

Supplementary Information

Cooling of hydrothermal fluids rich in carbon dioxide can create large karst cave systems in carbonate rocks

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The Supplementary Information Sections:

Supplementary Methods 1: Rock and fluid compositions used in the geochemical calculations

Supplementary Methods 2: Equilibrium model derivation

Supplementary Note 1: Effect of salinity on calcite retrograde solubility

Supplementary Note 2: Theoretical analysis of cooling-driven dissolution in a bedding horizon

Supplementary Note 3: Verification of the AHD model

Supplementary Note 4: Verification of the equilibrium model

Supplementary Note 5: Simulation results of evolution in time of maze cave

The Supplementary Information Figures and Tables:

Supplementary Fig. 1. Effect of salinity on calcite retrograde solubility

Supplementary Fig. 2. Comparison between the analytical and numerical solutions

Supplementary Fig. 3. Comparison between the kinetic model and the equilibrium model solutions

Supplementary Fig. 4. Simulation results: Evolution in time of maze cave

Supplementary Table 1. Nomenclature

Supplementary Table 2. Aquifer rock mineralogical compositions

Supplementary Table 3. Chemical composition of groundwaters

Supplementary Table 1. Nomenclature.

Roman		t_a	Characteristic timescale of advection, s
C_p	Specific heat capacity, J (kg °C) ⁻¹	t_d	Characteristic timescale of diffusion, s
c	Average solute concentration, mmol kg ⁻¹	t_{dis}	Characteristic timescale of dissolution, s
c_s	Solute saturation concentration, mmol kg	t_r	Characteristic timescale of reaction, s
c_{sol}	Concentration of soluble solid, mmol kg ⁻¹	u	Channel average volumetric flow rate, m ³ s ⁻¹
c_w	Concentration at the wall, mmol kg ⁻¹	V	Volume of rock dissolved, m ³
D	Diffusion coefficient, m ² s ⁻¹	V_{dis}	Volume of channel dissolved, m ³
g	Parameter group	V_f	Volume of fluid injected, m ³
h	Horizon aperture, m	v	Velocity, m/s
h_p	Maximal aperture, m	z	Vertical coordinate, m
J_D	Diffusive flux at the channel, mol (m ² s) ⁻¹	Greek	
K	Thermal conductivity, W (m °C) ⁻¹	α	Thermal diffusivity, m ² s ⁻¹
k	Mass-transfer coefficient, m s ⁻¹	β	Expansion constant, mol (m ³ °C) ⁻¹
L_{fr}	Fracture length, m	γ	Acid capacity number
L_{max}	Max fracture length, m	Δc_{s0}	Reference undersaturation, mmol kg ⁻¹
L_{min}	Min fracture length, m	δ	Parameter group, m ⁻²
l	Channel length, m	ε	Geometrical correction factor
l_c	Characteristic length-scale, m	η	Degree of dissolution focusing, h_p/l_v
l_{dis}	Cave formation range, m	Θ	Heat exchange term, m °C s ⁻¹
l_{en}	Entrance length, m	θ	Undersaturation
l_v	Inner length of the void, m	κ	Parameter group, m ⁻² ;
m	Exponent of fracture distribution	λ	Reaction rate coefficient, m s ⁻¹
m_{CaCO_3}	Calcite molar mass, kg mol ⁻¹	λ^{eff}	Effective reaction rate coefficient, m s ⁻¹
n	Random number from uniform distribution	μ	Fluid viscosity, Pa s
Pe	Péclet number	ν	Stoichiometric coefficient
p	Fluid pressure, Pa	ζ	Axial coordinate, m
Q	Total volumetric flow rate, m ³ s ⁻¹	ρ	Density, kg m ⁻³
q	Integrated fluid velocity, m ² s ⁻¹	χ	Parameter group, m ⁻¹
R	Channel radius, m	Ω	Reaction rate, mol (m ² s) ⁻¹
R_F	Conduit channels average radius, m	Subscripts	
R_M	Matrix channels average radius, m	in	Inlet
r		out	Outlet
r_o	Cylindrical channels' radial coordinate, m	i	Nodes index
$Sh_=$	Sherwood number for parallel plates	j	Neighboring nodes index
Sh_o	Sherwood number for cylindrical channel	0	Initial quantity
s	Channel surface area, m ²	f	Fluid
T	Temperature, °C	r	Rock
t	Time, s	Superscripts	
t'	Time parameter, s	—	Average quantity

Supplementary Methods 1: Rock and fluid compositions used in the geochemical calculations

Carbonate aquifer: we assume that the reacting system is composed of a 1.5 dm³ solution in contact with 3.5 dm³ of rock and a gas bubble of 0.002 moles of total gas with 100% CO₂ (gas volume is ~0.5 dm³). The initial porosity is 27.3% and the aquifer is comprised mainly of limestone with some dolomite content. The mineralogical composition and its conversion from volume % to moles is given in Supplementary Table 2. The initial solution composition based on groundwater samples from the Judea Group aquifer in the North Negev Desert is given in Supplementary Table 3 (Mk Tel Shoket 6 well)¹.

Clastic aquifer: we assumed that the reacting system is composed of a 1 dm³ solution in contact with 4 dm³ of rock and a gas bubble of 0.04 moles of total gas with 100% CO₂ (gas volume is ~0.5 dm³). The initial porosity is 27.3% and the aquifer is comprised of sandstone. The mineralogical composition and its conversion from volume (%) to moles is given in Supplementary Table 2. The initial solution composition based on groundwater samples from the deep Kurnub Group aquifer in the Negev Desert is given in Supplementary Table 3 (Shizafon 1 well)².

Supplementary Table 2. Rock mineralogical composition for the silicate and carbonate aquifers.

	Volume (%)	Density (cm ³ ·mol ⁻¹)	Moles
Clastic rock			
Quartz	76.5	22.688	134.87
K-feldspar	8	108.87	2.94
Albite	4	100.25	1.60
Calcite	0.5	36.934	0.54
Kaolinite	9	99.52	3.62
Dolomite	1	28.018	0.62
Siderite	1	29.378	1.36
Total	100		
Carbonate rock			
Calcite	85	36.934	80.58
Dolomite	10.5	28.018	5.64
Quartz	2.5	22.688	3.86
K-feldspar	1	108.87	0.32
Illite	0.5	140.556	0.12
Kaolinite	0.5	98.534	0.18
Total	100	36.919	

Supplementary Table 3. Chemical composition of groundwaters from the aquifers (see text and Supplementary Table 2).

	Na mmol·L ⁻¹	K	Ca	Mg	Cl	Br	SO4	Alkalinity	pH
Shizafon 1	13.502	1.046	8.281	4.308	17.113	0.019	9.300	3.629	6.78
Mk Tel Shoket 6	1.957	0.059	1.297	1.029	1.805	0.003	0.323	3.606	7.22

Supplementary Methods 2: Equilibrium model derivation.

Here, we assume that the initial CO₂ partial pressure, PCO₂, is relatively high and the kinetics are rapid, so the rate-limiting step for the reaction is the diffusion of reaction products away from the mineral surface and undersaturation is sustained. Consequently, the reaction rate can be calculated from the transport rate alone, regardless of kinetics (so-called equilibrium dissolution model)^{3,4}. Below, we provide an explicit expression for the mass-transfer coefficient, k , and the complete derivation of Eq. 5 in the main text comprising the equilibrium model^{3,4}. Verification of this equilibrium model is provided in Supplementary Note 4.

Assuming first-order reaction kinetics, the reaction rate at the horizon surface is

$$\Omega = 2\varepsilon\lambda[c_s - c_w], \quad (\text{SM. 2.1})$$

which depends on the difference between the solute concentration at the solid surface, c_w , and the saturation concentration, c_s . Here, λ is the kinetic reaction rate coefficient [L T⁻¹], ε is a geometrical correction term (see Eq. 6 in main text) and the factor of two accounts for the upper and lower surfaces.

Reaction products (i.e., calcium ions) then diffuse away from the mineral surface to the bulk fluid, and sustain undersaturation conditions at the wall^{5,6}. This diffusive flux can be expressed by

$$J_D = 2\varepsilon k(h)[c_w - c]. \quad (\text{SM. 2.2})$$

Next, k , the mass-transfer coefficient, which is inversely proportional to the aperture, h , is calculated using

$$k(h) = \frac{DSh_{\infty}}{2h}, \quad (\text{SM. 2.3})$$

where D is the molecular diffusion coefficient, h is the horizon aperture, Sh_{∞} is the Sherwood number for parallel plates, here assumed constant $Sh_{\infty} = 8.24^{7,8}$. This assumption is adequate as long as the solute entrance length, l_{en} , required to reach the asymptotic value is small, i.e., $l_{\text{en}} \ll l_{\text{dis}}$, where l_{dis} is the distance over which dissolution takes place and the cave forms. The entrance length increases with flow rate and with aperture h (for details see, e.g., ref. ⁷). Here, we further assume that h does not vary substantially along the length scale l_{en} . Note that since k in Eq. SM.2.3 is inversely proportional to the aperture, h , the diffusive flux drops as h increases.

The reaction rate and the diffusive flux (Eqs. SM.2.1 and SM.2.2) are equal at the steady-state and can be used to express the concentration at the wall in terms of the average one

$$c_s - c_w = \frac{[c_s(T) - c]}{1 + \frac{\lambda}{k(h)}}. \quad (\text{SM. 2.4})$$

Next, expressing the reaction rate (Eq. SM.2.1) in terms of the averaged concentration leads to

$$\Omega = 2\varepsilon\lambda^{eff}[c_s(T) - c], \quad (SM.2.5)$$

where the effective reaction rate coefficient^{9,10}, which incorporates both kinetics and transport effects on reaction rate, is

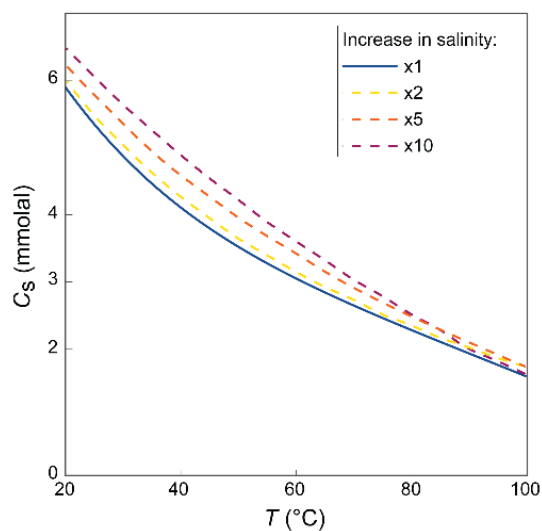
$$\lambda^{eff} = \frac{\lambda}{1 + g(h)}, \quad (SM.2.6)$$

with the function g , that is defined as

$$g(h) = \frac{\lambda}{k(h)}. \quad (SM.2.7)$$

The parameter $g(h)$ is the ratio between the characteristic timescales of diffusive transport, t_d , and reaction ($t_r = h/\lambda$) and accounts for the extent by which dissolution rate within a single channel is hindered by transport; when $g \ll 1$ reaction rate is surface-controlled and limited by kinetics and when $g \gg 1$ the reaction is transport-controlled and reaction rate depends on transport only and the equilibrium dissolution model can be assumed^{3,4,11}. Under the current conditions, of rapid reaction kinetics and large λ relative to k , $\lambda^{eff} \approx k$ (see Eqs. SM.2.6 and SM.2.7) and Eq. SM.2.5 reduces to Eq. 5, in which the reaction rate is calculated from the transport rate alone, regardless of kinetics. The validity of the equilibrium model for the conditions considered here is demonstrated in Supplementary Note 4.

Supplementary Note 1: Effect of salinity on calcite retrograde solubility



Supplementary Fig. 1. Solubility of calcite (C_s) as a function of temperature for different groundwater salinities (colored curves) at PCO_2 of 0.03 MPa. The solubility was calculated for the original groundwater salinity (solid blue line) and for salinities of 2, 5 and 10 times the original groundwater salinity (yellow, orange and purple dashed lines, respectively; given in Supplementary Table 3). For comparison with seawater, these salinities correspond to 0.25%, 0.5%, 2.5% and 5% of seawater salinity. The plots show clearly the small effect of salinity on calcite solubility, for example, at temperature of 60 °C, a salinity increase by a factor of 10 is accompanied by solubility increase of just ~20%.

Supplementary Note 2: Theoretical analysis of cooling-driven dissolution in a bedding horizon

This section presents a theoretical analysis for dissolution in a uniform horizon as a result of heat exchange with the rock and fluid cooling, which was developed as part of this work. The analysis involves similar settings and identical geometry as the AHD model (see Methods, AHD Model: Setup section), but several additional simplifying assumptions, which are elaborated below. The theoretical solution is then used to validate the numerical finite-difference AHD model (see Supplementary Note 3).

1.1. Horizon temperature

We consider a confined horizon between impermeable layers, initial temperature T_0 and flow in the radial direction, r , from an inlet point source of constant flow rate, Q , and temperature, T_{in} (i.e., so-called radial Lauwerier problem^{12,13}; see Fig. 7 in the main text). Assuming transport by advection in the horizon and only vertical heat conduction in the rock (i.e., neglecting the radial component), the solution for the temperature distribution in the horizon is,

$$T(r, t) = T_0 + (T_{in} - T_0) \operatorname{erfc}(\kappa(t)r^2), \quad (SN.1.1)$$

where t is time, and κ is

$$\kappa(t) = \frac{\chi\pi}{\sqrt{\alpha_r t'(t)}}, \quad (SN.1.2)$$

with α thermal diffusivity and $\chi = K_r/Q\rho_f C_{pf}$ with K is the thermal conductivity, ρ density and C_p the heat capacity, and subscripts r and f indicate rock and fluid, respectively. Finally, $t' = t - h^2 2\pi r^2 / Q$, where h is the aperture. Note that for longer times $t' \approx t$ ^{12,13}.

1.2. Reactive solute transport

Solute transport is calculated using quasi-static averaged advection-reaction equation^{14,15}, assuming transport is dominated by advection,

$$0 = -q \frac{\partial c}{\partial r} + \Omega(r, t), \quad (SN.1.3)$$

where c is solute concentration and q is the fluid velocity integrated over the horizon aperture h [$L^2 T^{-1}$] and calculated using $q(r) = Q/(2\pi r)$. The reaction rate, Ω , is proportional to the difference between the temperature-dependent saturation (equilibrium) concentration, $c_s(T)$, and the concentration of the dissolved ions

$$\Omega = 2\lambda[c_s(T) - c], \quad (SN.1.4)$$

where λ is the kinetic reaction rate coefficient [$L T^{-1}$] (i.e., surface-controlled reaction is considered here) and c_s is calculated using,

$$c_s(T) = c_s(T_0) - \beta(T - T_0), \quad (SN.1.5)$$

with the constant expansion β evaluated from the data presented in Results and Discussion section and Fig. 2b. Defining then undersaturation as

$$\theta(r, t) = [c_s(T) - c]/\Delta c_{s0}, \quad (SN.1.6)$$

where $\Delta c_{s0} = c_s(T_0) - c_s(T_{in})$ and plugging Eq. SN.1.6 into Eq. SN.1.3, we obtain

$$0 = -q \left[\frac{\partial c_s}{\partial r} - \Delta c_{s0} \frac{\partial \theta}{\partial r} \right] + 2\lambda \Delta c_{s0} \theta. \quad (SN.1.7)$$

The derivative $\partial c_s / \partial r$ can then be expressed by differentiating the expansion in Eq. SN.1.5,

$$\frac{\partial c_s}{\partial r} = -\beta \frac{\partial T}{\partial r}, \quad (SN.1.8)$$

and further substituting the derived solution for the temperature of Eq. SN.1.1 yields,

$$-\beta \frac{\partial T}{\partial r} = (T_{in} - T_0) \frac{4\beta\kappa r}{\sqrt{\pi}} e^{(-\kappa^2 r^4)}. \quad (SN.1.9)$$

Next, substituting Eqs. SN.1.9, SN.1.8 in SN.1.7, and further assuming saturation conditions at the inlet and the boundary condition of $\theta(r=0) = 0$, lead eventually to the solution

$$\theta = \beta(T_{in} - T_0)/\Delta c_{s0} \cdot e^{\left(\frac{\delta^2}{4\kappa^2} - \delta r^2\right)} \cdot \left[\operatorname{erf} \left[\frac{\delta}{2\kappa} \right] - \operatorname{erf} \left[\frac{\delta}{2\kappa} - \kappa r^2 \right] \right], \quad (SN.1.10)$$

where $\delta = 2\pi\lambda/Q$. Given the reaction rate (Eq. SN.1.4), the chemical erosion rate of the channels can be calculated based on the mass conservation

$$\frac{\partial h(r, t)}{\partial t} = \frac{2\lambda\theta\Delta c_{s0}}{vc_{sol}}, \quad (SN.1.11)$$

where c_{sol} is the concentration of soluble solid material and v accounts for the stoichiometry of the reaction. Substituting Eq. SN.1.10 to SN.1.11 and integrating over time results in a close form expression for h ,

$$\begin{aligned}
h(r, t) = h_0 + \frac{8 \lambda \beta \kappa t}{\delta^2 v c_{sol}} (T_{in} - T_0) & \left(\delta \kappa r^2 (\text{erf}[\kappa r^2] - 1) + \kappa e^{\delta/4 \left(\frac{\delta}{\kappa^2} - 4r^2 \right)} \text{erf} \left[\kappa r^2 - \frac{\delta}{2\kappa} \right] \right. \\
& + \kappa \text{erf} \left[\frac{\delta}{2\kappa} \right] e^{\delta/4 \left(\frac{\delta}{\kappa^2} - 4r^2 \right)} + \frac{\delta}{\sqrt{\pi}} (e^{-\kappa^2 r^4} - e^{-\delta r^2}) - \kappa (\text{erf}[\kappa r^2] - 1) \\
& \left. - \kappa e^{-\delta r^2} \right). \quad (SN. 1.12)
\end{aligned}$$

The inherent assumptions in this solution of surface-controlled reaction limit its applicability to narrow apertures, at which there is no substantial transport limitation. Furthermore, when large radial thermal gradients develop in the rock, the solution is no longer valid since the radial heat conduction component in the rock is neglected here. Consequently, the solution is valid only for high flow rates and when mild radial thermal gradients develop in the rock, and in addition conduction and diffusion in the fluid can be neglected.

1.3. Approximate solution

To obtain solution by computational means and to avoid integer overflow¹⁶, it is useful to derive an approximate solution for Eq. SN.1.10 using the first-order asymptotic expansion of *erfc*

$$\begin{aligned}
\theta = \beta(T_{in} - T_0)/\Delta c_{s0} \cdot e^{\left(\frac{\delta^2}{4\kappa^2} - \delta r^2 \right)} \\
\cdot \left[-e^{\left(-\frac{\delta^2}{4\kappa^2} \right)} \frac{2\kappa}{\delta} + e^{\left(-\frac{\delta^2}{4\kappa^2} - \delta r^2 + \kappa^2 r^4 \right)} \frac{1}{\frac{\delta}{2\kappa} - \kappa r^2} \right] \frac{1}{\sqrt{\pi}}, \quad (SN. 1.13)
\end{aligned}$$

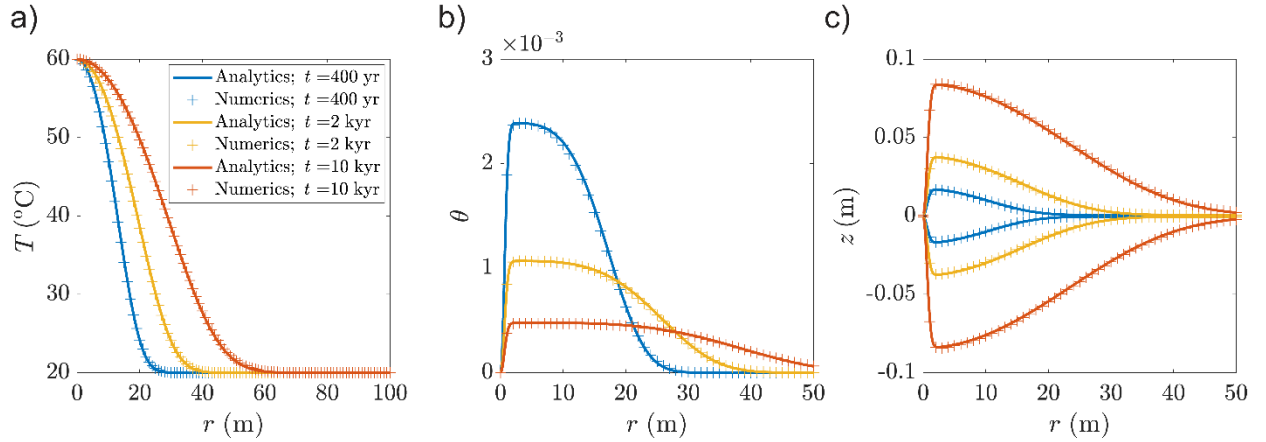
and after further rearrangement, we finally arrive to,

$$\theta = \beta(T_{in} - T_0)/\Delta c_{s0} \cdot e^{(-\delta r^2)} \cdot \left[-\frac{2\kappa}{\delta} + e^{(\delta r^2 - \kappa^2 r^4)} \frac{1}{\frac{\delta}{2\kappa} - \kappa r^2} \right] \frac{1}{\sqrt{\pi}}. \quad (SN. 1.14)$$

Eq. SN.1.14 uses to obtain solution for longer times presented in Supplementary Note 3.

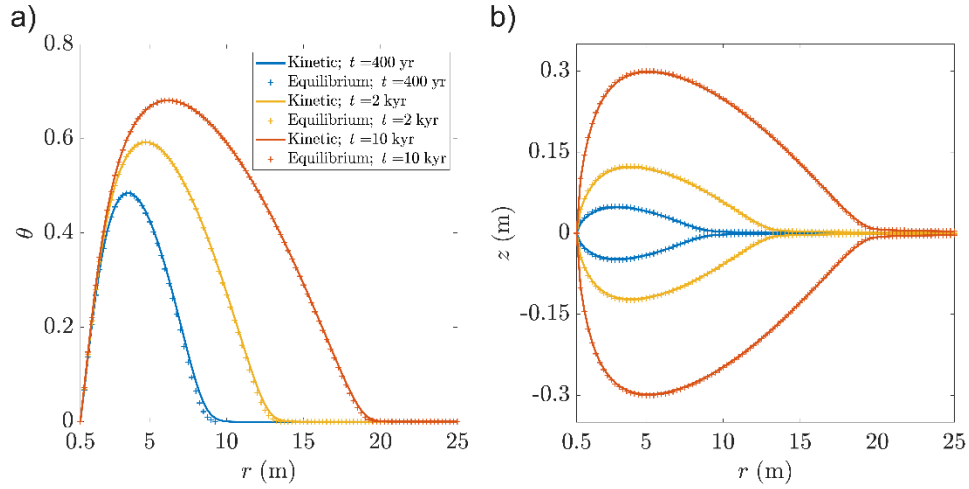
Supplementary Note 3: Verification of the AHD model

The AHD model accuracy was verified using the analytical solutions for conduction^{12,17} and for temperature, undersaturation and aperture developed above, which account both for the thermal and reactive processes (Eqs. SN.1.1, SN.1.10, SN.1.12, and SN.1.14; Supplementary Fig. 2). To perform the comparison, the AHD model is modified to incorporate the assumptions of the analytical solution: (i) conduction and diffusion in the fluid are neglected, (ii) the radial conduction component in the rock is neglected, (iii) the reaction is assumed to be surface-controlled reaction with perfect solute transverse mixing (in contrast to the numerical AHD model results in Fig. 3b-d, which were produced assuming transport limited reaction) and (iv) the inclination of the horizon surface following dissolution and the geometrical correction term (ε) are neglected. Supplementary Fig. 2 demonstrates our model validity, as it agrees with the analytical solution under these assumptions.



Supplementary Fig. 2. Comparison between the analytical and numerical solutions (solid lines and markers, respectively). Evolution of temperature, T , (a) solute undersaturation, θ , (b) and aperture profile, h , (c) at the horizon along the radial, r direction for different times.

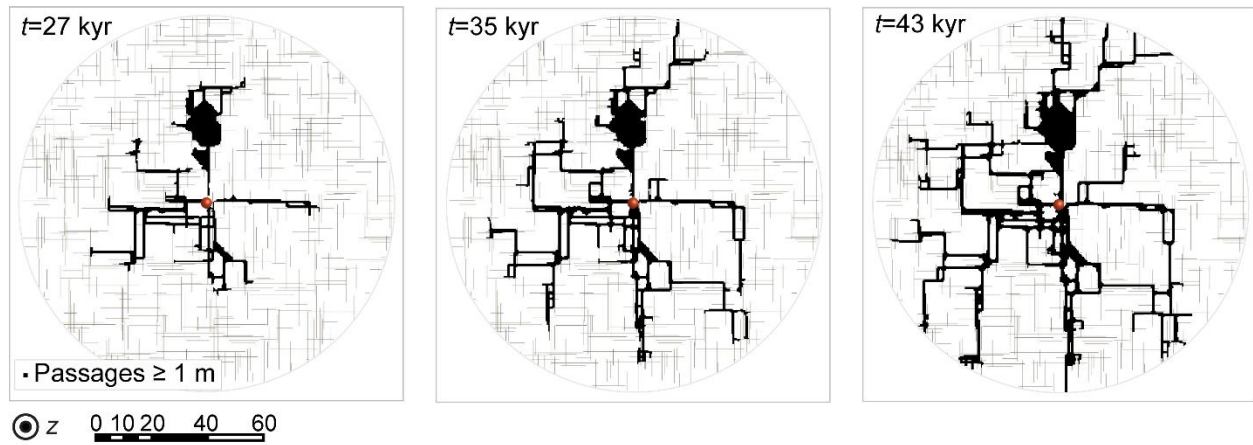
Supplementary Note 4: Verification of the equilibrium model



Supplementary Fig. 3. Comparison between the kinetic model (curves) and the equilibrium model (markers) solutions for solute undersaturation, θ , (a) and aperture profile, h , (b) at the horizon along the radial direction, r , at different times; $Q = 1 \text{ m}^3/\text{day}$.

In this section, the validity of the equilibrium dissolution model (Eq. 5 in the Methods, AHD Model: Setup section) for the conditions of dissolution by CHTF is tested by comparing numerical simulations with Eq. SM.2.5. In the analysis here, we exploit the linear behavior of reaction rate with calcite undersaturation observed over a particular range of PCO_2 values and undersaturation and use $\lambda = 10^{-6} \text{ m/s}$, appropriate for $\text{PCO}_2 = 0.03 \text{ MPa}$ and 25°C (see figure 8 and table 1 in ref. ¹⁸), which can be also higher if corrected for high temperature (i.e., kinetics is in fact more rapid and dissolution more transport-limited)^{18–20}. The comparison demonstrates a good fit between the the solutions for conditions of $\text{PCO}_2 > 0.03 \text{ MPa}$. The small deviation (associated with initial small aperture) diminishes as the aperture grows and the reaction can be regarded as fully transport limited (Supplementary Fig. 3).

Supplementary Note 5: Simulation results of temporal evolution of maze caves



Supplementary Fig. 4. Temporal evolution of a maze cave from a simulation using a network model for dissolution by CHTF in a fractured bedding horizon. The thin lines represent the initial fractures; the black represents dissolved areas and cave passages (only passages one meter wide or wider are shown). Simulations produce a typical maze-like pattern, characterized by many closed loops. Simulation duration was constrained by domain size, i.e., without reaching a steady-state. Simulation was halted when passages formed at the outlet boundary. For simulation details see the Network Model sections in the Methods.

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