Carbonates in the Critical Zone

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November 30, 2022

Abstract

Earth's Critical Zone (CZ), the near-surface layer where rock is weathered and landscapes co-evolve with life, is profoundly influenced by the type of underlying bedrock. Previous studies of the CZ have focused almost exclusively on landscapes dominated by silicate rocks. However, carbonate rocks crop out on approximately 15% of Earth's ice-free continental surface and provide important water resources and ecosystem services to ~1.2 billion people. Unlike silicates, carbonate minerals weather congruently and have high solubilities and rapid dissolution kinetics, enabling the development of large, interconnected pore spaces and preferential flow paths that restructure the CZ. Here we review the state of knowledge of the carbonate CZ and examine whether current conceptual models of the CZ, such as the conveyor model, can be applied to carbonate landscapes. We introduce the concept of a carbonate-silicate CZ spectrum. To obtain a holistic understanding of Earth's CZ we must understand CZ processes and architecture along the entire spectrum between the carbonate and silicate endmembers. We explore parameters that produce contrasts in the CZ in different carbonate settings and identify important open questions about carbonate CZ processes. We argue that, to advance beyond site-specific understanding and develop a more general conceptual framework for the role of carbonates in the CZ, we need integrative studies spanning both the carbonate-silicate spectrum and a range of carbonate settings.

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Key Points:

- A holistic understanding of Earth's critical zone requires integrative studies spanning the spectrum of carbonate and silicate landscapes.
- Porosity developed by congruent dissolution of carbonates decouples hillslopes from stream channels, altering topographic equilibrium.
- Shifts in carbonate critical zone structure from changing ecology, land use, and climate may be rapid because of fast dissolution kinetics.

Abstract

Earth's Critical Zone (CZ), the near-surface layer where rock is weathered and landscapes co-evolve with life, is profoundly influenced by the type of underlying bedrock. Previous studies employing the CZ framework have focused almost exclusively on landscapes dominated by silicate rocks. However, carbonate rocks crop out on approximately 15% of Earth's ice-free continental surface and provide important water resources and ecosystem services to ~1.2 billion people. Unlike silicates, carbonate minerals weather congruently and have high solubilities and rapid dissolution kinetics, enabling the development of large, interconnected pore spaces and preferential flow paths that restructure the CZ. Here we review the state of knowledge of the carbonate CZ, exploring parameters that produce contrasts in the CZ in different carbonate settings and identifying important open questions about carbonate CZ processes. We introduce the concept of a carbonate-silicate CZ spectrum and examine whether current conceptual models of the CZ, such as the conveyor model, can be applied to carbonate landscapes.We argue that, to advance beyond site-specific understanding and develop a more general conceptual framework for the role of carbonates in the CZ, we need integrative studies spanning both the carbonate-silicate spectrum and a range of carbonate settings.

Plain Language Summary

Carbonate landscapes, which cover ~15% of Earth's land surface and provide critical water resources and other services to ~1.2 billion people, require focused studies to understand how life and rocks interact. Most integrated studies of this "critical zone" focus on landscapes underlain by silicate minerals instead of considering the full spectrum of the minerals that make up bedrock. This review of the state of knowledge of the carbonate critical zone reveals that weathering extends to greater depths in carbonate landscapes compared with silicate landscapes, leading to the development of interconnected subsurface flow systems that transport both water and sediments. As a result, the flow of water and the movement of materials left behind by weathering rock may be disconnected from streams, unlike in silicate landscapes. Furthermore, changes in ecology, land use, and climate response may be rapid because carbonate dissolve faster than silicate rocks. Integrative studies of silicate, carbonate, and mixed silicate-carbonate landscapes will be required to further a holistic understanding of Earth's critical zone.

1 Introduction

The objectives of this paper are to review the state of knowledge of critical zone (CZ) processes in carbonate terrains, to advance a framework that serves to bridge the spectrum between carbonate and silicate CZ endmembers (Martin et al., 2021), and to identify key knowledge gaps in our understanding of the carbonate CZ. Earth's CZ is the region where landscapes co-evolve with life and is loosely defined as the zone from the base of continental crust weathering to the top of vegetation canopy (National Research Council, 2001). The CZ develops through interactions among geological, hydrological, chemical, biological, and climate processes. Understanding the scope of, and linkages between, these interactions requires interdisciplinary collaborations, to unravel how the CZ functions and responds to environmental perturbations, including human impacts on climate, land use, and global elemental cycling. As the concept of CZ science emerged, the U.S. scientific community engaged in focused research on Earth's CZ through the development of place-based Critical Zone Observatories (CZOs) (Brantley et al., 2017b), leading to the more recent development of theme-based Critical Zone

Networks (CZNs). The CZO/CZN sites span a variety of geological and climate settings across the U.S. However, the CZ framework is limited by a CZO/CZN focus on landscapes underlain by silicate rocks (Martin et al., 2021). Globally, scientists are beginning to establish CZ observatories on carbonate rocks (Gaillardet et al., 2018; Jourde et al., 2018; Quine et al., 2017), but carbonates remain underrepresented among the studies employing the CZ framework. Although prior and ongoing studies provide useful information about localized carbonate terrains, more synthesis and a better predictive understanding of the carbonate CZ will require integrative studies of multiple carbonate settings with varied characteristics. Such a synthesis could also improve fundamental understanding of the silicate dominated CZ, as weathering of carbonates is also important within (pre-)dominantly silicate settings (e.g. Brantley et al., 2013), and landscapes fall on a continuum between the carbonate and silicate endmembers.

A focus on terrains where the CZ is dominated by carbonate minerals is justified by their common occurrence, their influence on society and its resource base, and their role in the human experience and human culture. Approximately 15% of Earth's ice-free continental surface contains carbonate rock (Figure 1), and approximately 1.2 billion people, 16% of the Earth's population, reside on carbonate rock (Goldscheider et al., 2020). Landscapes developed by the dissolution of carbonate terrains, also known as karst, often appear as a central theme in cultural development among long-term communities around the world. Karst landforms and features have influenced Indigenous creation stories, place-naming (toponymy), culturally based geological interpretation, and local language adaptation in the Greater Antilles part of the Caribbean (Alvarez Nazario 1972; Dominguez-Cristobal 1989, 1992, 2007; Garcia et al., 2020; Pané 1999), as well as a form of wealth building in central Europe that goes back to the 17th century (Zorn et al., 2009). In addition, the conservation of karst features has become a global priority because they commonly link geological, ecological, cultural, archeological, and touristic resources (Williams, 2008a).

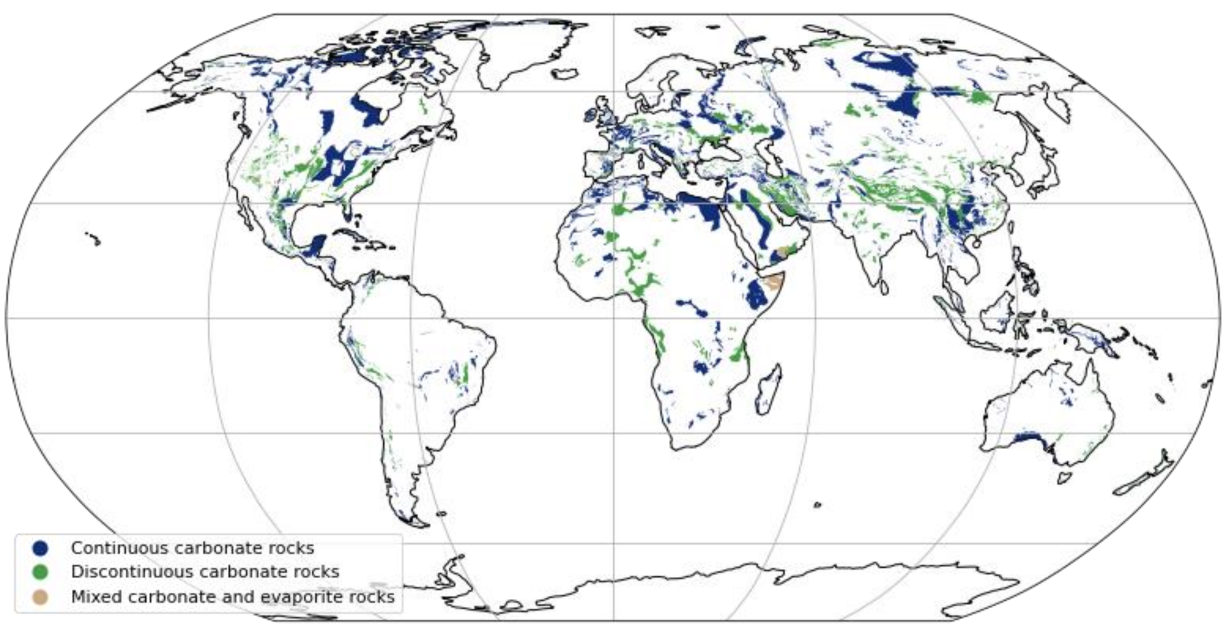

Figure 1. Carbonate exposures across the surface of earth using data from the World Karst Aquifer Map (data from Goldscheider et al., 2020). Areas with more than 65% carbonate rocks are mapped as continuous, whereas areas with between 15% and 65% carbonates are mapped

as discontinuous. Areas with greater than 15% of both carbonates and evaporites are mapped as mixed.

Carbonate terrains provide a wide range of societal and ecological services and present a variety of unique hazards. Given the favorable conditions for groundwater extraction from carbonates, and the ubiquity of springs within carbonate terrains, aquifers that develop in carbonate rocks are a crucial component of the global water supply (Ford and Williams, 2007; Worthington et al., 2016). Hazards unique to carbonate terrains, such as sinkholes and groundwater flooding, cause significant economic losses in densely populated areas (De Waele et al., 2011). Carbonate aquifers are particularly susceptible to contamination due to rapid travel times and limited natural remediation within large pores and conduits (White et al., 2016). Carbonate rocks are the largest global reservoir of carbon and have a potentially important, yet uncertain, role in the global carbon cycle over timescales relevant for rapid climate change (Baldini et al., 2018; Gaillardet et al., 2019; Martin, 2017). The raw materials for cement manufacturing are produced from carbonate rocks by calcination converting $CaCO_3$ to CaO plus CO_2, thereby producing 13% of the world's industrial CO_2 emissions (Fischedick et al., 2014). Carbonate minerals provide important pH buffering capacity within aquatic systems. Subterranean habitats within carbonate terrains host a wide variety of endemic species, many of which are threatened or endangered (Culver and Pipan, 2013). The carbonate CZ provides unique opportunities because of the ability for humans to access it at depth within caves. Interpretation of speleothem records within caves, which are an important source of paleoclimate information, requires substantial understanding of carbonate CZ processes, as signals recorded in speleothems are first filtered through the upper portion of the CZ (Fairchild et al., 2006; Fohlmeister et al., 2020). Consequently, studies of cave drip water have provided substantial insight into carbonate CZ dynamics (e.g., Tobin et al., 2021; Treble et al., 2022). Because of rapid mineral dissolution processes within, and subsurface fluxes through, the carbonate CZ, carbonate CZ systems may act as a bellwether for CZ responses to climatic and human perturbations (Sullivan et al., 2017). Furthermore, carbonate minerals often make up an important component of other sedimentary rocks (Hartmann and Moosdorf, 2012), and their distinct weathering characteristics can control weathering of non-carbonate minerals. The many impacts of carbonate minerals underscore the need for focused studies of carbonates in Earth's CZ.

2. Exploring the carbonate endmember

We begin with a review of current understanding of carbonate CZ processes. Within carbonate terrains, geological, hydrological, biological, geochemical, and climate variables produce a broad array of carbonate CZ characteristics. Here, we explore the range of parameters that create important differences within the carbonate CZ.

2.1 The importance of porosity distributions

Where the CZ occurs in nearly pure carbonate terrains, it is often transformed through congruent dissolution into karst, a landscape formed by dissolution of rock that develops underground drainage networks (Ford and Williams, 2007). Most karst landscapes form in carbonate bedrock, because of its common occurrence, although they also develop in evaporites (Klimchouk et al., 1996; Frumkin, 2013) and occasionally, in less soluble rocks (e.g., Wray and

Sauro, 2017). Dissolution integrates subsurface flow networks as water penetrates along heterogeneities in the rock until solutionally enlarged flow paths link input to outpoint points (Dreybrodt, 1990; Ford et al., 2000; Palmer, 1991). Such integrated flow paths, or karst conduits, are characterized by elevated permeability and exhibit rapid and turbulent flow that transports large quantities of solutes and gases between the surface and subsurface. High flow rates also allow the conduits to transport sediment through the subsurface (Cooper and Covington, 2020; Farrant and Smart, 2011; Herman et al., 2012). Once the capacity of the subsurface conduit network is sufficient to carry available surface runoff and sediment, closed basins develop on the land surface that route water and sediment into the subsurface. Conduit systems exit at springs, which frequently develop near the local hydrological base level. Together, these processes lead to the dolines, caves, and springs that characterize karst landscapes.

Karst aquifers are commonly conceptualized as a triple-porosity system, in which porosity is divided into a matrix component, a fracture component, and a conduit component (Quinlan et al., 1996; White, 2002; Worthington, 1999). The matrix component represents the primary porosity of the bedrock. The fracture component represents secondary porosity as a result of fractures and bedding partings. The conduit component represents dissolutionally enlarged flow paths that have increased connectivity as a result of positive feedback between dissolution and flow focusing (Worthington et al., 2016). While the dividing line between conduits and fractures is somewhat arbitrary, often the conduits are defined as the flow paths that carry turbulent flow (White, 2002). The three porosity components differ in their ability to store and transmit water. Primary porosity provides much more storage than the conduit network, because of its large total volume, whereas conduits transmit the most water, because of their high permeability (Worthington, 1999). These different hydrologic characteristics create a strong scale-dependent hydraulic conductivity in karst aquifers. Hydraulic conductivity over short distances is controlled by the primary porosity and is thus relatively low. Hydraulic conductivity increases over intermediate distances as fractures become important and is greatest at aquifer scales where flow through conduits dominates (Halihan et al., 2000; Király, 1975; Worthington, 2009). In general, heterogenous media exhibit an increase of hydraulic conductivity with measurement scale, up to some cutoff scale where the medium is well-represented by an equivalent porous medium (Schulze-Makuch et al., 1999). However, the range of variation in hydraulic conductivity is largest in karstified media, as karst exhibits the largest cutoff scale (Schulze-Makuch et al., 1999), with individual aquifers having measured values of hydraulic conductivity ranging over more than eight orders of magnitude (Worthington, 2009).

The primary porosity within a carbonate rock is a function of its diagenetic history and whether the rock has undergone burial diagenesis, which reduces primary porosity. The terms eogenetic karst and telogenetic karst are used to distinguish karst that is developed within relatively young carbonates that have primarily undergone meteoric (eogenetic) diagenesis from karst developed in older carbonates that have experienced burial diagenesis (telogenetic) and re-exposure to the surface via erosion (Vacher and Mylroie, 2002; Choquette and Pray, 1970). Integrated karst flow networks develop most easily in rocks with relatively low primary porosity and relatively high fracture porosity (Palmer, 1991; White, 1969; Worthington, 2014). Such conditions focus flow through higher permeability fractures, increasing flow velocities and the depth to which undersaturated water can penetrate the rock, ultimately leading to breakthrough of dissolutionally enlarged pathways that connect inlets to outlets (Dreybrodt, 1990). Positive feedback further focuses the flow, whereby the most efficient flow paths receive the most flow and therefore grow most rapidly, diverting even more flow into these pathways and further accelerating their growth (Ewers, 1982; Palmer, 1991; Siemers and Dreybrodt, 1998). The largest developing flow paths create troughs in the potentiometric surface, such that other competing pathways are drawn toward them, frequently producing a dendritic pattern like that found in surface stream networks. The overall conduit network geometry is strongly influenced by the nature of recharge to the aquifer and the locations of recharge and outlet points (Figure 2) (Palmer, 1991).

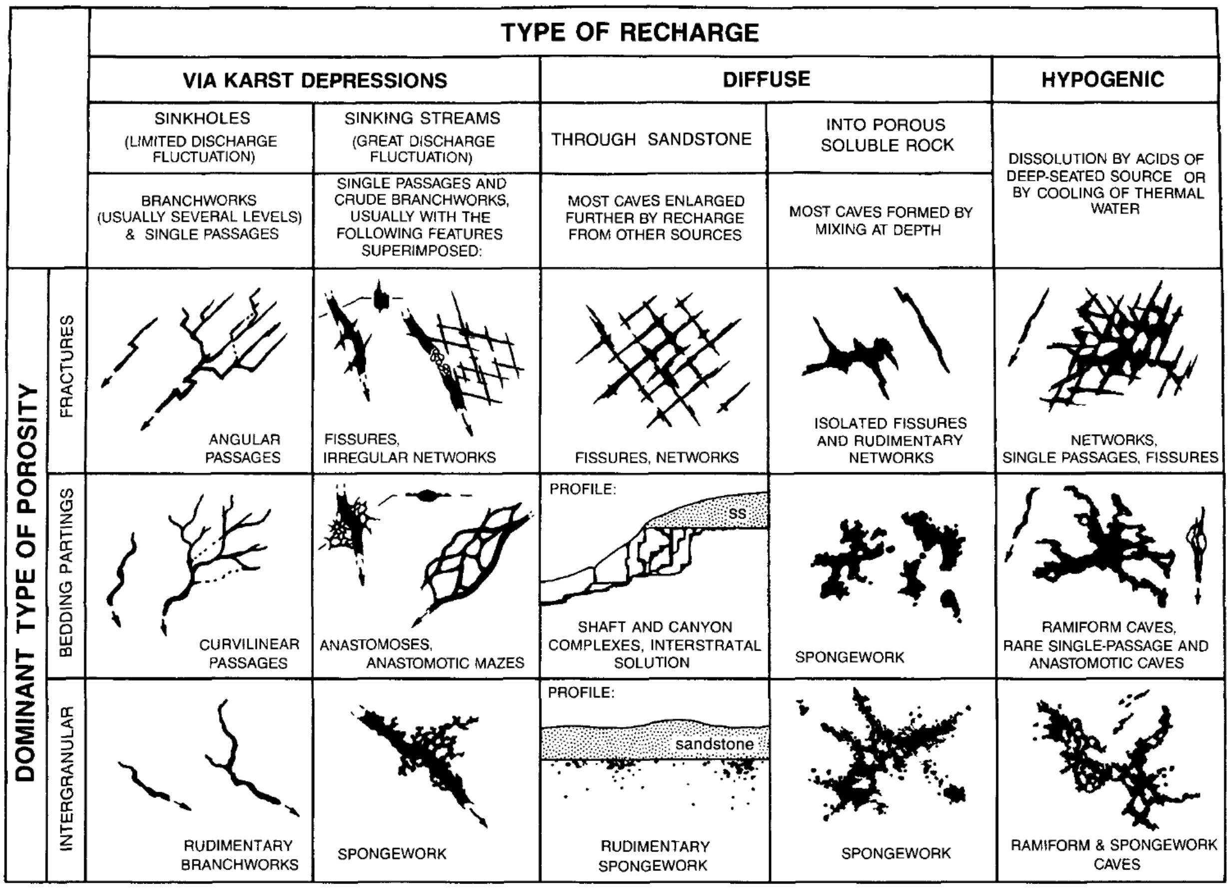

Figure 2. Relationship between recharge, dominant porosity, and the patterns of karst networks that develop (from Palmer, 1991).

Rocks with high primary porosity, as found in eogenetic karst, preferentially develop spongework caves (Palmer, 1991), which are often isolated voids that are not connected into an integrated conduit flow system (Vacher and Mylroie, 2002). Examples of such dissolutional voids include flank margin caves and "banana holes" that develop in carbonate island karst (Breithaupt et al., 2021; Mylroie and Carew, 1990; Vacher and Mylroie, 2002). In such settings, the locations of dissolutional voids may be controlled by zones of mixing (Mylroie and Carew, 1990) or by biological CO_2 production (Gulley et al., 2016, 2015). Consequently, voids frequently develop near the water table, where vadose zone CO_2 can boost dissolution rates (Gulley et al., 2014), or in zones of freshwater-saltwater mixing (Mylroie and Carew, 1990). While evolution of such voids produced by local mixing or CO_2 production may enhance local hydraulic conductivity and focus porous media flow toward enlarging voids (Mylroie and Carew, 1990; Vacher and Mylroie, 2002), it is less common for these processes to develop regionally integrated conduit systems (Palmer, 1991). However, long-range conduit connectivity that does develop in eogenetic karst is commonly associated with sinking streams (Martin and Dean, 2001; Monroe, 1976), reversing springs (Gulley et al., 2011; Moore et al., 2010), or large recharge areas, as found in the Yucatan Peninsula of Mexico (Back et al., 1986) and on large carbonate islands (Larson and Mylroie, 2018).

The primary porosity of carbonate rocks also impacts the magnitude of water exchange between conduits and the porous matrix. The matrix component is often considered negligible in models of flow and transport in telogenetic karst aquifers (Peterson and Wicks, 2005). However, in eogenetic karst, with high matrix porosity, transient head conditions within conduits, combined with the relatively high permeability of the matrix, can produce substantial exchange flows between the conduits and matrix, analogous to hyporheic exchange within rivers (Martin and Dean, 2001). Such exchange flows may dampen the hydraulic response of karst aquifers, which are typically flashy (Florea and Vacher, 2006; Spellman et al., 2019). The loss of water from conduits into small intergranular matrix porosity increases surface areas available for dissolution reactions. In some cases, dissolution by exchange flow may be the primary factor driving evolution of connectivity within a karst aquifer (Gulley et al., 2011; Moore et al., 2010). Exchange flows are also important drivers of a variety of other biogeochemical reactions, in large part because of their control of redox condition as water equilibrated with atmospheric oxygen and elevated in dissolved organic carbon is injected into reducing water stored in matrix porosity (Brown et al., 2014; 2019; Flint et al., 2021). Such exchange flows can occur both between conduits and matrix and between rivers and the surrounding aquifer.

2.2 Sources of undersaturation and dissolution

In the classic conceptual model of karst development, calcite dissolution is driven by carbonic acid. Meteoric water dissolves CO_2 within the atmosphere and soil and carries this CO_2 downward into the rock, dissolving carbonate minerals along its way (Adams and Swinnerton, 1937). Karst developed by such processes is often referred to as epigene karst, indicating its close relationship to surface processes, in contrast to hypogene karst, which develops at depth. This classic conceptual model has been expanded in several ways, particularly as it relates to the sources of CO_2. In some karst settings, CO_2 concentrations are higher at depth than within the soil, suggesting CO_2 production deep within the vadose zone, perhaps as the result of the remineralization of particulate organic matter that has infiltrated to depth (Atkinson, 1977b; Mattey et al., 2016; Noronha et al., 2015;Wood, 1985).

In addition to carbonic acid, carbonate dissolution can be driven by a variety of other acids, with sulfuric and nitric acids being the most common. Sulfuric acid is widely cited as a source of dissolution in hypogenic speleogenesis (Egemeier, 1988; Engel et al., 2004), in marine carbonate sediments (Beaulieu et al., 2011; Torres et al., 2014), and in landscapes affected by acid rain (Shaughnessy et al., 2021). Sulfuric acid can be produced through fossil fuel combustion, especially coal (Irwin and Williams, 1988). Sulfuric acid is also produced where oxygen-rich air or water encounters reduced sulfur species such as pyrite in sedimentary rocks or H_2S produced by coupled microbial organic carbon oxidation and sulfate reduction. Carbonate dissolution can also occur by nitric acid produced during microbial nitrification or industrial processes. Nitric acid production has been enhanced by anthropogenic production of reactive nitrogen species (Galloway, 1998; Galloway et al., 2008), for example by chemical fertilizer use in intensive agriculture and partial oxidation of atmospheric N_2 in internal combustion engines (Gandois et al., 2011; Perrin et al., 2008). Organic acids may also be important drivers of dissolution in some carbonate settings, although their concentrations are commonly lower than concentrations of sulfuric or nitric acids (Jones et al., 2015). High concentrations of organic acids have been suggested to cause rapid carbonate dissolution in a temperate rainforest setting (Allred, 2004; Groves and Hendrikson, 2011).

The source and type of acid causing carbonate dissolution is critical to global carbon cycling (Martin, 2017). Carbonate dissolution by carbonic acid is neutral with respect to long-term atmospheric CO_2 concentrations, because CO_2 consumed during weathering is balanced by CO_2 released during marine carbonate precipitation, with

CO_2 (atm) + H_2O (atm) + $CaCO_3$ (bedrock) → Ca^{2+} (river) + $2HCO_3^-$ (river) → $CaCO_3$ (marine) + CO_2 (atm) + H_2O (marine).

In contrast, dissolution of carbonates by sulfuric or nitric acids results in a net flux of CO_2 to the atmosphere (Martin, 2017), with

$H_2SO_4 + 2CaCO_3 + H_2O \rightarrow CaCO_3 + CaSO_4 * 2H_2O + CO_2$.

$2HNO_3 + CaCO_3 \rightarrow Ca^{2+} + 2NO_3^- + CO_2 + H_2O$

Considerable work over the last two decades has focused on hypogene speleogenesis, in which water undersaturated with respect to bedrock minerals forms at depth and is carried to the surface with regional groundwater flow (Klimchouk, 2007; Palmer, 1991). Undersaturated water may form through many mechanisms, including cooling of rising thermal waters, oxidation of reduced sulfur species, deep sources of CO2, and mixing of waters with different salinity or pCO_2. Dissolution deep within a karst aquifer may develop porosity that is disconnected from points of surface recharge, forming isolated porosity rather than regionally integrated flow networks. Alternatively, dissolution where deep and meteoric water mix may develop integrated flow networks if the pore spaces become linked. Karst conduit networks formed by hypogene processes typically develop complex mazes or ramiform passages, with less tendency toward the dendritic flow patterns common in epigene karst settings (Palmer, 1991). Porosity that develops in the deep subsurface may serve as a template for epigenetic karst processes when exhumation due to erosion brings that porosity closer to the surface (e.g., Tennyson et al., 2017).

2.3 Climate

Climatic factors impact the rates and forms of karst development (Lehmann, 1936). A theoretical relationship for the maximum possible rates of karst denudation ($D_{\max}$) based on equilibrium carbonate chemistry (White, 1984) provides a first order estimate of the impact of climate factors on rates of carbonate denudation,

$$D_{\max} = \frac{100}{\rho}\left(\frac{K_C K_1 K_{CO2}}{K_2}\right)^{\frac{1}{3}} pCO2^{\frac{1}{3}}(P-E) \qquad (1)$$

where ρ is rock density, K_c, K_1, K_{CO2} and K_2 are temperature-dependent equilibrium constants of the carbonate system, pCO_2 is the partial pressure of CO_2, and $P - E$ is precipitation minus evapotranspiration. Equation 1 shows the three main contributors to climate-driven differences in carbonate denudation rates: 1) changes in the equilibrium constants with changing temperature, 2) differences in pCO_2, which are strongly related to temperature, and 3) water availability. Among these three factors, water availability plays the strongest role in producing global variation in chemical denudation rates (Ryb et al., 2014; Smith and Atkinson, 1976). Well-developed karst surface features are less common within hot and arid settings or cold settings where water is rarely present in a liquid state (Ford and Williams, 2007). When karst surface features are present in such settings, they are sometimes inherited from landscapes that developed in past conditions that were wetter.

As temperature increases, solubility of calcite decreases, largely because of the decreased solubility of CO_2. However, carbonate mineral dissolution rates increase with warmer temperatures (Plummer et al., 1978). Elevated dissolution rates decrease the time required to reach equilibrium within the CZ and thus faster kinetics lead to more dissolution within the near subsurface (Gabrovšek, 2009). In addition, soil pCO_2 increases with increased temperature as biological activity increases (Drake, 1980). These two competing effects, of decreasing solubility and increasing pCO_2 with increasing temperature, are thought to produce the observed boomerang shape between $Ca^{2+} + Mg^{2+}$ concentrations and temperature within world rivers, which suggests carbonate weathering intensity peaks around a temperature of 10° C (Gaillardet et al., 2019). While a substantial body of work examines fluxes of solutes from carbonate basins and uses these to estimate average denudation rates (e.g., Erlanger et al., 2021; Gunn, 1981; Lauritzen, 1990) the role of kinetics in partitioning dissolution within the subsurface remains an area for further study.

While, broadly speaking, the impacts of climate on karst processes are well-understood, many open questions remain. For example, polygonal or cockpit karst develops preferentially in the humid tropics, whereas doline karst is more typical of humid temperate regions, and the reason for this difference is unclear (Ford and Williams, 2007). Interactions between climate and biological processes may be an important driver in the evolution of these landscapes.2.4 Vadose zone gases and open vs. closed system weathering

Vadose zone gases, particularly CO_2 and O_2, play an important role in weathering processes (e.g., Brantley et al., 2013; Kim et al., 2017). These gases are derived from Earth's atmosphere as a primary source (Kim et al., 2017; Wood and Petraitis, 1984) and are often assumed to be transported by diffusion in the vadose zone. However, connectivity among solutionally enlarged fractures and larger conduits in karst systems enables advective gas flows. Advection is forced by density contrasts between surface and subsurface air, largely through temperature variations at daily and seasonal time scales (Covington, 2016; Covington and Perne, 2015; Sanchez-Cañete et al., 2011), that drive seasonal and diurnal changes in subsurface gas concentrations (Benavente et al., 2010; Gulley et al., 2014; Kowalczk and Froelich, 2010; Lang et al., 2017; Mattey et al., 2016; Milanolo and Gabrovšek, 2009; Sekhon et al., 2021; Spötl et al., 2005; Wong et al., 2011). These variations are likely to extend throughout the vadose zone, even where it may be thick because of deep groundwater tables (Benavente et al., 2010; Covington, 2016; Mattey et al., 2016). In some cases, soil and the shallow subsurface may be aerated from below rather than directly from the atmosphere (Faimon et al., 2020). The ventilation through conduit systems, and the linked changes in vadose water chemical compositions and compositions at the water table, can thus provide controls on the spatial and temporal patterns of dissolution and precipitation of calcite (Covington et al., 2021; Covington and Vaughn, 2019; Gulley et al., 2014; Houillon et al., 2017; Spötl et al., 2005; Wong et al., 2011). Similar processes can impact CO_2 gas fluxes from, and carbonate weathering patterns within, the soil (Roland et al. 2013).

Weathering of carbonate minerals is often approximated as proceeding under open or closed system conditions with respect to a CO_2 gas phase. Under open system conditions, the solution is in contact with a large reservoir of CO_2 and evolves at fixed pCO$_2$, dissolving more CO_2 from the gas phase as CO_2 is consumed by carbonate dissolution. Under closed system conditions, the solution is isolated from the gas phase, and pCO$_2$ decreases as carbonate dissolution proceeds. Open and closed conditions are partly dictated by the water saturation state of the pore spaces, with complete water saturation producing closed conditions. Whether carbonate dissolution proceeds under open or closed conditions impacts both the rate of weathering processes (Buhmann & Dreybrodt, 1985a; Buhmann & Dreybrodt, 1985b) and trace element concentrations and isotopic compositions of dissolved species (Hendy, 1971; Stoll et al., 2022). A global study of spring water chemistry suggests that, on average, spring chemistry in carbonate regions is well-explained by weathering under conditions that are open to soil CO_2 (Romero-Mujalli et al., 2019).

The impact of carbonate weathering processes on the isotopic composition of speleothems was first investigated in the seminal work of Hendy (1971). Subsequent studies built on the model to discern the effects of prior calcite precipitation, which impacts trace element concentrations, and kinetic fractionation, which impacts stable isotope ratios, to confidently isolate climate signals from speleothems (e.g., Fohlmeister et al. 2011; Fohlmeister et al., 2020). The primary goal of these models is to illustrate the potential of speleothems to track changes in the climate. However, such studies also help us to better understand local hydrological processes dictating epikarst conditions, such as prior calcite precipitation, that are sensitive to open and closed system conditions and pore spaces in the CZ (Stoll et al., 2012). Recent work goes beyond the open/closed system framework and employs a reactive transport model to simulate carbonate weathering processes and gas transport in the carbonate CZ (Druhan et al. 2021; Oster et al., 2021). Such approaches provide a promising new avenue for future research on carbonate CZ processes. Lastly, to investigate the open versus closed system paradigm, variation in dead carbon fractionand Li isotopes of speleothems provide additional constraints on the relationship between climate and weathering. Dead carbon fraction in speleothems is primarily controlled by an uptick in limestone dissolution. This is typically indicative of closed system conditions during periods of increased hydrological activity (Griffiths et al., 2012; Bajo et al., 2017). Though enhanced decomposition of old, recalcitrant, carbon is another important source of dead carbon fraction (Rudzka et al., 2012; Noronha et al., 2015). Likewise, recent studies of Li isotopes within cave drip waters and analog experiments highlight the possibility of studying silicate weathering intensity using speleothem records (Day et al., 2021; Wilson et al., 2021).

2.5 Tectonic setting and base level

Tectonic uplift, sea level change, and other drivers of changes in base level provide important boundary conditions for the development of karst flow networks and the resulting landscapes. Karst conduit development is often focused near, or driven toward, the water table (Ford and Ewers, 1979). During periods of stable base level, karst conduit networks can preferentially develop within specific elevation ranges (Figures 3). Such cave levels are used to date phases of river incision using cosmogenic burial dating (Granger et al., 2001; Stock et al., 2005). Similarly, flat corrosion plains develop when the land surface approaches base level (Ford and Williams, 2007). In contrast, where rapid uplift occurs, the resulting high relief promotes the development of thick vadose zones, sometimes in excess of 2 km. In these cases, conduit development may be primarily vertical, along structural features such as faults, until water collects within subhorizontal conduits that drain the water laterally out of massifs into springs near base level (Audra et al., 2006; Turk et al., 2014; Klimchouk, 2019).

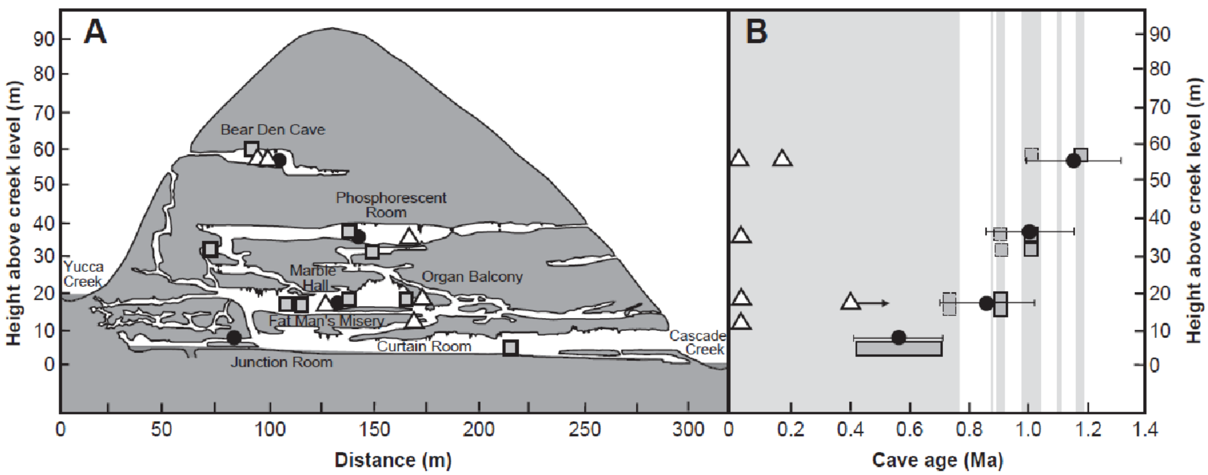

Figure 3. The development of horizontal cave levels in response to stream incision (from Stock et al., 2005). As the surface stream incised, new levels of cave passage were developed (A), rather than steepening of the existing channel, as would occur during a pulse of incision in a surface stream. Locations (A) and ages (B) of cave deposits are shown, including speleothem U-Th (white triangles), paleomagnetic (gray squares), and cosmogenic burial (black circles) samples. The cosmogenic burial ages of coarse sand and gravel are most indicative of the time when a cave passage was occupied by an active stream.

Uplift of carbonate platforms can also result from isostatic rebound caused by dissolution and the resulting reduction in platform density (Adams et al., 2010; Opdyke et al.,1984). In fold and thrust belts, the tendency for evaporites to act as planes of detachment frequently results in the formation of anticlines with evaporite cores (Davis and Engelder, 1985), and the buoyant effect of the evaporites may be an additional force contributing to uplift of the anticline (Lucha et al., 2012). The juxtaposition of evaporites below uplifted, fractured carbonate-rich rocks create ideal conditions for hypogene, sulfidic karst development, as in the Central Apennines, Italy (D'Angeli et al., 2019). In this setting, base level is controlled by river incision of the anticline, resulting in sulfidic springs that discharge in or near river valleys. Cycles of sea level rise and fall are important drivers of karst development in coastal settings, which are typical of most eogenetic karst. Voids that develop at sea-level low stands are subsequently flooded during sea level rise (Myroie and Carew, 1990; Smart et al., 2006; Gulley et al., 2013). Patterns of sea level change can often be tracked within speleothem records (Bard et al. 2002; Roy & Mathews, 1972; Surić et al., 2009).

2.6 Relative importance of chemical vs. mechanical weathering processes

Landscapes that develop on carbonate bedrock are impacted by the types and rates of mechanical weathering and erosion. In landscapes where mechanical processes are more efficient than chemical processes, karst features will be less pronounced, even if subsurface karst flow networks are well-developed. The instantaneous rate of chemical erosion tends to be slower than the instantaneous rates of mechanical erosion processes such as bedrock abrasion, hillslope mass wasting, and glacial erosion. However, chemical erosion processes are often relatively continuous, with chemical denudation rates depending primarily on climate (White, 1984) and dissolution rates within streams showing relatively low variability over time (Covington et al., 2015). In contrast, mechanical erosion and mass transport processes are frequently episodic. Consequently, the most extensive karst landscapes develop in humid environments where nearly continuous chemical weathering outpaces episodic mechanical processes – a tortoise and hare analogy (Simms, 2004). In environments where mechanical weathering processes are particularly effective, karst surface features may fail to develop because of the rapid breakup and accumulation of weathered rock. One such example is alpine karst settings, where frost cracking can erase surface expressions of karst (Ford, 1971).

In mixed carbonate and non-carbonate terrains, carbonates can behave either as weaker rock layers, forming topographic lows, or as strong layers that form topographic highs (Simms, 2004; Ott et al., 2019). When chemical weathering rates outpace tectonic uplift, as might be the case in either humid environments or tectonically passive settings, then carbonates tend to erode more quickly and develop lows in the topography. However, when tectonic uplift outpaces chemical weathering, as in arid or rapidly uplifting environments, then the mechanical strength of carbonates may result in the formation of topographic highs (Ott et al., 2019).

The diversion of surface water, and therefore geomorphic work, into the subsurface in sinking streams can influence the efficiency of fluvial erosion processes. For example, karst sink points can stall the propagation of knickpoints, reducing rates at which stream profiles adjust to changes in tectonic forcing (Fabel et al., 1996). Ott et al., (2019) quantified both chemical and mechanical erosion rates in carbonates and non-carbonates in Crete, showing that mechanical erosion processes dominate, even in the carbonates, where chemical denudation accounts for ~40% of total erosion. Their results suggest that the much greater relief that develops in the carbonates results from loss of water into the subsurface and subsequent steepening of stream channels to enable mechanical erosion rates to keep pace with uplift.Chemical and physical processes can also interact, potentially enhancing or inhibiting each other. Experiments in subcritical cracking demonstrate unique fracture propagation behaviors in carbonates, which may relate to dissolution processes at fracture tips (Atkinson, 1984; Henry, 1978). In general, models and experiments suggest that acids can enhance fracture propagation rates in carbonate rocks (e.g., Hu & Hueckel, 2019). Roots are an important agent in mechanical breakup of rock, particularly in areas with thin regolith (Brantley et al., 2017). In carbonates, roots can take advantage of subsurface porosity generated by dissolution processes (Estrada-Medina et al., 2013), and they can also generate subsurface porosity through dissolution by root exudates or CO_2 generated by root respiration (Klappa, 1980; Rossinsky and Wanless, 1992), potentially enhancing root-driven rock fracturing. It has also been hypothesized that chemical and mechanical erosion may enhance each other within stream channels (Covington, 2014; Covington & Perne, 2015), with chemical erosion potentially loosening grains that are then removed by mechanical processes (Emmanuel & Levenson, 2014), or with mechanical abrasion removing surface impurities to expose fresh weatherable carbonate minerals. Mechanical weathering processes can also inhibit chemical weathering processes. For example, buildup of fractured rock material on the surface, with high surface areas for reaction, may lead to saturation of meteoric water before it reaches unweathered bedrock. Similarly, high sediment loads within streams could armor the beds and inhibit dissolution except during periods of sediment mobility.

2.7 Biota

As in the CZ more generally, the activity and spatial architecture of carbonate CZ biological communities have important feedbacks to other CZ processes. Thanks to networks of large voids, the carbonate CZ is distinguished by the potential for macroscopic biota including fish, amphibians, and invertebrates to penetrate up to several km below the photic zone (Figure 4). Because both locomotion and passive transport in karst conduit networks are more constrained than at the surface, carbonate CZ biological communities often show a high degree of endemism. The resulting small population sizes leave carbonate CZ fauna especially vulnerable to extinction (Culver & Pipan, 2013).

Animal communities in the subsurface can be fed either by in situ microbial primary production or detrital dissolved and particulate organic carbon percolating downward from the surface soil. In some cases, sedimentation of particulate organic carbon in conduits creates a biological hot spot where CO_2 production from decomposition drives further carbonate dissolution (Covington et al., 2013; Gulley et al.,2016). In coastal karst landscapes where aquifers are density stratified and partially filled by anoxic seawater (i.e. anchialine), organic matter hot spots also facilitate H_2S production from microbial sulfate reduction. As water flows over the hot spot, H_2S is transported away and oxidized at redox interfaces elsewhere in the network, producing sulfuric acid that drives more carbonate dissolution. A striking example of this process can be observed in the Bahamas eogenetic karst. "Blue holes" (sinkholes) are extremely common in the landscape and collect surface vegetation, which is deposited at the bottom of the conduit in anoxic or dysoxic seawater. Tidal pumping exchanges low pH water between the blue hole and matrix porosity of these eogenetic karst features, enhancing dissolution reactions (Martin et al., 2012). Decomposition of the detrital plant material fuels intense H_2S production and, where the H_2S diffuses into the photic zone, associated blooms of sulfide-dependent photosynthetic bacteria thrive and fix additional carbon in the subsurface (Gonzalez et al., 2011, Haas et al., 2018).

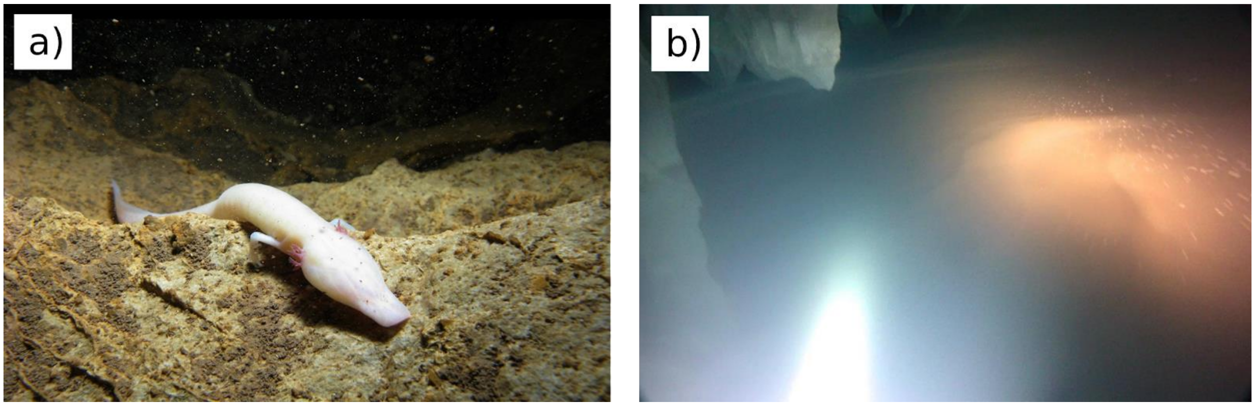

Figure 4. a) Proteus anguinus, an aquatic salamander found in the karst of the Dinaric Alps that is one of the largest cave adapted animals in the world (reaching up to 40 cm in length). Photo Gergő Balázs. b) A dense swarm of amphipods (Niphargus sp.) flee a diver exploring water-filled karst conduits ~400 m below land surface in the Frasassi cave system, Italy. Stable density stratification between sulfidic water and an overlying lense of oxic vadose water in the aquifer create enough chemical energy to support a rich food web based on microbial lithoautotrophy. Photo J. L. Macalady/A. Crocetti.

Vegetation on karst landscapes is affected by (1) rapid drainage and associated nutrient leaching due to thin soils and large bedrock pores, (2) phosphorous scarcity due to the low P content of carbonate bedrock and high phosphate complexation with abundant Ca^{2+} ions, (3) strong decimeter- to meter-scale spatial heterogeneity in topography, soil and hydrologic factors, and (4) slow soil formation due to limited silicate minerals with incongruent weathering to form clay minerals. The plant ecology of tropical and subtropical karst ecosystems has recently been reviewed in depth (Geekiyanage et al., 2019). Because water in thin karst soils is in short supply, plants growing on carbonate-dominated landscapes have adaptations for using alternative reservoirs of water, especially in dry seasons (Figure 5). Non-tree species often have particularly dense and extensive shallow root systems because they depend on soil water year-round (Ellsworth et al., 2015). Due to high bedrock porosity, water stored in the vadose zone (epikarst) represents a significant alternative to soil water for woody species that can penetrate into carbonate bedrock (e.g., Querejeta et al., 2007). Some woody species also have specialized, long roots that reach the water table (Deng et al., 2012; Swaffer et al., 2014). Adaptations for obtaining fog water (Fu et al., 2016), and a drought-deciduous strategy in which leaves are shed during dry seasons (Reich and Borchert, 1984; Wolfe and Jursar, 2015), have also been documented in plants growing in carbonate terrains.

Plant adaptations to obtain water resources in the carbonate CZ significantly alter the hydrologic balance at depths far below the soil zone, and therefore have feedbacks on weathering rates and nutrient and organic carbon transport out of the system that are different than in the silicate-dominated CZ (Huang et al., 2009; Dammeyer et al., 2016). Karst plant nutrient acquisition strategies may also differ significantly, with potential feedback to weathering rates. Plants growing on calcareous soils release organic acids from their roots in order to obtain phosphate (Ström et al., 2005). Subsequent microbial degradation of the organics further enhances CO_2 production near roots. In the presence of strong topographic heterogeneity leading to soil pockets in epikarst depressions, vegetation can reinforce CO_2-induced weathering hot spots in the landscape and thereby amplify dissolution along certain water flow paths. A well-studied example of vegetation-mediated positive weathering feedbacks can be seen in Big

Cypress National Preserve, South Florida, which is characterized by extensive spatial patterning (Dong et al., 2019a,b).

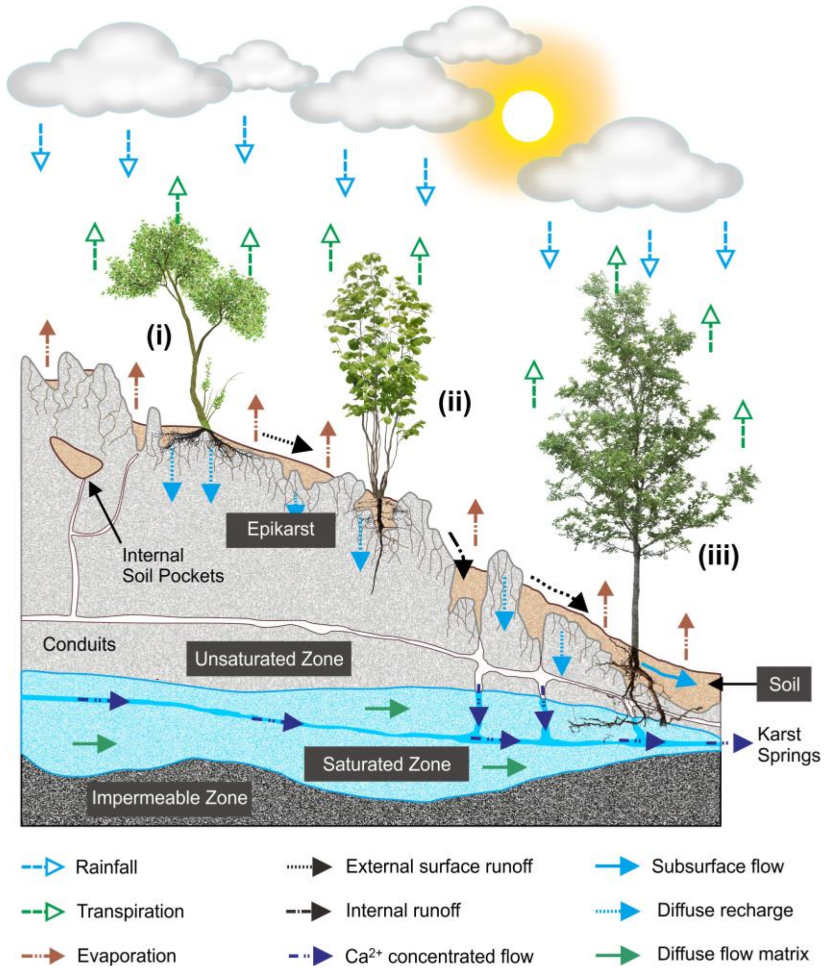

Figure 5. Water use strategies of karst plant species in a typical karst ecosystem during the dry season; (i) soil water dependent (species that predominantly take up soil water in both the dry and wet season), (ii) epikarst water dependent (species that use both soil and water stored in epikarst in both seasons and show a major shift to epikarst water when soil water is depleted during the dry season), and (iii) groundwater dependent (species that use groundwater in addition to soil and epikarst water and show a major shift to epikarst and groundwater when soil water is depleted during the dry season). Not illustrated here are (iv) fog water dependent plants, which use fog-derived water in addition to any of the above water sources, and (v) drought-deciduous (remain dormant by leaf shedding during the dry season). From Geekiyanage et al. (2019).

Plant roots and the microbial communities they support, including mycorrhizae, saprotrophic fungi, bacteria, and archaea have long been recognized as drivers of chemical weathering and the global carbon cycle (Beerling, 1998; Berner, 1992; Brantley et al., 2017a). Plant growth elevates soil pCO$_2$ and increases dissolved inorganic carbon (DIC) fluxes (Andrews and Schlesinger, 2001; Berner, 1997). Rooting systems (e.g., grass-, shrub- and woodlands) govern the distribution of soil carbon (both organic and inorganic), microbial biomass, and soil respiration (Billings et al., 2018; Drever, 1994; Jackson et al., 1996). For example, relatively deep root distributions in shrublands compared to grasslands lead to deeper soil carbon profiles (Jackson et al., 1996; Jobbágy and Jackson, 2000), which elevate CO_2 and therefore weathering at depth. The work described here was carried out almost exclusively at sites where the CZ is dominated by silicate minerals. Only recently have similar ideas been applied to carbonate terrains, particularly in connection with studies of land-use changes.

Changing land cover has been invoked to explain changes in carbonate weathering processes. In carbonate terrains, carbon sequestration has been found to be optimized in grasslands as compared to shrub, managed crop, soil denuded of vegetation, or bare rock dominated landscapes (Zeng et al., 2017). This optimization results from greater pCO_2 and greater depths of water penetration in grasslands as compared to other land cover types. Woody vegetation encroachment into grasslands underlain by carbonate systems causes shifts in flow paths, groundwater solute concentration, and the timing of solute delivery to streams as inferred from reactive transport models and observed changes in stream and groundwater chemical compositions (Sullivan et al., 2019), with deep root systems regulating how much CO_2 is transported downward to the deeper carbonate-rich zone (Wen et al., 2020). Changes in pCO2 as a response to vegetation and landscapes can also be discerned through ^{13}C variability in speleothems. Lechleitner et al. (2021) show that an increase in soil gas pCO_2 is recorded in speleothem carbon isotope ($\delta^{13}C_{spel}$), which may retain information on soil respiration. Similarly, Stoll et al. (2022), attribute trends in $\delta^{13}C_{spel}$ to soil gas and bedrock dissolution. They propose that higher temperatures increase vegetation productivity, thereby increasing soil CO2 production, which leads to more negative $\delta^{13}C$ in speleothems.

Bedrock type can control plant productivity through influencing the available nutrients and physical regolith structure (Hahm et al., 2014). Data from carbonate settings suggest that silicate percentage is negatively correlated with the rate of water drainage from regolith and positively correlated with primary productivity (Jiang et al., 2020). It is hypothesized that preferential drainage features are better developed within carbonate-rich rocks and that this leads to both water and regolith loss into the subsurface, reducing water availability during dry periods. Similarly, a global study of relationships between rock type and biodiversity in erosional landscapes demonstrates that regions rich in carbonates have less vegetation and lower animal richness (Ott 2020).

2.8 Humans and the carbonate CZ

Human activity over millennia is intimately tied to use of karst landscapes for agricultural purposes, water resources, and cultural traditions (Quine et al., 2017; Stevanović, 2018; Moyes et al., 2009). The study of human evolution is rooted in investigating hominin bearing fossils discovered in caves (Mijares et al., 2010; Zanoli et al., 2022; Pickering et al., 2011; Sutikna et al., 2016) as well as cave art (Brumm et al., 2021; Valladas et al., 2001). Excavations of fossils in cave deposits continue to be a crucial tool in piecing together the history of human evolution. However, destruction of cave sites through cave infilling because of construction, and visitors destroying artifacts, threaten these prehistoric records. Interdisciplinary research between social scientists, geographers, archaeologists, and earth scientists is required to better constrain the relationships between humans and their interactions with karst landscapes. Human activity through the Anthropocene is negatively impacting the karst landscape (Long et al., 2021; Beach et al., 2015). This delicate environment is susceptible to soil degradation, sinkhole development, groundwater contamination, and depletion in groundwater levels. Globally, many regions with carbonate aquifers are predicted to experience lower precipitation and higher temperatures, reducing recharge and stressing available water resources (Hartmann et al., 2014). Similar to geochemical processes, environmental impacts can occur more rapidly in karst and carbonate systems. The consequences of human activities in the carbonate CZ are highlighted below to draw attention to the vulnerability of karst that requires further research.

Karst uplands are vulnerable to runaway degradation if trees are removed. In the absence of forest vegetation protecting thin soils, rapid erosion into exposed karst fissures culminates in the creation of rocky deserts where forest vegetation can no longer get a foothold. Rocky desertification has occurred in significant areas of Mediterranean Europe (e.g., the Dinaric Karst), on islands such as Haiti and Barbados in the Caribbean, and especially and most recently in southwestern China (Jiang et al., 2014; Green et al., 2019). Over the past 50 years, a variety of human activities have played a substantial role in the expansion of rocky deserts in China including fuelwood collection, development of housing and tourism, slope cultivation, and animal grazing (Zhao and Hou, 2019). Populations are impacted as farmable land can switch from soil covered to denuded relatively rapidly (Zhao et al., 2020).

Sinkholes are one of the costliest hazards in karst regions, when collapse of underground voids intersects with human land use (Gutiérrez et al., 2014). Anthropogenic activities can accelerate sinkhole development, through lowering of the water table, diversion of recharge into karst depressions, or creation of water table fluctuations (e.g., Newton, 1987; Parise et al., 2015; Waltham, 2008; Yizhaq et al., 2017). Consequently, sinkhole hazards are closely linked to human activities through both water extraction and land development. These hazards may be exacerbated with future climate change as carbonate regions experience lower precipitation and more extreme precipitation events, further stressing water resources and creating higher runoff and larger water table variation.

Carbonate aquifers are particularly vulnerable to contamination (e.g., Hartmann et al., 2021; White et al., 2016), and because of enlarged passages a wider range of contaminants such as pathogens, contaminants sorbed to particles, and trash need to be considered (Ford and Williams, 2007; Vesper and White, 2003). Microplastics have recently been identified in karst systems but little is known of their sources, fate and impacts (Panno et al., 2019; Balestra and Bellopede, 2022). Predicting contaminant transport pathways is complicated by mixing of fast and slow flow paths, reflecting a need for an improved understanding of flow components and storage (Tobin et al., 2021). Furthermore, karst systems are more vulnerable to changing climate regimes, which increase or decrease precipitation inputs and may require special protection measures such as larger stormwater control structures (Veni et al., 2001). Recharge into karst aquifers can be enhanced because of heterogeneity, and a model of karst aquifer recharge suggests that heterogeneity influences recharge sensitivity to climate change, in some cases reducing sensitivity, and in some cases increasing it (Hartmann et al., 2017). Therefore, the heterogeneity of karst needs to be explicitly accounted for within water management strategies that consider impacts from climate change.

3 The carbonate-silicate spectrum

Due to fundamental differences in the properties of silicate and carbonate mineral groups, the percentage and spatial distribution of carbonate minerals within parent rocks drive important differences in the processes and architectures that develop as the CZ evolves. As a conceptual framework, we will consider a silicate-carbonate spectrum (Figure 6), with endmember landscapes completely dominated by either carbonate or silicate minerals. This framework provides a link between prior CZ studies and synthesis studies yet to be carried out in both carbonate and silicate-dominated sites along the spectrum. Understanding how CZ dynamics and processes change along this spectrum is a crucial next step towards integrating carbonate landscapes into existing knowledge of the CZ. We argue that studying the carbonate CZ will also contribute to new understanding of silicate settings by comparison.

3.1 Silicate-carbonate mineral mixtures and distributions in the CZ

Within Earth's CZ, silicate and carbonate minerals occur in mixtures across a range of scales, from the grain scale to stratigraphic scales (Figure 6). At the grain scale, all carbonate rocks contain some percentage of non-carbonate minerals, with common constituents including clays and slowly weathering silicate minerals such as quartz and feldspars (Ford and Williams, 2007). Silicate mineral fractions of carbonate rocks often take the form of sand- or silt-size quartz grains, or nodules or beds of authigenic chert (Figure 7a). These minerals may remain as lag deposits as the carbonate minerals are dissolved (Figure 7b-c). Similarly, many siliciclastic rocks contain some fraction of carbonate minerals, often in the form of a cement between grains. Carbonate-cemented sandstones, or impure carbonates, can form caves and karst landforms through the process of phantomization (Dubois et al., 2014; Häuselmann and Tognini, 2005; Kůrková et al., 2019), whereby preferential dissolution of the cement disintegrates the rock and then the remaining loose sand grains are removed physically by piping (Figure 7d). Counterintuitively, the effectiveness of the phantomization process is only weakly dependent on carbonate percentage, and instead disintegration is largely controlled by the grain-size and texture of the silicate component (Kůrková et al., 2019). This observation suggests that the change of landforms and CZ architecture along the carbonate-silicate spectrum depends on variables other than just the carbonate fraction of the lithology, such as how the mineral groups are distributed at the grain scale.

In addition to mixtures at the grain scale, silicate and carbonate rocks occur as relatively pure beds in layered stratigraphy (Figure 6). Terrains composed largely of carbonates may contain continuous beds of non-carbonates such as chert or shale. The layering creates heterogeneities in porosity and permeability with silicate mineral layers often less permeable than carbonate layers. The contrasts in permeability can create perched water tables and zones of focused conduit development in the carbonate layers (Figure 7e), while the impermeable silicate mineral layers tend to impede vertical flow of water. Sometimes carbonates are thinly interbedded with impure carbonates, shales, or other non-carbonate rocks, creating a landscape referred to as merokarst (Cvijic, 1925). Merokarst typically displays little surface topographical expression of karst but may still behave hydrologically like a karst system (Brookfield et al., 2017; Macpherson and Sullivan, 2019a; Sullivan et al. 2020).

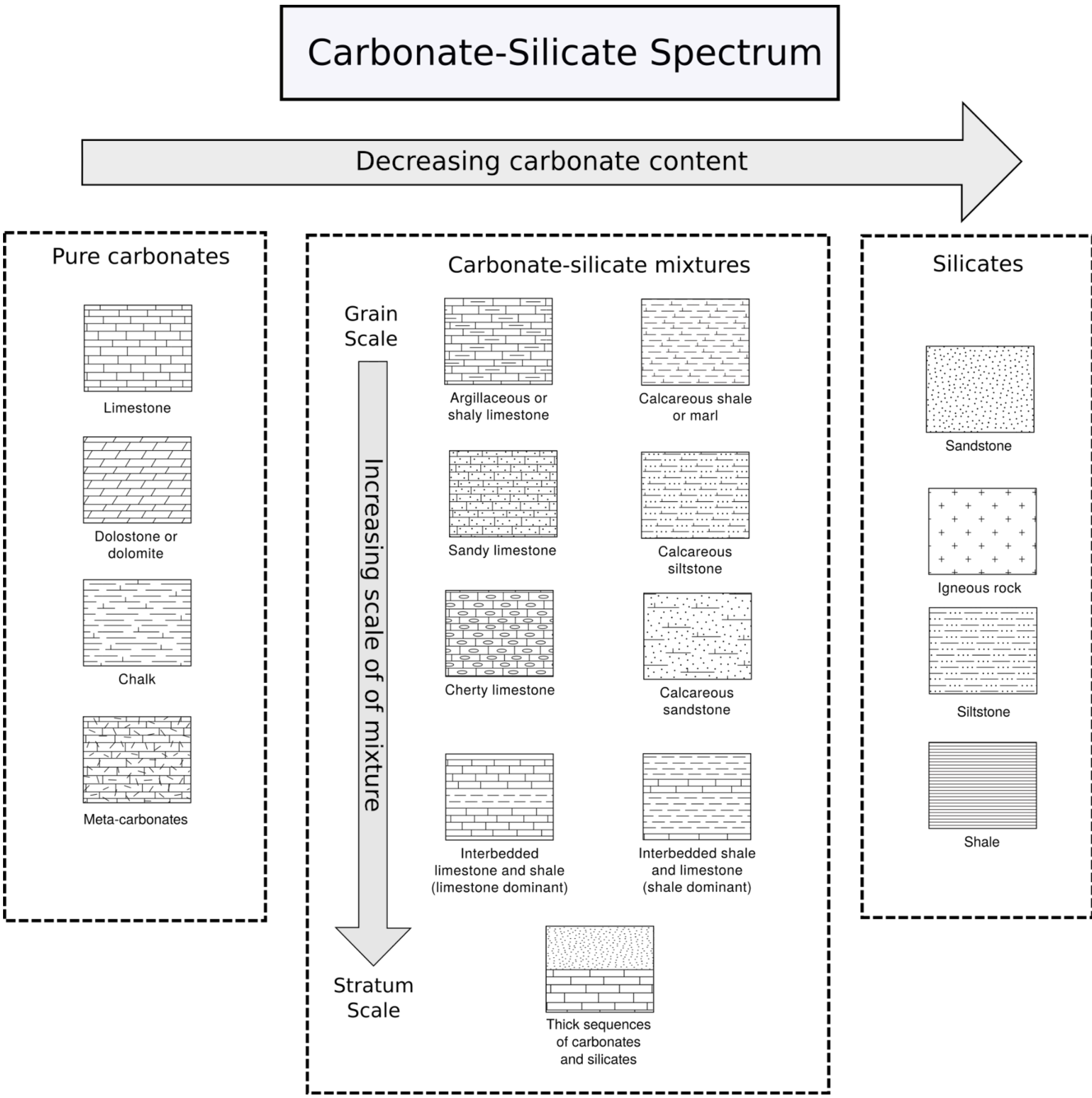

Figure 6. The carbonate-silicate spectrum. In addition to end-member cases of pure carbonate and silicate rocks, carbonates and silicates commonly occur as mixtures. Both the carbonate percentage and the scale over which the two mineral types mix are crucial parameters that will influence critical zone structure and evolution.

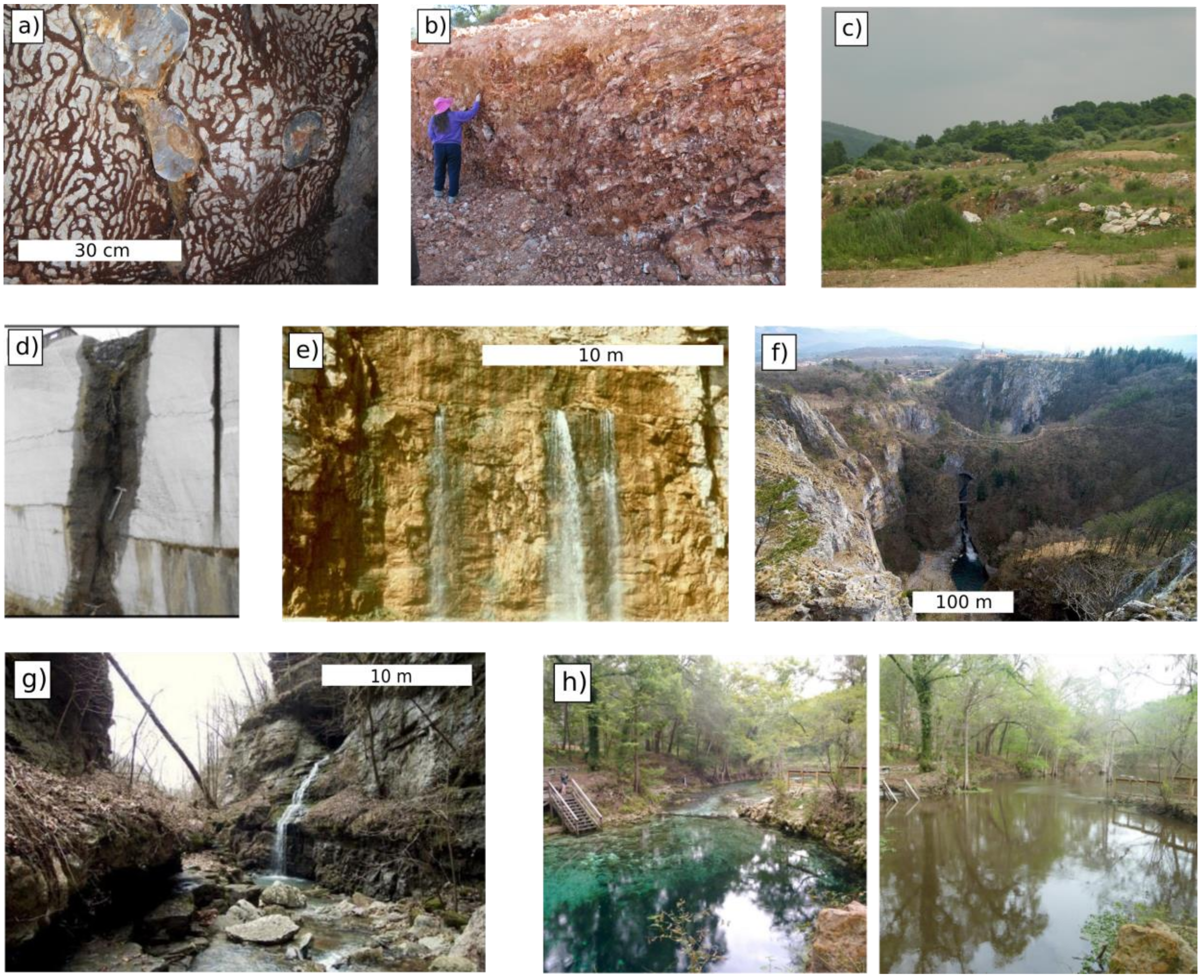

Figure 7. Features illustrating aspects of the carbonate-silicate spectrum. a) Differential weathering of chert nodules within micritic limestone in Grotta Sulfurea, Frasassi, Italy. The cave walls are colonized by microbial biofilms (biovermiculations) that prefer the carbonate to the silicate surface, b) A thick regolith layer of chert and clay left behind after dissolution of the Boone Limestone, Arkansas, c) Weathering residuum drapes crystalline dolomite of the Cambrian Ledger Formation in Pennsylvania, d) Ghost-rock karstification (phantomization), whereby weathering residuum is left behind within solutionally altered preferential flow paths, near Soignies, Belgium (from Dubois et al., 2014), e) Water emerges from a bedding plane on top of a chert layer within a carbonate rock, Arkansas, f) The Reka River in the classical karst region of Slovenia sinks after flowing from flysch onto limestone, creating two large 160-m deep collapse dolines and the upper entrance to Škocjan Caves, g) A perched spring creates a waterfall at the contact where a limestone unit overlies a sandstone, Indian Creek, Arkansas, h) Madison Blue Spring, Florida, an estavelle, which functions as a spring in baseflow conditions (left) and reverses flow direction to receive organic-rich water from the Withlacoochee River during flood events (right).

Thick carbonate layers may be juxtaposed laterally with non-carbonate rocks. Contacts between carbonates and non-carbonates that are exposed at the surface typically form regions of focused interaction between surface and subsurface hydrological, geomorphological, and biological processes (Atkinson, 1977a; Brucker et al., 1972; Gulley et al., 2013; Khadka et al., 2014; Martin and Dean, 1999; Palmer, 2001). When surface water flows from non-carbonate onto carbonate rocks, sinking streams, blind valleys, sinkholes, and open cave shafts often develop (Figure 7f). These vertical conduits capture surface runoff and route it into the subsurface. Likewise, springs are common features at contacts where confining non-carbonate rocks underlie carbonate rocks (Figure 7g). Such underlying confining units may produce a stratigraphically determined base level for the development of karst flow systems. Springs are also common where the water table intersects the land surface because erosion has removed silicate rocks and exposed high permeability zones in the underlying carbonates. Contact zones can also host estavelles (Figure 7h), features that alternate between acting as springs and sinks depending on the relative elevations of the water table and the surface water that receives spring discharge. When the surface water level at the spring rises above the hydraulic head at an estavelle, surface water may intrude into the spring, which can aid dissolution (Gulley et al., 2011) and alter concentrations of redox sensitive solutes (Brown et al., 2019).

3.2 Differences between carbonate and silicate settings

CZ architecture and dynamics differ substantially between settings that are dominated by either carbonates or silicates. Here we examine these differences, contrasting the end-member cases. Less is known about how these differences emerge along the carbonate-silicate spectrum, the parameters that control these changes, and whether changes occur smoothly with these parameters or exhibit non-linear, threshold responses. Understanding how the CZ varies along the entire carbonate-silicate spectrum is an important area for future research.

3.2.1 How deep is the CZ?

The dissolutional enhancement of permeability, and the resulting high flow velocities (Worthington et al., 2016), produce rapid advection of solutes into the subsurface. After development of preferential flow paths, substantial changes in flow and chemistry can be expected deep within and throughout the carbonate CZ over short time periods, such as individual storm events. Such variability is expected both within larger dissolutional conduits (e.g., Ashton, 1966; Birk et al., 2006; Brown et al., 2014; Covington et al., 2012; Groves and Meiman, 2005; Gulley et al., 2011; Liu et al., 2004; Vesper and White, 2004) and within smaller dissolutionally enlarged fractures and the epikarst (Kogovšek and Petrič, 2012; Liu et al., 2007; Miorandi et al., 2010; Musgrove and Banner, 2004; Tooth and Fairchild, 2003). Consequently, within the carbonate CZ, surface-like geochemical conditions can occur at substantial depth and at long distances from locations of point recharge. These changes deep within the carbonate CZ differ from the commonly assumed base of the silicate CZ as the depth where regolith formation begins (Figure 8). Thus, an important consideration in contrasting Earth's CZ in endmember carbonate and silicate settings lies in the definition of the CZ itself, specifically, its lower boundary, and the lower boundary's relationship with the mineralogical makeup of the CZ and active circulation of water (Condon et al., 2020).

Riebe et al. (2017) review possible criteria for defining the base of the CZ. Ultimately, they settle on an equilibrium-based definition, that is, the base of the CZ is the depth in the subsurface at which meteoric water and Earth materials are at chemical equilibrium. Although they do not explain why, they also note that a different definition may be needed for carbonate settings. We see two ways in which the equilibrium definition might be problematic in carbonates. First, given that active dissolution of calcite by meteoric water can occur at great depths, up to thousands of meters (Klimchouk, 2019), the lower boundary using this definition can be quite deep, leading to a picture of the CZ that differs substantially from the typical hillslope catena (Figure 8). However, given that deep karst conduits can provide important controls on the fluxes of water, gas, and sediment through the CZ, it seems that a holistic understanding of the carbonate CZ requires an incorporation of coupling between the near and deep subsurface. Therefore, the extreme depth of carbonate dissolution illustrates a meaningful difference in the dynamics and processes that occur in carbonate and silicate settings.

Perhaps ironically, the second potential problem that we can see with the equilibrium definition of the base of the carbonate CZ is that, due to rapid kinetics, meteoric water equilibrates quickly with carbonates. Consequently, water may be effectively saturated with calcite in the near subsurface, ending further chemical weathering. That is, the equilibrium definition may specify too shallow a depth of the CZ, with a bottom boundary that is above depths in which additional CZ processes occur. In fact, these two problems can be seen as opposite sides of the same coin. They both result from the non-planar nature of the weathering front within carbonates (Phillips et al., 2019). Although meteoric water often comes close to equilibrium with calcite in the near subsurface, non-linear kinetics reduce dissolution rates as water nears equilibrium with carbonate minerals, enabling undersaturated water to penetrate deep into the subsurface (Dreybrodt, 1990; Palmer, 1991). Even in the absence of such non-linear kinetics, flow fingering or "wormhole" development can drive undersaturated water deep into dissolving fractures (Szymczak and Ladd, 2011, 2012). Additionally, dissolutional capacity can be added to alter equilibrium conditions in the deep subsurface by many processes. These processes include CO_2 production (Atkinson, 1977b; Benavente et al., 2010; Gulley et al., 2015; Mattey et al., 2016), mixing of surface-derived meteoric water with water containing H_2S (Davis, 1980; Egemeier, 1987; Hill, 1990; Jagnow et al., 2000; Palmer, 1991; Martin, 2017), mixing of water with different partial pressures of CO_2 (Bögli, 1964; Wigley and Plummer, 1976), or mixing with salt water (Back et al., 1986; Mylroie and Carew, 1990; Plummer, 1975). Each of these processes may alter the equilibrium conditions deep within the CZ.

Despite potential difficulties outlined above, we think that an equilibrium-based definition of the lower boundary of the CZ in carbonates is a reasonable starting point. A working definition of the base of the CZ in carbonate settings would then be, "The depth below which there is no measurable dissolution of carbonate minerals by meteoric water." This definition comes with the caveats that: 1) much of the water between the surface and the base of the CZ will be near equilibrium with respect to carbonate minerals, even though it is within the CZ, and 2) some of the dissolution will be driven by subsurface acid production and/or mixing of meteoric water with deeper water. Perhaps the most difficult delineation to make is between dissolution processes that are driven by proximity to Earth's surface and those which can occur at great depth from rising thermal waters, H_2S-rich fluids, or volcanic production of CO_2. While many of these deeper processes may create a template for further permeability development by near-surface processes as rocks are exhumed, they can be considered as initial conditions for CZ development, much like the initial mineralogy, fabric, and structures of the exhumed rock layers, rather than an integral component of CZ processes. Here, we propose that dissolution processes that should be considered to define the bottom boundary of the CZ are those that produce feedback with the near-surface hydrological, geomorphological and biogeochemical processes, such that the dissolution processes both influence and are influenced by the flow of meteoric water.

3.2.2 The Conveyor model and CZ architecture

We use a conceptual model central to understanding CZ evolution within silicate terrains – the CZ conveyor (see e.g., Riebe et al., 2017) – to explore differences between the CZ in carbonate and silicate endmembers. Within the CZ conveyor model (Figure 8a), minerals are brought upward toward Earth's surface via erosion, exposing them to physical, chemical, and biological gradients. These gradients drive incongruent weathering that transforms bedrock into regolith that is transported down hillslopes toward stream channels. Through the migration of knickpoints, the stream channel network communicates erosion rate changes driven by tectonics or isostasy upward to the hillslopes. As channels at the base of hillslopes experience a change in erosion rate, hillslope topography and downslope transport of regolith adjust to accommodate the change. This system reaches topographic equilibrium when fluxes of fresh rock into the CZ are balanced by fluxes of solutes and sediments out of the channel network, resulting in a steady soil and regolith thickness. This conceptual model, in various forms, is ubiquitous throughout CZ studies (Amundson et al., 2007; Anderson et al., 2013, 2002; Brantley et al., 2017a; Heimsath et al., 2020; Hilley et al., 2010; Lebedeva et al., 2010; Patton et al., 2018; Rempe and Dietrich, 2014; Riebe et al., 2017).

Arguably the most fundamental difference between the weathering of silicates and carbonates is that carbonate minerals weather congruently, while silicate minerals weather incongruently. Incongruent weathering provides a key aspect of the conveyor model, whereby only a portion of the rock is removed in solution and the remaining sediment is transported to channels via hillslope processes (Figure 8a). This model thus predicts dynamic adjustment of soil and regolith thickness, producing negative feedback that drives soil production and rock lowering toward the average landscape erosion rate. When erosion rates increase, the down cutting of channels steepens the hillslopes and thins the soils, accelerating soil production. When erosion rates decrease, reduction in the rate of stream incision leads to reduction in hillslope relief, accumulation of soil, and reduction of weathering rates as soil thickens (Heimsath et al., 1997).

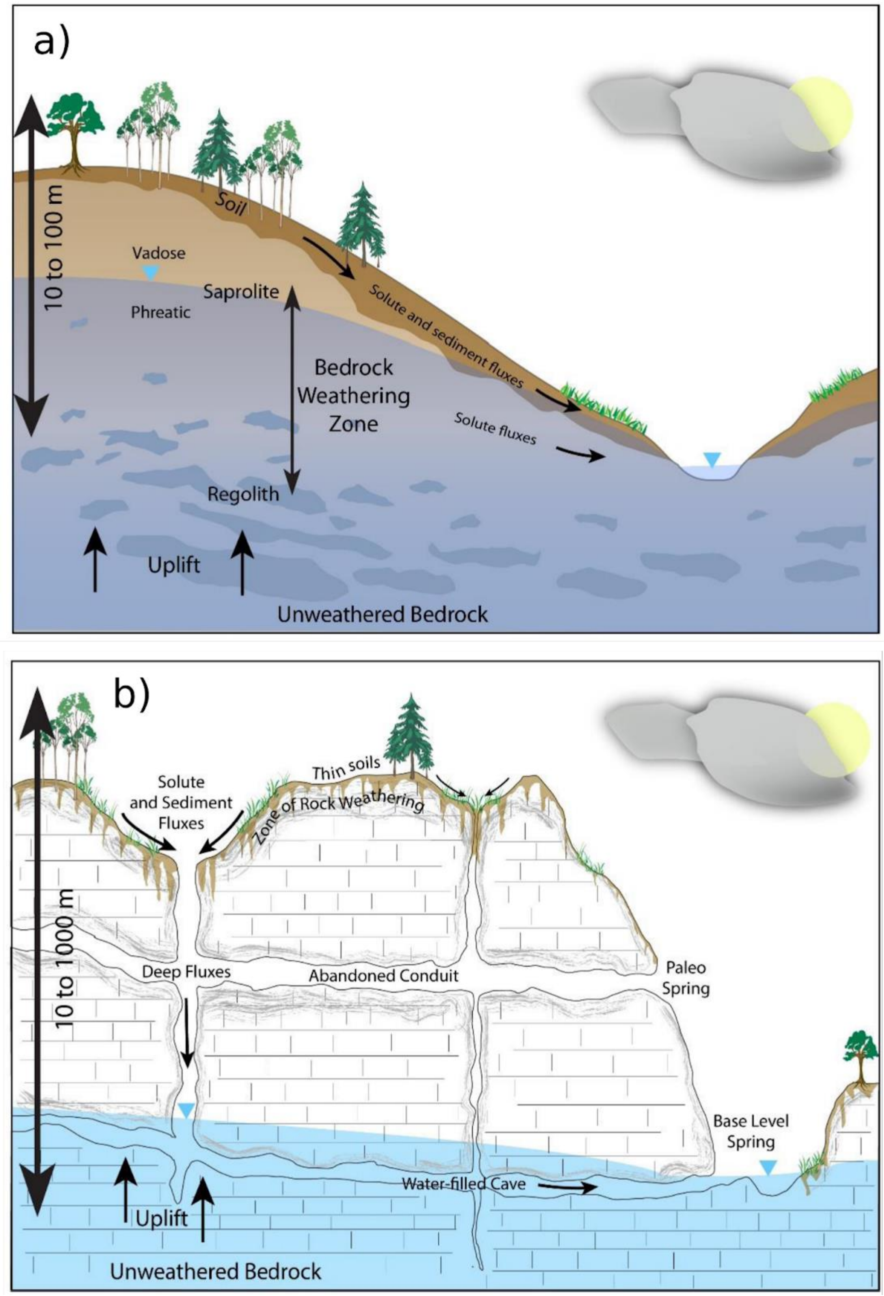

Figure 8. Carbonates and the conveyor model of the CZ. a) The conveyor model of the CZ, whereby uplift brings unweathered bedrock toward the surface. Weathering processes convert the bedrock into regolith and soil. Gravity transports sediment down the hillslopes, and stream channels carry away the solutes and sediments that are the byproducts of weathering. Communication between the hillslopes and channel network enables equilibration of the landscape to a rate of steady base level fall. b) Conceptual model of a well-developed karst in a carbonate setting. Surface drainage is limited. Congruent weathering of the carbonate rock leaves behind a thin soil. Much of the residuum from carbonate weathering may be routed through internally drained basins into the karst conduit network, potentially disconnecting hillslope response from changes in the rate of base level fall. Karst systems often respond to base level fall through the development of additional levels of conduits. Rapid carbonate weathering can occur deep within the subsurface in the vicinity of conduits and fractures.

Unlike silicate minerals, however, congruent weathering of carbonate minerals leaves only minor amounts of insoluble residue and therefore little soil or regolith (Figure 8b). Soils in carbonate terrains may develop largely from aeolian dust deposition (Macpherson and Sullivan, 2019b), and soil thickness may depend more on the carbonate purity or dust delivery rate rather than erosion rates such as in silicate terrains (Green et al., 2019; Moore et al., 2017). Additional differences result from the greater solubility and faster reaction kinetics of carbonate than silicate minerals (Plummer et al., 1979; Svensson and Dreybrodt, 1992). Carbonate dissolution is sufficiently fast that in some cases, chemical denudation rates can outpace mechanical denudation processes (Simms, 2004), such that solute fluxes may represent the majority of the seaward flux of weathering products.

Feedback mechanisms between soil development and denudation may be weakened, or even decoupled, within pure carbonate settings, particularly if the rate of soil development is controlled by allochthonous dust input. Carbonate denudation also may be controlled more by water availability and pH, rather than by topography or soil thickness as in silicate terrains (Gabrovšek, 2009; Gombert, 2002; Ryb et al., 2014; White, 1984). The weakening of feedback between soil formation rates and denudation rates may inhibit the approach to topographic equilibrium or at least increase the equilibration timescale. However, equilibrium landscape configurations that are entirely internal (autogenic) are also possible. For example, biogeomorphic feedbacks between soil thickness, CO_2 production, and weathering rates can produce equilibrium landscapes within low relief carbonate settings, where the water table is near the surface such as Big Cypress Swamp in southern Florida (Cohen et al., 2011; Dong et al., 2019a, 2019b). Here, modeling and field data suggest that initial development of a karst depression leads to the accumulation of both soil and colonization by rooting plants. As soil thickens, water becomes more available, and root respiration increases, increasing the pCO_2 at the rock surface and accelerating rates of rock weathering and depression growth. However, once sufficiently thick, soil cover inhibits the delivery of CO_2 to the rock surface. Ultimately, these feedbacks can produce a patterned equilibrium landscape that depends on internal controls rather than external erosional or tectonic forcing. Within the conveyor belt conceptual model for the silicate CZ, weathering occurs along planar fronts that are subparallel to the land surface (Figure 8a). In karstic carbonate terrains, weathering is focused along high permeability zones that create heterogeneous and irregular weathering patterns (Figure 8b) that are rarely subparallel to the surface (Phillips et al., 2019; Williams, 1985). Active weathering thus spans a range of depths, from exposed rock at the surface to rock that is hundreds, or even thousands, of meters below the surface (Audra et al., 2007; Klimchouk, 2019). The upper zone of weathering, often called the epikarst, typically has a higher degree of irregularity than the surface topography (Figure 9). This irregularity can grow over time through positive feedback resulting from flow-focusing (Klimchouk, 2004; Williams, 2008a, 1985) and generation of soil CO_2 that enhances shallow dissolution (Dong et al., 2019a; Gulley et al., 2015). The control of spatial weathering patterns in the subsurface of karst by geological structures and hydrological boundary conditions (Palmer, 1991), rather than soil properties or topography, indicates that models of carbonate CZ evolution will need to incorporate heterogeneity explicitly, as has been done in models of cave development (Dreybrodt, 1990; Gabrovšek and Dreybrodt, 2001; Groves and Howard, 1994; Hanna and Rajaram, 1998). These heterogeneities are missing from the lateral homogeneity of the conveyor belt model of the silicate CZ (Figure 8a).

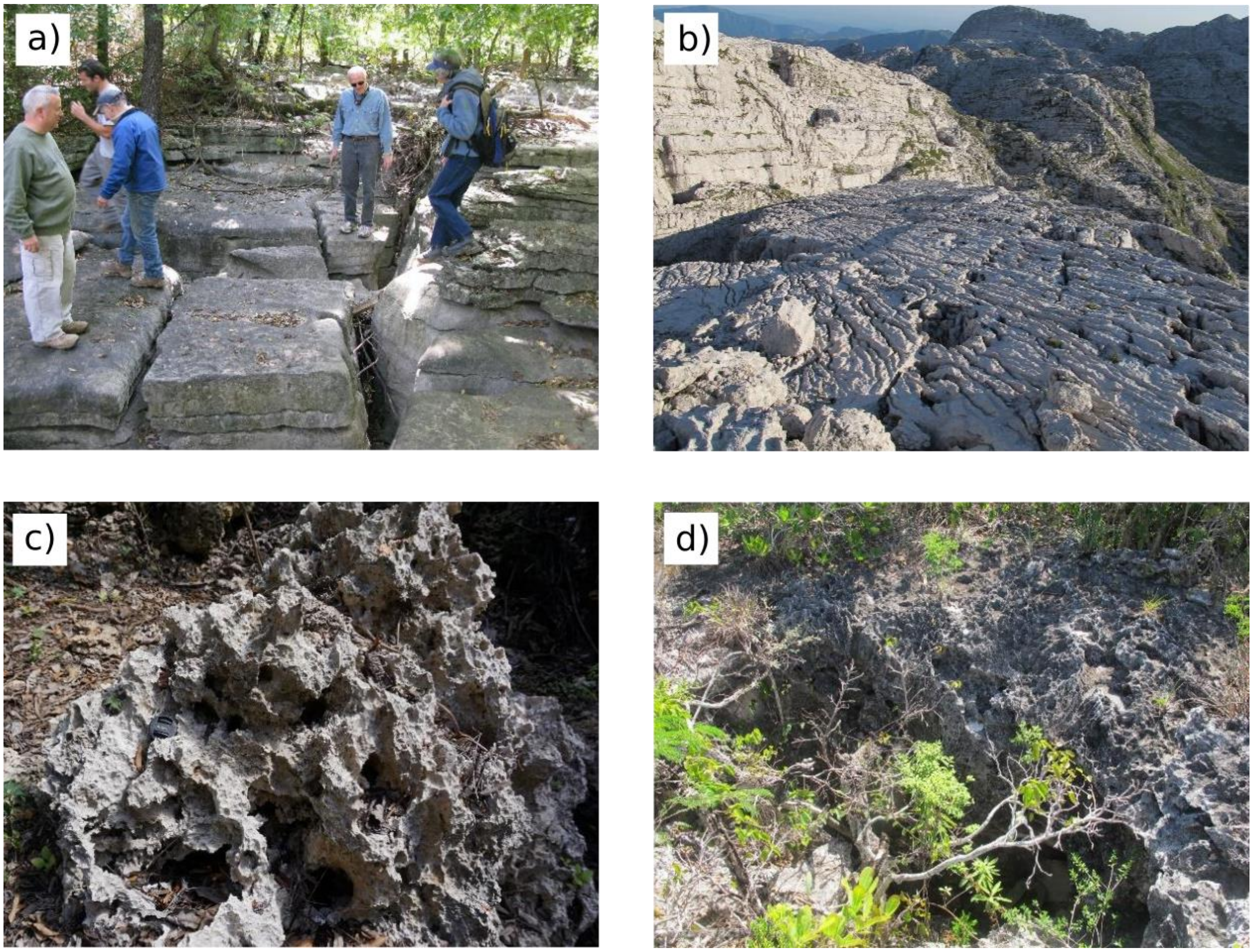

Figure 9. Weathering surfaces in carbonate terrains. a) Weathering along orthogonal joints in the St Joe Limestone in northern Arkansas. Floodwaters from a dam spillway have eroded the soil and exposed the weathering epikarst. b) Karren and epikarst surface on Dachstein Limestone on Mt. Kanin, Slovenia. c) Intense solutional weathering on an exposed piece of young, porous carbonate in Zanzibar. d) Thin soil and vegetation drape the weathering surface of young carbonates on San Salvador Island, Bahamas. In the center of the photo is the entrance of a 7-meter-deep solution shaft.

The focus of dissolution along high permeability zones in carbonate terrains causes an additional breakdown of the coupling between tectonic uplift and erosion rates found in the conveyor model. In the conveyor model, surface streams transport the sediment and solutes delivered to them by hillslopes (Figure 8a), enabling landscape-wide equilibration of erosion to uplift. However, surface streams are largely absent within a mature karst terrain, as all runoff and sediment generated near the land surface is diverted into the karst conduit system through closed basins (dolines or sinkholes) (Figures 8b, 10) (Ford and Williams, 2007). Thus, if the conveyor model of the CZ is transposed from silicate to carbonate terrains, dolines would represent hillslopes, and conduits would represent stream channels (Figure 8b). Even with relatively little relief (tens of meters), the hillslopes of dolines may be decoupled from base level, as dolines typically feed water and sediment vertically into the subsurface along solutionally enlarged fractures and conduits (Brucker et al., 1972; Klimchouk, 2004; Palmer, 1991; Williams, 1985). Therefore, many of the "hillslopes" of karst terrains terminate at the tops of vertical subsurface channels.

Even in the case of dolines feeding into subhorizontal conduits, changes at base level may not propagate through karst conduit networks as they do through surface channel networks. First, the geometry of karst conduits, including the profiles of the streams within them, are often controlled by structural heterogeneities in the rock, such as bedding partings and fractures (Filipponi et al., 2009; Lowe and Gunn, 1997; Palmer, 1991). Therefore, the initial profiles of streams within karst conduits may be far from the equivalent equilibrium channel morphologies (e.g., slope-discharge relationships) that would be expected within surface stream channels. Second, under conditions of rapid base level change, karst systems often respond by the development of new levels and abandonment of old cave channels (Figures 3 and 8b) (Audra et al., 2007; Gabrovšek et al., 2014; Granger et al., 2001; Stock et al., 2005; Wagner et al., 2011), rather than through the propagation of knickpoints. Similar shifts in cave development in coastal carbonate settings result from variations in sea level (Florea et al., 2007; Gulley et al., 2013). The development of new levels within karst systems may often be sufficiently fast that stream profiles within karst conduits do not have time to adjust their long profiles and erosion rates to accommodate changes in the rate of base level rise and fall.

4 A dissolving and leaky conveyor

The most basic concepts within the conveyor model remain intact within carbonate settings – rock is uplifted toward Earth's surface, it undergoes weathering, and the products of weathering are transported seaward. However, the details of the conceptual model need revision because of two fundamental ways in which carbonate settings diverge from the standard conveyor model. First, congruent weathering causes a large fraction of the total weathering flux to be exported from the system in a dissolved form. Second, the development of integrated subsurface drainage networks with high permeability and rapid, often turbulent, flow, allow solid weathering products to be transmitted to base level via subsurface conduits rather than along hillslopes and surface streams. Each of these two factors can be quantified using a dimensionless weathering flux fraction that varies between zero and one, with the first factor being quantified by

$$F_{dissolved} = \frac{W_{dissolved}}{W_{dissolved} + W_{solid}}, \qquad (2)$$

where $W_{\mathrm{dissolved}}$ is the dissolved weathering flux, W_{solid} is the solid weathering flux, and $F_{\mathrm{dissolved}}$ is the fraction of dissolved flux, and where all fluxes have dimensions of M L^{-2} T^{-1}. The second factor is quantified by

$$F_{solid,sub} = \frac{W_{solid,sub}}{W_{solid,sub} + W_{solid,surf}}, \qquad (3)$$

where $W_{\mathrm{solid,sub}}$ is the solid weathering flux that transits through subsurface conduits, $W_{\mathrm{solid,surf}}$ is the solid weathering flux that remains near the surface and is transmitted to base level via hillslopes and surface channels, and $F_{\mathrm{solid,sub}}$ is the fraction of the solid weathering flux that transits through subsurface conduits. We consider two modified versions of the conveyor model, which we call the "dissolving conveyor" (where $F_{\mathrm{dissolved}}$ is large) and the "leaky conveyor" (where $F_{\text{solid,sub}}$ is large). Both modifications of the original conveyor model result in a weakening of the negative feedback mechanisms that drive weathering rates toward uplift rates and produce equilibrium landscapes. The dissolving conveyor describes settings where the dissolved fraction of the total seaward flux of weathering products is close to one, meaning that most weathered materials exit the system as solutes. In this case, the buildup of soil and regolith is insufficient to retard denudation. In cases where tectonic uplift is rapid, topography may become extremely steep, until mechanical weathering and erosion processes match uplift (Ott et al., 2019). In this case, the system would be driven away from the dissolving conveyor state as solid material export increases due to steepened terrain. In contrast, where uplift trate is low, the lack of negative feedback enables the development of karst planation surfaces (e.g. Krklec et al. 2022 ; Simms, 2004; Smart et al. 1986). In this case, surface denudation is not arrested until the land surface approaches base level and the water table.

The leaky conveyor describes settings where the fraction of solid weathering products transported through the karst conduit network is high, meaning that both solid and dissolved weathering materials transit through the subsurface to base level rather than down hillslopes and stream channels. This fraction should govern the ability of karst landscapes to develop, with high subsurface flux fractions producing landscapes dominated by dolines (Figure 10) and lacking integrated surface drainage networks. Again, this subsurface transport weakens feedback between uplift, weathering, and erosion, as base level changes may not communicate through the subsurface as they would in a surface stream network. In such cases, autogenic processes may drive patterns in topography and regolith thickness (e.g., Dong et al., 2018) rather than external forcing by tectonics.

While each of these modified models can be considered separately, there is likely a strong correlation between the two governing dimensionless fractions in real landscapes. Settings with a higher fraction of dissolved weathering fluxes will tend to have a higher percentage of weathering fluxes transiting through the conduit network. In these settings, karst conduit networks will be better developed than where solid weathering products dominate as a result of reduction in the total volume of insoluble weathering products. Importantly, both of these weathering flux fractions could be quantified via field studies. While there are some studies that quantify the relative importance of chemical and physical fluxes (e.g. Erlander et al., 2021; Ott et al., 2019), we are not aware of any studies that have quantified surface vs. subsurface fluxes. The controls on these both flux fractions are currently poorly constrained. While position on the carbonate-silicate spectrum is undoubtedly important, other factors, such as climate and tectonics, should also impact these flux fractions. Further work is also needed to elucidate the impacts that these weathering flux fractions, and their external controls, have on CZ architecture, dynamics, and resilience.

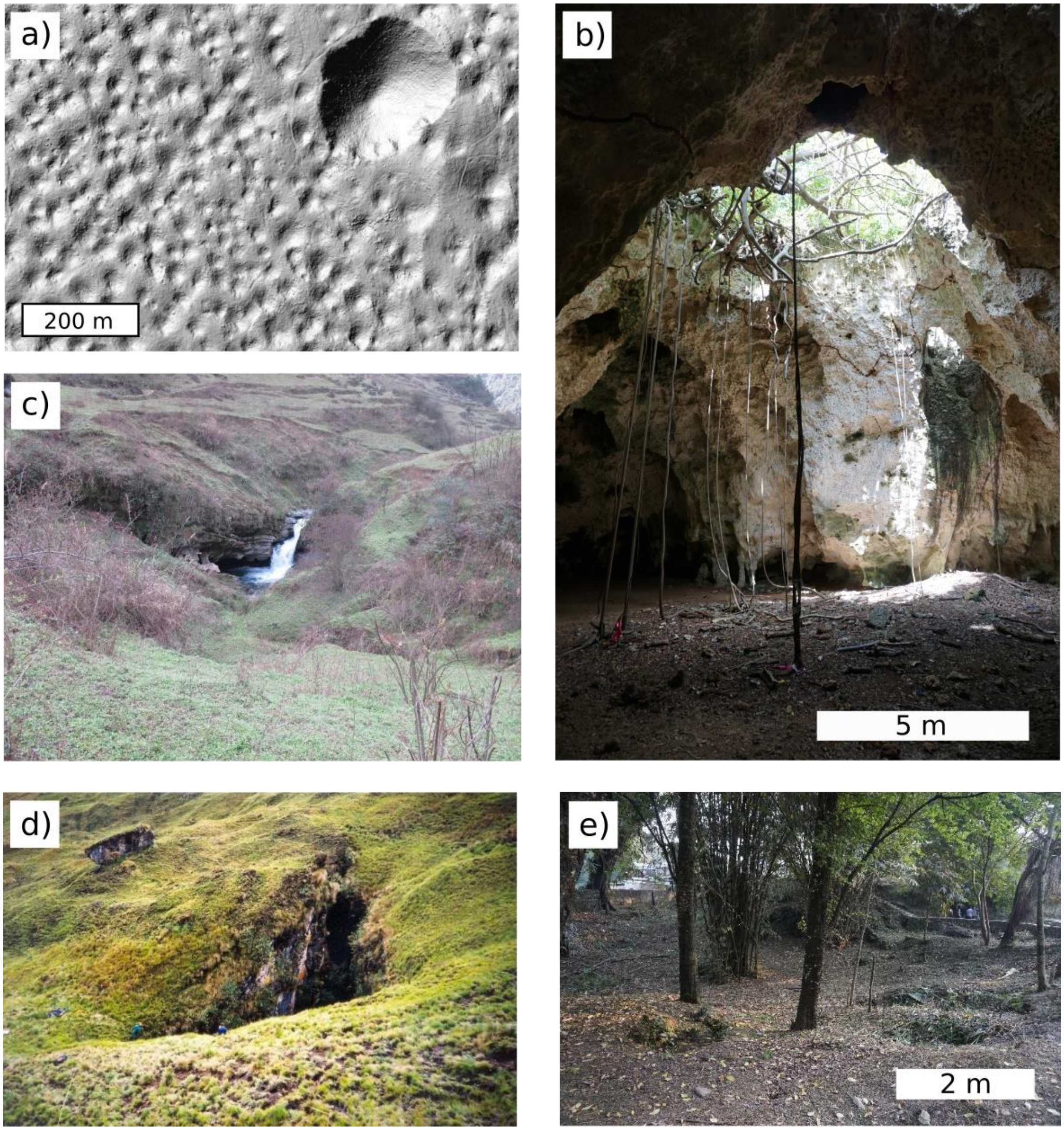

Figure 10. Dolines/sinkholes and shafts in karst terrains. a) A lidar hillshade of solution dolines, and a collapse doline, on Logaška Planota, Slovenia. b) Vegetation hangs into a collapse doline in a cave system on the island of Zanzibar. c) A stream channel within a blind valley sinks into a doline near the contact with carbonate rocks in Wulong County, China. d) A 60-meter-deep vertical shaft breaches a hillslope in the Andes of northern Peru (note cavers for scale). e) Small solutional dolines developed in a calcite-cemented conglomerate near Pokhara, Nepal.

5 Conclusions

Carbonates underlie a substantial portion of Earth's surface and represent an important fraction of Earth's CZ, providing crucial water resources and ecosystem services to more than a billion people. Our current state of knowledge suggests that the congruent weathering, high solubility, and fast kinetics of carbonate dissolution, lead to altered rates and patterns of CZ evolution in carbonates compared to silicate settings. When landscapes develop in relatively pure carbonate rocks, karst systems typically form, producing large contrasts in subsurface permeability and long-range subsurface connectivity that enable rapid fluxes of water, solutes, sediment, and gases through the CZ along routes of preferential flow. Direct relationships between biological CO_2 production and carbonate weathering by carbonic acid mean that production of porosity in the subsurface may be tied to biological processes in carbonates, potentially enabling carbonate-specific feedback loops between CZ development and ecosystem form and function. Because of the rapid kinetics of calcite dissolution, shifts in system dynamics and structure due to changes in ecology, land use, or climate may also be rapid.

These differences show that conceptual models developed to understand CZ architecture and evolution within silicate-rich rocks, such as the conveyor model, may require rethinking in their application to carbonates. We present the initial ideas of a "dissolving conveyor" and a "leaky conveyor" as starting points to incorporate carbonate CZ processes. The ability of karst conduits to transport mobile regolith can lead to decoupling of hillslopes from stream channels, potentially weakening or eliminating feedback mechanisms that drive landscapes underlain by silicate-rich rocks toward equilibrium topography and regolith thickness. The fast reaction kinetics and elevated solubility of carbonate minerals lead to distinct differences in the relationships between tectonism and carbonate and silicate CZ development, including in the interactions between base level and the depths of weathering processes. Because of the deep circulation of meteoric water in karst settings, the lower boundary of the CZ needs to be expanded, and the definition of the CZ may need modification to include carbonate terrains.

A better understanding of carbonate CZ development may inspire broader conceptual frameworks that incorporate roles for preferential flow and heterogeneity, which are present to some extent in all CZ settings. The triple porosity system of matrix, fractures, and karst provides opportunities to study a spectrum of flow-through timescales and weathering rates and depths in one setting. Scaling questions are also amplified when there are large contrasts in permeability that vary with the scale considered. The controlling processes in the conveyor model for weathering might be better understood by measuring rates in a faster transport system, particularly under anthropogenic stresses, harking back to the concept of carbonate rocks as a bellwether. Constraining the transport of gases through the subsurface may enhance our understanding of the global carbon cycle and how it is affected by biological and geochemical processes.

Understanding how the CZ evolves along the carbonate-silicate spectrum requires a broader conceptual framework than we currently have. Many questions arise. What controls the distribution of CO_2 in the subsurface? How do advective processes influence this distribution? How do pCO_2, water availability, plant growth, and rock structure interact to determine patterns of porosity development? Under what conditions do acids other than carbonic acid drive porosity development? How are feedbacks between biological, hydrological, and geological processes reflected at the landscape scale? What factors control the partitioning of weathering fluxes between dissolved vs. solid and subsurface vs. surface? How does this partitioning impact the dynamics and structure of the CZ? There is also a need to integrate knowledge across sites rather than focusing on the idiosyncratic or distinctive nature of individual sites. In addition to pure carbonates and pure silicates, there is an entire spectrum of mixtures that lie between these endmembers. What are the most important parameters along that spectrum that produce differences in CZ processes and architecture? Answers to these questions will require transdisciplinary study teams that are integrated into the CZ research community going forward.

Acknowledgments

This work was supported by the National Science Foundation grant CZ RCN: Research Coordination Network in Carbonate Critical Zones (1905259). PLS was also supported by CZ RCN: Expanding Knowledge of Earth's Critical Zone (1904527).

Open Research

No new data were presented in this review article.

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