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#### **Key Points:**

- Infiltration-driven replacement fronts can be unstable even if the permeability of the secondary rock is lower than that of the primary rock
- The instability is linked to the presence of a region of increased permeability in the replacement zone
   Initial perturbations of the
- replacement front are transformed into funnel-like solution pipes

#### Supporting Information:

- Supporting Information S1
- Movie S1
- Movie S2
- Movie S3
- Movie S4

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## Instabilities and finger formation in replacement fronts driven by an oversaturated solution

JGR

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**Abstract** We consider a simple model of infiltration-driven mineral replacement, in which the chemical coupling between precipitation and dissolution leads to the appearance of a reaction front advancing into the system. Such fronts are usually accompanied by a local increase of porosity. We analyze the linear stability of the replacement front to establish whether such a localized porosity increase can lead to global instability and pattern formation in these systems. We find that for a wide range of control parameters such fronts are unstable. However, both short- and long-wavelength perturbations are stabilized, whereas in a purely dissolutional instability only short wavelengths are stable. We analyze the morphologies of the dissolution patterns emerging in the later stages of the evolution of the system, when the dynamics are beyond the linear regime. Implications of these results for the natural systems are discussed, particularly in the context of karst formation in terra rossa-covered carbonate bedrock.

**Plain Language Summary** The geological forms we observe all around us were shaped over long periods of time by changes that are occasionally violent — for example, earthquakes and volcanos — but are more often gradual. One important mechanism for gradual change in rock morphology is chemical reactions, such as dissolution and precipitation, which slowly transform the rock matrix. In this paper, we are interested in the stability of the reaction fronts between the primary (dissolving) and secondary (precipitating) rock. Are these fronts moving in a stable way remaining planar, or could they form fingers or funnels in which the fluid flow is focused? As we show, the answer to this question depends on a subtle interplay between reactant transport, fluid flow, and rates of chemical reactions. In many cases we find that the fronts are unstable and finger-like structures are formed which then compete with each other: the shorter fingers are attracted to the longer ones and eventually merge with them. As a result the pattern coarsens with time, and the widths of the fingers and characteristic distance between them increase.

#### 1. Introduction

Whenever a fluid is out of equilibrium with the porous rocks it is infiltrating, dissolution and precipitation can take place in the pore space. As a result, the chemical composition and morphology of the rock might undergo significant changes, up to the complete replacement of the parent (primary) rock by a product (secondary) one. Natural examples of replacement include dolomitization [*Merino and Canals*, 2011], serpentinite carbonation [*Beinlich et al.*, 2012], and fluid-mediated feldspar replacement reactions [*Plümper and Putnis*, 2009; *Hofmann*, 1972]. Fluid-mediated replacement reactions have also been studied in the laboratory, although most of the experiments were conducted in the absence of the flow [*Putnis*, 2009]. The replacement of one rock by another is not instantaneous. Instead, replacement fronts form. These are regions of increased chemical activity, separating the secondary and the primary phase, which propagate in the direction of the flow, but with much lower velocity than that of the infiltrating water [*Ortoleva et al.*, 1986; *Bickle and Baker*, 1990; *Lake et al.*, 2002]. This time scale separation is due to the large molar concentration difference between ions in the fluid phase and the consolidated material in the solid phase.

When the upstream secondary phase is more permeable than the downstream primary phase, the reaction front is destabilized. Even if the reaction front is initially planar, small perturbations emerge, which absorb more flow and amplify into finger-like or funnel-like structures, such as wormholes or solution pipes [Daccord and Lenormand, 1987; Hoefner and Fogler, 1988; Petrus and Szymczak, 2016]. This mechanism is referred

©2017. American Geophysical Union. All Rights Reserved. to in the literature as the *reactive-infiltration instability* [*Chadam et al.*, 1986; *Hinch and Bhatt*, 1990; *Aharonov et al.*, 1995]. The classic example of this process is the dissolution of a carbonate matrix by an incoming acidic solution, giving rise to a rich variety of karstic forms[*Jennings*, 1985; *Palmer*, 1991]. On the other hand, precipitation reactions tend to stabilize the reaction front by decreasing the permeability of the rock [*Woods*, 2014]; nevertheless, in some instances localized precipitation can initiate an instability in the front [*Nagatsu et al.*, 2014; *Shukla and De Wit*, 2016] (see section 6).

Replacement fronts are sometimes characterized by centimeter-scale zones of increased porosity [Merino and Banerjee, 2008; Banerjee and Merino, 2011]. In such cases the permeability of the rock near the reaction front is higher than the permeability of both the parent and the product phase. Banerjee and Merino [2011] have proposed that kaolinite-for-calcite replacement, driven by an oversaturated solution of alumino-silicate ions, is a key process underlying terra rossa formation on limestone bedrock. A high-porosity region at the interface between primary and secondary minerals can also be observed in gypsum-for-calcite replacement, driven by an oversaturated gypsum solution [Plan et al., 2012], in the hydrothermal replacement of calcite by magnesium carbonates [Jonas et al., 2015], and in fluorite-for-calcite replacement [Putnis, 2009]. Merino and Banerjee [2008] have suggested that the presence of a highly porous intermediate zone might cause an instability in the replacement front, which would speed up karst formation and lead to the appearance of solution pipes and sinkholes in terra rossa-covered regions.

We have previously proposed a kinetic model for infiltration-driven replacement [Kondratiuk et al., 2015], which synchronizes the dissolution and precipitation fronts even when the incoming solution is oversaturated. The system dynamics (section 2) contain the key features of the mechanism for terra rossa replacement proposed by *Banerjee and Merino* [2011], including a region of high porosity separating the dissolution and precipitation fronts. In this paper, we investigate the evolution of precipitation-driven replacement fronts (section 3) derived from these model kinetics. A linear stability analysis (section 4) allows us to verify the Banerjee-Merino hypothesis that a high-porosity region can destabilize the replacement front. Subsequently, the nonlinear evolution of the replacement system is explored numerically (section 5), tracking the evolution of wormholes as they develop in time and space. The morphology of these simulated wormholes is compared with outcrops. The qualitative features of the evolving replacement fronts are compared with viscous fingering and localized precipitation systems (section 6), and the geological context of our results is discussed in section 7.

#### 2. The Mineral Replacement Model

The mineral replacement model used here is a simplified version of the model of *Banerjee and Merino* [2011], which is an example of a precipitation-dissolution process. A supersaturated solution of secondary ions  $A_s$  infiltrates a porous matrix of the primary mineral  $M_p$ , precipitating the secondary mineral  $M_s$  and releasing aqueous protons (or other coupling species) H, which in turn dissolve the primary mineral with release of ions  $A_p$ . Schematically, this can be represented as

$$A_{\rm S} \longrightarrow M_{\rm S} + \nu H \tag{1}$$

$$M_{\rho} + H \longrightarrow A_{\rho}, \tag{2}$$

where  $\nu$  is a stoichiometric coefficient. The model assumes irreversible reactions. The assumption is justified as long as the inlet solution is oversaturated by  $A_s$ , and the dissolution of the primary mineral is fast compared to the reverse reaction, as in the case of dissolution of calcite by acidic fluids. Similar models with reversible reactions were studied previously [Kondratiuk et al., 2015].

The overall setup is shown in Figure 1.

The flow through the rocks is assumed to follow Darcy's law:

$$\mathbf{v} = -K\nabla p,\tag{3a}$$

where **v** is the Darcy velocity,  $\varphi$  is the porosity, and  $K = K(\varphi)$  is the permeability. We adopt a cubic dependence of the rock permeability on its porosity,  $K(\varphi) \propto \varphi^3$ , which corresponds to the Kozeny's model with a constant surface area [*Bear*, 1972].



**Figure 1.** Schematic view of the replacement system, adapted from *Kondratiuk et al.* [2015]. Fluid infiltrates the system, bringing  $A_s$  ions. The ions precipitate, releasing coupling ions *H*, which dissolve the primary mineral.

We assume that the velocity field is incompressible,

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = \boldsymbol{0}, \tag{3b}$$

neglecting contributions to the fluid density from reactants or dissolved products. Under typical geological conditions, porosity evolution is slow in comparison to flow and transport processes; we can therefore assume a steady state in both the flow and transport equations [*Lichtner*, 1988]. The aqueous species ( $A_S$ , H, and  $A_P$ ) are transported by convection and dispersion. Since dissolution is taken as irreversible, the  $A_P$  species can be treated as inert, so that we need only to track the concentrations of  $A_S$  (denoted by  $c_S$ ) and  $H(c_H)$ :

$$\nabla \cdot (c_{\mathsf{S}} \mathbf{v}) - \nabla \cdot (D \nabla c_{\mathsf{S}}) = -r_{\mathsf{prec}}$$
(3c)

$$\nabla \cdot (c_H \mathbf{v}) - \nabla \cdot (D \nabla c_H) = \nu r_{\text{prec}} - r_{\text{diss}}.$$
(3d)

Here  $r_{\text{prec}}$  and  $r_{\text{diss}}$  are the rates of precipitation and dissolution, respectively, and *D* is the effective dispersion coefficient. In general, *D* is a function of both porosity and the fluid flow, but for simplicity we will assume it to be constant. The specific volumes of the solid phases,  $\phi_s$  and  $\phi_p$ , evolve due to the precipitation and dissolution reactions,

$$c_{\rm S}^{\rm sol}\partial_t\phi_{\rm S} = r_{\rm prec} \tag{3e}$$

$$c_{P}^{\rm sol}\partial_{t}\phi_{P} = -r_{\rm diss},\tag{3f}$$

where  $c_{P,S}^{sol}$  is inverse molar volumes of the primary and secondary minerals. Obviously, the relation between the porosity and the mineral volume fractions is

$$\phi_{\mathsf{S}} + \phi_{\mathsf{P}} + \varphi = 1. \tag{3g}$$

To facilitate an analytical treatment, we assume first-order reaction kinetics, with rate constants  $\alpha_{\text{prec}}$  and  $\alpha_{\text{diss}}$  respectively,

$$r_{\rm prec} = \alpha_{\rm prec} c_{\rm S} \theta(\varphi - \varphi_{\rm min}) \tag{3h}$$

$$r_{\rm diss} = \alpha_{\rm diss} c_H \theta(\phi_P). \tag{3i}$$

Both the dissolution and the precipitation are surface reactions, but we assume that the specific surface area is constant and incorporated into the kinetic constants  $\alpha_{prec}$  and  $\alpha_{diss}$ . The Heaviside functions ( $\theta$ ) in equations (3h) and (3i) indicate that the dissolution reaction ceases if there is no soluble mineral present and that the precipitation reaction stops if the porosity drops below a minimum value,  $\varphi_{min}$ . The introduction of residual porosity, which prevents a complete clogging of the flow paths, can be justified by the observation that precipitation in small pores is much slower than in large pores and thus only a fraction of the porosity is eliminated [*Jamtveit et al.*, 2014]. Moreover, reaction-generated stresses can keep a part of the pore network open and even induce microcracking in the matrix.

Equation (3) has to be supplemented with appropriate boundary conditions on the velocity and concentration fields as  $x \to \pm \infty$ . We require that the fluid flow is uniform both far upstream and far downstream from the replacement zone,

$$\mathbf{v}(x \to -\infty) = v_0 \mathbf{e}_x, \qquad v_y(x \to \infty) = 0.$$
 (4a)

The input stream contains  $A_s$  component only, whereas in the outlet stream the concentrations become x independent:

$$c_{\rm S}(x \to -\infty) = c_{\rm S}^{\rm in}, \qquad (\partial_x c_{\rm S})(x \to \infty) = 0,$$
 (4b)

$$c_H(x \to -\infty) = 0,$$
  $(\partial_x c_H)(x \to \infty) = 0.$  (4c)

Finally, the initial conditions on the mineral volumes are that the system is filled with a primary phase of volume fraction  $\phi_p^{\max}$ 

$$\phi_{\rm S}(t \to -\infty) = 0 \tag{4d}$$

$$\phi_{P}(t \to -\infty) = \phi_{P}^{\max}.$$
 (4e)

The replacement model defined above possesses two intrinsic features that are crucial for our study. First, its dynamics allows for the emergence of planar and stationary replacement fronts, whose stability with respect to small perturbations can then be analyzed. Second, as we show below, it produces a region of increased porosity at the front, which is consistent with field observations [*Banerjee and Merino*, 2011; *Lucke et al.*, 2012].

#### 3. Front Velocities and Stationary Planar Profiles

Let us first consider the velocities of the reaction fronts in the planar case, where all the fields (p,  $\mathbf{v}$ ,  $c_s$ ,  $c_p$ ,  $\phi_s$ , and  $\phi_p$ ) depend on the x coordinate only. The precipitation front can be defined as the rightmost position where the specific volume of the secondary mineral is equal to its maximum allowed value,  $\phi_s^{max} = 1 - \varphi_{min}$ .

Similarly, the dissolution front corresponds to the leftmost position where  $\phi_P$  is positive. The locations of the fronts are indicated by  $x_S$  and  $x_P$  in the sketch (Figure 1). The propagation velocities of these fronts follow from reactant mass balances. In the case of precipitation, there are  $v_0 c_S^{in}$  secondary ions entering the system per unit time and unit area. The same amount needs to be precipitated, since the outgoing concentration of  $A_S$  is 0. This gives the velocity of the precipitation front as

$$U_{\rm prec} = \frac{v_0 c_5^{\rm in}}{\phi_5^{\rm max} c_5^{\rm sol}}.$$
 (5)

On the other hand, since each mole of precipitated secondary ions produces  $\nu$  moles of protons, each mole dissolving a volume  $(c_p^{sol})^{-1}$ , the dissolution front moves with the velocity of

$$U_{\rm diss} = \frac{v V_0 C_s^{\rm in}}{\phi_p^{\rm max} c_p^{\rm sol}}.$$
 (6)

Note that in deriving equations (5) and (6) we have again assumed a complete separation of time scales between reactant transport and mineral dissolution ( $v_0 \ll U_{\text{prec}}, U_{\text{diss}}$ ). Obviously  $U_{\text{prec}}$  differs from  $U_{\text{diss}}$  in general, the only condition under which the front velocities can match being

$$\frac{\phi_{\rm S}^{\rm max}c_{\rm S}^{\rm sol}}{\phi_{\rm p}^{\rm max}c_{\rm sol}^{\rm sol}} = 1. \tag{7}$$

With the chemical kinetics in our model, all of the above parameters are independent:  $c_s^{sol}$  and  $c_p^{sol}$  are material properties of the respective minerals,  $\phi_p^{max}$  is controlled by the porosity of the primary rock, and  $\phi_s^{max}$  by the amount of the free space available to precipitate. Due to the oversaturation of the incoming solution, the reaction stops only when all of the available space is filled with precipitate. It would seem that there is no reason for the fronts to move with the same velocities, yet in nature, the precipitation and dissolution fronts are often synchronized. For example, during carbonate-for-clay replacement, both the precipitation and dissolution front have moved several meters over approximately 10 million years [*Meert et al.*, 2009]. At the same time, primary and secondary minerals are separated by a thin porous band only a few centimeters thick. This observation shows that the front velocities must be synchronized to within a few percent.

Two mechanisms of synchronization have been proposed for replacement fronts driven by an oversaturated solution of secondary ions: a mechanical one [*Banerjee and Merino*, 2011] and a chemical one [*Kondratiuk et al.*, 2015]. In the mechanical mechanism crystallization pressure suppresses the growth of the replacement phase, thereby synchronizing the fronts [*Maliva and Siever*, 1988; *Merino et al.*, 1993; *Minguez and Elorza*, 1994].



**Figure 2.** Stationary one-dimensional mineral replacement profiles for H = 1,  $\kappa = 2$ ,  $\nu = 1$ ,  $\rho = 1$  (14), and  $\phi_5^{max} = 0.9$ . (a) Volume fractions of the primary ( $\phi_P$ ) and the secondary ( $\phi_5$ ) minerals, and the porosity  $\varphi$ . The porosity is larger in the vicinity of the replacement zone. (b) Concentration profiles of the secondary ions  $c_5$  and of protons,  $c_H$ , scaled by the input concentration of secondary ions. The length scale  $I_d$  is the downstream penetration length of the secondary ions (equation (10)).

However, when the molar volume of the replacement phase is smaller than that of the primary, as for example in kaolinite-for-calcite replacement, there will be no confining stress. Rather, the primary phase will tend to run away from the precipitation front creating an increasing gap between them. *Kondratiuk et al.* [2015] proposed that in such cases, the excess protons could be consumed by a buffering reaction, which lowers the dissolution rate until it matches with the precipitation rate. The width of the zone separating the fronts decreases with increasing buffering rate; this is a self-regulatory process, which maintains a constant distance between the dissolution and precipitation fronts over a wide range of buffering rates. We consider this model in the simulations in section 5, but here we simply assume that the fronts move with the same velocities,

$$U = U_{\rm prec} = U_{\rm diss}.$$
 (8)

The system described by equations (3) and (4), together with the condition expressed in (8), possesses a class of solutions that correspond to planar reaction fronts propagating invariantly with velocity U, so that all the fields depend on only one variable x' = x - Ut (Appendix A).

A typical stationary solution is illustrated in Figure 2. In the reaction zone the volume of secondary mineral decays exponentially and is accompanied by a sharp rise of primary phase volume. The width of the reaction zone is controlled by the slowest rate constant. In most geochemical systems dissolution is much faster than precipitation and we will assume that the ratio

$$\kappa = \frac{\alpha_{\rm diss}}{\alpha_{\rm prec}} > 1. \tag{9}$$

In this case the relevant length scale is, from (3c),

$$I_{d} = \frac{2D}{\sqrt{v_{0}^{2} + 4\alpha_{\text{prec}}D - v_{0}}}.$$
 (10)

The associated time scale,

$$t_p = \frac{c_s^{\text{sol}}\phi_s^{\text{max}}}{c_s^{\text{in}}} \frac{l_d}{v_0},\tag{11}$$

is the characteristic time scale for the replacement front to propagate over a distance  $I_d$ . The Péclet number on the length scale  $I_d$ ,

$$Pe = \frac{v_0 l_d}{D} = \frac{2}{\sqrt{1 + 4H} - 1},$$
(12)

is a function of the dimensionless group

$$H = \alpha_{\rm prec} D / v_0^2, \tag{13}$$

which can also be interpreted as the inverse Péclet number associated with the precipitation length scale  $v_0/\alpha_{prec}$ .

The reaction zone is characterized by an increased porosity, which may lead to an instability in a planar replacement front (section 4). The concentration of the secondary aqueous species,  $c_s$ , decreases sharply

in the reaction zone, due to consumption by the secondary mineral precipitation reaction. Protons produced during precipitation initially increase the  $c_{\mu}$  concentration but are then consumed by the dissolution of primary mineral, leading eventually to an exponential decay of the  $c_{\mu}$  profile.

The morphology of the stationary front depends on a small number of dimensionless parameters: the transport parameter H, the ratio of the reaction rate constants  $\kappa$ , the stoichiometric coefficient  $\nu$ , and the ratio of the volume fractions,

$$=\frac{\phi_s^{\text{max}}}{\phi_p^{\text{max}}}.$$
(14)

In fact, a whole class of valid one-dimensional solutions can be found, which vary in the distance between the precipitation front and the dissolution front. In section 4 we will assume that these two fronts overlap,

ρ

$$x_{\rm S}(t) = x_{\rm P}(t) = x_{\rm front}(t). \tag{15}$$

Explicit formulas for the (one-dimensional) volume fractions and aqueous ion concentrations, illustrated in Figure 2, are given in nondimensional form in equations (A13)-(A16). The variable gap between the fronts is a result of the constraint imposed by matching the velocities of the two fronts (7), which maintains the separation imposed by the initial conditions. In section 5 we consider a more general model where the synchronization arises from the dynamics, but in this case the stability analysis is not analytically tractable.

#### 4. Stability of the Planar Mineral Replacement Front

The model described in section 2 has steady one-dimensional solutions (section 3) propagating with velocity U (5), provided that the condition (8) is fulfilled. In this section we investigate the stability of these solutions to infinitesimal perturbations in an initially planar reaction front,

$$x_{\text{front}}(y,t) = Ut + A\sin(ky)\exp(\sigma t);$$
(16)

here *A* is the (small) amplitude of the harmonic perturbation, *k* is its wave number, and  $\sigma$  the growth rate. The pressure, Darcy velocity, concentration, and volume fraction fields are also perturbed by small harmonic oscillations, growing (or decaying) exponentially in time. The perturbed fields are then inserted back into equations (3) with boundary conditions (4) and continuity conditions across the front. The resulting equations for the perturbations are linearized by neglecting terms which are of the second and higher order in the perturbation amplitudes. Eventually, a dispersion relation is obtained, relating the growth rate  $\sigma$  to the wave number *k* of the harmonic mode. Details of the derivation can be found in the Appendix B. The nondimensional dispersion relation, given by equation (B9), depends on only three parameters: the transport parameter *H* (13), the ratio of reaction rate constants  $\kappa$  (9), and the ratio of solid volume fractions  $\rho$  (14). Analytic expressions for the dispersion relation can be obtained in the limit that the permeability contrast  $K(\varphi_{max})/K(\varphi_{min})$  is close to unity (Appendix C). However, the dispersion relations shown in Figures 3–5 were obtained by a pseudospectral method [*Boyd*, 2001] and are valid for any permeability contrast.

Figure 3 shows a typical set of dispersion curves  $\sigma(k)$  for different values of H. For H > 0, there is a maximum growth rate,  $\sigma_{max}$ , at a specific wave number  $k_{max}$ . The sign of  $\sigma_{max}$  determines the stability of the front. If  $\sigma(k_{max}) > 0$ , the front is unstable; the mode with wave number  $k_{max}$  grows fastest and dominates the shape of the growing front in the early stages of replacement. Analogous to the reactive-infiltration instability, diffusion stabilizes small-wavelength perturbations [*Szymczak and Ladd*, 2014]. The relative magnitude of the diffusive flux on length scales  $v_0/\alpha_{prec}$  is controlled by the transport parameter H (equation (13)). Increasing H reduces the range of unstable wavelengths (Figure 3), but the long-wave ( $kI_d \ll 1$ ) part of the spectrum is not affected by diffusion, and all the plots collapse to a single curve in this domain.

The system is more unstable for smaller values of  $\rho$  (Figure 4): both the range of unstable wave numbers and the maximum growth rate ( $\sigma_{max}$ ) decrease with increasing  $\rho$ . The stability of the long-wave (small k) part of the spectrum is solely determined by  $\rho$ : it is unstable when  $\rho < 1$ , meaning that the slope of the dispersion curve  $\sigma'(k = 0) > 0$ , and vice versa. This agrees with our intuition: the long-wave part of the spectrum is related to the permeability difference between the bulk minerals,

$$\Gamma_{\infty} = \frac{K(x' \to \infty)}{K(x' \to -\infty)},$$
(17)



**Figure 3.** Dispersion curves for the replacement system with  $\kappa = 10$ ,  $\varphi_{\min} = 0.1$ ,  $\rho = 1$ , and H = 0, 0.002, 0.005, 0.01, and 0.02 (top to bottom). The length scale  $l_d$  is the penetration length for the secondary species (equation (10)), and  $t_p$  is the characteristic time scale of the precipitation reaction, equation (11).

but it does not depend on H or  $\kappa$ , which only affect the properties of the front itself. At long wavelengths the replacement front between the secondary and primary rock appears sharp and the system reduces to the classical reactive-infiltration instability [Ortoleva et al., 1987; Szymczak and Ladd, 2014]. The limiting slope of the dispersion curve can then be found analytically,

$$\left. \frac{\mathrm{d}\sigma}{\mathrm{d}k} \right|_{k=0} = \frac{1 - \Gamma_{\infty}}{1 + \Gamma_{\infty}} U. \tag{18}$$

A similar result can be derived for the replacement system in the limit of a small permeability contrast (Appendix C).

Perturbations with wavelengths comparable to the width of the reaction front can be

unstable even when  $\Gamma_{\infty} \ge 1$  (Figure 4). This behavior is fundamentally different from one-component reactive infiltration, where precipitation fronts ( $\Gamma_{\infty} \ge 1$ ) are always stable. This new instability arises from the presence of a negative slope in the porosity profile in the region of the front (Figure 2), meaning that the more permeable intermediate zone precedes the less permeable primary mineral. Our hypothesis is supported by the observation (Figure 4) that the wavelength of the most unstable mode is of the order of the width of the region of increased porosity near the reaction front. Diffusion (H > 0) stabilizes short-wave perturbations (Figure 4), but perturbations of the order of the front width ( $kI_d \sim 1$ ) remain unstable for  $\rho \gtrsim 1$ .

Cases with  $\rho \ge 1$  are particularly interesting, because they do not involve a destabilizing permeability contrast between the bulk minerals ( $\Gamma_{\infty} \ge 1$  for  $\rho \ge 1$ ). An instability must then be connected with the rearrangement of porosity within the reaction zone. In fact, if the porosities of both bulk mineral phases are the same ( $\rho = 1$ ), the total porosity in the system becomes a conserved quantity (Appendix D). However, despite the lack of porosity generation, a domain of unstable wavelengths exists (see Figures 3–5), but, contrary to the standard reactive-infiltration instability, long-wave perturbations are stable, as shown in the inset to Figure 5.

In Figure 5 we observe that the front is stabilized by an increasing contrast in the reaction rates ( $\kappa$ ). From equation (A16) in Appendix A we can deduce that increasing  $\kappa$  reduces the negative slope of the porosity in the region just after the permeability (or porosity) maximum (Figure 2). This supports our hypothesis that the front is being destabilized by the region where the slope of the porosity profile is negative. For smaller  $\kappa$  the permeability contrast between the reaction zone and the bulk primary mineral is higher, which results in a more unstable system.



**Figure 4.** Dispersion curves for the replacement system with  $\phi_s^{max} = 0.9$ ,  $\kappa = 5$ , H = 0 (solid lines) or H = 0.01 (dashed lines), and  $\rho = 0.95$ , 1, and 1.02 (top to bottom, either in the zero- or finite-*H* case). Inset: long-wave perturbations are unstable for  $\rho < 1$  and stable for  $\rho > 1$ .



**Figure 5.** Dispersion curves for the replacement system with  $\phi_S^{max} = 0.9$ ,  $\rho = 1$ , H = 0 (solid lines) or H = 0.01 (dashed lines);  $\kappa = 2$ , 5, and 10 (top to bottom, either in the zero- or finite-*H* case). Inset: negativity of the long-wavelength ( $kl_d \ll 1$ ) part of the spectrum indicates that long-wavelength perturbations are stable, even in the case of neutral ( $\rho = 1$ ) permeability contrast between the primary and secondary rock.

So far, we have focused on the convection-dominated case, H < 1, which implies either relatively large fluid flows or small precipitation rates. For example, in kaolinite-for-calcite replacement the rate limiting step is the precipitation reaction [*Banerjee and Merino*, 2011], which results in convective replacement (H < 0.1) for groundwater flow rates in excess of 1 m/yr [*Kondratiuk et al.*, 2015]. In such cases, the most unstable wavelength is of the order of the front width, ( $k_{max}I_d \sim 1$ ). On the other hand, when the flow velocity is small (or the reaction rate large) such that H > 1, the unstable region moves toward longer length scales. Now the system is controlled by an interplay of convection and diffusion in the upstream region. The relevant length scale is then given by the transport length  $I_u = D/v_0$ , which can extend from meters to kilometers depending on the flow rate. Again, at these length scales, the system reduces to the thin-front limit of classical reactive-infiltration instability [*Ortoleva et al.*, 1987]. The dispersion relation

$$\sigma = \frac{U}{l_u (1 + \Gamma_{\infty})} \left[ 1 + (1 - \Gamma_{\infty}) k l_u - \sqrt{1 + 4(k l_u)^2} \right]$$
(19)

has then a maximum

$$\sigma_{\max} = \frac{U}{l_u(1+\Gamma_{\infty})} \left[ 1 - \frac{\sqrt{(3-\Gamma_{\infty})(1+\Gamma_{\infty})}}{2} \right]$$
(20)

at a wave vector

$$k_{\max} I_u = \frac{1 - \Gamma_{\infty}}{2\sqrt{(3 - \Gamma_{\infty})(1 + \Gamma_{\infty})}}.$$
(21)

Note that  $k_{max}/_u$  depends only on the permeability contrast, not on the reaction rates. In this case, the instability appears only if  $\Gamma_{\infty} < 1$ , and fronts where the secondary phase is less porous than the primary one are always stable.

#### 5. Later Stages of Evolution: The Growth of Replacement Fingers

The results of the linear stability analysis show that the replacement front is unstable over a wide range of the control parameters, even if the permeabilities of the product and parent rock do not differ. In the parameter space we have explored, the maximally unstable wavelength is of the order of the penetration length of the secondary species. This is the largest length scale in our system, and thus, the width of the porous region at the replacement front is of the same order of magnitude. *Merino and Banerjee* [2008] and *Lucke et al.* [2012] have measured this width to be of the order of 5 cm. However, this is far smaller than the spacing between any of the karst features observed in terra rossa-covered regions, like the ones depicted in Figure 6. As a possible solution to this problem, *Merino and Banerjee* [2008] suggested that the replacement pattern can coarsen with time, analogous to what is observed in dissolution systems [*Szymczak and Ladd*, 2006].



**Figure 6.** (left) Solution pipes in limestone bedrock overlaid with terra rossa at Greatstone Winery near Coonawarra, South Australia. The height of the outcrop is about 7 m. The photo is courtesy of Les Sampson (Claremont Wines, South Australia). (right) Closeup of one of the pipes, showing the terra rossa layer (dark red) and more recent siliceous sands overlaying it. The hammer indicates the scale.

To test these ideas, we have carried out numerical simulations of equations (3) and (4) in two spatial dimensions. To make the simulations more realistic, we have included the dependence of the dispersion coefficient *D* on the porosity,

$$D = \varphi D_{\rm mol},\tag{22}$$

where  $D_{mol}$  is the (constant) molecular diffusion coefficient. The evolution of porosity and precipitated (secondary) mineral is illustrated in Figure 7. As predicted by linear stability analysis, an initially planar front is unstable, with spontaneous protrusions developing as the reaction proceeds. With time, these protrusions



**Figure 7.** The basic mineral replacement system. Development of wormhole-like structures from spontaneous protrusions in the replacement front: H = 1/16,  $\kappa = 2$ ,  $\rho = 1$ , and  $\phi_5^{\text{max}} = 0.9$ . (top row) The initially planar replacement front. (middle row) Initial protrusions in the front. (bottom row) Well-developed wormholes. (left column) The rescaled porosity field,  $\hat{\varphi} = (\varphi - \varphi_{\min})/(1 - \varphi_{\min})$ . (right column) Secondary mineral volume fraction ( $\hat{\phi}_5 = \phi_5/\phi_5^{\text{max}}$ ). Movies S1 and S2 in the supporting information illustrate the full evolution of this system.



**Figure 8.** Dispersion relations for the extended replacement model, recovered from two-dimensional simulations. The parameters are  $\rho = 1$ ,  $\kappa = 100$ ,  $\phi_{S}^{max} = 0.9$ , and H = 0.001 (red circles), H = 0.005 (green squares), or H = 0.01 (blue diamonds). The system has finite width and the longest wavelength corresponds to  $kI_d \approx 0.4$ .

extend and transform themselves into fingers. The fingers interact with each other in a strongly nonlinear way, which gives rise to a complex dynamics at the front. A striking feature in Figure 7 is the concentration of porosity in disjoint regions associated with the tips of the fingers. Since precipitation produces the protons needed for the dissolution reaction, the presence of free space is essential for the replacement to proceed. Therefore, except for the finger tips, the pattern becomes frozen and no longer evolves. The effect is illustrated in Movie S1 (supporting information), which shows the evolution of the volume fraction of the secondary mineral.

A characteristic phenomenon is attraction of shorter fingers by the longer

ones, which is due to the flow convergence near the bases of the longest fingers [*Szymczak and Ladd*, 2006], which causes the shorter fingers to bend toward their longer neighbors. As the fingers merge, the longer finger absorbs the porosity concentrated at the tip of the shorter one. This predatory behavior is further illustrated in Movie S2, which shows the evolution of porosity in the system. Since precipitation occurs only at the tips of the active fingers, their trajectories are regions with the highest concentration of the secondary phase. This gives rise to tree-like structures of the fingers, as shown in Figure 7. Interestingly, although the evolution of the system is highly nonlinear and complex, the total porosity in the system is time independent (Appendix D).

The morphology of these structures is markedly different from terra rossa-filled fingers in nature (Figure 6). A possible reason for this discrepancy is the simplicity of the replacement model with the matching condition



**Figure 9.** System with the same parameters as in Figure 7 but with the additional reaction (23) characterized by  $\alpha_{\text{buff}} = \alpha_{\text{prec}}$ . Movies S3 and S4 in the supporting information illustrate the full evolution of this system.



(8) externally imposed. We therefore consider a more sophisticated model [Kondratiuk et al., 2015], where the velocity synchronization (8) is achieved by introducing a buffering reaction to deplete the excess protons,

The buffering reaction gives rise to

$$B + H \longrightarrow Y.$$
 (23)

**Figure 10.** Average distance between the pipes as a function of time for the buffering model with H = Da/Pe = 5/8,  $\kappa = 2$ ,  $\rho = 1$ , and  $\phi_s^{max} = 0.9$ . The functional form of the solid line is given by  $d/l_d = 14.4 + 4.7\sqrt{t/t_p}$ . The functional form of the solid line is given by  $d/l_d = 14.4 + 4.7\sqrt{t/t_p}$ .

quently move with equal velocities. In kaolinite-for-calcite replacement, the buffering might be provided by the reaction of  $H^+$  ions with bicarbonate anions. Due to the excess of  $(HCO_3^-)$ , the kinetics are expected to be roughly linear in the proton concentration

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$$r_{\rm buff} = \alpha_{\rm buff} c_H. \tag{24}$$

Such a system is also unstable with respect to small perturbations. The dispersion curves in Figure 8 were recovered by analyzing the initial growth of perturbations in the nonlinear system, sampling over seven initial conditions to reduce the statistical noise. The plots are qualitatively similar to the ones obtained for the system without the buffering reaction (Figure 4).

As suggested by the resemblance of the dispersion curves for the two models, the initial development of the systems is similar (compare middle rows in Figures 7 and 9). However, their further evolution is markedly different. For the buffering system, more compact, funnel-like structures emerge, and the high-porosity layer remains continuous, although still mostly concentrated at the finger tips (Figure 9, bottom). The overall morphology of the fingers is now much more akin to the natural systems shown in Figure 6.

The fingers again interact with each other (see Movies S3 and S4), with the smaller fingers attracted to the longer ones (see, for instance, the second finger from the right in Figure 9, bottom, which is leaning toward its neighbor and is about to merge with it). There is a fundamental difference in the dynamics when compared to the system without the buffering reaction (Figure 7). In the buffered system the precipitation reaction takes



**Figure 11.** The effect of *H* on the replacement patterns. The successive columns correspond (from left to right) to H = 1, 1/4, 1/16, and 1/64 at a time  $t = 30 t_p$ ; the other parameter values are the same as in Figure 9. (top row) Rescaled porosity; (bottom row) rescaled volume fraction of the secondary mineral.



**Figure 12.** Long time limiting form for the (left) porosity, (middle) secondary mineral volume fraction, and (right) Darcy velocity. The parameters are H = 1,  $\kappa = 2$ ,  $\rho = 1$ ,  $\phi_{S}^{max} = 0.9$ , and  $\alpha_{buff}/\alpha_{prec} = 1$ . Due to competition and merging a single finger with a time-independent shape has eventually developed.

place along the entire front, not just at the finger tips, and the front propagates throughout the system, wiping out all of the preexisting patterns, including the remnants of the shorter fingers. The pattern coarsens, and the characteristic distance between the fingers increases with the square root of time, as illustrated in Figure 10. Thus, after a while, the size of the fingers and the distance between them are unrelated to the values predicted by linear stability analysis. Interestingly, analogous  $\sqrt{t}$  coarsening has been observed in the growth of viscous fingers [*Wooding*, 1969; *Menon and Otto*, 2005], which is another indication that these phenomena share many common features. Importantly, the  $\sqrt{t}$  dependence is not connected with a transverse spreading of the fingers by diffusion, but it is rather a consequence of the convective coalescence of nearby fingers [*Menon and Otto*, 2005]. The shapes of the fingers are influenced by the value of *H*, becoming more elongated as *H* decreases (Figure 11), which, according to equation (13), corresponds to increased flow through the rock.

Looking more closely at the distribution of porosity within the body of the finger, in Figure 12 (left) we notice regions of enhanced porosity (green) at the sides of the finger and along its centerline. The enhanced porosity along the edges of the finger coincide with the position of the replacement front, where protons produced by precipitation result in an increased leaching intensity. The reason behind a porous zone along the centerline of the finger is less obvious, but a careful examination of the porosity evolution (Movie S4) shows that this is a remnant of the passing finger tip, still visible because of the delay in the filling of the pores by the precipitation reaction. This zone of enhanced porosity results in an increased flow in the center of the finger, as shown in Figure 12 (right). We hypothesize that the concentration of flow in the center of the fingers might be the reason why siliceous sands, deposited later than the terra rossa layer, have been transported predominantly along the centerline of a solution pipe; an example can be seen in Figure 6 (right).

#### 6. Comparison With Other Fingering Instabilities

Instabilities in precipitation-dissolution systems resemble a particular viscous fingering in which a thin slice of fluid of viscosity  $\mu_c$  is inserted between two fluids of viscosities  $\mu_A$  (upstream) and  $\mu_B$  (downstream); the fluids are confined within a Hele-Shaw cell and driven by an applied pressure gradient [*De Wit et al.*, 2005;

Mishra et al., 2008; Daripa, 2008; Hejazi et al., 2010; Pramanik and Mishra, 2015]. The special case  $\mu_A = \mu_B$ , analogous to the replacement instability with  $\rho = 1$ , is characterized by an absence of mobility contrast in the bulk phases; nevertheless, one of the two fluid-fluid interfaces is always unstable. When a slice of a more viscous solution ( $\mu_C > \mu_A, \mu_B$ ) is sandwiched in-between the bulk phases, the rear interface of the injected slice becomes unstable while the forward one is stable. Conversely, when the plug has a lower viscosity than the bulk fluids ( $\mu_C < \mu_A, \mu_B$ ), fingers develop at the forward interface of the sample while the rearward one remains stable [*De Wit et al.*, 2005]. These conclusions have been verified experimentally [*Catchpoole et al.*, 2006; *Shalliker et al.*, 2007]. Even if the fluid upstream is more viscous than the fluid downstream ( $\mu_A > \mu_B$ ), the presence of the additional middle layer can destabilize the front, provided that its viscosity  $\mu_C$  is either lower or higher than both viscosities of the neighboring fluids. Such a case is analogous to our examples with  $\rho > 1$ , where the downstream (primary) mineral has a higher porosity than the upstream one.

Although the instability in hydrogeochemical systems is conceptually similar to viscous fingering, there are important distinctions. In a replacement system, the characteristic wavelength of the perturbation is comparable to the width of reaction zone, but in the viscous fluid case the width of the central slice of fluid has a minimal impact on the dynamics [*Daripa*, 2008].

Although one-component precipitation fronts are stable, multicomponent reactions can sometimes lead to an unstable front [*Nagatsu et al.*, 2014; *Shukla and De Wit*, 2016]. For example, if an aqueous phase *A* infiltrates another aqueous phase *B* and *A* reacts with *B* to form a precipitate, there is a localized decrease in porosity in the reaction front separating *A* and *B*. The reduced mobility generates an instability in the interface with the more mobile upstream solution *A*, leading to fingering. In contrast, the precipitation-dissolution system described in this paper is initially destabilized on the downstream (dissolution) front.

#### 7. Discussion

The reactive-infiltration instability is an important source of pattern formation in geology [*Ortoleva*, 1990]. During infiltration-driven dissolution the reaction front is destabilized by the upstream permeability increase, which results from porosity generated by the passing dissolution front. In this paper we have shown that a replacement front is similarly unstable whenever the secondary mineral is more permeable than the primary one ( $\rho < 1$ ). Moreover, for convection-dominated systems (H < 1) a precipitation-driven replacement is unstable even when the secondary phase is the less permeable ( $\rho > 1$ ). The appearance of an instability in this case is linked to the creation of a region of increased porosity in the vicinity of the front, something which can also observed in the field [*Banerjee and Merino*, 2011; *Lucke et al.*, 2012]. The size of the porous zone reflects the length scale over which the slowest reaction comes to equilibrium. The localized region of enhanced porosity destabilizes a planar front, even when the secondary phase is less permeable ( $\rho \ge 1$ ) than the primary mineral. However, in this case long-wavelength perturbations are stabilized by the favorable permeability contrast between bulk phases and only perturbations on the scale of the thickness of the zone of enhanced porosity (Figure 4) are unstable. This is reminiscent of certain kinds of viscous fingering and precipitation experiments (section 6). Both viscous and reactive instabilities are generated by mobility contrast, with a mobile upstream phase penetrating a less mobile downstream one.

We have previously argued [Kondratiuk et al., 2015] that in cases where the secondary phase has a smaller molar volume than the primary mineral a replacement front cannot be synchronized by crystallization pressure. Instead, we suggested two chemical mechanisms by which a steadily propagating front could be obtained. In this paper we studied the buffering mechanism (23), which can operate when replacement is driven by an oversaturation of secondary ions. However, when the two minerals share a common ion, replacement can also be initiated by undersaturated solutions of secondary ions, as for example in KCl-for-KBr replacement [*Putnis*, 2009]. The rising concentration of the common ion, by dissolution of the primary mineral, then leads to precipitation of the secondary mineral. The stability of these fronts [*Kondratiuk et al.*, 2015] will be investigated in future work. Interestingly, recent studies [*Raufaste et al.*, 2011; *Kar et al.*, 2016] report fingering at a microscopic scale (~100  $\mu$ m), presumably connected with self-generated convective flows by the process of diffusion osmosis [*Kar et al.*, 2016; *Ajdari and Bocquet*, 2006].

Although the high permeability of the upstream phase destabilizes the front, the growth of an instability depends on its length scale and the lateral dimensions of the replacement front. If the lateral span of the front is too small in comparison with the wavelength of the instability, its growth is quenched by diffusion. For example, serpentinite carbonation is characterized by sharp, almost flat fronts [*Beinlich et al.*, 2012],

with no suggestion of fingering. This is because serpentinite is highly impermeable; Kawano et al. [2011] suggests a permeability of  $0.1 - 1\mu$ D for unconfined serpentinite, corresponding to flow velocities  $v_0 \sim 10^{-10}$  cm/s. In that case the replacement reactions are entirely transport limited ( $H \gg 1$ ) and a sharp discontinuity between the two phases is to be expected [Ortoleva et al., 1987]. The characteristic length scale of the instability (21) is then of the order of kilometers and the time scale for the growth of perturbations (20) exceeds  $10^{12}$  years. Even over geological times, instabilities of such large length scales cannot develop and the front will remain flat. The sharpness of the serpentinite front is therefore consistent with the diffusion-dominated ( $H \gg 1$ ) character of this replacement process.

The qualitative features of the dispersion curves are insensitive to details of the chemical kinetics, provided that the high-porosity zone is present. However, the subsequent, nonlinear stages of the dynamics can be markedly different, as shown by the figures in section 5. When an isovolumetric replacement is imposed by fiat (section 2) the fingering patterns (Figure 7) do not resemble the shapes observed in nature (Figure 6). Much more realistic morphologies (Figures 9 and 11) are obtained by allowing the isovolumetric condition to emerge naturally via the buffering reaction (23). The instability leads to the breakup of the front and the formation of finger-like funnels in the replacement zone. Once formed, the fingers continue to grow, focusing an ever-increasing portion of the flow but also competing with each other: the shorter fingers are attracted to the longer ones and eventually merge with them. As a result the pattern coarsens with time, and the widths of the fingers and characteristic distance between them increase as  $\sqrt{t}$  (Figure 10). Thus, as suggested by Merino and Banerjee [2008], chemical replacement can in principle trigger the formation of large-scale karst structures. However, there are caveats to these conclusions. First, we have assumed that the only source of protons is the precipitation reaction (1), but in reality other sources of acidity can be present, such as meteoric carbonic acid or soil waters. Second, the assumption of equal porosities of product and parent phase [Merino and Baneriee, 2008] can be treated as an approximation only. For both of the above reasons, one would expect that both the reactive-infiltration instability and the replacement-associated instability could contribute to karst formation in terra rossa-covered limestone terrains.

#### **Appendix A: The Scaled Equations and Their One-Dimensional Solutions**

In one dimension the equations for reactant transport (3c) and (3d) can be integrated directly, noting that  $\mathbf{v}(x) = v_0 \mathbf{e}_x$ . For example, from equations (3c) and (3e)

$$\frac{c_{S}^{1D}}{c_{S}^{in}} = 1 - \frac{e^{x'/l_{u}}}{1 + Pe}, \qquad \phi_{S}^{1D} = \phi_{S}^{max} \qquad x' < 0, \qquad (A1)$$

$$\frac{c_{\rm S}^{1D}}{c_{\rm S}^{\rm in}} = \frac{e^{-x'/l_d}}{1+Pe^{-1}}, \qquad \qquad \frac{\phi_{\rm S}^{1D}}{\phi_{\rm S}^{\rm max}} = e^{-x'/l_d} \qquad \qquad x' > 0, \tag{A2}$$

where x' = x - Ut is the spatial coordinate in the reference frame moving with the front. The upstream penetration length is  $l_u = D/v_0$ , and the downstream penetration length of the secondary ions is  $l_d = 2D/(\sqrt{v_0^2 + 4\alpha_{prec}D} - v_0)$  [Szymczak and Ladd, 2013]. We define the Péclet number with respect to the downstream penetration length,

$$Pe = \frac{v_0 l_d}{D} = \frac{2v_0}{\sqrt{v_0^2 + 4\alpha_{\text{prec}}D} - v_0}},$$
(A3)

and the Damköhler number similarly,

$$Da = \frac{\alpha_{\text{prec}}I_d}{v_0} = \frac{2\alpha_{\text{prec}}D}{v_0\left(\sqrt{v_0^2 + 4\alpha_{\text{prec}}D} - v_0\right)}.$$
 (A4)

The ratio of upstream and downstream length scales,  $I_d/I_u = 2/(\sqrt{1+4H} - 1)$ , is a function of *H* only (equation (13)); in fact, both *Pe* and *Da* can be expressed as functions of *H* [*Szymczak and Ladd*, 2013],

$$Pe = \frac{2}{\sqrt{1+4H}-1}, \quad Da = \frac{\sqrt{1+4H}+1}{2}.$$
 (A5)

The flow and transport equations can now be simplified by scaling space by the downstream penetration length,  $I_d$  (10), and time by the characteristic time for secondary phase precipitation,  $t_o$  (11). We define dimensionless coordinates:

$$\xi = x'/I_d, \quad \eta = y/I_d, \tag{A6}$$

and time

$$\tau = t/t_p. \tag{A7}$$

Next, we rescale the concentration, velocity, and volume fractions:

$$=\mathbf{v}/v_0,\tag{A8}$$

$$\hat{c}_S = c_S / c_S^{\text{in}}, \quad \hat{c}_H = c_H / c_S^{\text{in}}, \tag{A9}$$

$$\hat{\phi}_{S} = \phi_{S}/\phi_{S}^{\max}, \quad \hat{\phi}_{P} = \phi_{P}/\phi_{S}^{\max}, \quad \hat{\varphi} = \frac{\varphi - \varphi_{\min}}{1 - \varphi_{\min}}.$$
(A10)

The rescaled volume fractions are bounded on [0, 1]. The dimensionless equations are then as follows: Ŷ

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$$\cdot \hat{\mathbf{v}} = 0$$
 (A11a)

$$\hat{\mathbf{v}} = -\hat{K}(\hat{\varphi})\hat{\nabla}\hat{\rho} \tag{A11b}$$

$$\hat{\nabla} \cdot (\hat{c}_{S} \hat{\mathbf{v}}) - \frac{1}{Pe} \hat{\nabla}^{2} \hat{c}_{S} = -\theta (1 - \hat{\phi}_{S}) Da \, \hat{c}_{S} \tag{A11c}$$

$$\hat{\nabla} \cdot (\hat{c}_H \hat{\mathbf{v}}) - \frac{1}{Pe} \hat{\nabla}^2 \hat{c}_H = \nu \theta (1 - \hat{\phi}_S) Da \, \hat{c}_S - \kappa \theta (\hat{\phi}_P) Da \, \hat{c}_H \tag{A11d}$$

$$(\partial_{\tau} - \hat{U}\partial_{\xi})\hat{\phi}_{S} = \theta(1 - \hat{\phi}_{S})Da\,\hat{c}_{S} \tag{A11e}$$

$$\nu \rho (\partial_{\tau} - \hat{U} \partial_{\xi}) \hat{\phi}_{\rho} = -\kappa \theta (\hat{\phi}_{\rho}) Da \, \hat{c}_{H} \tag{A11f}$$

$$1 - \hat{\varphi} = \hat{\phi}_{\varsigma} + \hat{\phi}_{\rho}, \tag{A11g}$$

where  $\hat{K} = K/K_{\min}$  and  $\hat{p} = p/\partial_{\hat{x}}p_0$ .

In the moving reference frame the initial conditions ((4d)-(4e)) transform into boundary conditions and together with the conditions (4a) - (4c) read as follows:

$$\hat{\boldsymbol{v}}|_{\xi \to -\infty} = \mathbf{e}_{\xi} \qquad \qquad \hat{\boldsymbol{u}}_{\eta}\Big|_{\xi \to \infty} = 0 \qquad (A12a)$$

$$\hat{c}_{S}\Big|_{\xi \to -\infty} = 1$$
  $\partial_{\xi} \hat{c}_{S}\Big|_{\xi \to \infty} = 0$  (A12b)

$$\hat{c}_{H}|_{\xi \to -\infty} = 0$$
  $\hat{\partial}_{\xi} c_{H}|_{\xi \to \infty} = 0$  (A12c)

$$\left. \hat{\phi}_{\mathsf{S}} \right|_{\xi \to \infty} = 0 \qquad \left. \hat{\phi}_{\mathsf{P}} \right|_{\xi \to \infty} = \rho^{-1}.$$
 (A12d)

There is the additional condition at the front,

$$\hat{\phi}_{S}(\xi=0) = 1,$$
 (A12e)

which follows from the requirement that the front velocity remains constant (see the discussion in Szymczak and Ladd [2014]). A number of matching conditions are necessary to close the equations. The concentration fields and their first derivatives must be continuous to enforce continuity of reactant flux across each front. The pressure and normal component of the fluid velocity also have to be continuous across the front.

We use the one-dimensional solutions as the base state for the linear stability analysis. In the scaled variables, the secondary ion profile and the secondary mineral volume fraction profile, equation (A2), take the form

$$\hat{c}_{\varsigma}^{1D}(\xi) = \begin{cases} 1 - (DaPe)^{-1} e^{Pe\xi}, & \xi < 0\\ Da^{-1}e^{-\xi}, & \xi > 0 \end{cases}$$
(A13)

$$\hat{\phi}_{S}^{1D}(\xi) = \begin{cases} 1, & \xi < 0\\ e^{-\xi}, & \xi > 0. \end{cases}$$
(A14)

It can be seen that the concentration and porosity profiles satisfy the continuity conditions at the interface ( $\xi = 0$ ).

In the absence of the buffering reaction, the dissolution front ( $x_p$  in Figure 1) is located at an arbitrary position with respect to the precipitation front ( $x_s$ ), depending on the amount of porosity initially present in the system. Here we will assume that their positions coincide, which leads to profiles for  $\hat{c}_H$  and  $\hat{\phi}_p$  with the following form:

$$\hat{c}_{H}^{1D}(\xi) = \begin{cases} \frac{\nu}{\kappa-1} \left( Da^{-1} - Da_{\kappa}^{-1} \right) e^{Pe\,\xi}, & \xi < 0\\ \frac{\nu}{\kappa-1} \left( Da^{-1}e^{-\xi} - Da_{\kappa}^{-1}e^{-Pe\,\xi/Pe_{\kappa}} \right), & \xi > 0 \end{cases}$$
(A15)

$$\hat{\phi}_{\rho}^{1D}(\xi) = \begin{cases} 0, & \xi < 0\\ \frac{1}{\rho} - \frac{1}{\rho(\kappa-1)} \left( \kappa e^{-\xi} - e^{-\rho e \,\xi/\rho e_{\kappa}} \right) . & \xi > 0 \end{cases}$$
(A16)

The Péclet and Damköhler numbers associated with the dissolution of the primary mineral are

$$Pe_{\kappa} = \frac{2v_0}{\sqrt{v_0^2 + 4D\alpha_{\text{diss}}} - v_0}} = \frac{2}{\sqrt{1 + 4\kappa H} - 1},$$
(A17)

$$Da_{\kappa} = \frac{2D\alpha_{\rm diss}}{v_0 \left(\sqrt{v_0^2 + 4D\alpha_{\rm diss}} - v_0\right)} = \frac{\sqrt{1 + 4\kappa H} + 1}{2}.$$
 (A18)

#### **Appendix B: The Linear Stability Analysis Framework**

The linear stability analysis proceeds by considering an infinitesimal perturbation to a planar reaction front,

$$\xi_0(\eta,\tau) = \zeta \sin(\hat{k}\eta) \exp(\hat{\sigma}\tau) \tag{B1}$$

In the above,  $\zeta \ll 1$  is the amplitude of the perturbation,  $\hat{k}$  is its dimensionless wave number, and  $\hat{\sigma}$  is the (dimensionless) growth rate. The pressure, Darcy velocity, concentration, and volume fraction fields are similarly perturbed, e.g.,

$$\hat{\phi}_{\mathsf{S}}(\xi,\eta,\tau) = \hat{\phi}_{\mathsf{S}}^{1D}(\xi) + f_{\phi_{\mathsf{S}}}(\xi)\sin(\hat{k}\eta)\exp(\hat{\sigma}\tau). \tag{B2}$$

and analogously for the other fields. The perturbed fields are then inserted back into equation (3), with boundary conditions (A12) and continuity conditions across the front. The resulting equations for the perturbations are linearized by neglecting terms which are of the second and higher order in the perturbation amplitudes.

Due to the presence of step functions in the transport equation, one needs to solve the resulting differential equations separately in the upstream ( $\xi < 0$ ) and the downstream ( $\xi > 0$ ) domains. In the upstream domain the porosity perturbations vanish and, as a result, the equations can be solved analytically. In the downstream domain, however, the problem is more complex. One can note that all the (downstream) perturbation amplitudes can be derived from the  $f_{\phi_c}$  amplitude,

$$f_{c_{5}} = Da^{-1}(\hat{\sigma} - \partial_{\xi})f_{\phi_{5}}$$
(B3)

$$f_{\nu_{\xi}} = Da^{-1} \mathcal{P}(\hat{\sigma} - \partial_{\xi}) f_{\phi_{\xi}}$$
(B4)

$$f_p = (Da\,\hat{k}^2\hat{K}(\hat{\varphi}^{1D}))^{-1}\partial_{\xi}\mathcal{P}(\hat{\sigma} - \partial_{\xi})f_{\phi_{\xi}}$$
(B5)

$$f_{\phi_{\mathcal{P}}} = -\left(1 - \frac{1}{\hat{k}^2 Da} \left(\frac{1}{W} \hat{\nabla}^2 - (\partial_{\xi} \hat{\varphi}^{1D}) \partial_{\xi}\right) \mathcal{P}(\hat{\sigma} - \partial_{\xi})\right) f_{\phi_{\mathcal{S}}}$$
(B6)

$$f_{c_{H}} = \frac{\nu\rho}{\kappa Da} \left( 1 - \frac{1}{\hat{k}^{2} Da} (\hat{\sigma} - \partial_{\xi}) \left( \frac{1}{W} \hat{\nabla}^{2} - \hat{\varphi}' \partial_{\xi} \right) \mathcal{P} \right) (\hat{\sigma} - \partial_{\xi}) f_{\phi_{S}}$$
(B7)

where 
$$\mathcal{P} = -(\partial_{\xi}\hat{c}_{S}^{1D})^{-1} \left( Da + \partial_{\xi} - Pe^{-1}\hat{\nabla}^{2} \right), \hat{\nabla}^{2} = \partial_{\xi}^{2} - \hat{k}^{2}, \text{ and}$$
  

$$W(\xi) = \partial_{\hat{a}^{1D}} \ln \hat{K}(\hat{\varphi}^{1D}). \tag{B8}$$

The set of coupled equations for the  $f_*(\xi)$  amplitudes can be combined into a single eighth-order ODE for  $f_{\phi_5}(\xi)$ ,

$$\left(\kappa Da + \partial_{\xi} - Pe^{-1}\hat{\nabla}^{2}\right)\left(\hat{\sigma} - \partial_{\xi}\right)\left(\frac{1}{W}\hat{\nabla}^{2} - \left(\partial_{\xi}\hat{\varphi}^{1D}\right)\partial_{\xi}\right)\mathcal{P}(\hat{\sigma} - \partial_{\xi})f_{\phi_{5}}$$

$$= \hat{k}^{2}Da\left(\kappa Da(1 - \rho^{-1}) + \partial_{\xi} - Pe^{-1}\hat{\nabla}^{2} + \left(\partial_{\xi}\hat{c}_{H}^{1D}\right)\frac{\kappa}{\nu\rho}\mathcal{P}\right)\left(\hat{\sigma} - \partial_{\xi}\right)f_{\phi_{5}}, \quad \xi > 0,$$
(B9)

which can be only solved numerically. The boundary conditions for equation (B9) follow from boundary conditions (A12) and the linearized continuity conditions across the (now perturbed) reaction front. Eventually, three boundary conditions at  $\xi = 0$  can be constructed:

$$\left(\partial_{\xi} - \frac{Pe}{2}\left(1 + \sqrt{1 + \left(\frac{2\hat{k}}{Pe}\right)^{2}}\right)\right)f_{\zeta_{5}}(0) - \left(\partial_{\xi}\hat{\zeta}_{5}^{1D}\right)(0)\left(1 + \frac{Pe}{2\hat{k}} - \sqrt{1 + \left(\frac{Pe}{2\hat{k}}\right)^{2}}\right)f_{v_{\xi}}(0) = -\zeta Pe \qquad (B10)$$

$$\left(\partial_{\xi} - \frac{Pe}{2}\left(1 + \sqrt{1 + \left(\frac{2\hat{k}}{Pe}\right)^{2}}\right)\right)f_{\zeta_{\mu}}(0) - \left(\partial_{\xi}\hat{\zeta}_{\mu}^{1D}\right)(0)\left(1 + \frac{Pe}{2} - \sqrt{1 + \left(\frac{Pe}{2}\right)^{2}}\right)f_{v_{\xi}}(0)$$

$$\left( \partial_{\xi} - \frac{re}{2} \left( 1 + \sqrt{1 + \left(\frac{2\kappa}{Pe}\right)} \right) \right) f_{c_{H}}(0) - \left( \partial_{\xi} \hat{c}_{H}^{DD} \right)(0) \left( 1 + \frac{re}{2\hat{k}} - \sqrt{1 + \left(\frac{re}{2\hat{k}}\right)} \right) f_{v_{\xi}}(0)$$

$$= -\xi_{0} \frac{\nu Pe}{\kappa - 1} \left( 1 - \frac{Pe}{Pe_{\kappa}} \right)$$
(B11)

$$(\partial_{\xi} - \hat{k})f_{\nu_{\varepsilon}}(0) = 0 \tag{B12}$$

as well as five at  $\xi \to \infty$ ,

$$\left. f_{\phi_5} \right|_{\xi \to \infty} = 0 \tag{B13}$$

$$f_{\phi_{\mathcal{P}}}\Big|_{\xi \to \infty} = 0 \tag{B14}$$

$$\left. f_{c_{S}} \right|_{\xi \to \infty} = 0 \tag{B15}$$

$$f_{c_H}\Big|_{\xi \to \infty} = 0 \tag{B16}$$

$$f_{v_{\xi}}\Big|_{\xi \to \infty} = 0.$$
(B17)

Note that the amplitude of the perturbation,  $\zeta$ , is arbitrary, which is to be expected, since the perturbation equation (B9) is linear. The above boundary conditions allow us to find the solution to (B9) and then the stationarity condition (7), which can be put in the form

$$f_{\phi_5}(0) = \xi_0,$$
 (B18)

allows us to obtain the dispersion curve  $\hat{\sigma}(\hat{k})$ . We solve the problem numerically using the pseudospectral, boundary-bordering method [*Boyd*, 2001], and a cubic permeability model. As a result, we obtain the dispersion curves shown in Figures 3–5.

#### Appendix C: Linear Stability Analysis for Small Permeability Contrasts

In some cases the change in porosity across the front may be small, such that the porosity contrast

$$\Delta = \frac{\varphi_{\max} - \varphi_{\min}}{\varphi_{\min}} \tag{C1}$$

is much less than 1. It is then more convenient to rescale the porosity by  $\varphi_{\max} - \varphi_{\min}$ ,

$$\hat{\varphi} = \frac{\varphi - \varphi_{\min}}{\varphi_{\max} - \varphi_{\min}},\tag{C2}$$

rather than by  $1 - \varphi_{\min}$  (A10), so that  $\hat{\varphi}$  remains bounded in [0, 1]. The linear stability analysis still follows Appendix B but with the rescaled porosity now defined by (C2). When the porosity contrast is sufficiently small, the permeability varies approximately linearly with  $\hat{\varphi}$ ,

$$\hat{K}(\hat{\varphi}) = 1 + W\hat{\varphi} + \mathcal{O}(\Delta^2).$$
(C3)



**Figure C1.** Dispersion curves for the replacement system with the exponential permeability model assumed, for W = 0.1,  $\kappa = 2$ , H = 0 (convection-limited case), and  $\rho = 0.63$ , 0.71, 0.83, 1.0, and 1.25 (top to bottom). Solid lines—exact numerical solutions; dashed lines—the approximate analytical results, equation (C7).

For the cubic permeability law,  $K \propto \varphi^3$ ,  $W = 3\Delta$ . Here we show that when W is small the dispersion relation can be solved analytically, adding additional insight.

If the permeability contrast is not too large it is possible to obtain an approximate dispersion relation by expanding  $f_{\phi_c}(\xi)$  and  $\hat{\sigma}$  in powers of W [Szymczak and Ladd, 2014],

$$f_{\phi_5} = f_0 + W f_1 + W^2 f_2 + \dots \tag{C4}$$

$$\hat{\sigma} = \hat{\sigma}_0 + W\hat{\sigma}_1 + W^2\hat{\sigma}_2 + \dots$$
(C5)

Neglecting diffusion ( $H \rightarrow 0$ ), analytical solutions up to first order can be relatively easily obtained. At zeroth order

$$\hat{\sigma}_0 = 0, \tag{C6}$$

so  $\hat{\sigma}$  is of the order of W. To first order in W, the dispersion relation is given by

$$\hat{\sigma} = W\hat{\sigma}_1 = W \frac{\hat{k}[\kappa \left(\rho^{-1} - 1\right)(\kappa + 1 + \hat{k}) - \hat{k}]}{2(\kappa + 1)(\hat{k} + 1)(\kappa + \hat{k})}.$$
(C7)

As shown in Figure C1, equation (C7) is a good approximation to  $\hat{\sigma}$  when W < 1. For this comparison we used an exponential permeability model

$$\hat{K}(\hat{\varphi}) \propto e^{W\hat{\varphi}},$$
 (C8)

which also has a constant W but a nonlinear dependence of  $\hat{K}$  on  $\hat{\varphi}$ . It is sometimes used to model the permeability of partially soluble rocks [*Hinch and Bhatt*, 1990], for example, sandstones containing carbonate cement. The dispersion curves for small W share some common features with the cubic permeability model. The system again becomes more unstable with decreasing  $\rho$  (Figure C1), but when  $\rho \ge 1$  the front is always stable, with  $\hat{\sigma} \le 0$  for all  $\hat{k}$ .

At long wavelengths the dispersion curves are linear in  $\hat{k}$ , with a slope

$$\frac{d\hat{\sigma}}{d\hat{k}}\Big|_{\hat{k}=0} = \frac{1}{2} \left(\rho^{-1} - 1\right) W = \frac{W}{2} \left(\frac{\phi_{\rho}^{\max} - \phi_{S}^{\max}}{\phi_{S}^{\max}}\right) = \frac{1 - \Gamma_{\infty}}{2},\tag{C9}$$

again making use of the linearly varying permeability (C3). The stability of the front with respect to long-wavelength ( $kl_d \ll 1$ ) perturbations is solely determined by the permeability difference between the bulk mineral phases, as in equation (17); the two expressions are equivalent when  $\Gamma_{\infty} \simeq 1$ .

Unstable systems ( $\rho < 1$ ) have a characteristic wave number

$$\hat{k}_{\max} = \frac{\kappa}{\kappa+1} \left( \kappa \left(\rho - 1\right)^{-1} + \sqrt{\rho^{-1} \left(\kappa^2 \left(\rho^{-1} - 1\right) + 1\right)} - 1 \right),$$
(C10)

corresponding to the largest growth rate. All wavelengths are unstable if the porosity contrast is small enough,  $\rho^{-1} < 1 + \kappa^{-1}$ . For intermediate values of  $\rho$ , i.e.,  $1 < \rho^{-1} < 1 + \kappa^{-1}$ , long-wave ( $\hat{k} < \hat{k}_{cr}$ ) perturbations are

unstable but short-wave ( $\hat{k} > \hat{k}_{cr}$ ) perturbations are stable. The critical wave number  $\hat{k}_{cr}$  separating stable and unstable regions is

$$\hat{k}_{cr} = \frac{1+\kappa}{\left(\kappa \left(\rho^{-1}-1\right)\right)^{-1}-1}.$$
(C11)

The stabilization of short waves by chemical reactions is fundamentally different from the stabilization by diffusion, which was discussed in section 4.

#### **Appendix D: Total Porosity Balance**

Let us calculate the time derivative of the total porosity in the system:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}\hat{t}} \iint_{S} \mathrm{d}S\,\hat{\varphi}(\hat{x},\hat{y},\hat{t}) &= \iint_{S} \mathrm{d}S\,\partial_{\hat{t}}\hat{\varphi} = -\iint_{S} \mathrm{d}S\,(\partial_{\hat{t}}\hat{\varphi}_{S} + \partial_{\hat{t}}\hat{\varphi}_{\rho}) \\ &= -\iint_{S} \mathrm{d}S\,\left(-\nabla\cdot\mathbf{j}_{S} + \frac{1}{\nu\rho}\left(\nu\nabla\cdot\mathbf{j}_{S} + \nabla\cdot\mathbf{j}_{X}\right)\right) \\ &= \iint_{\partial S} \mathrm{d}I\,\hat{\mathbf{n}}\cdot\left(\left(1-\rho^{-1}\right)\,\mathbf{j}_{S} - \frac{1}{\nu\rho}\,\mathbf{j}_{X}\right) \\ &= \int_{\partial S} \mathrm{d}\hat{y}\left(-\mathbf{e}_{\hat{x}}\right)\cdot\lim_{\hat{x}\to\infty}\left(\left(1-\rho^{-1}\right)\,\mathbf{j}_{S} - \frac{1}{\nu\rho}\,\mathbf{j}_{X}\right) \\ &+ \int_{\partial} \mathrm{d}\hat{y}\,\mathbf{e}_{\hat{x}}\cdot\lim_{\hat{x}\to\infty}\left(\left(1-\rho^{-1}\right)\,\mathbf{j}_{S} - \frac{1}{\nu\rho}\,\mathbf{j}_{X}\right) \\ &= \left(\rho^{-1}-1\right)\int_{\partial} \mathrm{d}\hat{y}. \end{aligned}$$
(D1)

The fluxes of aqueous species are  $\mathbf{j}_{s} = \hat{\mathbf{u}} \hat{c}_{s} - Pe^{-1}\hat{\nabla}\hat{c}_{s}$  and  $\mathbf{j}_{x} = \hat{\mathbf{u}} \hat{c}_{x} - Pe^{-1}\hat{\nabla}\hat{c}_{x}$ . Total porosity increases for  $\rho < 1$  and decreases for  $\rho > 1$ . In the special case of  $\rho = 1$ , the total porosity in the system remains constant.

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