2005; Oskierski et al., 2019; Pogge von Strandmann et al., 2023; Cheung et al., 2026) and laboratory (Zheng et al., 2019; Pogge von Strandmann et al., 2019; Baldermann et al., 2025) settings demonstrate the importance of secondary phase formation, particularly in mafic and ultramafic systems where rapid clay formation can occur (Pogge von Strandmann et al., 2019, 2023). The observed systematic fractionation of these isotopes between the dissolved and solid phases highlights the importance of accounting for secondary minerals in the dissolved geochemical budget. Consistent with our sensitivity analysis, the geochemical inversion responds strongly to the inclusion of a solute sink, suggesting that neglecting secondary mineral formation in tropical mafic and ultramafic systems can introduce additional uncertainty.

5.2 Strontium isotope geochemistry

Generally, mafic and ultramafic lithologies have greater mantle-derived composition which typically have lower Rb/Sr ratios, resulting in less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values than felsic rocks (Bataille and Bowen, 2012). The relatively unradiogenic Sr signatures of rivers in the East subgroup, as well as the Lawis, Bucao, and Maloma Rivers in the West subgroup are consistent

with the water and basalt $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from other island and volcanic arcs as documented in the literature (Allègre et al., 2010; Bednarick et al., 2024). The inversion analysis indicates that these ratios are largely accounted for by contributions from unradiogenic silicate endmembers (Fig. 10), whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were constrained by the whole-rock analysis of the low-Na and high-Na silicate samples (0.70427 and 0.70391, respectively, Table 4) and the lower end of the range measured in serpentinized ultramafic samples (0.70279 to 0.70333, Table 4). Additionally, the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values in the PMB river waters are largely attributed to precipitation and the dissolution of carbonate lithology within those catchments (Fig. 10b).

However, several of the river water samples, particularly within the SC and West subgroups, exhibit more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values than expected from a simple mantle-derived ultramafic endmember ($\sim 0.705\text{--}0.708$; Fig. 10). Given the wide range of the input $^{87}\text{Sr}/^{86}\text{Sr}$ distribution, the inversion analysis assigned relatively radiogenic signatures to the serpentinized ultramafic endmember in these catchments. The isotopic heterogeneity among serpentinized ultramafic rock samples may reflect variable overprinting of their primary Sr isotope compositions depending on the extent of fluid–rock interactions, as documented in other ultramafic complexes globally (e.g. Kawahata et al., 2001; Scott et al., 2019; Schwarzenbach et al., 2021; Hochscheid et al., 2022).

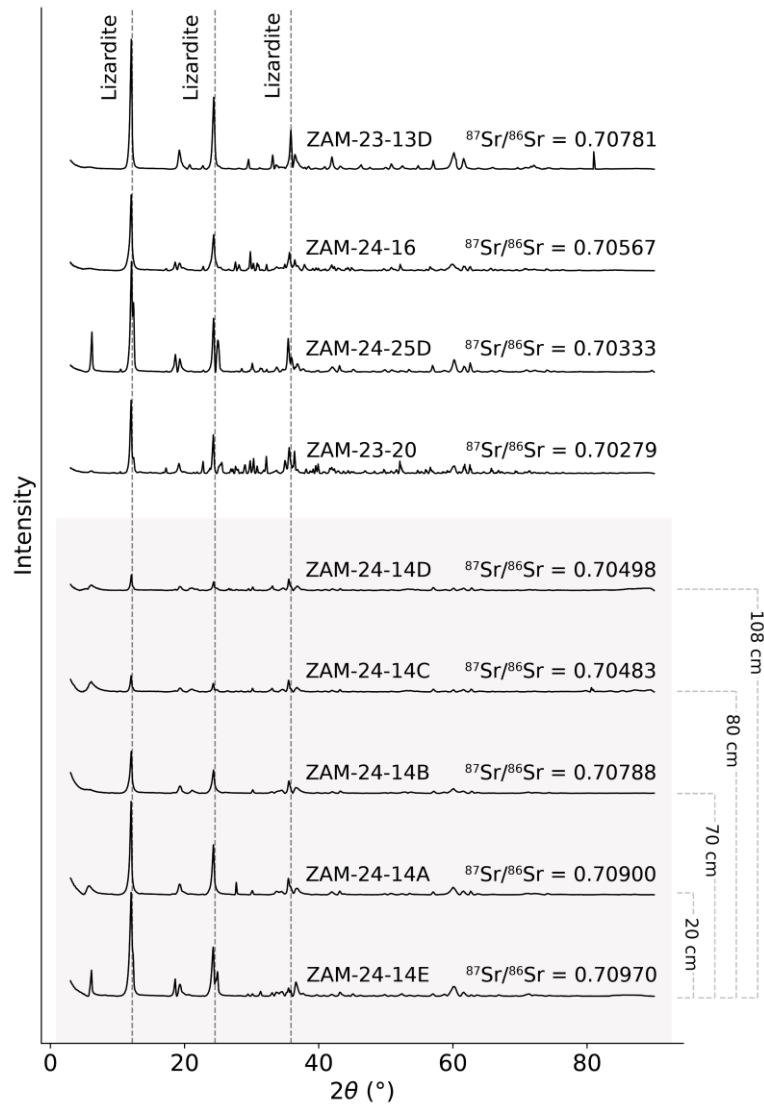


Figure 12. X-ray diffraction (XRD) patterns of selected serpentinized ultramafic samples and their corresponding bulk $^{87}\text{Sr}/^{86}\text{Sr}$ values ratios. Dashed lines mark diagnostic lizardite peaks. Samples ZAM-24-14E through ZAM-24-14D (shaded area) were collected along a soil profile and are arranged from regolith (ZAM-24-14E) to upper soil horizons (ZAM-24-14D); the remaining samples were collected from other locations (Fig. S1). Vertical offsets between patterns are for clarity and are not to scale.

Few studies have investigated the alteration of the mafic and ultramafic rocks in the ZOC. Based on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements of serpentine separates, which were predominantly

identified as lizardite, Sturchio et al. (1989) proposed that isotopically distinct meteoric fluids facilitated the serpentinization process within the critical zone of the Acoje chromite mining area, roughly near the SC catchments. This mineralogy is consistent with the XRD spectra of the serpentinized ultramafic samples analyzed in this work. Additionally, petrographic analysis of saprolite layer samples from a nickel laterite deposit in the SC catchments suggest multiple episodes of serpentinization, as described by Aquino et al. (2022). Together, these studies provide a plausible mechanism of the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ of the rock and river samples in several catchments, particularly in the SC subgroup.

Bulk XRD and $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of several samples obtained from a soil profile within the SC catchments (Fig. 12) suggest that serpentinite minerals primarily carry the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature. The decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ along the inferred weathering progression, which is based on the decreasing lizardite peak intensity from the regolith to the upper soil horizons, suggests the preferential loss of this radiogenic Sr component during weathering. Strontium isotopes have been shown to trace specific mineral-weathering processes across other watersheds (e.g. Bain and Bacon, 1994; Pett-Ridge et al., 2009). However, this relationship between lizardite peak intensity and $^{87}\text{Sr}/^{86}\text{Sr}$ is not evident in the other rock samples. This suggests that the extent of rock-fluid interactions and serpentinization varies across the ZOC, requiring systematic sampling for mineralogical and geochemical characterization.

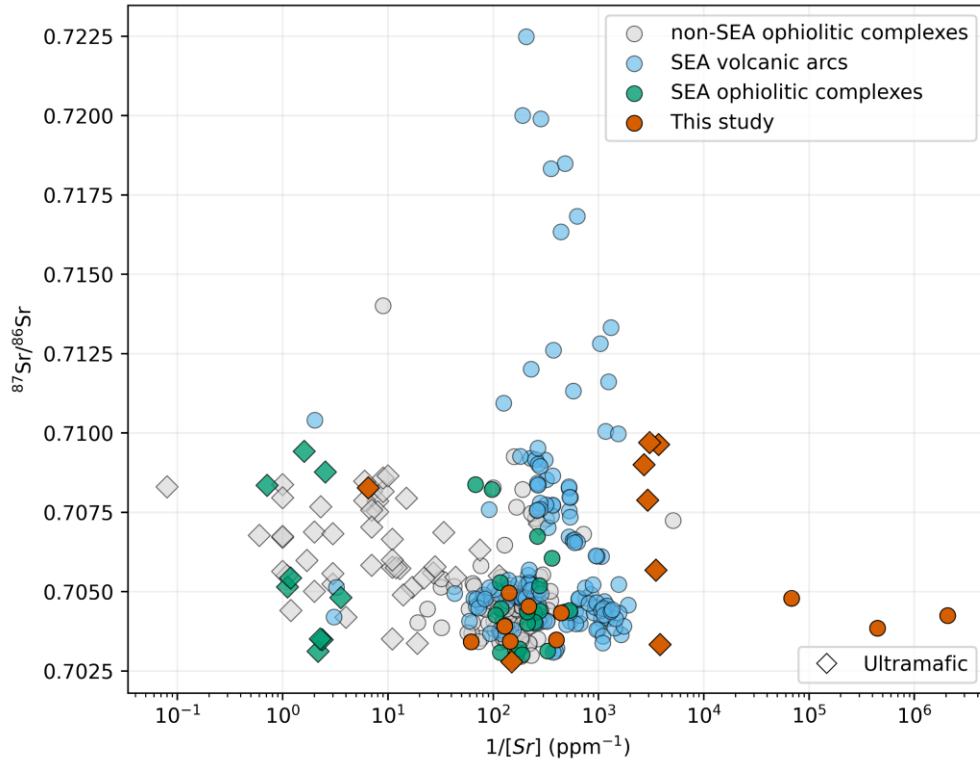


Figure 13. Reported bulk $^{87}\text{Sr}/^{86}\text{Sr}$ of various igneous rocks, plotted as a function of inverse Sr concentration ($1/[\text{Sr}]$). Illustrated data come from this study and compiled samples from SEA (Smith and Compston, 1982; Vidal et al., 1989; Vroon et al., 1993; Encarnación et al., 1999; M. A. Elburg and Foden, 1999; M. Elburg and Foden, 1999; Falloon et al., 2006; König et al., 2010; Yu et al., 2020; Gibaga et al., 2020; Tian et al., 2024) and non-SEA (Richard and Allegre, 1980; Kawahata et al., 2001; Scott et al., 2019; Schwarzenbach et al., 2021) geological settings. Diamond markers denote samples of ultramafic lithology.

Considering the reported bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ data from other catchments, the majority of mafic and ultramafic rocks, as expected, have strontium isotope ratios of <0.705 . However, radiogenic igneous rocks also occur in other volcanic arcs and ophiolitic complexes within and outside SEA (Fig. 13). Within SEA, volcanic rocks in the Banda Arc and Sulawesi, Indonesia and unaltered peridotites in Hili Manu, Timor-Leste all exhibit relatively radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, albeit proposed mechanisms differ from those observed in this study. Both Vroon et al. (1993) and Elburg

and Foden (1999) invoke mixing of subducted continental material and mantle-derived magma in the mantle wedge or arc crust as a mechanism for the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ in andesites (0.705-0.709) and lamprophyres ($\sim$ 0.710) in the Banda Arc and Central Sulawesi, respectively. Similarly, the radiogenic signatures of two peridotites from Hili Manu (0.7088-0.7094) have been attributed to the infiltration and reaction with isotopically distinct melts in a supra-subduction setting, with the complex subsequently emplaced during the Miocene collision between the Banda Arc and the Australian continental margin (Falloon et al., 2006). Collectively, these examples demonstrate that tectonically complex settings such as maritime SEA can produce mafic and ultramafic rocks with varying $^{87}\text{Sr}/^{86}\text{Sr}$ through interactions between continental material, melts, or fluids.

5.3 Regional and global comparisons of annual long-term CO_2 consumption

Watershed characteristics, particularly those related to topography, hydrology, and forest cover, appear to exert first-order control over the magnitude of area-normalized CO_2 consumption rates in the study area (Fig. 11). Additionally, the geochemical inversion also shows considerable variations in the relative contributions of the three silicate endmembers to the total silicate weathering-derived CO_2 consumption across catchments. This variability highlights the role of lithological heterogeneity of the ZOC, in addition to the broad influence of topographic and hydrological features of the catchments.

While runoff and lithology have been identified as major controls on silicate weathering and have been used to estimate fluxes at large spatial scales, the individual influences of topographic factors such as slope and relief remain difficult to assess because of the confounding effects of variations in runoff and geochemistry across different watersheds (Bluth and Kump, 1994; Hartmann, 2009; Hartmann et al., 2009, 2010; Hartmann and Moosdorf, 2011). Gaillardet et al. (1999) showed that weathering rates in major global watersheds do not exhibit a clear

relationship with basin relief. However, our principal component analysis indicates that slope and relief have some association with the estimated CO₂ consumption rates, presumably due to their impact on physical denudation and the supply of fresh minerals available for weathering (Bluth and Kump, 1994; Maher and Chamberlain, 2014). Therefore, topography may be important to consider at local to regional scales.

With the exception of SC-1, high-Na silicates consistently have a minor contribution to the CO₂ consumption across catchments (1.34% to 10.92%, Table 6), reflecting the dominance of the mafic-ultramafic lithology and the limited influence of the exposed Na-rich silicates. In contrast, the elevated contribution of high-Na silicates in the SC-1 catchment (34.51%) compared to other SC sites (<3%) may reflect the combination of a comparatively less harzburgite-lherzolite coverage and flatter slopes (Fig. 1). Domingo et al. (2021, 2023) mapped much of the SC-1 catchment as Quaternary alluvium, indicating the accumulation of weathered materials which may include a higher abundance of Na-rich silicates. However, more detailed geologic mapping and lithologic data is needed to better characterize the sources of solutes in this catchment.

The majority of the PMB and SC catchments derive most of their long-term CO₂ consumption from serpentinized ultramafics (>70%), consistent with its geological setting dominated by harzburgite-lherzolite lithology supplying most of the dissolved Mg²⁺ (Fig. 1a). With the exception of SC-1, SC catchments (75.11% to 78.15%, Table 6) have slightly higher ultramafic influence than PMB catchments (71.62% to 73.70%), presumably due to the influence of some enhanced weathering of exposed nickel laterites and the higher contribution of carbonate lithology in PMB catchments, as discussed in Section 5.1.1.

The relatively higher contribution of low-Na silicates to long-term CO₂ consumption than serpentinized ultramafics in seven out of nine catchments in the East subgroup appears to be

consistent with the dominance of mafic-ultramafic cumulates and basalt-diabase lithology (Fig. 1a). In comparison, western catchments exhibit greater variability, reflecting the variable extent of mafic-ultramafic cumulates and harzburgite-lherzolite rocks across the catchments. This variability extends to the magnitude of total silicate weathering, although seasonal variations in precipitation and sea spray additionally influence the partitioning of individual silicate endmembers.

Fig. 14 compares the calculated long-term CO₂ consumption rates from this work against estimates for other catchments with various lithologies. Generally, estimates from each watershed occupy the upper range of the trend followed by the CO₂ consumption of basaltic, volcanic, and ultramafic terrains with runoff. The mean area-weighted CO₂ consumption in the ZOC is approximately 1.5 times higher than the estimate of Dessert et al. (2003) for large basaltic provinces and small island arcs, and consistent with other studies, an order of magnitude higher than the average for major global watersheds reported by Gaillardet et al. (1999). Among other ultramafic landscapes, the ZOC appears to be comparable to the Monte del Estado Massif in Puerto Rico, USA ($1.59 \times 10^6 \text{ mol CO}_2 \text{ km}^{-2} \text{ yr}^{-1}$; Moore et al., 2025) and ~7 times higher than the Voltri Massif in Italy ($3.02 \times 10^5 \text{ mol CO}_2 \text{ km}^{-2} \text{ yr}^{-1}$; Frondini et al., 2019). The lower CO₂ consumption reported for the Voltri Massif likely reflects the substantially lower runoff from its catchments (215 mm/yr to 947 mm/yr; Frondini et al., 2019), highlighting the importance of hydrology, consistent with the watershed-scale controls identified in Fig. 11b.

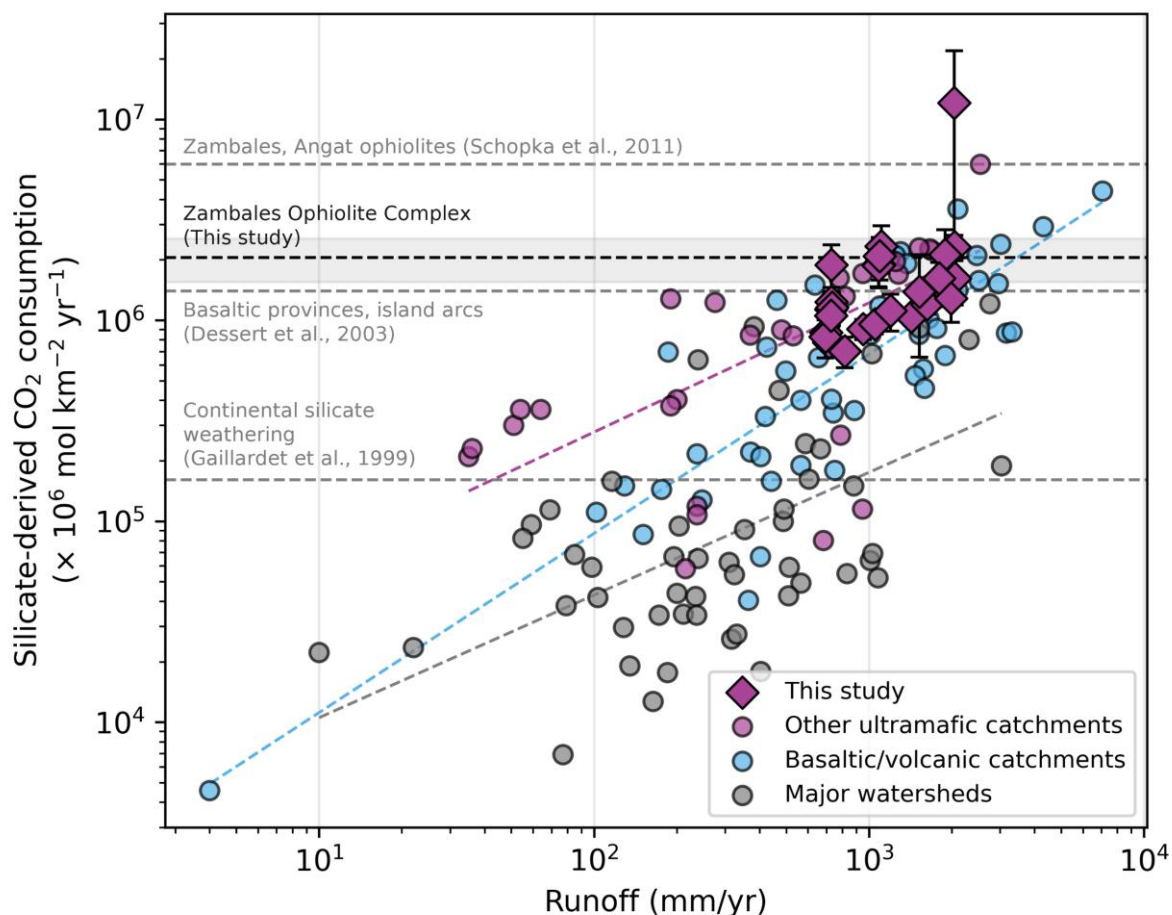


Figure 14. Area-normalized CO₂ consumption from this study and previous estimates. Both axes are in logarithmic scales. Other ultramafic catchments include the Zambales and Angat ophiolites, Philippines (Schopka et al., 2011), Putah Creek watershed, California, USA (McClain and Maher, 2016), Voltri massif, Italy (Frondini et al., 2019) and Monte del Estado massif, Puerto Rico, USA (Moore et al., 2025). Data for basaltic and volcanic catchments were compiled from Louvat and Allègre (1997), Dessert et al. (2001, 2003), Goldsmith et al. (2008, 2010), Gaillardet et al. (2011), and da Conceição et al. (2015). Major watershed estimates are from Gaillardet et al. (1999). The gray envelope around the dashed line representing the area-normalized mean from this study represents the calculated CV (Table 6).

While the fluxes shown in Fig. 14 are predominantly derived from river geochemistry, it is important to recognize that the geochemical approaches to estimate weathering fluxes vary across each study. The CO₂ consumption of the ZOC as estimated in this work is approximately three times lower than the combined value reported by Schopka et al. (2011) for the Zambales and Angat ophiolites ($5.99 \times 10^6 \text{ mol CO}_2 \text{ km}^{-2} \text{ yr}^{-1}$). This discrepancy likely arises from several methodological differences, particularly temporal variability in river chemistry due to sampling seasonality, as most samples in Schopka et al. (2011) were collected during the dry season, and differences in the geochemical modeling framework used for source partitioning. These factors were systematically evaluated by Moon et al. (2014) as significant sources of uncertainty in estimates of weathering rates and motivated this work.

Rather than treating silicate weathering as a single lithologic source, the geochemical inversion model adopted in this study incorporates lithological heterogeneity by implementing multiple silicate endmembers (serpentinized ultramafics, high-Na silicates, and low-Na silicates), together with carbonate dissolution and precipitation, to reconstruct the measured major ions (Ca²⁺, Mg²⁺, Na⁺) as well as dissolved Si, Sr²⁺, and ⁸⁷Sr/⁸⁶Sr ratios. Additionally, accounting for a solute sink provides further constraint to the mass balance calculations. Fig. S7b shows that the contribution of serpentinized ultramafic endmember, which supplies most of the Mg²⁺ ions, is considerably higher in inversion scenarios that separately exclude secondary mineral precipitation and ⁸⁷Sr/⁸⁶Sr ratios. Furthermore, successful reconstruction of the measured dissolved Si required the inclusion of a sink endmember, highlighting the sensitivity of the inversion to this process (Section 4.2.2.2). These additional independent constraints, which were not considered in previous geochemical partitioning works (e.g., Gaillardet et al., 1999; Schopka et al., 2011; Kemeny et al.,

2021), can limit the range of acceptable mass balance solutions and produce more conservative estimates of silicate-derived CO₂ consumption.

5.4 Implications

5.4.1 Sensitivity of geochemical inversion models: Implications for estimating modern silicate weathering budgets

Accurately constraining silicate weathering fluxes requires geochemical frameworks that can account for the complexity of natural weathering systems (Hartmann, 2009; Hartmann et al., 2010; Moon et al., 2014). In this study, representing the lithologic heterogeneity and secondary mineral formation within the ZOC demonstrates that inversion modeling is sensitive to these parameters and can substantially alter solute partitioning. Despite the relatively conservative approach adopted in this study leading to lower area-normalized fluxes than previous estimates from the same catchments (cf. Schopka et al., 2011), the estimated area-normalized CO₂ consumption of the ZOC remains among the highest reported for silicate catchments worldwide (Fig. 14), reinforcing the potential importance of tropical mafic and ultramafic landscapes to the global weathering budget (Dessert et al., 2003; Hartmann et al., 2009; Gaillardet et al., 2011).

Given current investments in exploring enhanced rock weathering (ERW) as a potential mechanism for atmospheric carbon dioxide removal (CDR), this study provides a natural watershed-scale analog for tropical mafic and ultramafic landscapes. Among the many uncertainties in evaluating the scalability and effectivity of ERW as a CDR strategy are limitations in our understanding of how alkalinity moves through the land-ocean continuum and the potential for release of toxic trace metals (McClain and Maher, 2016; Zeng et al., 2019; Schiedung et al., 2026). Estimates from this work provide useful constraints on natural weathering, as areas in the

tropics like the ZOC represent the higher end of global weathering fluxes. Additionally, the demonstrated sensitivity of our geochemical approach to additional constraints, such as lithology-specific geochemical signatures and secondary mineral formation, represents the complexity of estimating silicate weathering-derived solute and CO₂ export at the watershed scale. Accounting for these factors can improve the representation of weathering processes in modern carbon cycle models.

5.4.2 Scaling weathering fluxes to Southeast Asia: Implications for global silicate weathering rates and Neogene cooling

An extrapolation can be made by estimating the areal distribution of different lithologies across maritime SEA (Brunei, Indonesia, Malaysia, the Philippines, Singapore, and Timor-Leste) and assuming that the corresponding area-normalized CO₂ consumption rates calculated for the ZOC are representative of ophiolitic, ultramafic, mafic, felsic, and carbonate lithologies across the region (Table 6). Table 7 summarizes the estimated lithological distribution across maritime SEA using global and regional geospatial information from the Global Lithological Map (GLiM) database (Hartmann and Moosdorf, 2012) and the geological map generated by the Geological Survey of Japan for Southeast Asia (Peucker-Ehrenbrink and Miller, 2004; Wakita et al., 2004), complemented by geological datasets from governmental agencies for Indonesia, Malaysia, and the Philippines (Menteri Energi dan Sumber Daya Mineral, 2017; Jabatan Mineral dan Geosains Malaysia, 2025; Mines and Geosciences Bureau, 2026).

Table 7. Estimated lithological distribution and regional weathering CO₂ consumption in maritime Southeast Asia extrapolated from calculated ZOC weathering rates.

Weathering class	Estimated area (km ²)	% total SEA area*	Area-normalized consumption (Table 6, mol CO ₂ km ⁻² yr ⁻¹)**	Extrapolated consumption (mol CO ₂ yr ⁻¹)
Felsic (<i>high-Na sil.</i>)	1.99×10^5	6.64	1.42×10^5	2.82×10^{10}

Mafic (low-Na sil.)	2.48×10^5	8.30	9.62×10^5	2.39×10^{11}
Ultramafic (serp. ultramafic)	6.78×10^3	0.23	9.44×10^5	6.40×10^{09}
Ophiolitic (overall ZOC)	4.17×10^4	1.40	2.05×10^6	8.55×10^{10}
Other (inc. sedimentary rocks)***	2.14×10^6	71.57	1.42×10^5	3.04×10^{11}
Total silicate	2.99×10^6	88.13	-	6.63×10^{11}
Carbonate	3.54×10^5	11.84	3.16×10^5	1.14×10^{11}

*Not included in the table are polygons marked as 'Excluded', which accounts for the remaining 0.03% of the area

** The 'Other' category is assigned the area-normalized consumption for the 'Felsic' weathering class

*** The 'Other' category includes sedimentary rocks (35.68%), unconsolidated sediments (19.49%), metamorphic rocks excluding metacarbonates (7.88%), and areas assigned identified as intermediate (5.09%), mixed (2.50%), and unknown (0.92%) lithologies. The latter categories represent areas where the provided geological descriptions were insufficient to confidently assign a lithological class.

Following this approach, CO₂ consumption in maritime SEA via silicate weathering is estimated to be 6.63×10^{11} mol CO₂ yr⁻¹ $\pm$ 26.46% (1 σ). This flux is ~74% of the estimate for tropical volcanic arcs (9×10^{11} mol CO₂ yr⁻¹; Schopka et al., 2011), ~16% of global basaltic weathering (4.08×10^{12} mol CO₂ yr⁻¹; Dessert et al., 2003), and ~7.6% of global silicate weathering CO₂ consumption (8.70×10^{12} mol CO₂ yr⁻¹; Gaillardet et al. 1999). Given that the area represented by this estimate represents only <2% of the total global continental area, our findings support the previous inferences of disproportionate contribution of volcanic arcs, particularly maritime SEA, to global silicate weathering rates (Dessert et al., 2003; Gaillardet et al., 1999, 2011; Hartmann et al., 2009; Schopka et al., 2011; Moon et al., 2014).

The ongoing discussion regarding the climatic influence of the tectonic uplift of SEA has largely centered on the exposure and subsequent weathering of mafic and ultramafic rocks, an event that has not been clearly expressed in the marine ⁸⁷Sr/⁸⁶Sr and ¹⁸⁷Os/¹⁸⁸Os records (Zhang and Planavsky, 2019; Park et al., 2020; Rugenstein et al., 2021; Bayon et al., 2023; Chiang et al., 2024; Liu et al., 2026). Based on our data, the ZOC exports 5.87×10^6 mol Sr yr⁻¹ $\pm$ 62.10% (1 σ), partitioned among the contributions of silicate weathering (61.47% of the total flux), carbonate

weathering (15.15%), and precipitation (23.38%). A flux-weighted Sr isotope ratio of 0.7055 can then be calculated, with the total silicate endmember having a flux-weighted $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7033. This indicates that radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ catchments are offset by the higher Sr fluxes from less radiogenic rivers.

However, scaling the ZOC $^{87}\text{Sr}/^{86}\text{Sr}$ value is not straightforward, given that (1) precipitation appears to significantly contribute to the Sr flux, which in the past would have likely varied as seawater $^{87}\text{Sr}/^{86}\text{Sr}$ changed, and (2) the demonstrated range of Sr isotopic compositions reported in this study and elsewhere within SEA (Fig. 14) highlights the importance of accounting for the tectonic and geochemical complexity of volcanic arc settings. This suggests that seawater $^{87}\text{Sr}/^{86}\text{Sr}$ alone may not adequately constrain the magnitude of silicate weathering in SEA and its role in the atmospheric CO_2 consumption during the Neogene, as the isotopic signature of the regional Sr export may not have been associated with a single, predictable value. Additional studies investigating the alteration history of mafic and ultramafic rocks and its geochemical expression may help better reconcile marine isotope (Sr, Os, Li) records with independent estimates of silicate weathering-derived CO_2 consumption.

6 Conclusion

In this work, we report a new geochemical dataset from rivers draining the Zambales Ophiolite Complex and applied inversion modeling to partition solutes derived from silicate weathering. Using newly measured and existing major ion and $^{87}\text{Sr}/^{86}\text{Sr}$ data, we constrained source and sink endmembers to estimate disproportionately high area-normalized long-term CO_2 consumption rates, consistent with other mafic and ultramafic landscapes. Explicitly accounting for lithological heterogeneity and secondary mineral precipitation in the inversion model provided new insights into the sensitivity of geochemical source-partitioning approaches. The results from

1127 this study reinforce previous work demonstrating that tropical volcanic arcs contribute
1128 substantially to the global silicate weathering budget, despite the more conservative inversion
1129 framework adopted here.

1130 However, important uncertainties remain in estimating silicate weathering fluxes, and we
1131 demonstrate that the variability in the geochemical signals of the lithologies present in the ZOC,
1132 particularly their $^{87}\text{Sr}/^{86}\text{Sr}$ signatures, introduces an additional dimension to estimating the modern
1133 weathering rates and evaluating the role of Southeast Asian uplift on the late-Cenozoic climate
1134 evolution. In addition to these geochemical controls, the PCA identified associations between
1135 long-term CO_2 fluxes and catchment features related to topography and hydrology. Future work
1136 could include explicitly accounting for these landscape parameters to reveal solute production
1137 mechanisms, providing insights into kinetic or transport limitations. Investigating such
1138 variabilities in the ZOC can improve estimates of modern and paleo-weathering fluxes from the
1139 Southeast Asian region.

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Supplementary material

Ultramafic weathering in the tropics: Geochemistry and inverse modeling of rivers draining the Zambales Ophiolite Complex (ZOC), Philippines

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The contents of this supplementary material include:

- Figure S1 to S8
- Tables S1 and S2

Data analysis scripts and MEANDIR input and output files are uploaded separately at <https://doi.org/10.5281/zenodo.22945851>.

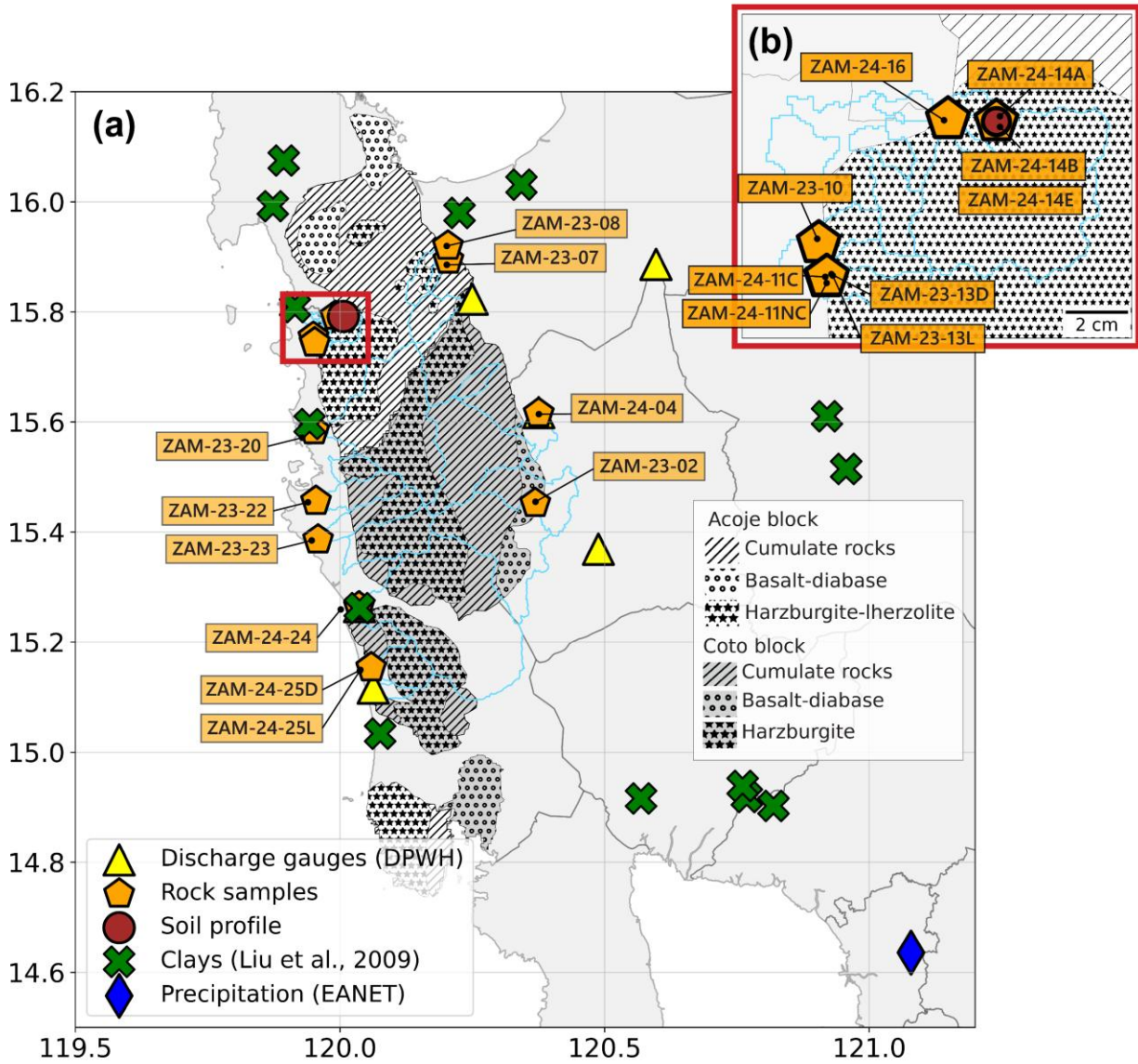


Figure S1. (a) Sampling locations of the rock and soil samples collected in this study, clay-fraction sediment samples from Liu et al. (2009), the Acid Deposition Monitoring Network in East Asia (EANET) precipitation monitoring station, and the discharge gauging stations used in this study. (b) Zoomed in map highlighting samples from the SC and PMB sub-catchments within the red box in (a).

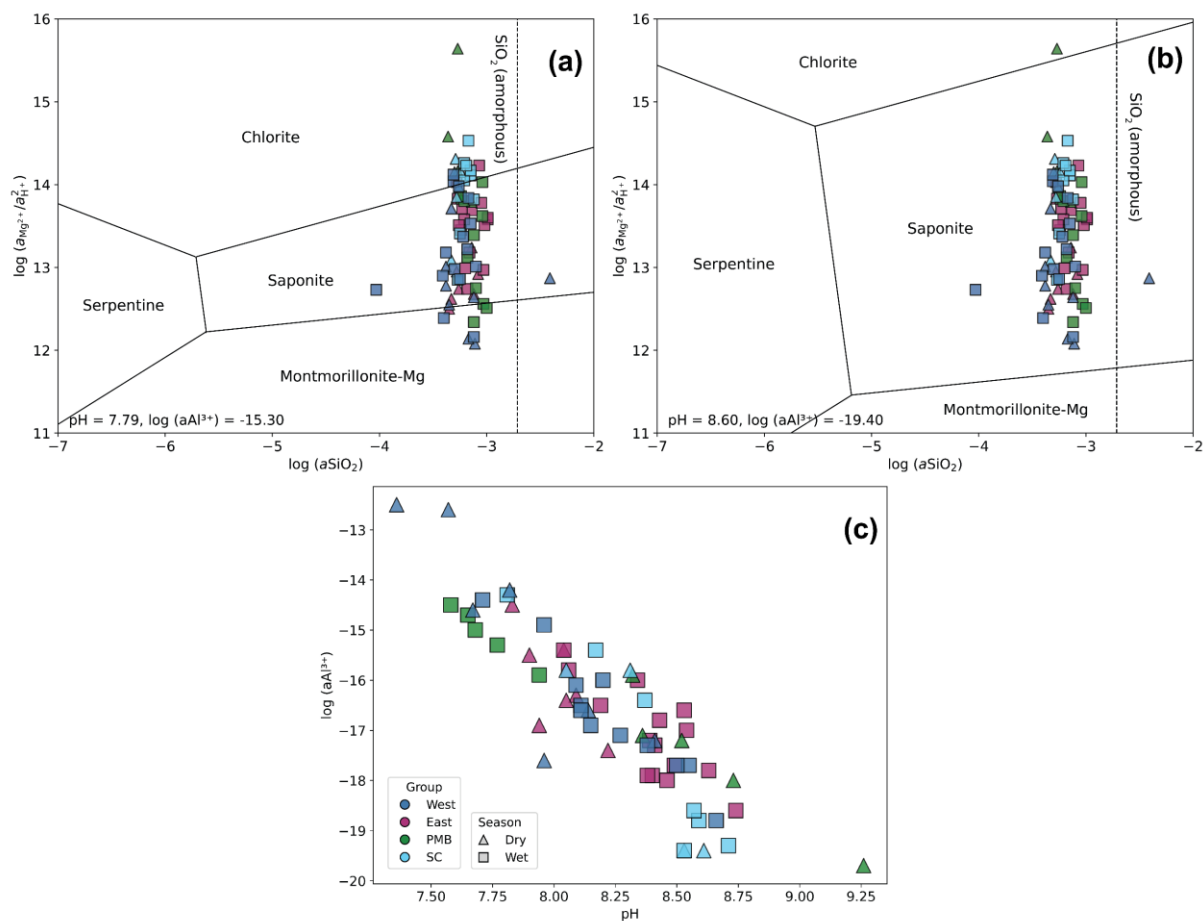


Figure S2. Mineral activity diagrams at (a) low and (b) high pH values and their corresponding $\log(a_{\text{Al}^{3+}})$. The linear relationship between pH and $\log(a_{\text{Al}^{3+}})$ is shown in (c).

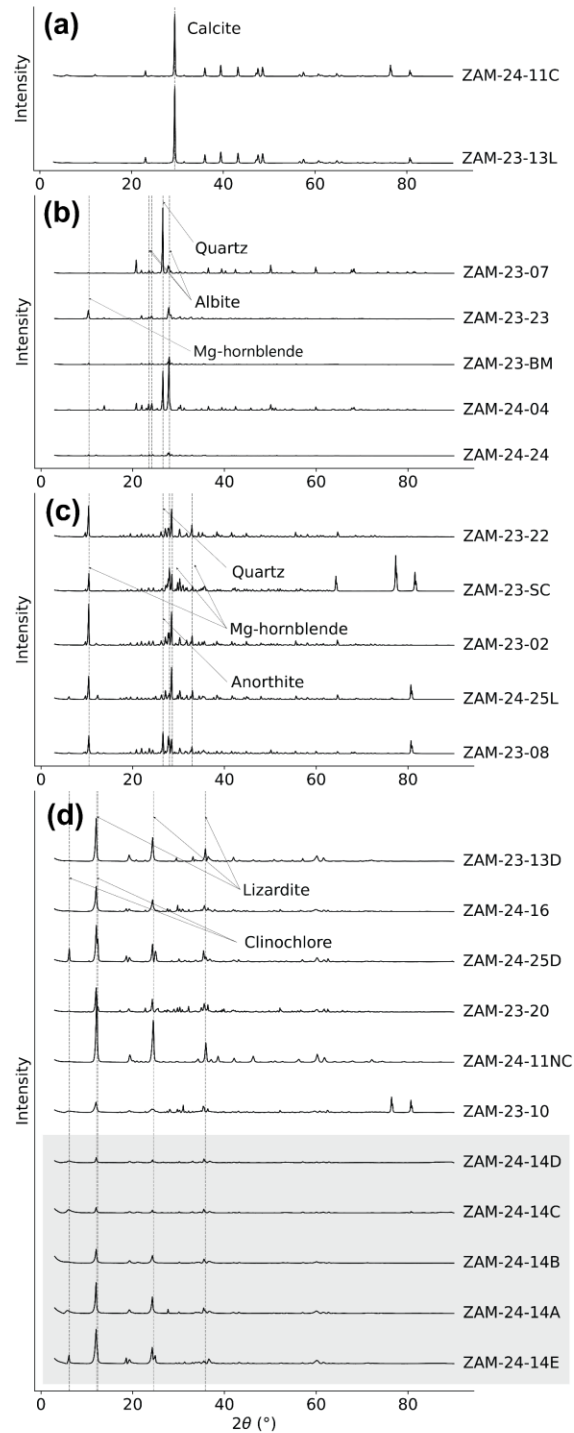


Figure S3. XRD spectra of hand rock and soil samples grouped according to lithological classification: (a) carbonates, (b) high-Na silicates, (c) low-Na silicates, and (d) serpentized ultramafics. Spectra in the shaded region in (d) correspond to the samples obtained from the soil profile site (Fig. S1). Note that the y-axes are not to scale; comparisons among spectra are only valid for within each lithological classification.

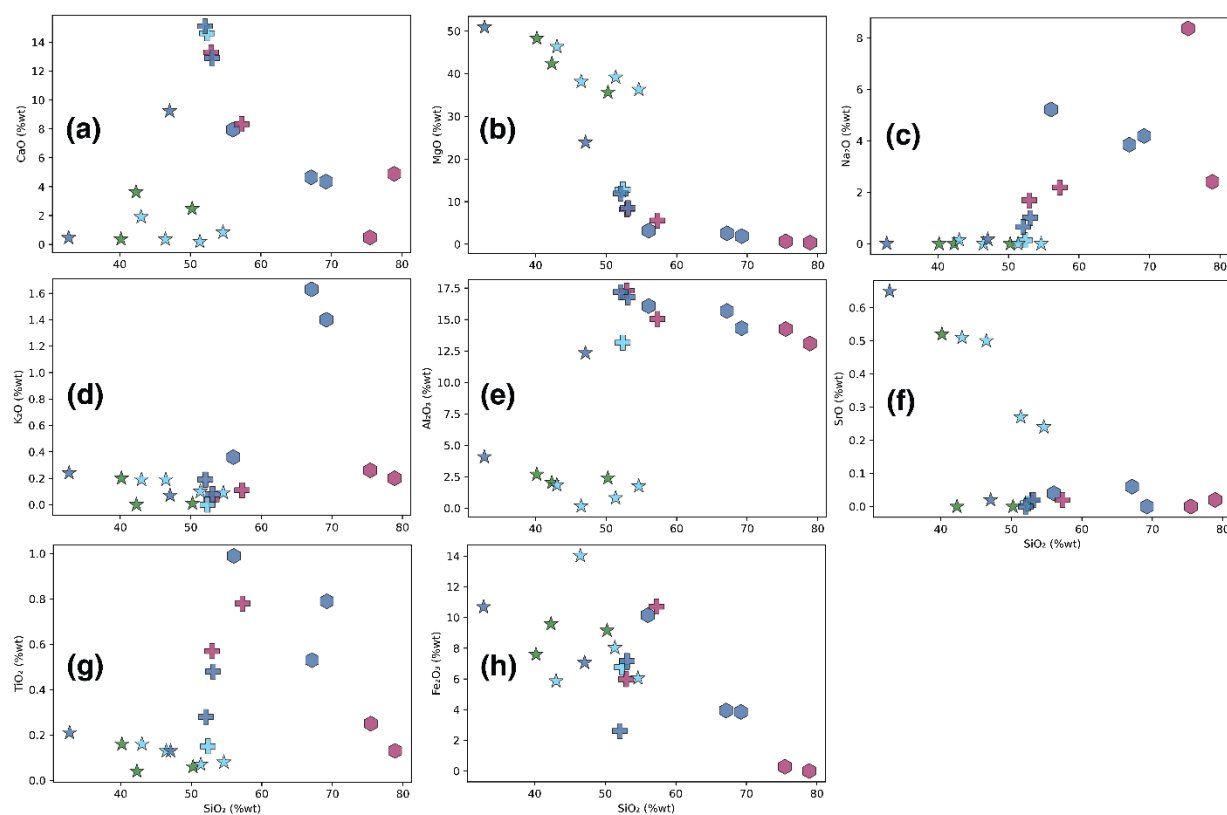


Figure S4. Harker-type diagrams for the elemental composition of the rock samples with wt. % SiO₂ composition. (a) CaO, (b) MgO, (c) Na₂O, (d) K₂O, (e) Al₂O₃, (f) SrO, (g) TiO₂, and (h) Fe₂O₃.

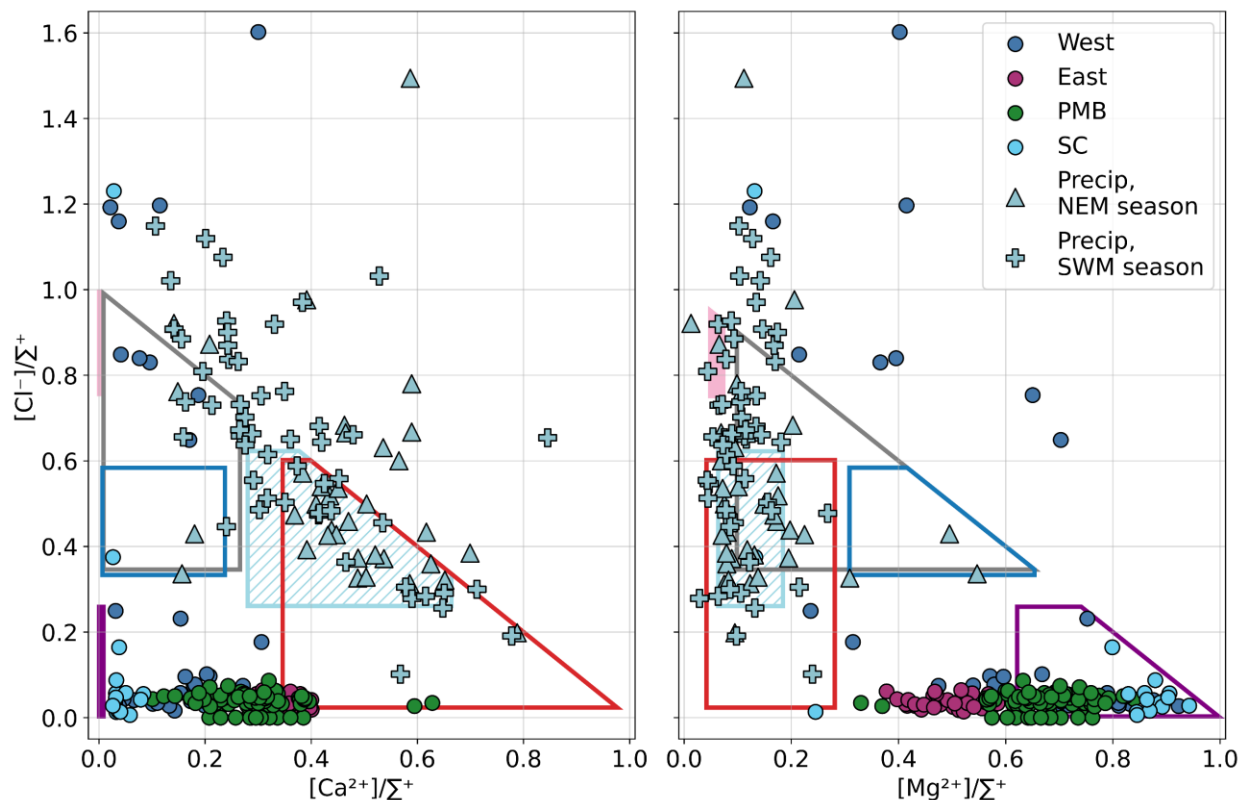


Figure S5. Elemental molar ratios calculated from river water and precipitation data (Network Center for EANET, 2024) plotted as (a) $[Ca^{2+}]/\Sigma^+$ vs. $[Cl^-]/\Sigma^+$ and (b) $[Mg^{2+}]/\Sigma^+$ vs. $[Cl^-]/\Sigma^+$. The polygons represent the range of endmember ratios as listed in Table 5, following the colored labels in Fig. 7a-b. The polygons are truncated due to the compositional constraint imposed by the normalization variable ($\Sigma^+ = [Na^+] + [Ca^{2+}] + [Mg^{2+}]$), where any combination of $[Na^+]/\Sigma^+$, $[Ca^{2+}]/\Sigma^+$, and $[Mg^{2+}]/\Sigma^+$ values cannot have a sum exceeding one. The actual precipitation data from Network Center for EANET have a significantly wider range than what was used for the inversion, as only the average of the 25th and 75th percentile values from both the wet (Southwest Monsoon, SWM) and dry (Northeast Monsoon, NEM) seasons were utilized. Initial inversion runs using the minimum and maximum values produced a broader range than required to solve the mass balance.

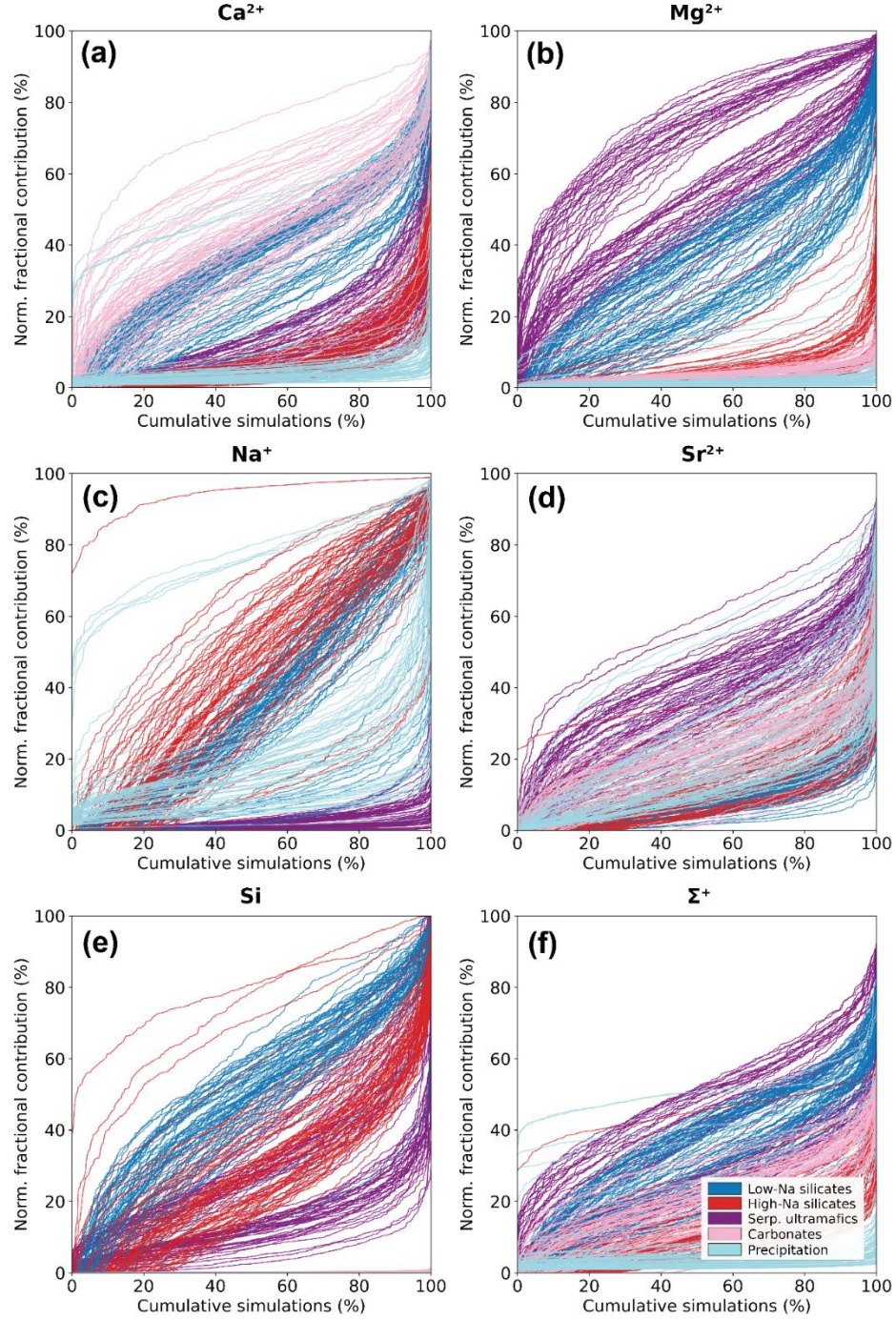


Figure S6. Cumulative distribution function (CDF) plots of the 400 successful simulations for the full model inversion scenario. Each plot corresponds to (a) Ca^{2+} , (b) Mg^{2+} , (c) Na^+ , (d) Sr^{2+} , (e) dissolved Si, and (f), the normalization parameter, where $\Sigma^+ = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+]$.

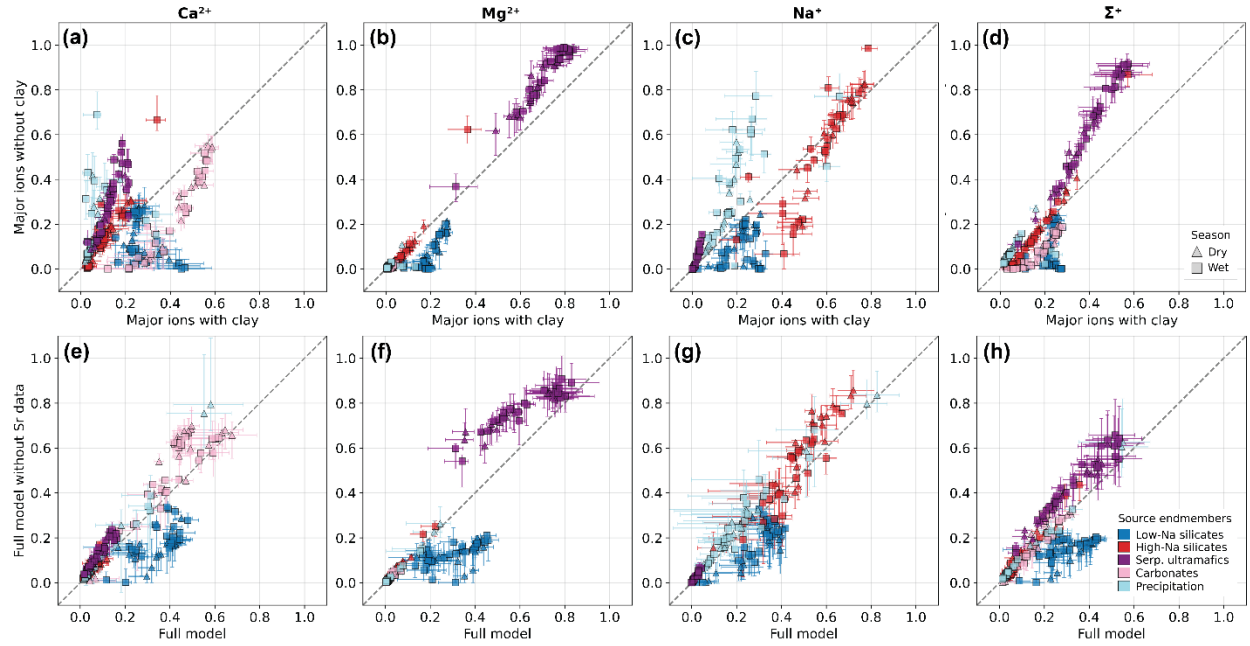


Figure S7. Sensitivity of the geochemical inversion results to the incorporation of clay endmember and Sr isotopic data. Panels (a-d) correspond to the normalized source partitions for $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{Na}^+]$, and the normalization variable (Σ^+) calculated for inversions constrained only by major ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^-) with the clay endmember included (x-axis) and excluded (y-axis). Panels (e-h) show the normalized source partitioning for inversions using the full geochemical model that include (x-axis) and exclude (y-axis) $[\text{Sr}^{2+}]$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data. Diagonal broken line represents perfect correlation ($y=x$). Markers denote data for both dry (triangles) and wet (squares) seasons, color-coded by the source endmembers. Error bars are based on the 25th and 75th percentile fractions from the successful simulations.

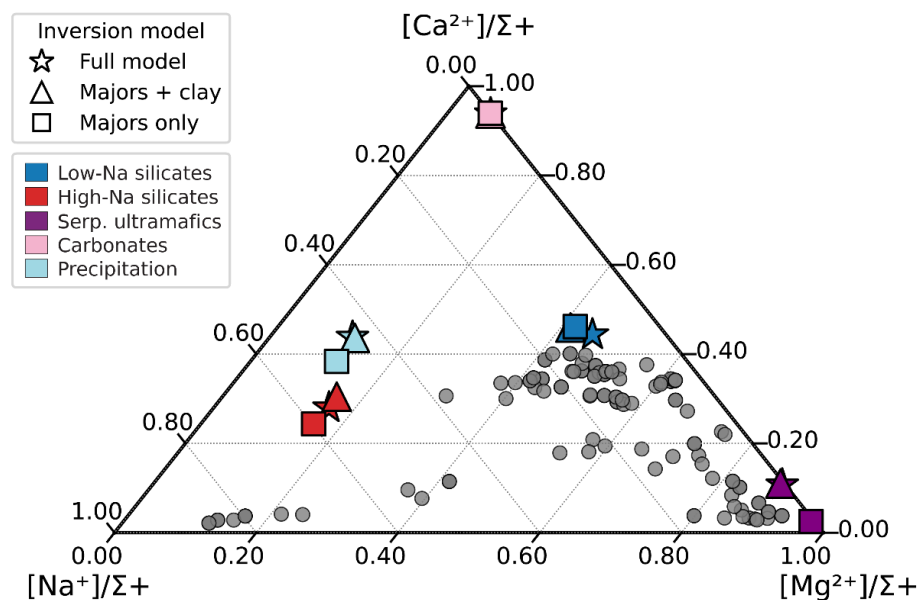


Figure S8. Sensitivity of the inversion-constrained composition of source endmembers to the incorporation of a sink endmember in the inversion model. Gray markers are the elemental ratios of the river samples, while colored markers are the inversion-constrained source endmembers. Endmember compositions (identified by color) are shown as the median from the calculated elemental ratios. Inversion scenarios shown are the full model (star), major ions and full suite of endmembers (triangle), and major ions and full suite of endmembers without the sink term (square).

Table S1. Gauge records used to estimate discharge from ungauged study catchments. Data can be retrieved from https://apps.dpwh.gov.ph/streams_public.

River	Latitude	Longitude	Drainage area (m ²)	Start year	End year	Raw data units	Temp. Reso.	Study catchments applied to
Agno River	15.88639	120.5969	2402.14	1983	2001	L/s	Daily	Malabobo River, Mapita River, Dumoloc River, Bayaoas River, SC catchments
Bangot River	15.36889	120.4881	92.15	1993	2020	L/s	Daily	Camiling River, Bulsa River us, Bancal River, Dapya River, Maloma River, Bucao River
Bayaoas River	15.82333	120.25	66.32	1983	2015	L/s	Daily	Bayaoas River, Mapita River, Dumoloc River, Camiling River, Masinloc River, Lawis River, SC and PMB catchments
Bucao River	15.26417	120.0367	646.01	2010	2020	L/s	Daily	Bucao River, Masinloc River, Lawis River, Salasa River, Bulsa River ds, Dapya River, Maloma River
Camiling River	15.61694	120.3753	284.96	1985	2020	L/s	Daily	Camiling River, Mapita River, Dumoloc River, Bayaoas River, Malabobo River, Masinloc River, Lawis River, Salasa River, Bulsa ds, Bagsit River, SC and PMB catchments
Maloma River	15.11611	120.0628	150.29	1984	2020	L/s	Daily	Maloma River, Salasa River, Bagsit River, Bancal River, Dapya River, Maloma River, Bucao River

Table S2. Visual description of hand rock samples

Sample ID	Site	PCA classification	Description	Representative ophiolite sequence
ZAM-23-13L	PMB4	Carbonate	White, massive carbonate rock	Overlying sedimentary sequence
ZAM-23-PMB	PMB3-PMB4 confluence	Carbonate	White, massive carbonate rock	Overlying sedimentary sequence
ZAM-24-11C	PMB3	Carbonate	White, massive carbonate rock	Overlying sedimentary sequence
ZAM-23-07	Dumloc River	High Na silicate	Light-colored silicate rock with banded ("tiger-striped") gneissic appearance; possibly metamorphosed chert	Overlying rocks, possibly younger
ZAM-23-23	Bagsit River	High Na silicate	Fine-grained quartz-rich metasedimentary rock, possibly metamorphosed mudstone or turbidite	Overlying rocks, possibly younger
ZAM-23-BM	Bucau River	High Na silicate	Light-colored pumice with vesicular texture	Overlying rocks, possibly younger
ZAM-24-04	Camiling River, ds	High Na silicate	Coarse-grained felsic igneous rock	Overlying rocks, possibly younger
ZAM-24-24	Bucau River	High Na silicate	Light-colored pumice with vesicular texture	Overlying rocks, possibly younger
ZAM-23-02	Bulsa River, us	Low Na silicate	Fine-grained mafic volcanic rock with basaltic appearance	Basalt-diabase
ZAM-23-08	Bayaoas River	Low Na silicate	Fine-grained mafic volcanic rock with basaltic appearance	Basalt-diabase
ZAM-23-22	Salasa River	Low Na silicate	Fine-grained mafic volcanic rock with basaltic appearance	Basalt-diabase
ZAM-23-SC	SC6-SC7 confluence	Low Na silicate	Medium- to coarse-grained mafic intrusive rock with gabbroic texture	Mafic cumulate sequence
ZAM-24-25L	Selbang River	Low Na silicate	Altered metamafic igneous rock	Mafic cumulate sequence

ZAM-24-14E	Soil profile	Serpentinized ultramafic	Strongly serpentinized ultramafic rock with visible pyroxene surfaces	Serpentinized peridotites
ZAM-24-14A	Soil profile	Serpentinized ultramafic	Strongly serpentinized ultramafic rock with visible pyroxene surfaces	Serpentinized peridotites
ZAM-23-10	PMB2	Serpentinized ultramafic	Highly weathered serpentinized ultramafic rock	Serpentinized peridotites
ZAM-23-20	Lawis River, ds	Serpentinized ultramafic	Coarse-grained mafic rock containing white plagioclase, gray pyroxene, and dark vein networks	Serpentinized peridotites
ZAM-24-14B	Soil profile	Serpentinized ultramafic	Strongly serpentinized ultramafic rock with visible pyroxene surfaces	Serpentinized peridotites
ZAM-24-16	SC7	Serpentinized ultramafic	Dense gray ultramafic rock with reddish weathered rinds and fresh pyroxene surfaces	Serpentinized peridotites
ZAM-23-13D	PMB4	Serpentinized ultramafic	Green, highly serpentinized ultramafic rock with smooth, locally slick surfaces	Serpentinized peridotites
ZAM-24-11NC	PMB3	Serpentinized ultramafic	Green serpentinized ultramafic rock	Serpentinized peridotites
ZAM-24-25D	Selbang River	Serpentinized ultramafic	Green serpentinized ultramafic rock	Serpentinized peridotites
