

Diagenesis and fault valve seismicity of crustal faults

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Abstract. Dehydration and hydration reactions can significantly change permeability and fluid pressure in fault zones. Conversely, sudden drops in fluid pressure caused by faulting, or gradual increases in fluid pressure caused by fault sealing, can cause subsequent long-term dehydration or hydration of minerals in fault zones. Reactions with gentle Clapeyron slopes are most susceptible to changes in fluid pressure and produce nonintuitive results—dehydration reactions reduce fluid pressure, whereas hydration reactions increase fluid pressure. Dehydration and hydration reactions also influence fault-valve behavior. The strength of the effect depends on the rate of reaction relative to the rate of fault sealing. Reactions with steep PT slopes operate together with sealing processes to decrease $P_{\text{H}_2\text{O}}$, but they oppose the decrease in porosity caused by sealing. Reactions with gentle PT slopes work in concert with sealing to change $P_{\text{H}_2\text{O}}$ and porosity. Regardless of the type of reaction, where reaction rates exceed sealing rates, $P_{\text{H}_2\text{O}}$ can be maintained near the equilibrium pressure of the reaction until the reactant minerals or fluids are exhausted, sharply modifying the timescale for earthquake recurrence.

1. Conventional Fault Valve Behavior

The shear strength σ_s of faults undergoing frictional sliding is commonly modeled using the Coulomb fracture criterion:

$$\sigma_s = C + \mu (\sigma_n - P_f),$$

where C is the cohesion, μ is the coefficient of internal friction, σ_n is the normal stress, and P_f is the fluid pressure. The conventional “fault valve” hypothesis (Figure 1) [Sibson, 1992] holds that interseismic periods in a fault zone are characterized by rising fluid pressure caused by the precipitation of minerals from the fluid, that the rising fluid pressure eventually triggers an earthquake and dilatation that lowers fluid pressure, and then the whole cycle repeats. Central to the hypothesis are cyclic changes in permeability, fluid pressure, and fluid flow. Thus far, the major processes considered to influence permeability and fluid pressure during interseismic periods are precipitation, solution-transfer creep, diffusion creep (including crack healing), and dislocation creep—in aggregate these processes produce fault sealing. This paper argues that dehydration and hydration reactions can have equally strong or bigger influences on permeability and fluid pressure and thus on seismicity.

2. Background: Fluid and Solid Volume Changes During Reactions

The effects that mineral reactions have on permeability and fluid pressure depend largely on the change in fluid volume ΔV_f and change in solid volume ΔV_s , that accompanies reaction. There are fundamentally two types of dehydration and hydration reactions, distinguished by the relative changes in solid and fluid volume (Table 1 and Figure 2). In a dehydration reaction ΔV_f is always positive and ΔV_s , while generally negative, may be positive. In a fluid-dominated reaction, ΔV_f is greater in

magnitude than ΔV_s ; thus the total volume change of the reaction $\Delta V_{rxn} = \Delta V_s + \Delta V_f$ is dominated by ΔV_f . In a dehydration reaction, ΔV_{rxn} is positive, whereas ΔV_{rxn} of a fluid-dominated hydration reaction is negative. In a solid-dominated reaction $|\Delta V_s| > |\Delta V_f|$. In a solid-dominated dehydration reaction, ΔV_{rxn} is negative, whereas ΔV_{rxn} of a hydration reaction is positive. As examples of these types of reaction, consider the fluid-dominated equilibrium laumontite \leftrightarrow wairakite + 2 H₂O, which has a steep Clapeyron slope, and the solid-dominated equilibrium laumontite \leftrightarrow lawsonite + 2 quartz + 2 H₂O, which has a gentle Clapeyron slope (Figure 3). Although these reactions are emphasized in this paper for illustrative purposes, they have occurred in active fault zones. For instance, as much as 50% of the cataclasite in the San Gabriel fault is made up of laumontite veins and clay, and several generations of veins with varying degrees of deformation are present [Evans and Chester, 1995].

2.1. Fluid-Dominated Reaction

The dehydration of laumontite to wairakite + H₂O produces a ΔV_s of -10% (Figure 2a and Table 1, reaction A); if a laumontite rock has zero porosity ϕ before reaction, its porosity is 10% after complete dehydration. During the dehydration of laumontite the fluid volume increases 70% faster than the solid volume decreases ($\Delta V_f/\Delta V_s = -1.7$); thus the reaction produces “excess” fluid which causes the fluid pressure to rise. If the fluid pressure rises to the equilibrium pressure of the reaction, transformation will cease, and further transformation may be limited by the rate at which the excess fluid can dissipate by hydrofracturing or percolation. Importantly, the rate of fluid pressure change is not constant because the reaction rate slows as the pressure difference driving reaction wanes. This nonlinearity is in addition to changes in reaction rate that may occur as a result of changes in reaction mechanism [Rubie and Thompson, 1985]—such that an important enhancement to hydrodynamic models [e.g., Wong et al., 1997] will be to include reaction rates that vary with thermodynamic potential.

In the reverse reaction, wairakite + H₂O \rightarrow laumontite, the fluid volume decreases 70% faster than the solid volume

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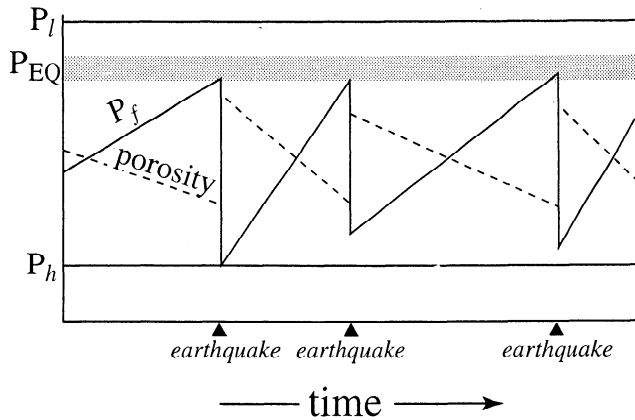


Figure 1. Conventional fault valve behavior. Earthquakes (denoted by triangles) produce near-instantaneous porosity increases and fluid pressure decreases in the rupture region. During interseismic periods, fault-sealing processes cause porosity to decrease and fluid pressure to increase. Eventually, the fluid pressure reaches a level high enough to initiate another earthquake and the cycle begins anew. P_l , lithostatic pressure, P_h , hydrostatic pressure, P_f , fluid pressure, P_{EQ} , pressure at which earthquake is triggered.

increases (Figure 2b and Table 1, reaction B). Every 1 cm³ increase in solid volume (i.e., laumontite produced minus wairakite consumed) requires the consumption of 1.7 cm³ of H₂O. If the initial porosity is greater than about 20%, then enough H₂O will be present in local pores to permit 100% transformation. If the initial porosity is less than about 20%, then all the H₂O in local pores will be consumed prior to 100% transformation. Thus this hydration reaction is limited by the availability of fluid, and its rate may be determined by the rate at which fluid can be drawn into the reaction site.

2.2. Solid-Dominated Reaction

An entirely different situation prevails during solid-dominated reactions. If a rock composed of lawsonite + quartz with H₂O-filled pores undergoes hydration to form laumontite, the ΔV_s is a staggering +29% (Figure 2d and Table 1, reaction D). Concomitantly, the fluid volume decreases only 59% as fast as the solid volume increases ($\Delta V_f/\Delta V_s = -0.59$). If the porosity is <30%, new laumontite grains fill the pore space faster than the fluid is consumed. If the reaction is to consume all available pore space, the fluid must be forced from remaining pores by percolation or hydrofracturing.

In the reverse reaction, laumontite \rightarrow lawsonite + quartz + H₂O, the fluid volume increases at only 59% of the rate at which the solid volume decreases (Figure 2c and Table 1, reaction C). Every 1 cm³ of laumontite consumed produces enough void space for 1.7 cm³ of H₂O. For this reaction to go to completion, additional fluid must flow into the growing pore space.

Table 1. Changes in Solid, Fluid, and Total Volume at STP of Two Reactions in the System CaAl₂Si₄O₁₂•4H₂O

Dehydration		Hydration	
<i>Fluid-Dominated Reaction</i>			
Reaction A. dehydration driven by decreasing P_{H_2O} lm \rightarrow wr + 2 H ₂ O $\Delta V_f = +36$ cm ³ /mol $-\Delta\phi = \Delta V_s = -21$ cm ³ /mol or -10% $\Delta V_{rxn} = +15$ cm ³ /mol or +7% $-\Delta V_f/\Delta V_s = +1.7$		Reaction B. hydration driven by increasing P_{H_2O} wr + 2 H ₂ O \rightarrow lm $\Delta V_f = -36$ cm ³ /mol $-\Delta\phi = \Delta V_s = +21$ cm ³ /mol or +10% $\Delta V_{rxn} = -15$ cm ³ /mol or -7% $\Delta V_f/\Delta V_s = -1.7$	
<i>Solid-Dominated Reaction</i>			
Reaction C. dehydration driven by increasing P_{H_2O} lm \rightarrow lw + 2 qz + 2 H ₂ O $\Delta V_f = +36$ cm ³ /mol $-\Delta\phi = \Delta V_s = -61$ cm ³ /mol or -29% $\Delta V_{rxn} = -25$ cm ³ /mol or -12% $-\Delta V_f/\Delta V_s = +0.59$		Reaction D. hydration driven by decreasing P_{H_2O} lw + 2 qz + 2 H ₂ O \rightarrow lm $\Delta V_f = -36$ cm ³ /mol $-\Delta\phi = \Delta V_s = +61$ cm ³ /mol or +29% $\Delta V_{rxn} = +25$ cm ³ /mol or +12% $\Delta V_f/\Delta V_s = -0.59$	
Phase	Symbol	Composition	Molar Volume [Helgeson et al., 1978]
laumontite	lm	CaAl ₂ Si ₄ O ₁₂ •4H ₂ O	208 cm ³ /mol
wairakite	wr	CaAl ₂ Si ₄ O ₁₂ •2H ₂ O	187
lawsonite	lw	CaAl ₂ Si ₂ O ₈ •2H ₂ O	101
quartz	qz	SiO ₂	22.5
water	H ₂ O	H ₂ O	18

The molar volume of H₂O was fixed at 1 g/cm³; this is correct to within 10% over much of the pressure and temperature range of Figure 3 [Johnson and Norton, 1991]. ΔV_f : fluid volume change; ΔV_s , solid volume change; ΔV_{rxn} , total volume change; $\Delta\phi$, porosity change.

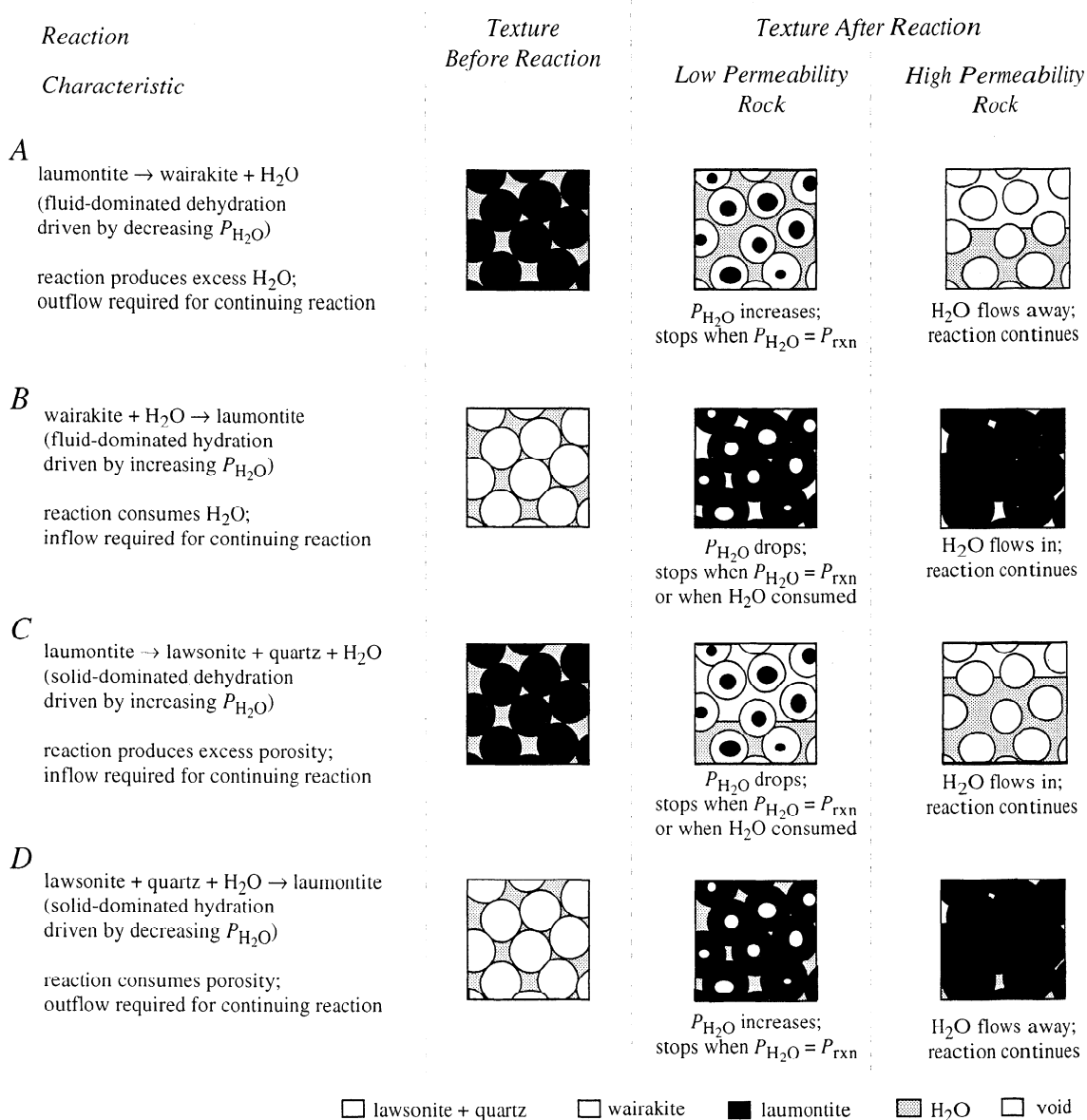


Figure 2. Characteristics of the four types of dehydration and hydration reactions and their influences on fluid pressure and fluid flow in rocks of high and low permeability. At low permeability (second column), changes in P_{H_2O} are limited by the equilibrium pressure of the reaction. At high permeability (third column) reactions are not necessarily limited by changes in P_{H_2O} and can run to completion.

3. Qualitative Implications: Influence of Reactions on Permeability and Porosity

The magnitude of the effect that dehydration and hydration reactions have on the porosity, permeability, and fluid pressure of a rock depends greatly on whether the local permeability is high or low relative to the production or consumption rate of fluid (Figure 2). If the permeability is high enough that fluids produced or consumed by metamorphic reactions do not affect the fluid pressure, then the reaction can only influence porosity. If the permeability is low, permeability and fluid pressure as well as porosity can be dictated by reaction.

3.1. Reactions Following Fault Rupture

Although phase transformations cannot, in general, keep pace with seismic deformation, the change in physical conditions

caused by an earthquake can drive long-term interseismic reactions. The equilibrium relations among solid phases in contact along grain boundaries are determined primarily by lithostatic pressure, whereas equilibria among phases in contact with fluids are chiefly a function of fluid pressure [Bruton and Helgeson, 1983]. Fault rupture can produce a large enough drop in fluid pressure to cause minerals in a fault zone that were stable at high fluid pressure to become unstable after the earthquake and break down to other phases that reflect the lower post-seismic fluid pressure. Coombs [1993] cited numerous field examples of low-temperature dehydration reactions in fault zones that he interpreted to have been caused by earthquake-related falls in pore pressure.

As detailed above, fluid-dominated dehydration reactions (e.g., laumontite → wairakite + H₂O), produce H₂O faster than they generate porosity (Figure 4a). Solid-dominated hydration

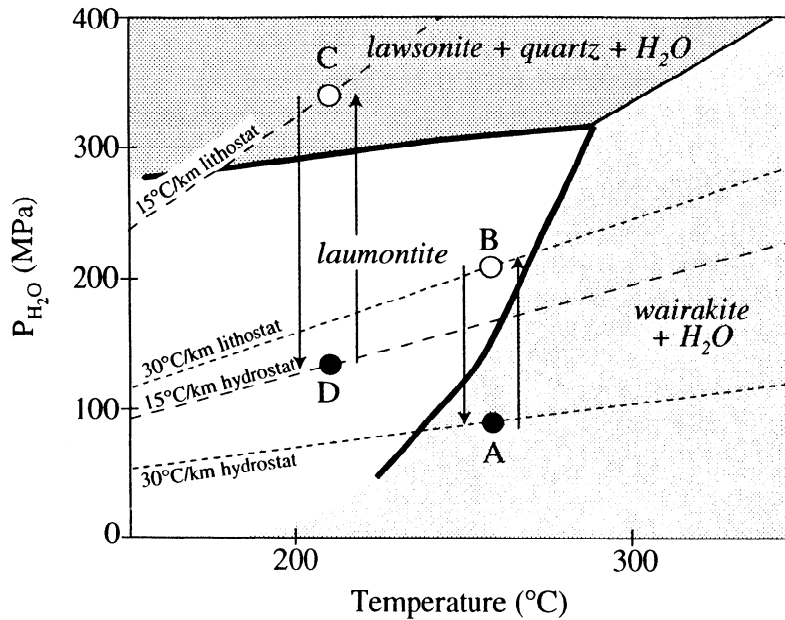


Figure 3. Equilibrium curves for reactions among the phases laumontite, wairakite, lawsonite, quartz, and H₂O. Dashed lines are lithostatic and hydrostatic gradients of ~15°C/km and 30°C/km, computed using fluid and rock densities of 1 and 2.5 g/cm³. Earthquakes cause fluid pressure to drop (down pointing arrows) from near-lithostatic pressures (open circles) where reactions B and C are operative to near-hydrostatic pressures (solid circles) where reactions A and D are operative. Fluid pressures rise during interseismic periods as shown by up-pointing arrows. A, fluid-dominated dehydration reaction; B, fluid-dominated hydration reaction; C, solid-dominated dehydration reaction; D, solid-dominated hydration reaction.

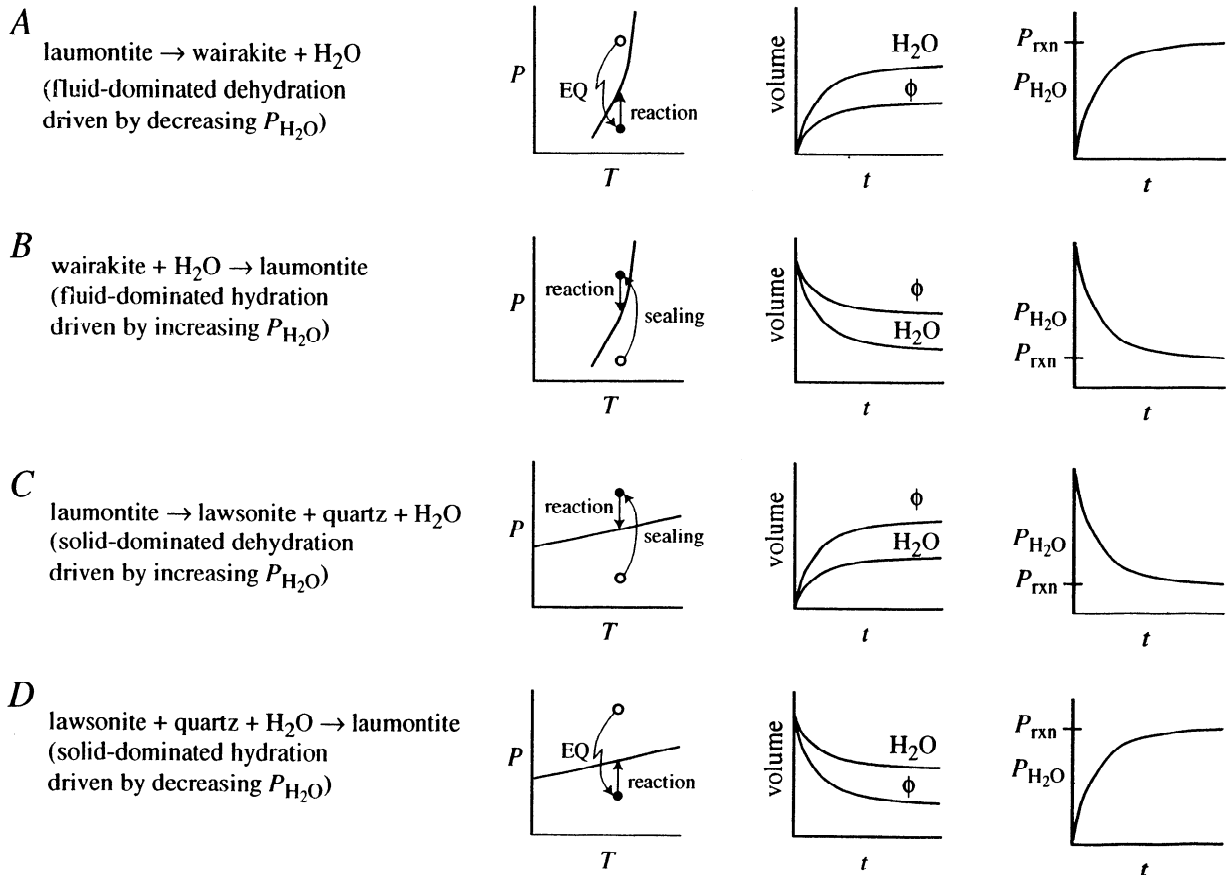


Figure 4. Changes in amount of H₂O, porosity ϕ and fluid pressure P_{H_2O} produced by the four types of hydration/dehydration reactions. Open circles indicate an initial pressure where no reaction occurs. Solid circles indicate pressure immediately after sudden change, and straight arrow indicates change in pressure caused by subsequent reaction.

reactions (e.g., lawsonite + quartz + H₂O → laumontite), consume pore space faster than they take up H₂O (Figure 4d). Both types of reaction produce the same result: at high permeabilities the “excess” H₂O flows away from the reaction zone. At low permeabilities, $P_{\text{H}_2\text{O}}$ increases, and the rate of increase slows as $P_{\text{H}_2\text{O}}$ approaches the equilibrium pressure P_{rxn} .

Thus at high permeability, fluid-dominated dehydration reactions and solid-dominated hydration reactions, both of which can be driven as a result of faulting, can potentially aid or initiate further faulting by producing H₂O that can flow to other sites within the fault zone. At low permeabilities these reactions can partially restore the drop in $P_{\text{H}_2\text{O}}$ caused by faulting (Figure 4). Whether the reaction-produced elevation of $P_{\text{H}_2\text{O}}$ is significant compared to other changes in $P_{\text{H}_2\text{O}}$ depends on the rates of other processes affecting porosity and permeability, and on the pre- and post-seismic stresses relative to P_{rxn} .

3.2. Reactions Preceding Fault Rupture

Fault sealing can increase fluid pressure enough to destabilize minerals in fault zones and promote the growth of phases stable at higher (preseismic) fluid pressures. Solid-dominated dehydration and fluid-dominated hydration reactions can both be active in such situations. The former (e.g., laumontite → lawsonite + quartz + H₂O) produce H₂O more slowly than they create porosity (Figure 4c), whereas the latter (e.g., wairakite + H₂O → laumontite) consume porosity more slowly than they take up H₂O (Figure 4b). During both types of reaction in high-permeability rocks, H₂O is drawn into the reaction zone to maintain constant $P_{\text{H}_2\text{O}}$. At low permeabilities, $P_{\text{H}_2\text{O}}$ decreases during reaction—the rate of decrease depending on the difference from the equilibrium pressure of the reaction, P_{rxn} .

Thus at high permeability, fluid-dominated dehydration reactions and solid-dominated hydration reactions, which can be driven as a result of fault sealing, inhibit faulting by drawing H₂O from the country rock or the fault zone. Under low-permeability conditions, solid-dominated dehydration and fluid-dominated hydration reactions both can partially reverse the increase in $P_{\text{H}_2\text{O}}$ caused by sealing. Whether the reduction in $P_{\text{H}_2\text{O}}$ is significant depends on the rates of reaction relative to the rates of sealing.

4. Quantitative Implications: Rates of Hydration/Dehydration and Sealing Reactions

Quantitative models of porosity and fluid pressure change were presented by Hanshaw and Bredehoeft [1968] and developed further, most recently, by Wong et al. [1997] but applied specifically only to fluid-dominated dehydration reactions. Here we explore qualitatively the effects of fluid-dominated and solid-dominated, hydration and dehydration reactions.

Hydration/dehydration reactions are only one among several processes collectively referred to as sealing that influence permeability and fluid pressure, including crack healing [Smith and Evans, 1984]; precipitation of minerals, such as quartz, from a fluid [Rimstidt and Barnes, 1980]; and solution-transfer, diffusion, and dislocation creep [Blanpied et al., 1995]. The relative importance of these processes varies under the range of fluid pressures, effective pressures, temperatures, and fluid compositions in the Earth, but each can be calculated after some simplifying assumptions.

Walther and Wood [1984] argued that at small degrees of overstepping, numerous reactions involving the interface-

controlled dissolution of hydrous or anhydrous phases within an H₂O-rich fluid display a consistent relationship between reaction rate (dm/dt), temperature (T), and reaction free energy (ΔG_{rxn}):

$$\frac{dm}{dt} = -K \frac{\Delta G_{\text{rxn}}}{RT} = -10^{-(2900/T - 6.85)} \frac{\Delta G_{\text{rxn}}}{RT}$$

If the rate constant K is written as an Arrhenius equation,

$$K = Ae^{-\Delta G/RT}$$

the preexponential constant A is $10^{6.85}$ and the apparent activation energy is:

$$\Delta G^* = \ln(10) \times 2900 \times 8.314 \text{ J/mol} = 55.5 \text{ kJ/mol.}$$

In other words, Walther and Wood suggested that reactions controlled by interfacial attachment/detachment of atoms that diffuse rapidly through an H₂O-rich fluid all have activation energies in the neighborhood of 55 kJ/mol. Their prediction does not apply to transformations involving diffusion through a solid nor to reactions controlled by transport through a fluid. Similarly, Lasaga [1984] noted that activation energies for dissolution reactions generally lie between 40 and 80 kJ/mol, with a mean of ~60 kJ/mol. Pertinent to the reactions used in this paper as examples, Jové and Hacker [1997] determined that the activation energy for the wairakite → laumontite + 2 H₂O reaction lies within this range, at 72 ± 13 kJ/mol.

Activation energies for quartz dissolution or precipitation in the presence of excess H₂O are similar—roughly 75 kJ/mol [Rimstidt and Barnes, 1980; Dove and Crerar, 1990; Brantley, 1992; Dewers and Hajash, 1995]; thus the rates of interface-controlled hydration/dehydration reactions and quartz dissolution/precipitation show similar temperature dependencies.

The rate of change of porosity caused by the precipitation of aqueous silica as quartz can be compared quantitatively to the rate of porosity change due to hydration/dehydration reactions—take the laumontite → wairakite reaction as an example. Quartz precipitation rate depends on temperature, the degree of supersaturation of the fluid, and the activities of aqueous H₄SiO₄, H⁺, H₂O, and organic compounds [Rimstidt and Barnes, 1980; Abercrombie et al., 1994]. Assuming intermediate pH and that the aqueous species have unit activities, the rate of quartz precipitation can be calculated from Rimstidt and Barnes' [1980] data. As an example, in the San Joaquin basin the degree of silica supersaturation relative to quartz varies from ~10 at 100°C to ~1 at 150°C [Abercrombie et al., 1994]. At higher temperatures, San Joaquin basin fluid is expected to be undersaturated and dissolving quartz: the predicted degree of undersaturation is ~0.5 at 200°C [Abercrombie et al., 1994]. Rimstidt and Barnes' experimental data yield for these conditions a precipitation rate of 0.1 μm/yr at 100°C and a dissolution rate of 0.9 μm/yr at 200°C (Table 2). Laumontite growth rates calculated using the equation of Walther and Wood [1984] and reaction free energies calculated using SUPCRT92, range from 0.05 to 0.7 μm/yr for the same temperature interval at 100 MPa. At 100°C, quartz and laumontite growth rates are the same order of magnitude. At 150°C, where the fluid is at exactly quartz saturation, the laumontite reaction is unopposed by silica precipitation. At higher temperatures, laumontite grows while quartz dissolves. Although the effects of grain-grain contact stresses, fluid composition, fluid pressure, and fluid flow, have been ignored in this simple exercise, the calculations demonstrate that rates of mineral growth as a result of reaction with a fluid can be comparable to rates of quartz precipitation and even run in the opposite sense.

Table 2. Growth Rates of Quartz and Laumontite

	Temperature, °C		
	100	150	200
Degree of supersaturation	10	1	0.5
Quartz growth rate, $\mu\text{m}/\text{yr}$	0.1	0	-0.9
Laumontite growth rate, $\mu\text{m}/\text{yr}$	0.05	0.3	0.7

5. Reactions and Fault Valve Behavior

Sealing processes reduce porosity and increase fluid pressure, decreasing the effective stress and increasing the likelihood of fault rupture. Phase transformations can enhance or counteract this process, depending on the equilibrium pressure of the reaction, the local permeability, and the local fluid pressure (Table 3).

5.1. High-Permeability Fault Zones

At high permeabilities, fluid-dominated dehydration reactions and solid-dominated hydration reactions may pump H_2O from one part of a fault to distant sites by mechanisms outlined above. Processes at those distant sites may be affected by this fluid influx if the fluid being pumped is enriched or impoverished in Si or other species of influence such as H^+ . Likewise, at high permeabilities, fluid-dominated hydration reactions and solid-dominated dehydration reactions may draw H_2O from distant sites, potentially removing solutes and inhibiting sealing processes, and they can transfer the solutes to the reaction site where accelerated sealing could result. If permeabilities are low, however, reactions may strongly influence faulting.

5.2. Fault Valve Behavior of Fluid-Dominated Reactions

At low permeabilities, fluid-dominated dehydration reactions increase $P_{\text{H}_2\text{O}}$ ("rxnA" curves Figure 5) until the pressure reaches the equilibrium pressure of the reaction, P_{rxn} . The porosity increase of fluid-dominated dehydration reactions works against the porosity decrease produced by fault sealing processes ("sealing" curves Figure 5; see Table 3). Whether the net change in porosity ("sum" curves Figure 5) is positive or negative is determined by the relative rates of the competing processes and the timescale over which both operate. If diagenetic/metamorphic reactions dominate sealing processes, the porosity will increase (Figure 5b); if not, porosity will decrease (Figure 5a). However, the sum effect of both processes, regardless of rates, is an

increase in $P_{\text{H}_2\text{O}}$. As $P_{\text{H}_2\text{O}}$ reaches P_{rxn} (at the time indicated by the vertical dashed line in Figure 5), the reaction slows and ultimately stops.

If sealing processes continue to decrease porosity and to build $P_{\text{H}_2\text{O}}$ above P_{rxn} ("sealing" curves Figure 5), eventually the fluid-dominated hydration reaction can begin ("rxnB" curves Figure 5), reversing the progress of the earlier reaction. This reaction decreases porosity, but the reduction in $P_{\text{H}_2\text{O}}$ is opposite to that produced by sealing processes. If reaction is subordinate to sealing processes (Figure 5a), eventually $P_{\text{H}_2\text{O}}$ may become high enough to trigger an earthquake (at P_{EQ}) and the cycle can begin anew. If reaction is faster than sealing (Figure 5b), $P_{\text{H}_2\text{O}}$ fluctuates above P_{rxn} until the reacting minerals are consumed; after that $P_{\text{H}_2\text{O}}$ is controlled solely by nonreaction sealing processes. Pore pressure may rise high enough eventually to trigger another seismic event, but in a system controlled by fluid-dominated reactions (Figure 5b), earthquakes are much farther apart than they are in a system controlled by sealing processes (Figure 5a).

5.3. Fault Valve Behavior of Solid-Dominated Reactions

Solid-dominated hydration reactions increase $P_{\text{H}_2\text{O}}$ and decrease porosity ("rxnD" curves Figure 6). Other sealing processes produce the same effects ("sealing" curves Figure 6). As $P_{\text{H}_2\text{O}}$ nears P_{rxn} (at the time indicated by the vertical dashed line in Figure 6), the reaction slows and sealing processes dominate. Once $P_{\text{H}_2\text{O}}$ has been pushed far enough above P_{rxn} by sealing, the solid-dominated dehydration reaction can begin ("rxnC" curves Figure 6). The porosity increase of the reaction works against the porosity decrease of sealing processes, and the reduction in $P_{\text{H}_2\text{O}}$ counteracts the $P_{\text{H}_2\text{O}}$ increase caused by sealing. If reaction is subordinate to sealing processes, $P_{\text{H}_2\text{O}}$ eventually becomes high enough to cause faulting (at P_{EQ}) and the cycle can repeat (Figure 6a). In fault zones where solid-dominated reactions are faster than sealing processes, $P_{\text{H}_2\text{O}}$ fluctuates above P_{rxn} , just as for fluid-dominated reactions.

6. Limitations

This study focused on the most fundamental interactions among hydration/dehydration reactions, porosity, and fluid pressure and has ignored some aspects that may bear further inquiry. I have assumed that $P_{\text{H}_2\text{O}}$ less than confining pressure is the result of sublithostatic fluid pressures of pure H_2O , but $P_{\text{H}_2\text{O}}$ can be less than the total fluid pressure if other volatiles such as hydrocarbons or CO_2 are present [e.g., Greenwood, 1961; Barnes and Ernst, 1963]. Variations in $P_{\text{H}_2\text{O}}$, which drive hydration/dehydration reactions considered here, are distinct from

Table 3. Changes in Porosity and $P_{\text{H}_2\text{O}}$ Caused by Reactions and Other Sealing Processes in Low Permeability Rocks.

Process	Porosity	$P_{\text{H}_2\text{O}}$
Sealing: precipitation/creep/crack healing	decrease	increase
Fluid-dominated dehydration reaction (A)	increase	increase
Fluid-dominated hydration reaction (B)	decrease	decrease
Solid-dominated dehydration reaction (C)	increase	decrease
Solid-dominated hydration reaction (D)	decrease	increase

Letters in parentheses refer to example reactions in Table 1.

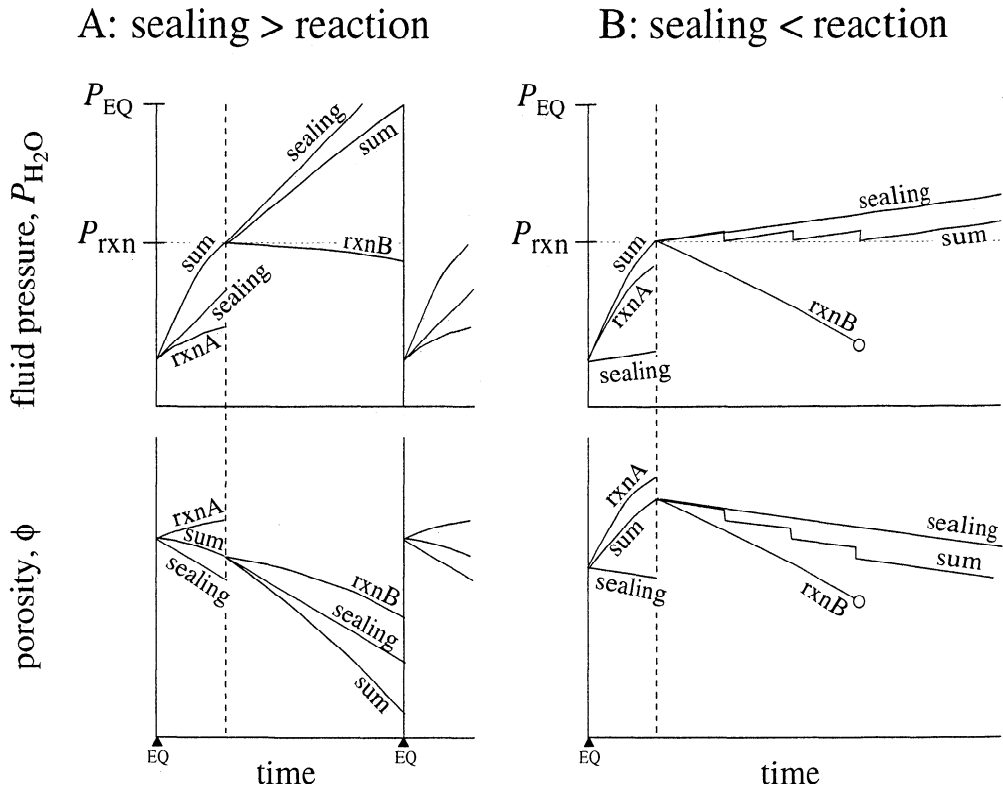


Figure 5. Cycles in fluid pressure and porosity resulting from fluid-dominated reactions and fault sealing processes. a) Effects of reaction are subordinate to those of sealing processes. b) Effects of reaction dominate those of sealing processes. P_{rxn} indicates equilibrium pressure of reaction. P_{EQ} indicates fluid pressure necessary to trigger an earthquake. The small triangles labeled “EQ” denote earthquakes. “rxnA” and “rxnB” match reactions in Table 1. Circles denote end of reaction caused by consumption of solid reactants. Compare with Figure 1.

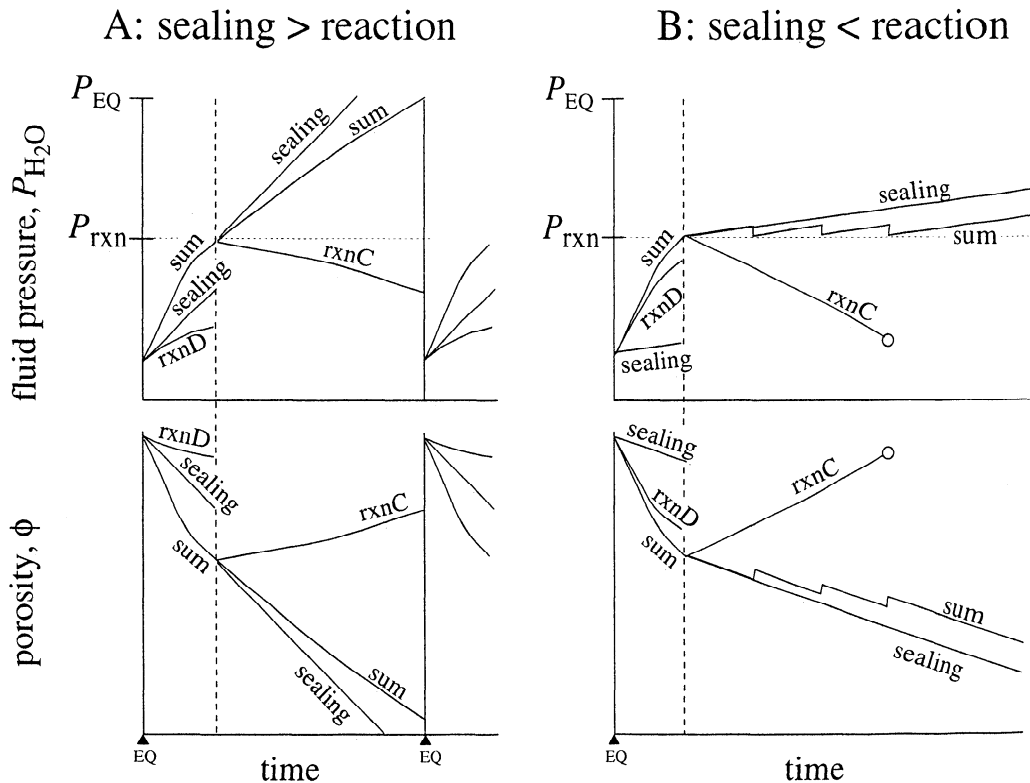


Figure 6. Cycles in fluid pressure and porosity resulting from solid-dominated reactions and fault sealing processes. See caption of Figure 5 for full explanation.

variations in total fluid pressure, which influence mechanical behavior. Changes in fluid composition brought about by the introduction or withdrawal of other volatile species can also drive phase transformations that depend on P_{H_2O} . For example, a fault could be entirely plugged at some level with laumontite in equilibrium with a pure H_2O fluid. If CO_2 migrates up the fault to the laumontite plug, the reduction in P_{H_2O} could cause the laumontite to break down to wairakite. This reaction creates porosity that would allow the CO_2 to move farther up the fault. In this manner the CO_2 could create its own dynamic porosity wave and move up the fault until it reached the top of the laumontite zone. Multicomponent fluids, where one component controls the rates of phase transformations and the other controls sealing, might have particularly significant influences on the behavior of fault zones.

One important limit to the effectiveness of transformations in fault zones is that ultimately, every reaction is limited by the mass of solid or fluid reactants that are present at or can be delivered to the reaction site. At moderately low permeability, precipitation and crack healing can continue forever as long as solutes can be drawn into cracks, whereas phase transformations are limited by the amount of solid reactants. Conversely, at very low permeabilities, some phase transformations may continue as a closed system, consuming local pore fluid and filling local pores, while precipitation can be inhibited if solute cannot be drawn into cracks.

Another limit is provided by the rate at which heat required (generated) by a reaction can flow to (from) the reaction site [Lasaga, 1986; Ridley, 1986]. The discussion in this paper applies strictly only to situations where the rate of heat flow does not limit reaction rates. Qualitatively, in the absence of heat flow, the effect of reaction enthalpy is to retard reaction rate; exothermic reactions (B and C in this paper) cool the system toward equilibrium and endothermic reactions (A and D) increase the local temperature toward equilibrium. Quantitative assessment of the interplay among heatflow, fluid flow, reaction rate, sealing rate, and fault slip rate is an important objective [Rutter and Brodie, 1990].

Although solid-dominated reactions produce more provocative mechanical effects, they are far less common, within the crust, than fluid-dominated reactions. At higher pressures, however, reactions of gentle Clapeyron slope are increasingly important, and interactions described in this paper are pertinent to subduction zones. For example, the breakdown reactions of the hydrous phases chloritoid, lawsonite, amphibole and serpentine [Pawley and Holloway, 1993; Ulmer *et al.*, 1994] are solid dominated; devolatilization in subducting mafic slabs thus does not necessarily mean an increase in pore pressure.

We have considered the mechanical effects of reactions only from the simple Coulomb fracture perspective of strength linearly related to effective pressure. Reactions have other important rheological effects, including, for example, changing stress concentrations around pores, causing change from faulting to cataclastic flow as a result of increasing effective pressure [e.g., Hirth and Tullis, 1989], and changing the efficacy of stress solution [e.g., Rutter, 1983]. As mentioned repeatedly above, permeability exerts strong influence on rates of (de)hydration reactions, and, thus, fluid pressure and fluid flow. Ko *et al.* [1997], for instance, showed that an initial 0.5% dehydration of a gypsum rock produced weakening due to increased fluid pressure in isolated pores and that greater extents of dehydration caused hardening because the evolved fluid was able to escape.

7. Conclusions

The conventional "fault valve" paradigm should be modified to take account of the effects of diagenetic/metamorphic reactions. As expected, fluid-dominated dehydration reactions increase fluid pressure and porosity, and hydration reactions decrease fluid pressure and porosity. Surprisingly, however, solid-dominated dehydration reactions actually decrease fluid pressure while increasing porosity, because the rate at which solid phases are consumed exceeds the rate at which fluid is produced. Solid-dominated hydration reactions are equally interesting in that they increase fluid pressure while decreasing porosity. Depending upon physical conditions, the rates of porosity and fluid pressure change effected by diagenetic/metamorphic reactions may be slower or faster than conventional fault sealing processes such as precipitation, crack healing, and solution-transfer, diffusion, and dislocation creep. The effect that diagenetic/metamorphic reactions have on fault valve behavior is complex: reactions either aid sealing by increasing fluid pressure and decreasing porosity or oppose sealing by decreasing fluid pressure and increasing porosity. Moreover, any reaction triggered by an earthquake will likely reverse itself before the next earthquake occurs—as a result of rising fluid pressure—and thus the fluid pressure and porosity effects of the reaction will also reverse. Regardless, reactions accelerate the fluid pressure increase during the early stages of a fault valve cycle and retard the fluid pressure increase during the waning stages, modifying fault valve behavior.

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