

Supporting Information for “Calcite dissolution-precipitation reactions are a key control on the Sr/Ca, Mg/Ca and $\delta^{88/86}\text{Sr}$ compositions of Himalayan river waters”

Emily I. Stevenson^{1,2a}, Kevin W. Burton³, Ian J. Parkinson⁴, Rachael H. James⁵, Basak Kisakürek⁶, Ed Tipper¹, Mike Bickle¹,

Contents

- 1) References for Fig. 1.
- 2) Supplementary Table S1: River water data.
- 3) Supplementary Table S2: Standard $\delta^{88/86}\text{Sr}$ data using MC-ICP-MS.
- 4) Supplementary Table S3: Major element composition of acetic acid leaches of bedload samples.
- 5) Solutions to equations (2) to (5) in the main text.
- 6) References

S1. References for Figure 1 (see section S6):

Hydrothermal: Pearce et al. (2015); Krabbenhöft et al. (2010); Andrews & Jacobson (2017).
Soils & Plants: Halicz et al., 2008; de Souza et al. (2010); Bullen and Chadwick (2016).
Silicates: Moynier et al. (2010); Charlier et al. (2012); Neymark et al. (2014); Pearce et al., (2015); Stevenson et al. (2016); Andrews et al., (2016), Andrews and Jacobson (2017); Andrews & Jacobson (2018); Amsellem et al. (2018); de Souza et al., 2010
Carbonates: Fietzke & Eisenhauer (2006); Halicz et al. (2008); Ohno & Hirata (2008); Rüggeberg et al. (2008); Krabbenhöft et al. (2010); Böhm et al. (2012); Raddatz et al. (2013); Neymark et al. (2014); Stevenson et al. (2014); Vollstaedt et al. (2014); Fruchter et al., (2016, 2017); Alkhatib & Eisenhauer (2017a,b); Liu et al. (2017); Shalev et al. (2017), Voigt et al., (2015).
Water: de Souza et al (2010); Krabbenhöft et al. (2010); Wei et al. (2013); Neymark et al. (2014); Chao et al. (2013, 2015); Pearce et al. (2015); Voigt et al. (2015); Stevenson et al. (2016); Andrews et al. (2016); Fruchter et al. (2016, 2017); Andrews & Jacobson (2017, 2018); Liu et al. (2017); Shalev et al. (2017); Stevenson et al. (2018).

Table S4 Definition of variables (Subscripts *cc* original high Mg, Sr calcite, *F* fluid)

Variable	Definition	Units	Value
Sr_F	Sr in fluid (Sr^0 is fluid Sr at $x=0$)	mmol.m^{-3}	
Sr_{CC}	Sr in calcite	mmol.m^{-3}	
Sr_F'	Dimensionless Sr in fluid (eq 6)		
Ca_F	Ca in fluid (Ca^0 is fluid Ca at $x=0$)	mol.m^{-3}	
Ca_{CC}	Ca in calcite	mol.m^{-3}	2×10^4
Ca_F'	Dimensionless Ca in fluid (eq 6)		1
t	Time	s	
x	distance along flow path (x' dimensionless distance)	m	
h	Flow path length	m	
$\omega_0\phi$	Fluid flux	m.s^{-1}	
$K_D^{Sr/Ca}$	Sr/Ca solid/fluid partition coefficient (eq 1)		
$K_D^{Mg/Ca}$	Mg/Ca solid/fluid partition coefficient		
N_D	Damköhler Number (water) (Equ. 7)		
N_D^{rock}	Damköhler Number (rock) (Equ. 8)		
RCa	Rate of Ca exchange between fluid and calcite	$\text{mol.m}^{-3}.\text{s}^{-1}$	
$1+\epsilon$	Rate of precipitation of Ca relative to dissolution		
Γ	Sr/Ca ratio of calcite being dissolved	mmol/mol	
Γ'	Dimensionless Sr/Ca ratio of calcite being dissolved		
$\delta^{88/86}\text{Sr}$	$\delta^{88/86}\text{Sr} = 10^3 ({}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{samp}}/{}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{SRM987}} - 1)$	‰	
$\Delta^{88/86}\text{Sr}$	Sr fractionation factor for calcite-water ($\delta_{\text{calcite}} - \delta_{\text{water}}$)	‰	
$\delta^{44/40}\text{Ca}$	$\delta^{44/40}\text{Ca} = 10^3 ({}^{44}\text{Ca}/{}^{40}\text{Ca}_{\text{samp}}/{}^{44}\text{Ca}/{}^{40}\text{Ca}_{\text{SRM915a}} - 1)$	‰	
$\Delta^{44/40}\text{Ca}$	Fractionation factor for calcite-water ($\delta_{\text{calcite}} - \delta_{\text{water}}$)	‰	
X_{wat}^i	Concentration of cation, i in water	$\mu\text{mol/L}$	
X_j^i	Concentration of cation, i in phase j (carbonate or silicate)	mol/kg	
F_j	Weight of phase j (carbonate or silicate) added to the water	kg/L	
E_{Sr}	Enrichment factor for Sr		
E_{Mg}	Enrichment factor for Mg		

S5. Solutions to equations 2 to 5 in the main text

Equation numbers follow from main text. Equation (2) in terms of the dimensionless variables (eq 6) reads

$$\frac{\partial Ca_F'}{\partial x'} = -N_D \cdot \epsilon \quad (\text{S12})$$

and the solution to equation (S12) is

$$Ca_F' = 1 - N_D \cdot \epsilon \cdot x' \quad (\text{S13})$$

The solution to equation (3), the variation in Ca-isotopic values with reactive transport with Ca_F given by

equation (S13), for $\epsilon=0$ is

$$\delta^{44/40}Ca = (\delta^{44/40}Ca_{CC} - \Delta^{44/40}Ca) - c4 \cdot e^{-N_D \cdot x'} \quad (S14)$$

where

$$c4 = -\Delta^{44/40}Ca, \quad (S15)$$

and the solution when $\epsilon \neq 0$

$$\delta^{44/40}Ca = (\delta^{44/40}Ca_{CC} - (1 + \epsilon) \cdot \Delta^{44/40}Ca) - c5 \cdot (1 - N_D \cdot \epsilon \cdot x')^{\frac{1}{\epsilon}} \quad (S16)$$

where the integration constant, c5 is given by

$$c5 = -(1 + \epsilon) \cdot \Delta^{44/40}Ca$$

If $\epsilon=0$, the solution to equation (4), the variation of Sr concentration with distance, is

$$Sr'_F = \frac{1}{K_D^{Sr/Ca}} \left[\Gamma' - (\Gamma' - K_D^{Sr/Ca}) \cdot e^{-N_D \cdot K_D^{Sr/Ca} \cdot x'} \right] \quad (S17)$$

where Γ' is the dimensionless Sr/Ca ratio of calcite being dissolved.

If ($\epsilon \neq 0$) the solution to equation (4) is

$$Sr'_F = \frac{\Gamma'(1 - N_D \cdot \epsilon \cdot x')}{[(1 + \epsilon) \cdot K_D^{Sr/Ca} - \epsilon]} + c2 \cdot (1 - N_D \cdot \epsilon \cdot x')^{(1 + \epsilon) \cdot K_D^{Sr/Ca} / \epsilon} \quad (S18)$$

where the integration constant c2 for the boundary conditions Ca'_F and $Sr'_F = 1$ at $x'=0$ is given by

$$c2 = 1 - \frac{\Gamma'}{[K_D^{Sr/Ca} \cdot (1 + \epsilon) - \epsilon]} \quad (S19)$$

*Note equation numbering continues from the main text.

The analytical solution to equation (5) where $\delta Sr'_F / \delta x'$ and Sr'_F are given by equations (4) & (S17) for the case $\epsilon=0$ is

$$\delta^{88/86}Sr'_F = \frac{\left[\delta^{88/86}Sr_{CC} \cdot \frac{\Gamma'}{K_D^{Sr/Ca}} - N_D \cdot \Delta^{88/86}Sr \cdot \left(\frac{\Gamma'}{N_D \cdot K_D^{Sr/Ca}} - (\Gamma' - K_D^{Sr/Ca}) \cdot x' \cdot e^{-N_D \cdot K_D^{Sr/Ca} \cdot x'} \right) \right]}{\left(\frac{\Gamma'}{K_D^{Sr/Ca}} \right) \left[1 - (1 - K_D^{Sr/Ca} / \Gamma') \cdot e^{-N_D \cdot K_D^{Sr/Ca} \cdot x'} \right]}$$

$$+ \frac{c3}{1 + \Gamma' / K_D^{Sr/Ca} \left(e^{-N_D \cdot K_D^{Sr/Ca} \cdot x'} - 1 \right)} \quad (S20)$$

where the integration constant, $C3$, is given by

$$c3 = \delta^{88/86} Sr_{CC} - \frac{\Gamma'}{K_D^{Sr/Ca}} \cdot [\delta^{88/86} Sr_{CC} - \Delta^{88/86} Sr] \quad (S21)$$

When $\varepsilon \neq 0$ equation (5) has been solved numerically by finite differencing. The numerical solutions reproduce the analytical solutions (eq S20) as $\varepsilon \rightarrow 0$ and Rayleigh fractionation when ε is large.

S6. References

- AlKhatib, M., & Eisenhauer, A. (2017a). Calcium and strontium isotope fractionation in aqueous solutions as a function of temperature and reaction rate; I. Calcite. *Geochimica et Cosmochimica Acta*, 209, 296-319. <http://dx.doi.org/10.1016/j.gca.2016.09.035>
- AlKhatib, M., & Eisenhauer, A. (2017b). Calcium and strontium isotope fractionation during precipitation from aqueous solutions as a function of temperature and reaction rate; II. Aragonite. *Geochimica et Cosmochimica Acta*, 209, 320-342. <https://doi.org/10.1016/j.gca.2016.09.035>
- Amsellem, E., Moynier, F., Day, J., M.D., Moreir, M., Puchtel, I.S., Teng, F.-Z. (2018). The stable strontium isotopic composition of ocean island basalts, mid-ocean ridge basalts, and komatiites. *Chemical Geology*, 483, 595-602. <https://doi.org/10.1016/j.chemgeo.2018.03.030>
- Andrews, M.G., & Jacobson, A.D. (2017). The radiogenic and stable Sr isotope geochemistry of basalt weathering in Iceland: Role of hydrothermal calcite and implications for long-term climate regulation. *Geochimica et Cosmochimica Acta*, 215, 247-262. <https://doi.org/10.1016/j.gca.2017.08.012>
- Andrews, M.G., Jacobson, A.D., (2018). Controls on the solute geochemistry of subglacial discharge from the Russell Glacier, Greenland Ice Sheet determined by radiogenic and stable Sr isotope ratios. *Geochimica et Cosmochimica Acta* 239, 312-329. <https://doi.org/10.1016/j.gca.2018.08.004>
- Andrews, M.G., Jacobson, A.D., Lehn, G.O., Horton, T.W., Craw, D. (2016). Radiogenic and stable Sr isotope ratios ($^{87}Sr/^{86}Sr$, $\delta^{88/86}Sr$) as tracers of riverine cation sources and biogeochemical cycling in the Milford Sound region of Fiordland, New Zealand. *Geochimica et Cosmochimica Acta*, 173, 284-303. <https://doi.org/10.1016/j.gca.2015.10.005>
- Böhm, F., Eisenhauer, A., Tang, J.W., Dietzel, M., Krabbenhöft, A., Kisakürek, B., Horn, C. (2012). Strontium isotope fractionation of planktic foraminifera and inorganic calcite. *Geochimica et Cosmochimica Acta*, 93, 300-314. <https://doi.org/10.1016/j.gca.2012.04.038>
- Bullen, T.D., Chadwick, O. (2016). Ca, Sr and Ba stable isotopes reveal the fate of soil nutrients along

atropical climosequence in Hawaii. *Chemical Geology*, 422, 25-45.

<https://doi.org/10.1016/j.chemgeo.2015.12.008>

Chao, H.-C., You, C.-F., Liu, H.-C., Chung, C.-H. (2013). The origin and migration of mud volcano fluids in Taiwan: Evidence from hydrogen, oxygen, and strontium isotopic compositions. *Geochimica et Cosmochimica Acta*, 114, 29-51. <https://doi.org/10.1016/j.gca.2013.03.035>

Chao, H.C., You, C.F., Liu, H.C., Chung, C.H. (2015). Evidence for stable Sr isotope fractionation by silicate weathering in a small sedimentary watershed in southwestern Taiwan. *Geochimica et Cosmochimica Acta*, 165, 324-341. <https://doi.org/10.1016/j.gca.2015.06.006>

Charlier, B.L.A., Nowell, G.M., Parkinson, I.J., Kelley, S.P., Pearson, D.G., Burton, K.W. (2012). High temperature strontium stable isotope behaviour in the early solar system and planetary bodies. *Earth and Planetary Science Letters*, 329-330 31-40. <https://doi.org/10.1016/j.epsl.2012.02.008>

de Souza, G.F., Reynolds, B.C., Kiczka, M., Bourdon, B. (2010). Evidence for mass-dependent isotopic fractionation of strontium in a glaciated granitic watershed. *Geochimica et Cosmochimica Acta*, 74, 2596-2614. <https://doi.org/10.1016/j.gca.2010.02.012>

Fietzke, J., Eisenhauer, A. (2006). Determination of temperature-dependent stable strontium isotope ($\text{Sr-}^{88}/\text{Sr-}^{86}$) fractionation via bracketing standard MC-ICP-MS. *Geochemistry Geophysics Geosystems*, 7, Q08009. <https://doi.org/10.1029/2006GC001243>

Fruchter, N., Eisenhauer, A., Dietzel, M., Fietzke, J., Bohm, F., Montagna, P., Stein, M., Lazar, B., Rodolfo-Metalpa, R., Erez, J. (2016). $^{88}\text{Sr}/^{86}\text{Sr}$ fractionation in inorganic aragonite and in corals. *Geochimica et Cosmochimica Acta*, 178, 268-280. <https://doi.org/10.1016/j.gca.2016.01.039>

Fruchter, N., Lazar, B., Nishri, A., Almogi-Labin, A., Eisenhauer, A., Be'eri Shlevin, Y., Stein, M. (2017). $^{88}\text{Sr}/^{86}\text{Sr}$ fractionation and calcite accumulation rate in the Sea of Galilee. *Geochimica et Cosmochimica Acta*, 215, 17-32. <https://doi.org/10.1016/j.gca.2017.07.026>

Halicz, L., Segal, I., Fruchter, N., Stein, M., Lazar, B. (2008). Strontium stable isotopes fractionate in the soil environments? *Earth and Planetary Science Letters*, 272, 406-411.

<https://doi.org/10.1016/j.epsl.2008.05.005>

Kisakürek, B., James, R. H., & Harris, N. B. W. (2005). Li and delta Li-7 in Himalayan rivers: Proxies for silicate weathering? *Earth and Planetary Science Letters*, 237, 387-401.

<https://doi.org/10.1016/j.epsl.2005.07.019>

Kisakürek, B. (2005). Utility of lithium and magnesium isotopes as tracers of continental weathering processes. Unpublished PhD thesis, Open University

Krabbenhöft, A., Eisenhauer, A., Bohm, F., Vollstaedt, H., Fietzke, J., Liebetrau, V., Augustin, N., Peucker-

- Ehrenbrink, B., Muller, M.N., Horn, C., Hansen, B.T., Nolte, N., Wallmann, K. (2010). Constraining the marine strontium budget with natural strontium isotope fractionations ($^{87}\text{Sr}/^{86}\text{Sr}$ *, $\delta^{88/86}\text{Sr}$) of carbonates, hydrothermal solutions and river waters. *Geochimica et Cosmochimica Acta* 74, 4097-4109. <https://doi.org/10.1016/j.gca.2010.04.009>
- Liu, H.-C., You, C.-F., Zhou, H., Huang, K.-F., Chung, C.-H., Huang, W.-J., Tang, J. (2017). Effect of calcite precipitation on stable strontium isotopic compositions: Insights from riverine and pool waters in a karst cave. *Chemical Geology*, 456, 85-97. <https://doi.org/10.1016/j.chemgeo.2017.03.008>
- Moynier, F., Agranier, A., Hezel, D.C., Bouvier, A. (2010). Sr stable isotope composition of Earth, the Moon, Mars, Vesta and meteorites. *Earth and Planetary Science Letters*, 300, 359-366. <https://doi.org/10.1016/j.epsl.2010.10.017>
- Neymark, L.A., Premo, W.R., Mel'Nikov, N.N., Emsbo, P. (2014). Precise determination of $\delta^{88}\text{Sr}$ in rocks, minerals, and waters by double-spike TIMS: A powerful tool in the study of geological, hydrological and biological processes. *Journal of analytical atomic Spectrometry*, 29, 65-75. <https://doi.org/10.1039/C3JA50310K>
- Ohno, T., Komiy, T., Ueno, Y., Hirata, T., Maruyama, S. (2008). Determination of $^{88}\text{Sr}/^{86}\text{Sr}$ mass-dependent isotopic fractionation and radiogenic isotope variation of $^{87}\text{Sr}/^{86}\text{Sr}$ in the Neoproterozoic Doushantuo Formation. *Gondwana Research*, 14, 126-133. <https://doi.org/10.1016/j.gr.2007.10.007>
- Parkhurst, D.L., and Appelo, C.A.J. (2013), Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497p. <https://pubs.usgs.gov/tm/06/a43/>
- Pearce, C.R., Parkinson, I.J., Gaillardet, J., Charlier, B.L.A., Mokadem, F., Burton, K.W. (2015). Reassessing the stable ($\delta^{88/86}\text{Sr}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) strontium isotopic composition of marine inputs. *Geochimica et Cosmochimica Acta*, 157, 125-146. <https://doi.org/10.1016/j.gca.2015.02.029>
- Raddatz, J., Liebetrau, V., Rüggeberg, A., Hathorne, E., Krabbenhöft, A., Eisenhauer, A., Böhm, Vollstaedt, H., Fietzke, J., López Correa, M., Freiwald, A., Dullo, W.-C. (2013). Stable Sr-isotope, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in the scleractinian cold-water coral *Lophelia pertusa*. *Chemical Geology*, 352, 143-152. <https://doi.org/10.1016/j.chemgeo.2013.06.013>
- Rüggeberg, A., Fietzke, J., Liebetrau, V., Eisenhauer, A., Dullo, W.-C., Freiwald, A. (2008). Stable strontium isotopes ($\delta^{88/86}\text{Sr}$) in cold-water corals—a new proxy for reconstruction of intermediate ocean water temperatures. *Earth and Planetary Science Letters*, 269, 570-575.

<https://doi.org/10.1016/j.epsl.2008.03.002>

Shalev, N., Gavrieli, I., Halicz, L., Sandler, A., Stein, M., Lazara, B. (2017). Enrichment of ^{88}Sr in continental waters due to calcium carbonate precipitation. *Earth and Planetary Science Letters*, 459, 381-393. <https://doi.org/10.1016/j.epsl.2016.11.042>

Stevenson, E.I., Aciego, S.M., Chutcharavan, P., Parkinson, I.J., Burton, K.W., Blakowski, M.A., Arendt, C.A. (2016). Insights into combined radiogenic and stable strontium isotopes as tracers for weathering processes in subglacial environments. *Chemical Geology*, 429, 33-43.

<https://doi.org/10.1016/j.chemgeo.2016.03.008>

Stevenson, E.I., Hermoso, M., Rickaby, R.E.M., Tyler, J.J., Minoletti, F., Parkinson, I.J., Mokadem, F., Burton, K.W. (2014). Controls on stable strontium isotope fractionation in coccolithophores with implications for the marine Sr cycle. *Geochimica et Cosmochimica Acta*, 128, 225-235. <https://doi.org/10.1016/j.gca.2013.11.043>

Stevenson, R., Pearce, C.R., Rosa, E., Hélie, J-F. & Hillaire-Marcel, C. (2018). Weathering processes, catchment geology and river management impacts on radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) and stable ($\delta^{88/86}\text{Sr}$) strontium isotope compositions of Canadian boreal rivers . *Chemical Geology*, 486, 50-60.

<https://doi.org/10.1016/j.chemgeo.2018.03.039>

Voigt, J., Hathorne, E.C., Frank, M., Vollstaedt, H., Eisenhauer, A. (2015). Variability of carbonate diagenesis in equatorial Pacific sediments deduced from radiogenic and stable Sr isotopes. *Geochimica et Cosmochimica Acta*, 148, 360-377. <https://doi.org/10.1016/j.gca.2014.10.001>

Vollstaedt, H., Eisenhauer, A., Wallmann, K., Bohm, F., Fietzke, J., Liebetrau, V., Krabbenhöft, A., Farkas, J., Tomasovych, A., Raddatz, J., Veizer, J. (2014). The Phanerozoic $^{88/86}\text{Sr}$ record of sea-water: New constraints on past changes in oceanic carbonate fluxes. *Geochimica et Cosmochimica Acta*, 128, 249-265. <https://doi.org/10.1016/j.gca.2013.10.006>

Wei, G.J., Ma, J.L., Liu, Y., Xie, L.H., Lu, W.J., Deng, W.F., Ren, Z.Y., Zeng, T., Yang, Y.H. (2013). Seasonal changes in the radiogenic and stable strontium isotopic composition of Xijiang River water: Implications for chemical weathering. *Chemical Geology*, 343, 67-75.

<https://doi.org/10.1016/j.chemgeo.2013.02.004>