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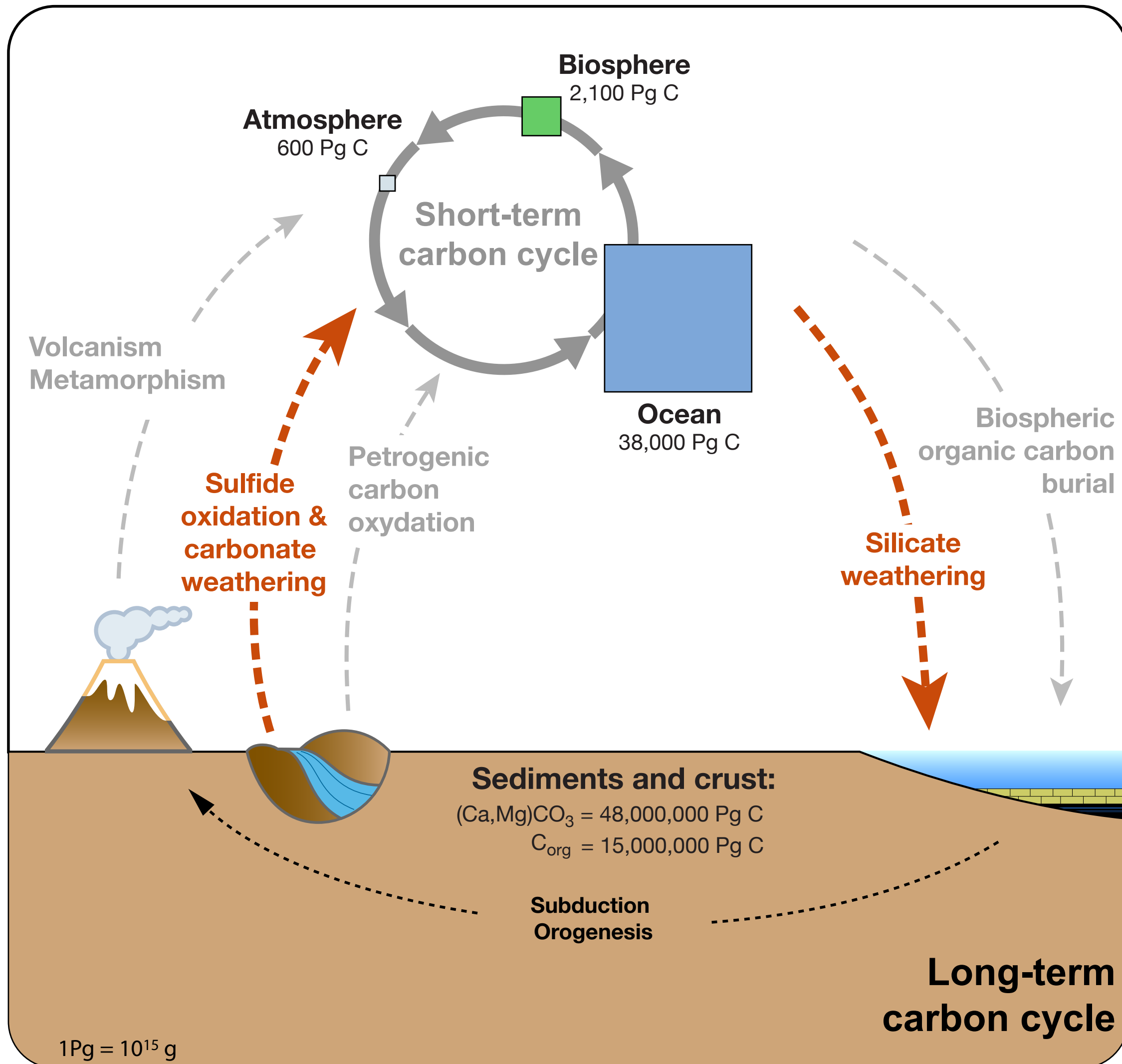
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Chemical weathering pathways in the central Himalaya

new constraints from $DI^{14}C$ (& $\delta^{34}S$)

Chemical weathering and the long-term carbon cycle



Background:

- On Myr time-scales, carbon is exchanged between Earth's surface reservoirs (atmosphere, biosphere, ocean) and crustal reservoirs within the **long-term carbon cycle**.
- These exchanges of carbon are mainly operated through :
 - Volcanic and metamorphic reactions (source)
 - The organic carbon cycle (source and sink)
 - The inorganic carbon cycle (chemical weathering, source and sink)
- Any imbalance in the these C-exchange fluxes (as sources or sinks) may result in significant changes in the amount of C in the atmosphere.

This study focuses on better quantifying the chemical weathering pathways involved in long-term carbon exchange between the crust and the atmosphere

Chemical weathering and the long-term carbon cycle

The carbon budget of weathering differs depending on the chemical weathering reaction pathway:

e.g. carbonic acid (derived from atmospheric CO₂) weathering of silicates, coupled to carbonate precipitation in the ocean is a carbon sink; sulfuric acid (derived from sulfide oxydation) weathering of carbonates, coupled to carbonate precipitation, is a carbon source to the atmosphere:

		Moles carbon relative to atmosphere
Carbonic acid weathering of silicates	$CaSiO_3 + \overset{\text{atmosphere}}{2H_2CO_3} + H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2HCO_3^-$	-2
Carbonic acid weathering of carbonates	$CaCO_3 + \overset{\text{atmosphere}}{H_2CO_3} \rightarrow Ca^{2+} + 2HCO_3^-$	-1
Sulfuric acid weathering of silicates	$CaSiO_3 + \overset{\text{sulfide}}{H_2SO_4} + H_2O \rightarrow Ca^{2+} + H_4SiO_4 + SO_4^{2-}$	na
Sulfuric acid weathering of carbonates	$CaCO_3 + \overset{\text{sulfide}}{\frac{1}{2}H_2SO_4} \rightarrow Ca^{2+} + 2HCO_3^- + \frac{1}{2}SO_4^{2-}$	0
Coupled to carbonate precipitation in the ocean	$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$	+1

A carbon budget of weathering therefore requires to partition weathering products into weathering pathways

Chemical weathering pathways

The radiocarbon signature of dissolved inorganic carbon (**DI¹⁴C**) in river water is a tracer of the carbon source, and hence of the chemical weathering reaction (e.g. Blattmann et al., 2019) :

		DI ¹⁴ C (Fm)
Carbonic acid weathering of silicates	$CaSiO_3 + 2H_2^{Fm=1}CO_3 + H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2H^{Fm=1}CO_3^-$	1
Carbonic acid weathering of carbonates	$Ca^{Fm=0}CO_3 + H_2^{Fm=1}CO_3 \rightarrow Ca^{2+} + 2H^{Fm=0.5}CO_3^-$	0.5
Sulfuric acid weathering of silicates	$CaSiO_3 + H_2SO_4 + H_2O \rightarrow Ca^{2+} + H_4SiO_4 + SO_4^{2-}$	na
Sulfuric acid weathering of carbonates	$Ca^{Fm=0}CO_3 + \frac{1}{2}H_2SO_4 \rightarrow Ca^{2+} + 2H^{Fm=0}CO_3^- + \frac{1}{2}SO_4^{2-}$	0

DI¹⁴C can be combined with the ionic composition measured in river water to constrain the importance of each reaction

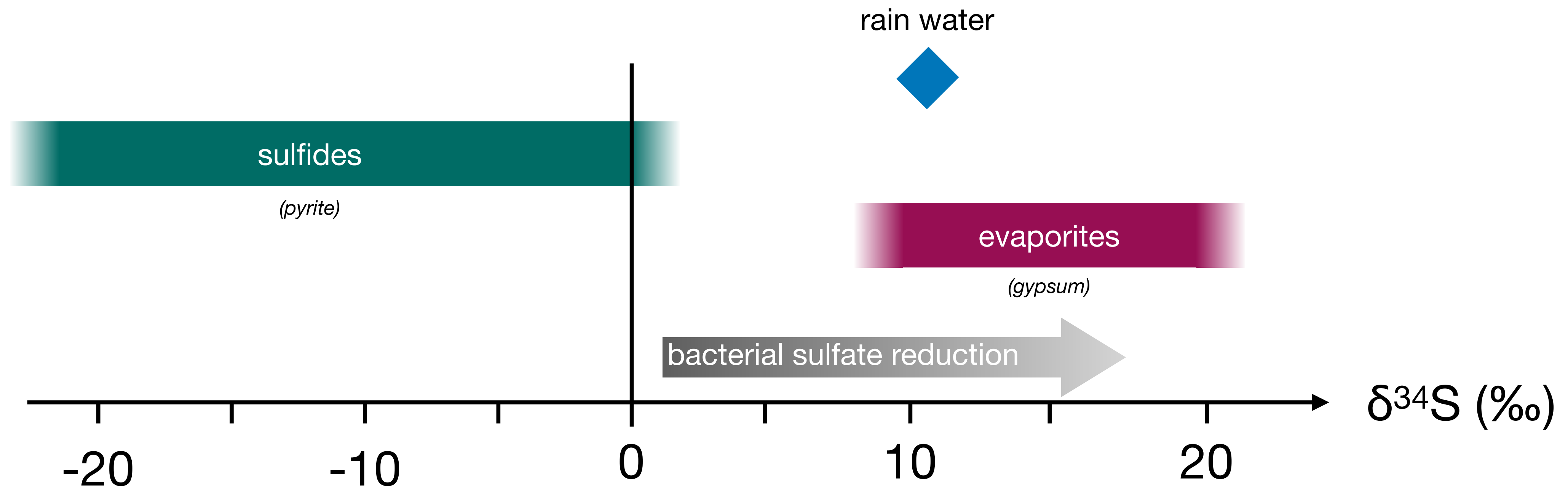
Radiocarbon signatures are reported as fraction modern (Fm):

- Fm = 1 radiocarbon modern (ca. atmosphere, biosphere...)
- Fm = 0 radiocarbon dead (carbonate rocks)

Chemical weathering pathways

However, not all sulfate (SO_4^{2-}) in the river dissolved load can be assigned to sulfide (pyrite) oxidation. Important evaporite inputs need to be accounted for as they cannot always be well quantified by dissolved ion compositions (and not at all by DI^{14}C).

The sulfur isotopic composition of dissolved sulfate ($\delta^{34}\text{SO}_4^{2-}$) is linked to the weathered mineralogy :



e.g. Huh et al., 1998; Karim & Veizer, 2000; Kampschulte & Strauss, 2004; Calmels et al., 2007; Turchyn et al., 2013; Torres et al., 2016; Burke et al., 2018...

Study outline

Objectives of the study:

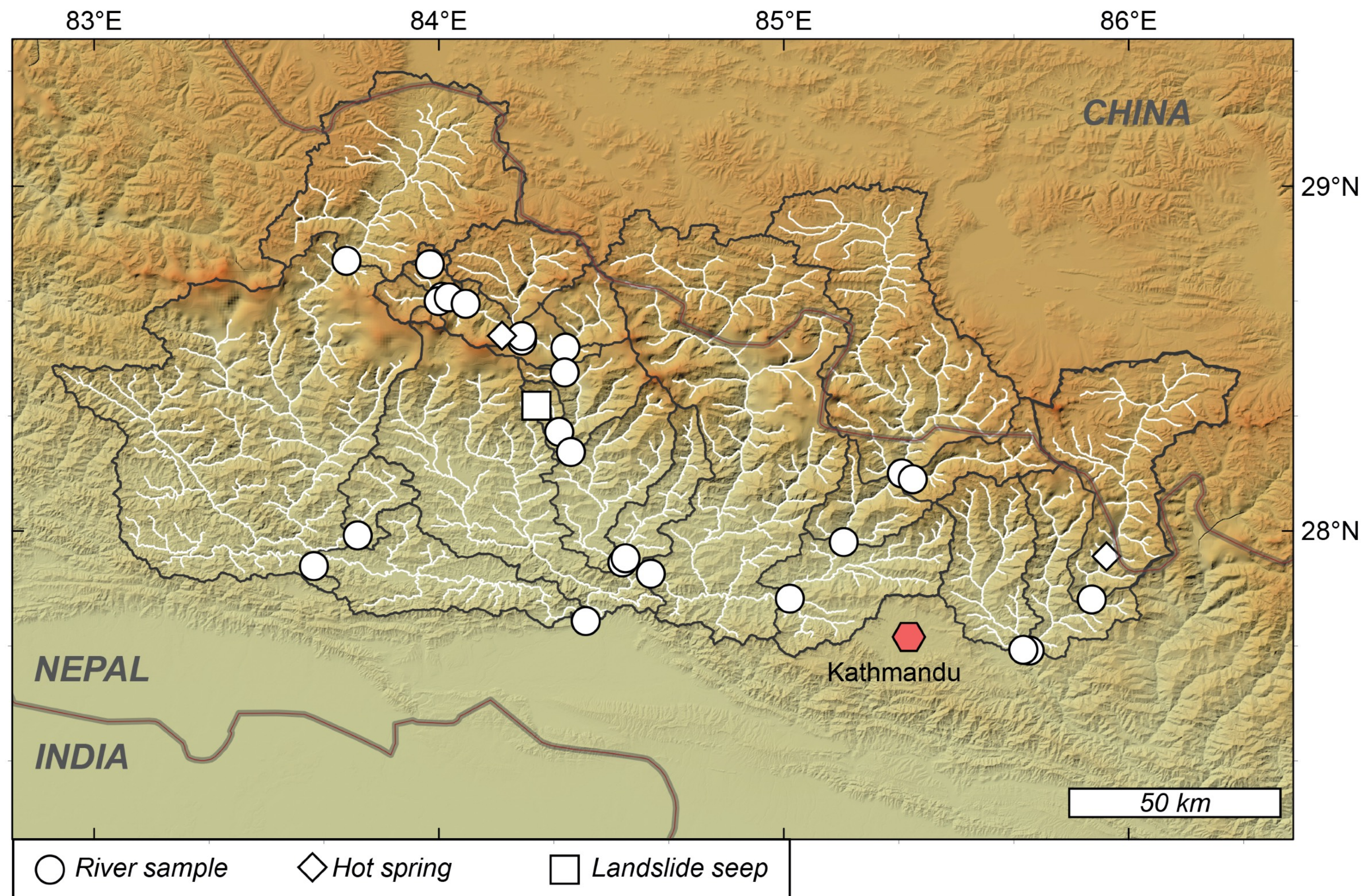
- Refine the carbon budget of chemical weathering in the Himalaya.
- Identify possible controls on the intensity of the sulfuric acid weathering pathway as a carbon source.

Approach :

Combine DI^{14}C & $\delta^{34}\text{S}$ and river water dissolved major ion compositions in an inversion model to constrain chemical weathering pathways.



Study outline



Samples (0.2 μm filtered):

sampled May through October 2014 - 2018

River water (x43)

- catchments from 15 to 30'000 km²
- carbonate and silicate lithologies
- elevation from 150 to 4500 m asl

Hot springs (x2)

Landslide seeps (x4)

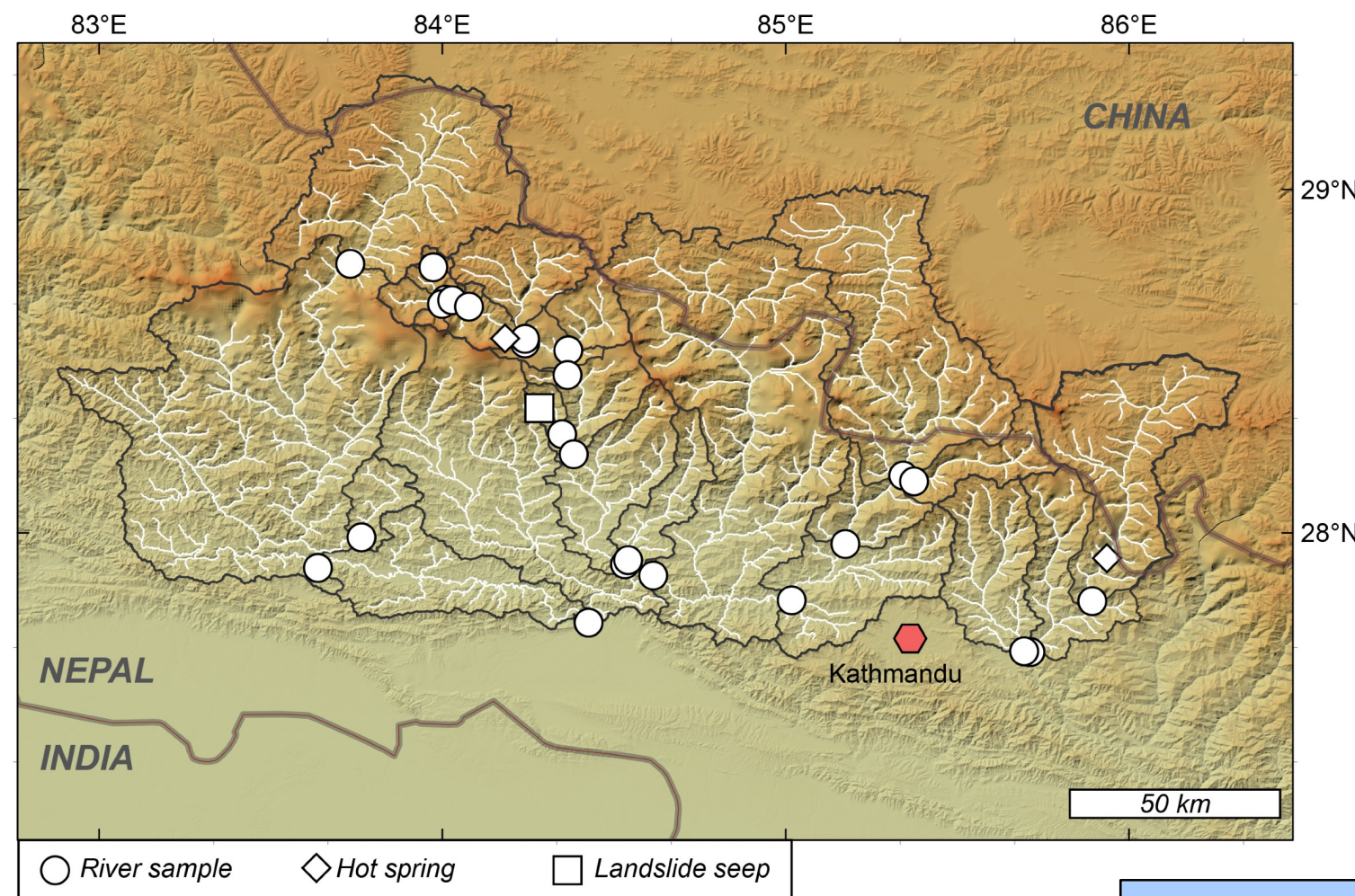
Analytical :

Anions & cations: ion chromatography

DI¹⁴C: gas-bench & AMS (ETH)

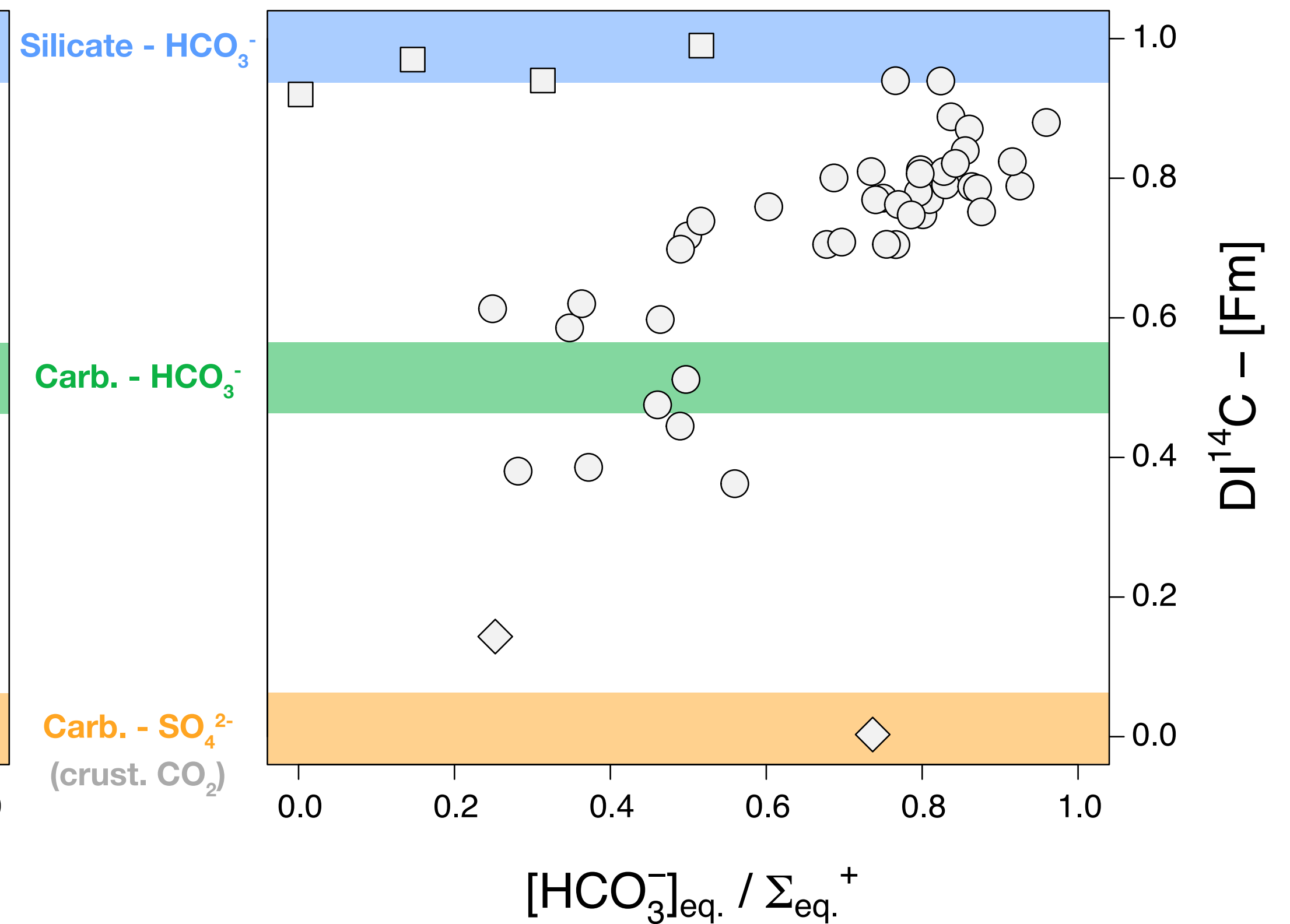
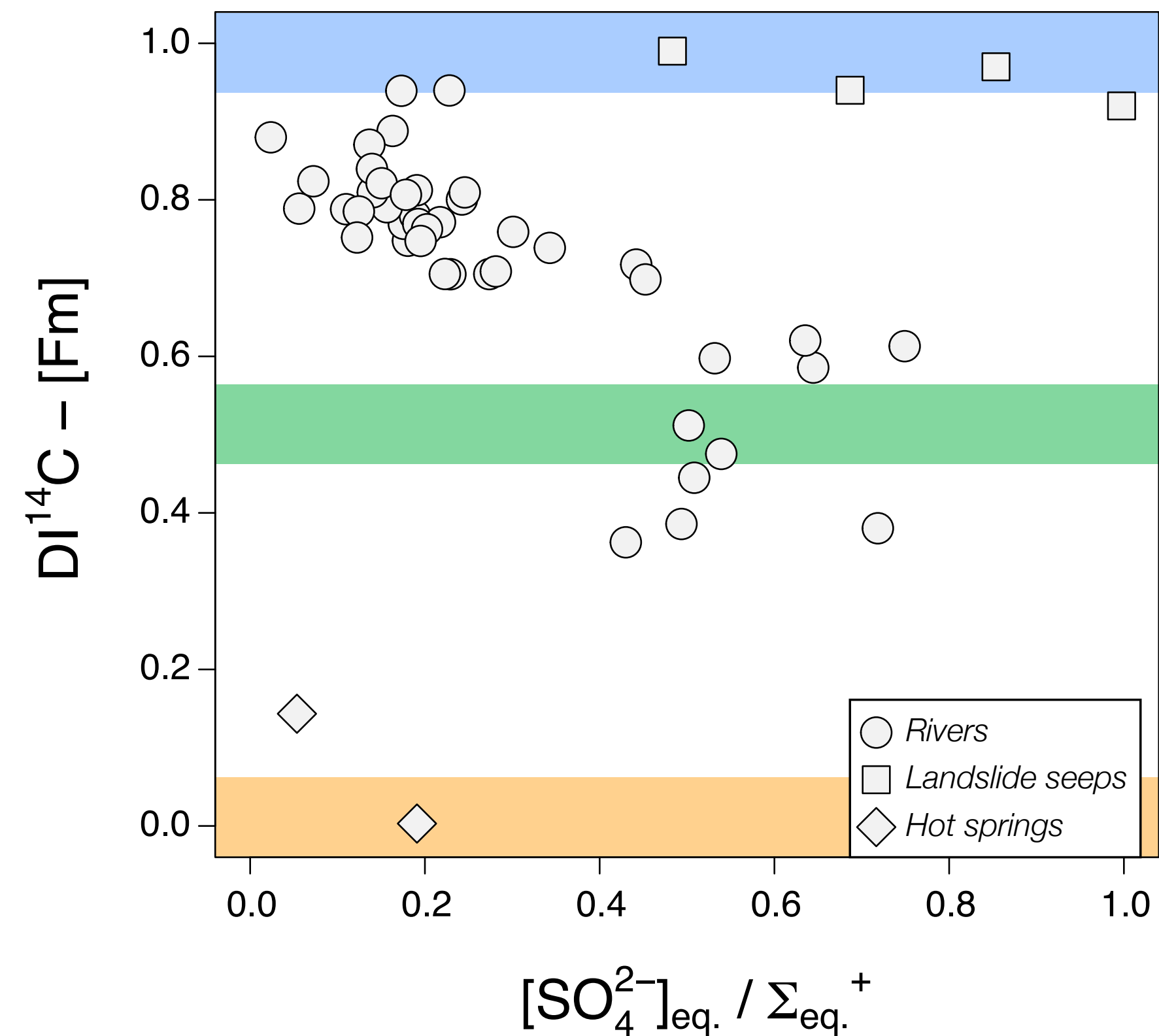
$\delta^{34}\text{S}$: MC-ICPMS (CRPG)

Chemical weathering pathways with DI^{14}C



Main anionic charge: HCO_3^- and SO_4^{2-}

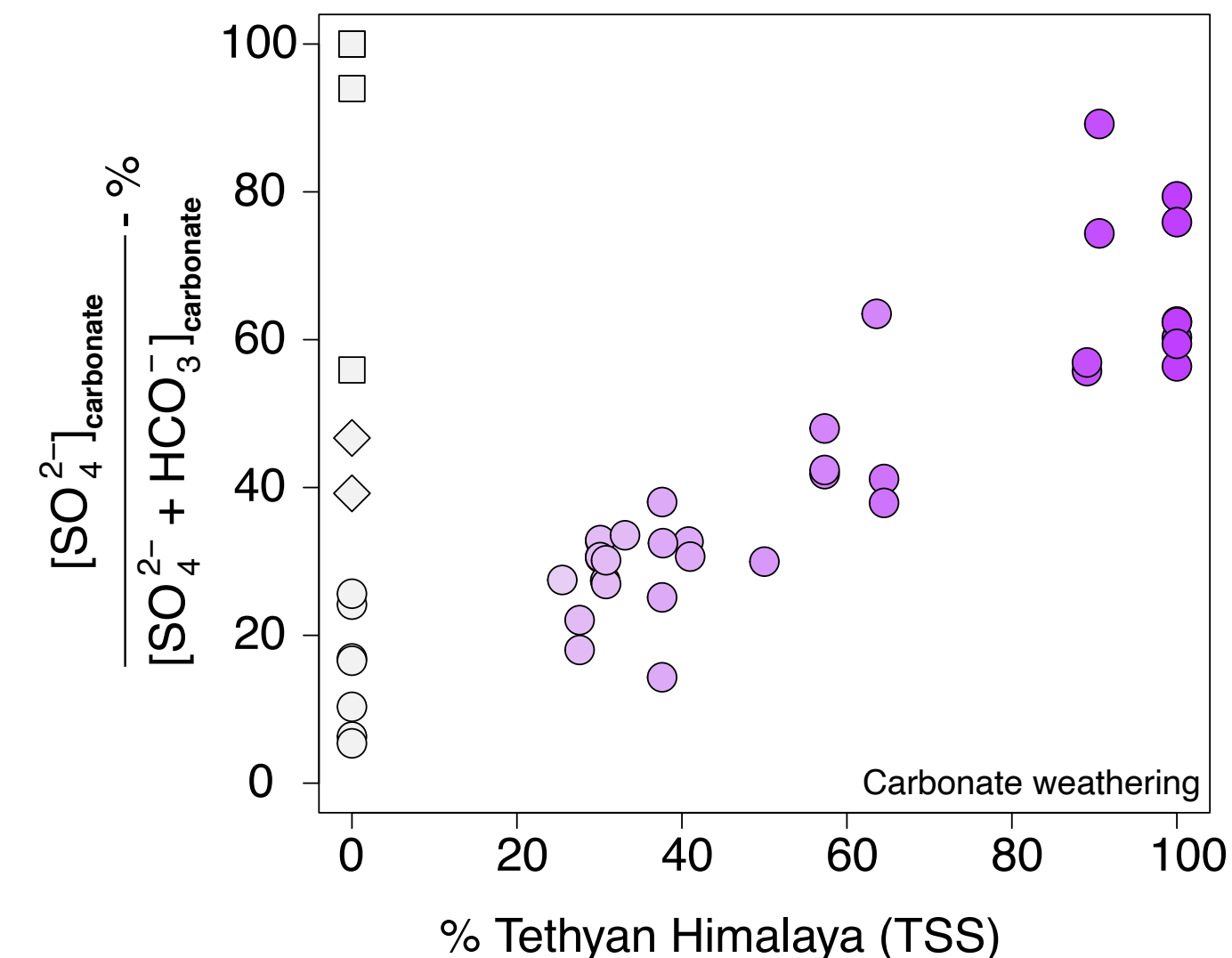
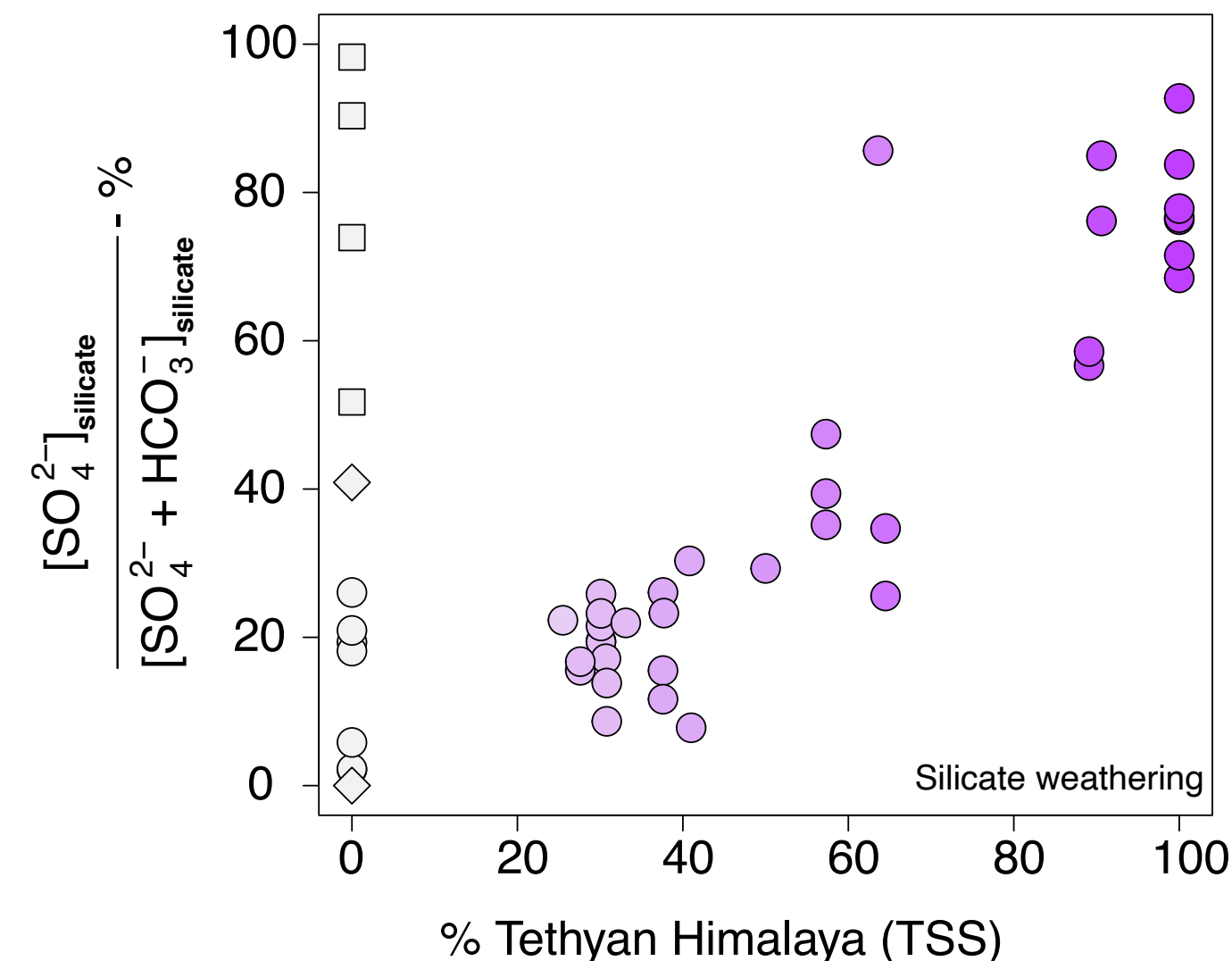
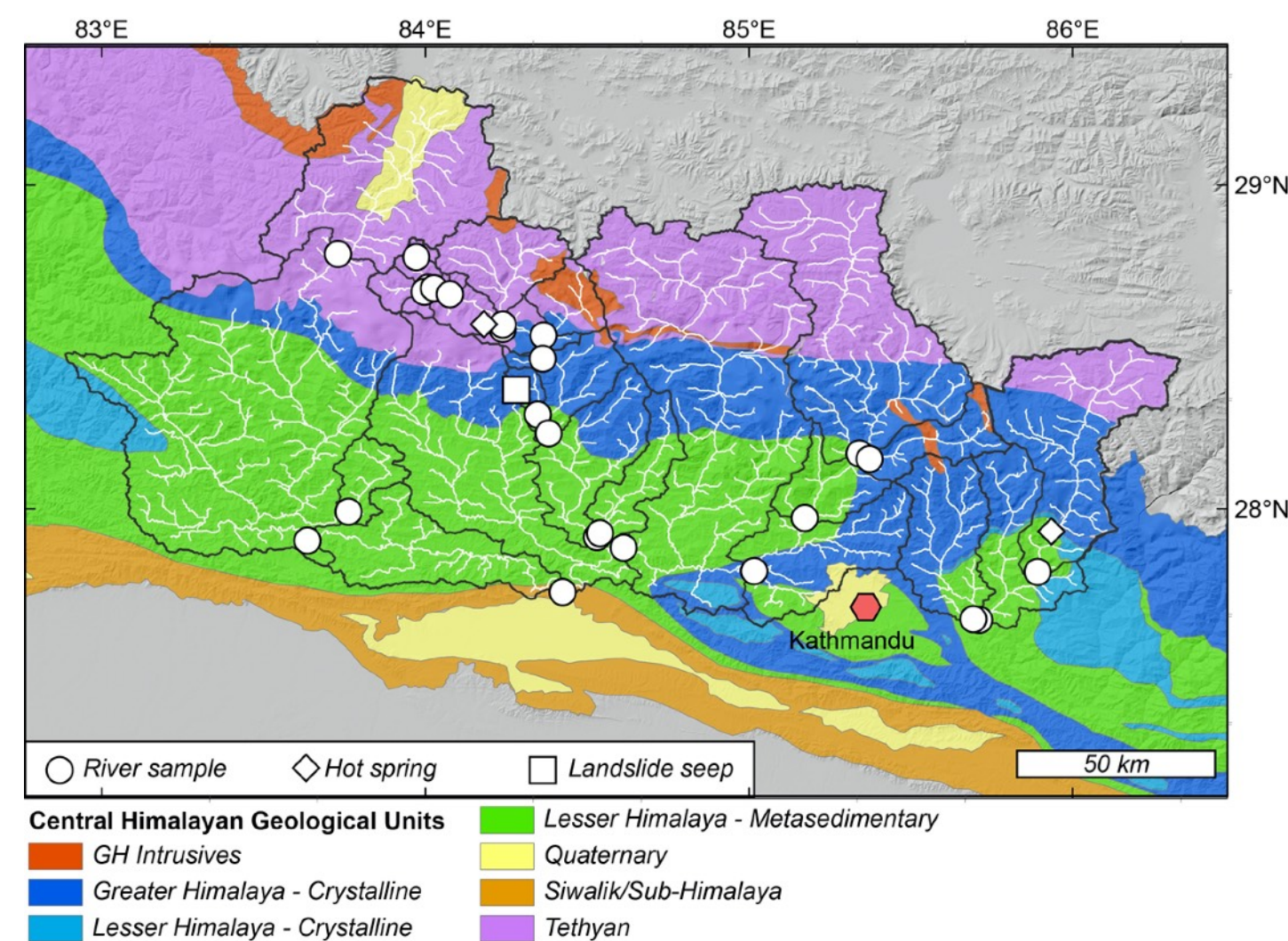
DI^{14}C values span a wide range $\text{Fm} = 0.05$ to 0.99



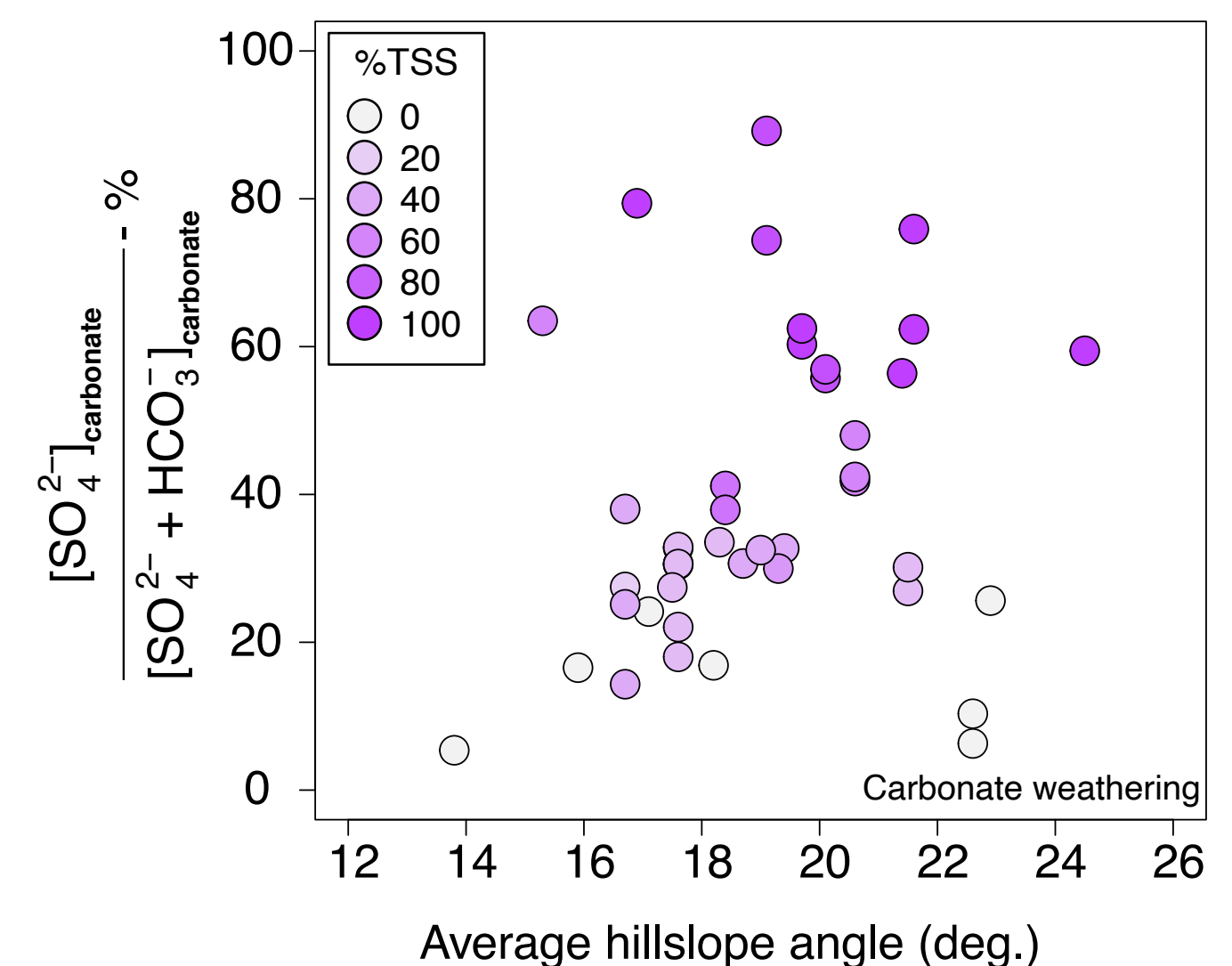
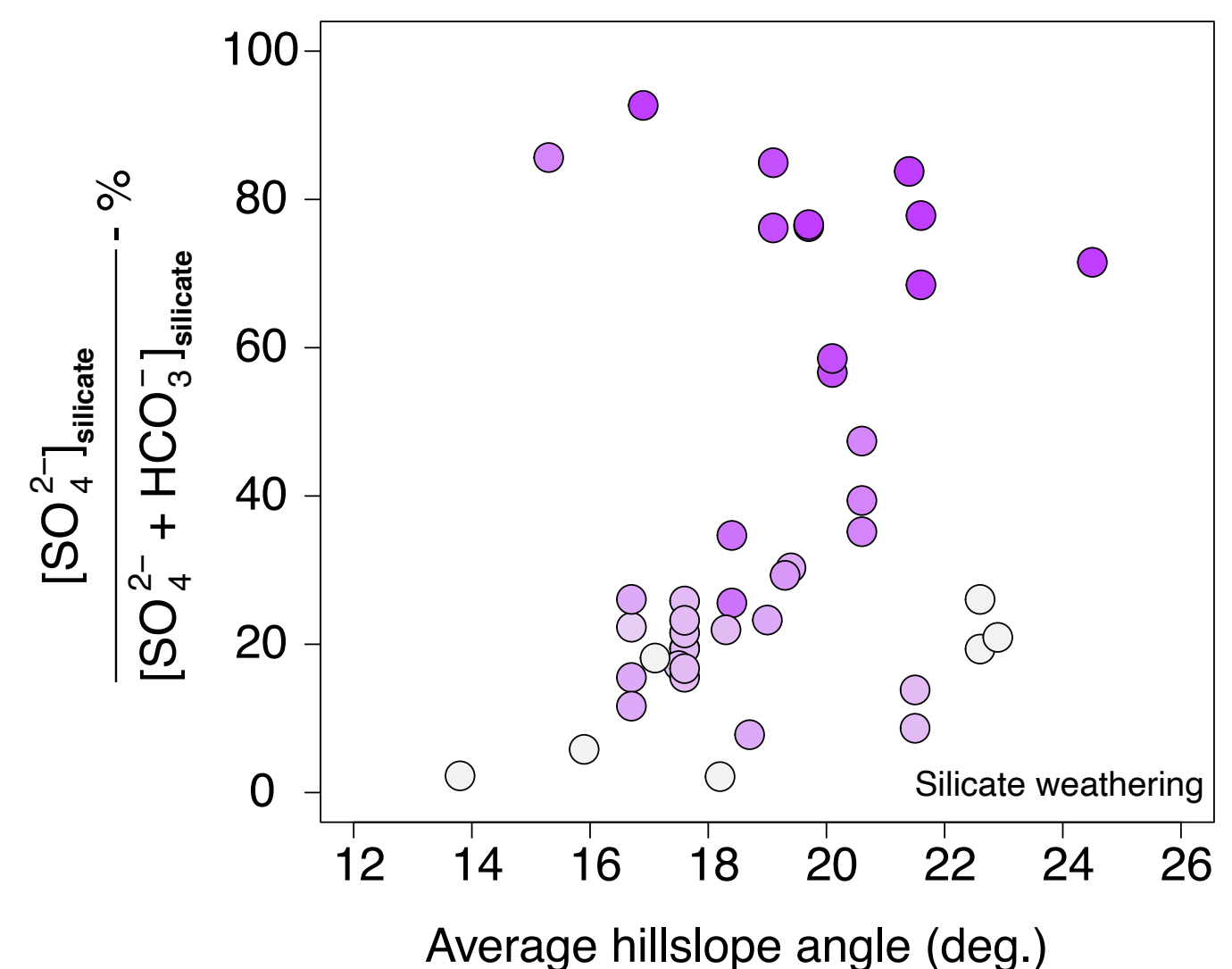
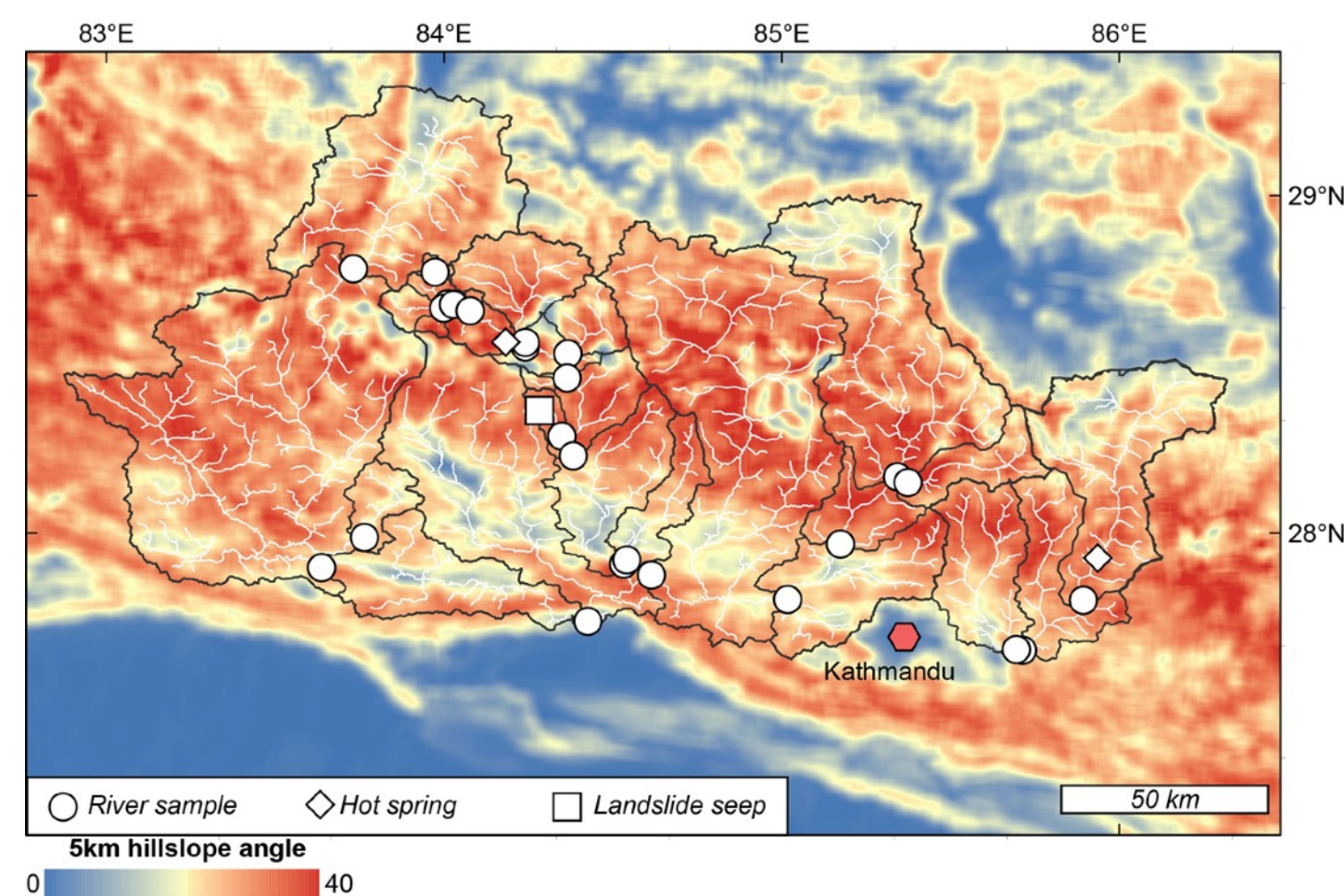
Chemical weathering pathways with DI^{14}C

Sulfuric acid weathering of carbonates and silicates is mainly controlled by the lithology outcropping in the catchment (the proportion of Tibetan Sedimentary Sequences (TSS) or Tethyan Himalaya, which are poorly metamorphosed sedimentary sequences at the southern edge of the Tibetan plateau).

Lithology

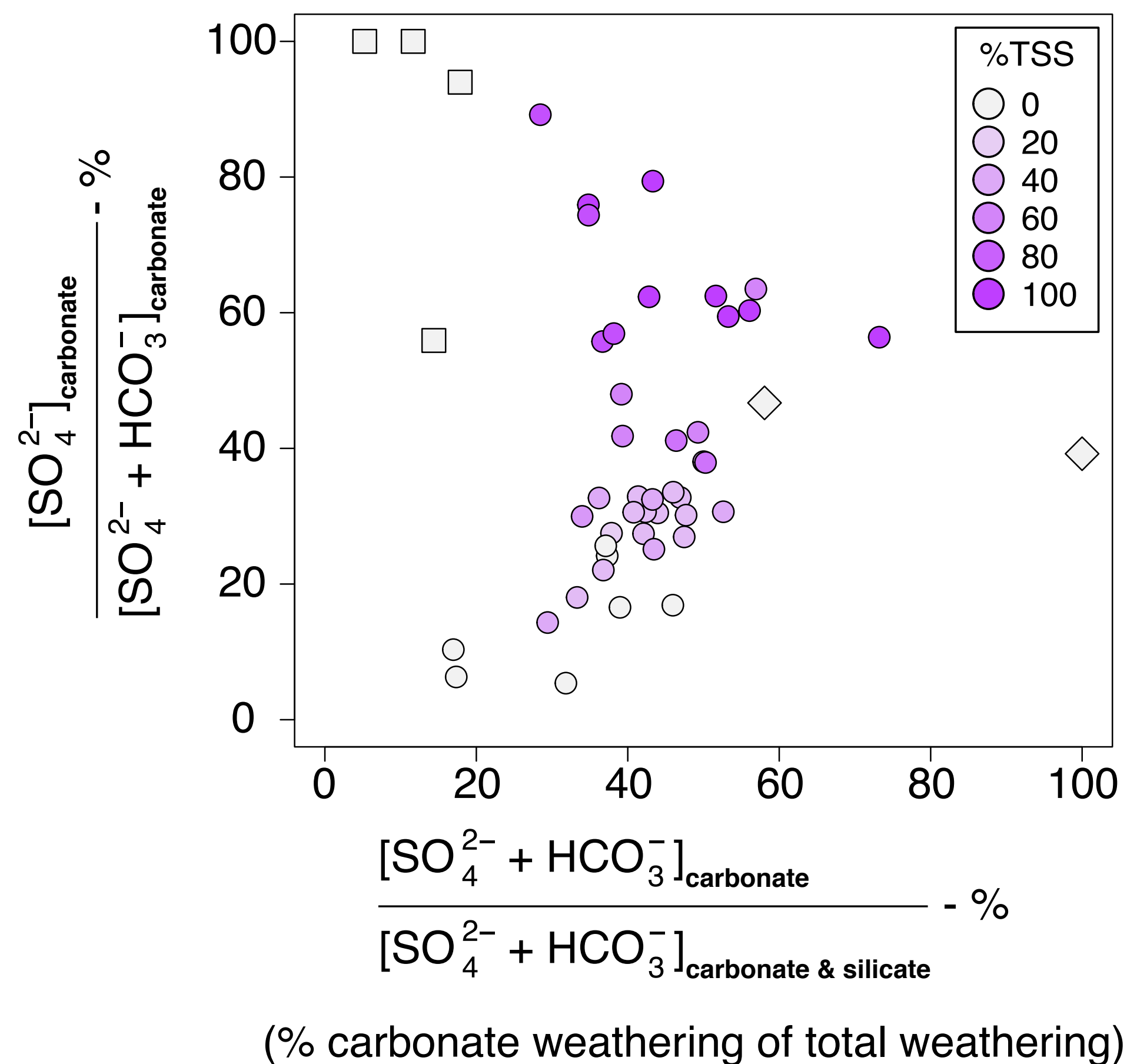


Hillslope



Chemical weathering pathways with DI¹⁴C

Sulfuric acid weathering of carbonates does not seem correlated to total carbonates weathering at the catchment-scale (is the intensity of carbonate sulfuric acid weathering controlled at the mineralogical level by sulfide associations to either carbonates or silicates, i.e. at the μm - mm - cm scale ?)



!! Preliminary data !!

Inversion results are sensitive to allowed range of end-member compositions (especially $[\text{Ca}^{2+}] / \Sigma^+$ for the silicate / carbonate partitioning).

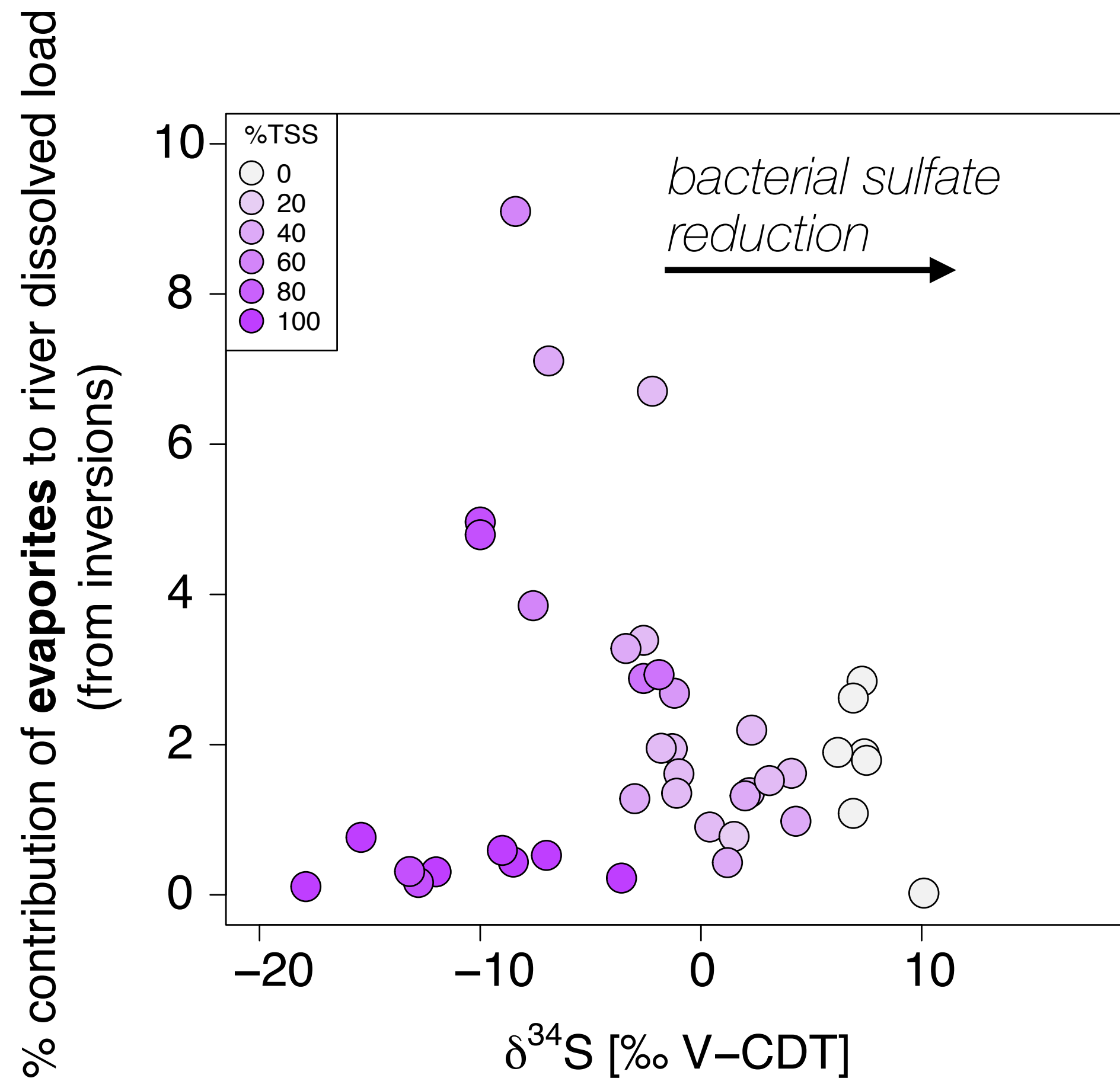
→ Since these ranges are possibly variable across lithological units, there is a possible bias in the silicate vs carbonate contributions that are calculated (?)

Next step:

- Inversions with end-members varying as a function of upstream catchment lithology
- Incorporate possible non-conservative behavior of Ca^{2+} and DIC in the inversions

Ion compositions and DI^{14}C inversions suggest limited evaporite inputs, in line with earlier studies

(e.g. Galy & France-Lanord, 1999; Tipper et al., 2006; Wolff-Boenisch et al., 2009; Turchyn et al., 2013; Hemingway et al., 2020...)

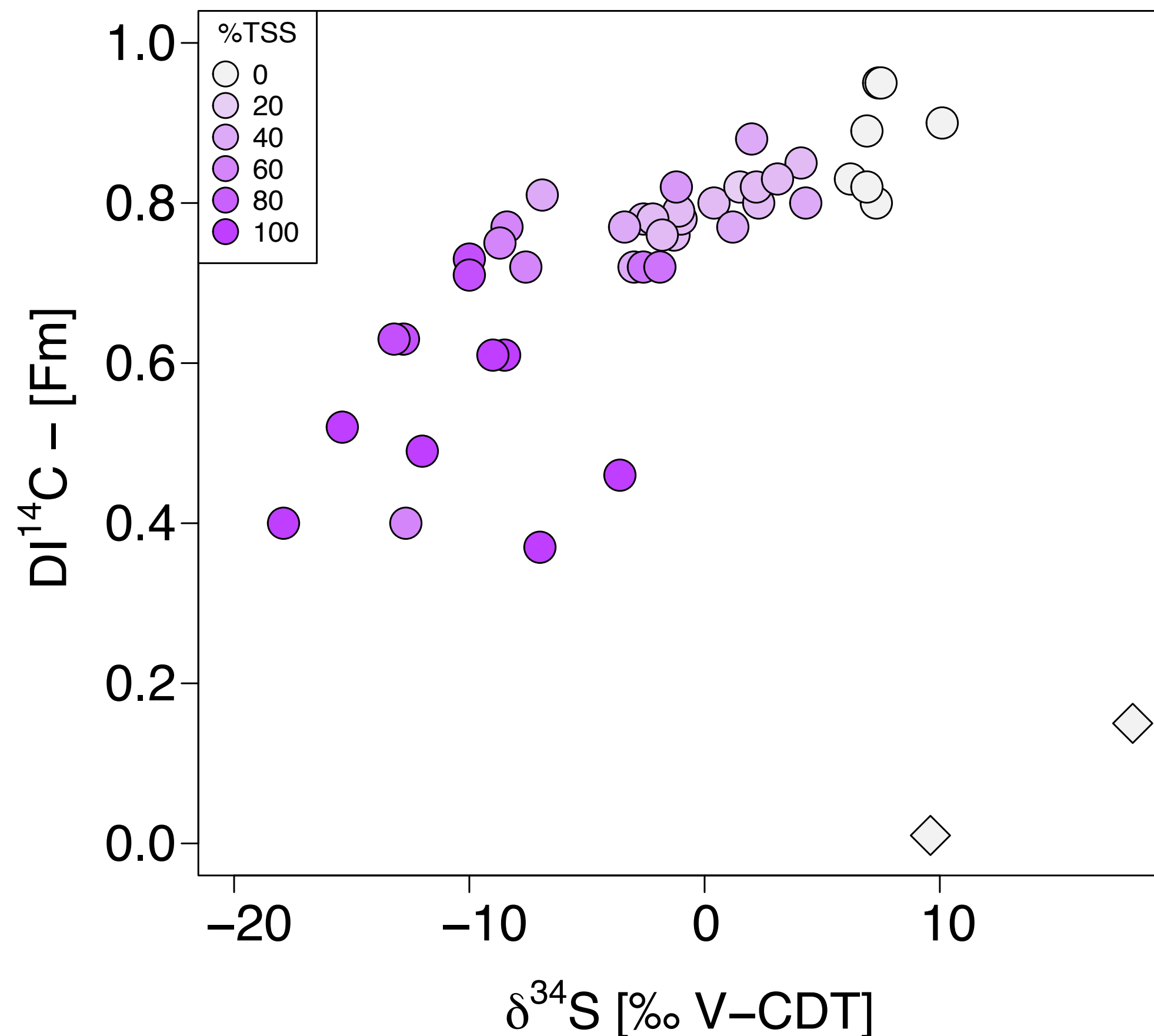


No relation between inverted evaporite contributions and sulfate $\delta^{34}\text{S}$ signature.

→ Information with respect to sulfate sources (evaporite vs sulfide) from $\delta^{34}\text{S}$ compositions have been suggested to be overprinted by bacterial sulfate reduction in the Himalayas (Turchyn et al., 2013; Hemingway et al., 2020)

Ion compositions and DI^{14}C inversions suggest limited evaporite inputs, in line with earlier studies

(e.g. Galy & France-Lanord, 1999; Tipper et al., 2006; Wolff-Boenisch et al., 2009; Turchyn et al., 2013; Hemingway et al., 2020...)



Other preliminary data (not shown) suggests a possible greater variability in sulfide $\delta^{34}\text{S}$ isotopic compositions in Himalayan bedrock as previously assumed.

→ Pending $\delta^{34}\text{S}$ measurements on bedrock samples will help better constrain the isotopic composition of sulfide sources

→ Required before incorporating $\delta^{34}\text{S}$ in weathering pathways inversions

Conclusions

- DI^{14}C spans the whole range of possible compositions (Fm 0.05 to 0.99) in the Himalaya.
- DI^{14}C can be used in combination with major ion compositions to disentangle chemical weathering pathways (see Blattmann et al. 2019).
- Inversion suggests that sulfuric acid weathering of carbonates (a carbon source to the atmosphere) is mostly controlled by lithology and does not seem to be limited by the availability of carbonates.
- Sulfate, S-isotopic compositions used to infer sulfate sources is still limited by sulfate reduction processes or possibly by the lack of constraints on source sulfide compositions.
- Ongoing work will refine inversion approaches & complement $\delta^{34}\text{S}$ measurements with bedrock samples.

This work is part of Lena Märki's PhD project

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References

- Burke, A., Present, T.M., Paris, G., Rae, E.C.M., Sandilands, B.H., Gaillardet, J., Peucker-Ehrenbrink, B., Fischer, W.W., McClelland, J.W., Spencer, R.G.M., Voss, B.M., Adkins, J.F., 2018. Sulfur isotopes in rivers: Insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle. *Earth and Planetary Science Letters* 496, 168–177. doi:10.1016/j.epsl.2018.05.022
- Calmels, D., Gaillardet, J., Brenot, A., France-Lanord, C., 2007. Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: Climatic perspectives. *Geology* 35, 1003. doi:10.1130/G24132A.1
- Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges–Brahmaputra basin and the riverine alkalinity budget. *Chemical Geology* 159, 31–60. doi:10.1016/S0009-2541(99)00033-9
- Hemingway, J.D., Olson, H., Turchyn, A.V., Tipper, E., Bickle, M.J., Johnston, D., 2020. Triple oxygen isotope insight into terrestrial pyrite oxidation. *Proceedings of the National Academy of Sciences*. doi:10.1073/pnas.1917518117/-/DCSupplemental
- Huh, Y., Tsoi, M.-Y., Zaitsev, A., Edmond, J.M., 1998. The fluvial geochemistry of the rivers of Eastern Siberia: I. tributaries of the Lena River draining the sedimentary platform of the Siberian Craton. *Geochimica et Cosmochimica Acta* 62, 1657–1676. doi:10.1016/S0016-7037(98)00107-0
- Kampschulte, A., Strauss, H., 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology* 204, 255–286. doi:10.1016/j.chemgeo.2003.11.013
- Karim, A., Veizer, J., 2000. Weathering processes in the Indus River Basin: implications from riverine carbon, sulfur, oxygen, and strontium isotopes. *Chemical Geology* 170, 153–177. doi:10.1016/S0009-2541(99)00246-6
- Tipper, E.T., Bickle, M.J., Galy, A., West, A.J., Pomiès, C., Chapman, H.J., 2006. The short term climatic sensitivity of carbonate and silicate weathering fluxes: Insight from seasonal variations in river chemistry. *Geochimica et Cosmochimica Acta* 70, 2737–2754. doi:10.1016/j.gca.2006.03.005
- Torres, M.A., West, A.J., Clark, K.E., Paris, G., Bouchez, J., Ponton, C., Feakins, S.J., Galy, V., Adkins, J.F., 2016. The acid and alkalinity budgets of weathering in the Andes–Amazon system: Insights into the erosional control of global biogeochemical cycles 1–11. doi:10.1016/j.epsl.2016.06.012
- Turchyn, A.V., Tipper, E.T., Galy, A., Lo, J.-K., Bickle, M.J., 2013. Isotope evidence for secondary sulfide precipitation along the Marsyandi River, Nepal, Himalayas. *Earth and Planetary Science Letters* 374, 36–46. doi:10.1016/j.epsl.2013.04.033
- Wolff-Boenisch, D., Gabet, E.J., Burbank, D.W., Langner, H., Putkonen, J., 2009. Spatial variations in chemical weathering and CO₂ consumption in Nepalese High Himalayan catchments during the monsoon season. *Geochimica et Cosmochimica Acta* 73, 3148–3170. doi:10.1016/j.gca.2009.03.012