1 Introduction

Silicate weathering, whereby silicate minerals are dissolved by carbonic acid, sequesters atmospheric CO_2 over long (10^6 year) timescales, influencing global climate regulation. As water passes through the subsurface, it interacts with the surrounding rock. This causes the addition of solute species to the groundwater, and the formation of stable secondary minerals through the dissolution of primary minerals. Large mountain ranges in particular are thought to be most sensitive to weathering (Tipper et al., 2006). The Himalayan mountain range spans more than 590,000 km^2, and is the source of major rivers, including the Ganges, Brahmaputra, and Indus. The dissolution kinetics of the silicate rocks in Himalayan catchments are thought to be sensitive to temperature and runoff because the weathering reactions have not gone to completion. Silicate weathering in the Himalayas as a result of their uplift and erosion in the Cenozoic may have contributed significantly to the global cooling over the past 40 million years (Raymo and Ruddiman, 1992; West et al, 2005, Kump et al, 2000). Clearly, understanding the strongest control on weathering in these key regions for the global carbon cycle is of utmost importance to inform climate policy. In highly erosive regions like the Himalayas where the supply of silicate minerals far exceeds the weathering rate, silicate weathering reactions are thought to be more sensitive to temperature than runoff. These are regions are called ”kinetically-limited” (Stallard & Edmund 1983 JGR, West et al, 2005). Reactive transport models are widely used in Earth Sciences to simulate the flow of groundwater through the subsurface (Bethke, 2011). Reactive transport models built on this temperature sensitivity (”Fontorbe models” from now on, after Fontorbe et al., 2013) are used to simulate groundwater through one-dimensional flow paths based on a few key parameters, which make up the ”weathering fingerprint” of a catchment. More recent models have proposed silicate weathering is more sensitive to runoff than to temperature (Maher, 2011). These (”Maher models” from now on, after Maher, 2011) assume that all weathering paths approach equilibrium. This study looks at Melamchi, a Himalayan catchment north-east of Kathmandu in Nepal, to act as a case study for Himalayan weathering. Determining the greatest control on weathering in Melamchi is complicated, however, and a proxy is needed for the comparison of the two models.

Estimation of residence time from the Maher and Fontorbe models using measured spring chemistry in Melamchi will act as the proxy for weathering control. The weathering fingerprints of these catchments contain many unknowns, namely the residence time of the water, flow path direction and length, rate of reaction, and extent to which equilibrium is reached. Spring chemistry is reflective of the weathering processes that occur in the subsurface, and can therefore be used to estimate these fingerprint parameters. Residence time, also called the advective age, is defined by how long a given water packet spends from rain recharge into groundwater to exiting at a spring (McCallum et al, 2015). Understanding residence time in particular is important because the geochemical and biogeochemical reactions that contribute to the solute load during weathering are time-dependent; generally, longer residence times promote greater solute accumulation in the water (Berner, 1978). These geochemical reactions are also controlled by the reaction rate which is thought to vary as equilibrium is approached (White and Brantley, 2003; Maher, 2011). Therefore, an understanding of residence time will provide insight into how long weathering reactions take place in a given catchment, whether they reach equilibrium, and what this means for the carbon cycle as a whole. Residence time will also reflect the variety of flow routes within a catchment because of physical constraints like Darcy's law, which will help to improve hydrological models. Calculating residence time using the spring chemistry in Melamchi will allow the assumptions underlying the two models to be tested, and assess their applicability to a real-world catchment.

From the model comparison will also come a better understanding of fluid residence times in Himalayan catchments, for which tracer data is already commonly used to infer how long a water packet spends in the subsurface (Atwood et al, 2021). Previous studies on Melamchi have used CFC and SF_6 gases to determine a mean age on the order of ten years for groundwater at the base of the catchment ridge (Atwood et al, 2021) (ref map). Using the chemical composition of the water will provide a different way of obtaining residence times, and give a benchmark for the tracer data, which is often reported to be limited in its application (McCallum et al, 2015). If the residence time of a particular water packet is long enough, the reaction will reach chemical equilibrium, meaning the free energy of the system will be close to zero (Kampman et al., 2013). Comparison of these residence times with separate estimates of free energy derived from the measured concentration of springwater in the catchment will test the validity of the two models and their assumptions. Finally, this will help to inform whether weathering in catchments like Melamchi is most strongly controlled by temperature or runoff.

The rate of weathering is dependent on the mineralogy of the rock. Different minerals weather at different rates. Therefore, the most reactive minerals will disproportionately contribute to the solute load of the water (Shand et al, 1999). Differences in lithology are therefore also thought to affect weathering. Geological differences lead to differences in soil composition, landscape features, vegetation, and climate which in turn affect the rates of reaction. Logically, the contribution of one lithology to weathering is at least in part correlated to its spatial extent in the catchment (Stallard and Edmond, 1983). In the Melamchi catchment, only weathering through carbonic acid is considered. Weathering through sulfuric acid also significantly contributes to the global weathering budget, but its impact is not considered in this study because the marine deposits required for its formation are not present in the Melamchi region (Bufe et al., 2021).

Weathering regimes can be classified as either transport-limited or kinetically limited (West et al., 2005). West et al. (2005) distinguish the two regimes by the rate of erosion in the catchment. In low erosion rate settings, weathering is transport-limited due to limited mineral supply. Weathering here is proportional to the material eroded. In high erosion rate settings, weathering is kinetically-limited due to an abundant mineral supply. Rapidly eroding catchments like Melamchi are likely kinetically-limited. Soil properties and topography can be used to identify different weathering regimes in the subsurface (Pedrazas et al, 2021). Indeed, bedrock strength is thought to be more dependent on weathering than mineral or textural differences between the metamorphic lithologies in the Himalayas (Medwedeff et al, 2021). Understanding the extent of weathering can therefore also serve to predict the stability of bedrock in rapidly eroding regions.

Estimation of porosity is essential for understanding the extent of weathering in a catchment. Understanding how open a rock is to water flow and reaction can constrain the reactive transport models used to estimate residence time. Porosities vary widely across a catchment depending on the rock type encountered (Singh et al, 1987; David et al, 1994). Porosity also increases as a rock becomes more weathered (Marques et al, 2009). Note that in the following models, the porosity value is taken to be an average over a given depth in the subsurface. In Earth Sciences, models of fluid flow – whether in the subsurface or deep within the Earth – are typically categorized based on whether the flow occurs through a porous medium or within large open channels (Pedrazas et al, 2021; Maher, 2011; Kelemen et al, 1999; Jackson et al., 2018). This remains an open debate beyond the scope of this study (though note that in later sections flow paths are depicted as "channels" to facilitate the explanation of reactive transport). Hence, the porosity value used for residence time calculation is assumed to be an average. This allows for both types of flow to be plausible, whether in a highly porous medium or large channels surrounded by less porous rock.

Rates of reaction during weathering comprise both dissolution and precipitation, and chemical equilibrium is defined as that state where these are balanced and equal. Rates of reaction are thought to be different depending on whether they are measured in the field or in a laboratory (Maher et al., 2009). This difference has been explained by denoting 'extrinsic' qualities that are variable in the field, such as permeability, mineral/fluid ratios and different surface areas available to react (White and Brantley, 2003). The rate of reaction of a system has also been linked to the free energy of the system, with laboratory rates being calculated significantly further away from equilibrium than field rates (Kampman et al, 2009). This implies that field localities are closer to equilibrium than laboratory-derived rates might suggest.

The strontium isotope composition of different rock types is indicative of different formation mechanisms and conditions. This is used to track the relative contributions of weathering and hydrothermal circulation inputs in seawater (Edmond, 1992). The rock signature imparts a strontium isotopic composition to groundwater that reacts with it in the subsurface. Hence, measuring the strontium isotopic composition of springs can provide information on provenance and mixing between groundwaters that react with different lithologies (Faure, 2001).

The Indian Summer Monsoon (ISM) in Nepal is characterised by a strong seasonal reversal of winds, which brings heavy rainfall to the region during the summer months, and dry conditions during the winter (Bookhagen and Burbank, 2010). The monsoon brings a large amount of precipitation to the region. Oxygen isotope measurements suggest most of the precipitation occurs in the higher elevation parts of the catchment, and this is supported by remotely sensed rainfall estimates in the region (Acharya et al, 2020; Bookhagen and Burbank, 2010). Precipitation and discharge relationships in the Himalayas have been used to suggest that there is a three month lag in the response of the river to precipitation (Andermann et al., 2012). The residence time of groundwater can be used to quantify this delay and nature of its origin, given that rain is the main source of recharge to the groundwater system (Illien et al, 2021). Seasonal variation in rainfall is thought to relate to different hydrological regimes, whereby river discharge and precipitation are 'coupled' when there is a significant enough amount of water to recharge the groundwater system. (Illien et al, 2021) The seasonal variation in precipitation therefore also translates to a variation in runoff, whereby this is twelve times stronger during the monsoon than during the dry season (Sharma, 1997).

Changes in climate contribute to changes in the monsoonal system dynamics. The start of the monsoon has not changed in Nepal, but the end has been delayed. This has led to more intense precipitation on a per day basis, which is detrimental for crops in the winter season due to lack of moisture. Intense precipitation is also considered the main climatic cause of flooding (Panthi et al, 2015; Baniya et al, 2012). "One-off" landslide events transport as much as four times the flux of sediment deposited in the valley in a year (Chen C et al., 2023). These events are thought to be increasing in frequency over recent years as a result of climate change, increasing the erosion rate in these areas (Adhikari et al, 2023). In particular, effects of a flash flood in 2021 are still visible in the area, with damage done to several bridges and hundreds of families.

In this study, spring and rain samples from the Melamchi region of Nepal are used as a case study to investigate the weathering rates in a kinetically-limited catchment. (ref map) The sample dataset consists of 372 samples spanning four field campaigns over three years (2021-2024), as well as more recent year-long bi-weekly timeseries data from stream and spring samples in sites across the catchment. Of those, 68 were collected in September 2024 by a team with researchers from the University of Cambridge and Kathmandu University for this study. This dataset comprises major ion concentrations, alkalinity, and radiogenic strontium isotopes from the Melamchi catchment.