Implications of replacement for reaction–transport modeling

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Abstract

Mineral replacement in rocks consists of growth of guest mineral and dissolution of host. The two reactions are coupled by the grain–grain stress generated by growth of the guest grain in a rigid or very viscous rock in which it has initially no available room. This stress self-adjusts to make the volumetric rates of guest growth and host dissolution equal to each other, which accounts for the volume conservation typical of replacement. Volume preservation during replacement is required by conservation of mass and momentum as well. The two reactions are also simultaneous and proceed by a sequence of many tiny alternating increments; where these increments are small enough, internal textural details of the host grain or grain aggregate are morphologically preserved (as ghost textures) by the replacement. The strong variation of mineral reaction rates with stress required by replacement is evidenced also experimentally. Reported widespread replacement in many rocks (laterites, diagenesis of siliciclastics and carbonates, metasomatic ores, metamorphic rocks, and hydrothermal alteration) warrants creating water–rock reactive transport models that predict when and where in a system replacement should take place.

Current geochemical models implicitly view replacement as sequential, uncoupled dissolution of host and growth of guest; this sequence of reactions may also occur in rocks, but crucially differs from replacement. Implications of replacement for water–rock reaction modeling include:

1. balancing of replacement reactions on volume;
2. use of Helmholtz (rather than Gibbs) free energies of minerals involved in replacement;
3. taking account of the strong stress-dependence of mineral growth and dissolution rates in rocks; and
4. taking account of possible accommodation of growth by local deformation (as well as pressure solution) of the host rock, and of the effect of strain rate (= growth rate) on local rock viscosity. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mineral replacement is the striking and widespread phenomenon whereby a guest authigenic mineral grain or aggregate chemically comes to occupy the space previously occupied by the host grains while preserving ghost textures of them. The purpose of this note is to bring out the uniqueness of the reactions and conditions that produce replacement in rocks, and to point out consequences and implications of replacement for the reaction–transport modeling of water–rock interactions. Current published models do not take account of replacement reactions, because they contain no provision for their origin, which has

remained obscure in spite of Lindgren's work (1912 and later). We summarize below a theory of the genesis of replacement which accounts well for its petrographic features (Maliva and Siever, 1988; Merino et al., 1993, 1994; Nahon and Merino, 1997). The theory incorporates a rheological–kinetic view of replacement and provides for possible deformation of the host rock (Nahon and Merino, 1997). Also discussed here briefly are: recent experimental work on the dependence of mineral reaction rates on stress; application of the momentum and mass conservation conditions to replacement; and current work on accommodation of growth by both pressure solution and local deformation of the host rock (Fletcher and Merino, 1997a, b).

2. Replacement

The petrographic characteristics of replacement are that the volume and textural details of an A host crystal or crystal aggregate are preserved by the new mineral, B, the guest. Excellent descriptions, photomicrographs, criteria, and discussion of replacement are given by Bastin (1950, pp. 33–53), and by many others before and since. In Fig. 1 a whole outcrop of sandstone in Senegal has been replaced by gibbsite, hematite, and kaolinite during lateritic weathering, obviously preserving undeformed the morphology of the cross bedding and the bulk volume (photo in Fig. 1 and description were provided by D. Nahon, Univ. Aix-Marseille III). Where the guest mineral is not one crystal, but an aggregate of crystals as in the case of this outcrop there is the potential for the aggregate to grow with its own built-in intercrystalline microporosity. The volume that gets preserved by replacement is now the *bulk* volume, that is, old volume = new volume + microporosity. Regardless of the genetic role of this microporosity (which may have to do with the need to let ions in and out of the current replacement site), one can still include it phenomenologically in mass balance calculations, see below just after Eq. (8). Another impressive mega-replacement is that of Upper Precambrian and Lower Paleozoic rocks of the US midcontinent by K-feldspar, reported by Hay and colleagues (Hay et al., 1988; Duffin, 1989; Duffin et al., 1989).
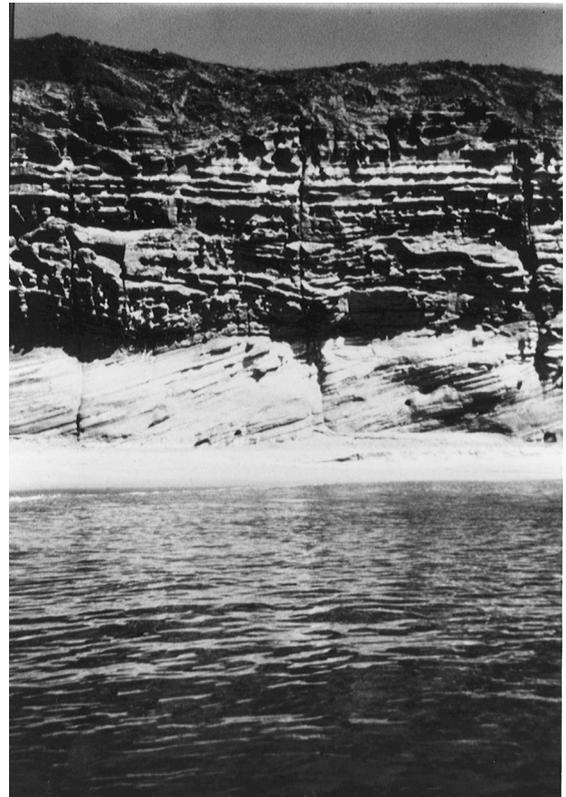
In Fig. 2, modified from Pettijohn (1957, plate

Fig. 1. Ten-meter-thick lateritic weathering profile developed after a Cretaceous glauconitic sandstone in western Senegal. Below the one-meter thick iron crust (black) at top, the sandstone is completely replaced by gibbsite, kaolinite, and hematite. Original cross-bedding of the bottom third and bedding of upper two thirds are preserved undeformed by the saprolite, implying that no change in bulk volume has taken place during lateritization. This is a replacement of an entire formation. (Photograph and description provided by D. Nahon, Univ. of Aix-Marseille III.)

39E), a quartz overgrowth has developed during diagenesis within a calcium carbonate oolite without bursting the oolite or deforming its concentric layers of inclusions (also Hesse, 1989). Obviously the quartz replaced the calcium carbonate preserving the original volume. The replacement is called automorphic because the quartz imposed its own crystal shape. (Pyrite and garnet also adopt their own crystal shapes easily as they replace other minerals.)

In Fig. 3, modified from Wallace (1976), quartz has replaced alkali feldspar clasts during diagenesis of a Precambrian sandstone in Utah, preserving the volume and shape of the initial feldspar grain (hence this replacement is called pseudomorphic). Wallace's
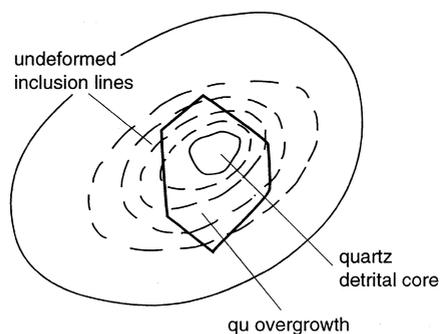
From Pettijohn, 1957

Fig. 2. Partial replacement of a carbonate oolite by quartz during diagenesis of the Pennsylvanian Hale Formation (Fayetteville, Arkansas). Sketch drawn after plate 39E in Pettijohn (1957). The quartz overgrowth replaced the carbonate without bursting the oolite, and without displacing the lines of inclusions, which still preserve the original concentric structure of the oolite. The overgrowth developed its own crystal faces (hence the replacement is called automorphic).

petrographic description is particularly compelling: the replacements can be conclusively said to be in-situ because they are in optical continuity with overgrowths on detrital grains adjacent to the feldspar clasts. When the overgrowths started to pressure-
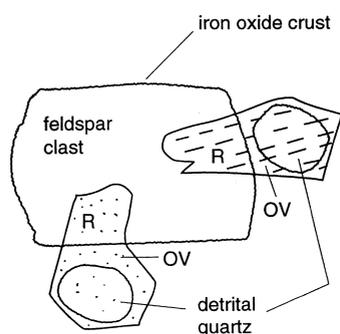
From Wallace, 1976

Fig. 3. Replacement of portions of an alkali feldspar sand grain by quartz in the Uinta Mountain Group, Utah. Sketch drawn after figures in Wallace (1976). Outlines of detrital grains are marked by dark thin crusts of iron oxide. Overgrowths, OV, on quartz clasts continued to grow into the feldspar clast without deforming its boundary, still preserved by the iron oxide crust, thus showing the replacement preserved volume as well as shape. Preservation of the old grain shape makes this replacement pseudomorphic. Each replaced portion, R, is in optical continuity (shown with the dashed or stippled patterns) with its overgrowth and corresponding clast, showing that the replacement occurred in situ.

dissolve the feldspar, the margin of the feldspar remained fixed in space, as marked by a thin crust of early iron oxide cement, proving that solid volume was preserved exactly.

Provided there is sufficient affinity for its growth, any mineral may in principle replace any neighbor, regardless of whether the two have an element in common, of whether the two are isostructural or not, and of which mineral has the greater formula volume. Replacement is in fact ubiquitous or widespread in: laterites (e.g., references listed in Nahon and Merino, 1997), pedogenic calcretes (e.g., references listed in Wang et al., 1994), and other soils (e.g., Buciak and Merino, 1996); in the diagenesis of sedimentary rocks (e.g., Pettijohn, 1957 (e.g., plate 39E,F); Coombs, 1954; Millot, 1964; Cook, 1970; Merino, 1975; Wallace, 1976; Williams et al., 1954, see numerous cases under 'replacement'; Maliva and Siever, 1988; Hesse, 1989; Tucker and Bathurst, 1990; and many more); a diagenetic mega-replacement mentioned above of uppermost Precambrian and lower Paleozoic rocks of the North-American mid-continent by low-temperature K-feldspar is reported by Hay and colleagues (Hay et al., 1988; Duffin, 1989; Duffin et al., 1989). Replacement is also widespread or ubiquitous in metamorphic and metasomatic rocks and ores (e.g., Lindgren, 1912, 1918, 1925; Bastin et al., 1931; Bastin, 1950; Lufkin, 1983; Biino, 1994 and many more); in serpentinization (e.g., Wicks and Whittaker, 1977); and in hydrothermally altered rocks.

Preservation of the *morphology* of the A-host's internal details (such as twin planes, cleavages, inclusions) or texture (such as fossil features, wood cells, or sedimentary or other structures) requires that B growth and A dissolution be simultaneous. (If grain or grain aggregate A had dissolved first, wholesale, there would be no structural, textural, or intra-crystalline details left for B to preserve when it grew later.) Preservation of volume requires that the two simultaneous reactions had to proceed with mutually equal volumetric rates, and that therefore the two had to be somehow coupled. Otherwise, why should two reactions—say, growth of pyrite and dissolution of quartz—proceed at the same rate? This kinetic and coupled nature of replacement was grasped by Bastin et al. (1931, p. 603, Fig. 12), who, commenting on an automorphic replacement of

schist by large pyrite cubes, wrote: ''A further implication not generally recognized is that the several minerals of the schist must have been replaced at essentially the same *rate*, a somewhat astonishing fact in view of the diverse solubilities of these several minerals under most circumstances.'' It was also recognized by Lindgren (1912), Carmichael (1986), Maliva and Siever (1988).

Thus, the petrographic characteristics of replacement imply that the two 'half' reactions that are always involved in producing a replacement—growth of guest B and dissolution of host A—are simultaneous, adjacent, and coupled.

Note that the term 'replacement' has been used also, confusingly, to denote cases where a secondary pore produced by dissolution is later filled, wholly or partly, by cement (e.g., Milliken, 1989, Davidsson et al., 1994, and comment by Merino, 1995). Because here the two 'half' reactions are separated by a time gap, are uncoupled, and do not necessarily preserve volume (since the cementation is accidental—it may or may not take place), it seems advisable to use the term as it has always been used by alert petrographers, namely to denote the phenomenon that preserves volume and (often, but not always—see below) ghost textures.

3. Genesis of replacement

In the hypothesis proposed by Merino et al. (1993); Nahon and Merino (1997, part II), as the guest mineral grows (unless it grows in a pore) it must exert a stress on its neighbor grains, the hosts, because there is otherwise no room to grow into. This stress has been called induced stress (Carmichael, 1986); since early in this century, force of crystallization (e.g., Maliva and Siever, 1988); and, in translation, excess pressure (Ostapenko, 1976). If the rock is locally rigid or viscous enough, that local growth-driven stress between guest and host has two immediate effects: it must increase the solubility and rate of pressure solution of the host, A, and it must decrease the rate of growth of the guest itself, B. (This decrease results from the stress-driven increase in the solubility of B, which brings down the supersaturation that drives B growth.) The two volumetric rates—growth of guest B and dissolution of host A—thus are coupled

through the grain/grain, growth-driven stress, and necessarily evolve in opposite ways (one up, the other down) until they quickly become equal (Nahon and Merino, 1997, Fig. 7). From this point on, they remain equal, with the A/B stress *self-adjusting* to that value for which the two rates become equal. This is why replacement preserves volume. Because the two reactions proceed by alternative minute increments, internal morphological or textural details of the host grain that are larger in scale than those minute increments should be preserved also (as so-called ghost textures)—which accounts for the other crucial petrographic characteristic of replacement. The intervention of stress in the replacement of a plagioclase by albite is evident in a photomicrograph of an experiment by Scholz et al. (1995), where the partly-unreplaced host grain is strained. Ostapenko (1976) measured the force of crystallization on the solid grains developed by the replacement of periclase by brucite at various temperatures and pore water pressures in samples packed in steel cylinders. Ion transport generally needed for replacement is probably nonlimiting, since occurrences of replacement are so common in various rock types.

The idea that replacement proceeds by dissolution-precipitation was explained by among others Carmichael (1969, p. 246) and is widely adopted, to the extent that replacement is often taken as synonymous with ''dissolution-precipitation''. But, not involving the growth-driven stress we discuss above, the idea does not account for the systematic ability of replacement in rocks of all kinds to preserve both volume and internal textural details — the very characteristics that define replacement petrographically. Carmichael said that the incongruent dissolution-precipitation mechanism he described could operate ''holding constant any of several extensive variables [such as the volume], depending on how the boundaries of a system are defined.'' However, how the system often ''knows'' to apply to itself the constant-volume boundary condition (thus yielding replacement, which is widespread) was left by Carmichael undiscussed.

Current geochemical modeling of water–rock reactions—whether of the reaction–path type (Helgeson, 1968, Bethke, 1996) or of the continuity type, reviewed by Steefel and Lasaga (1994)—does not

include the coupled reactions involved in producing replacement in rocks. The petrographic characteristics and occurrence of replacement have been well known for a hundred years, but awareness of its physico-chemical, petrological, and modeling implications lags behind in spite of both early (Lindgren, 1912, Bastin et al., 1931) and recent (Ostapenko, 1976, Carmichael, 1986, Maliva and Siever, 1988, Dewers and Ortoleva, 1989) insight.

In summary, replacement is driven by supersatura-tion with respect to a particular mineral at a point in a rock. The rock must be rigid enough (or viscous enough on the time scale of the replacement) for replacement to take place—otherwise the grain–grain stress locally developed by growth would instead physically displace the host grains, producing local deformation or creep, which is also possible where local rock viscosity is low enough (Nahon and Merino, 1997, pp. 410–412). In the model, replacement fundamentally requires a strong depen-dence of mineral growth or dissolution rates on stress: it is thanks to that stress dependence that the rates can become mutually equal and yield the observed volume preservation. Volume constancy is imposed on the local system by sufficient rigidity, or by sufficient viscosity. Replacement is thus best under-stood as one consequence of a rheological–kinetic phenomenon.

The dependence of mineral rates on stress is probably the same regardless of whether the stress is tectonic (or applied on the sample in an experiment) or growth-generated, but it is only growth-generated stress that (as argued above) can produce replacement.

4. Dependence of mineral rates on stress: experiments

Several authors have obtained experimental evidence for the operation and kinetics of pressure solution under applied stress. Hellmann et al. (1995) have demonstrated pressure solution in a halite aggre-gate (with various circulating fluids) under triaxial stress, and have measured its rate. Hickman and Evans (1995) also give evidence for pressure solution plus mass transfer through intergranular fluid films at single halite–clay contacts. Other experiments link compactional porosity loss to a (chemical) pressure

solution mechanism largely by microtextural evidence, or by fitting data to theoretical rate equations (Spiers and Schutjens, 1990, Schutjens, 1991, De Meer and Spiers, 1997, Tenthorey et al., 1998). There is limited direct evidence of a link between deformation and mineral–fluid reaction kinetics, except perhaps in the realm of defect-influenced reaction kinetics (Brantley et al., 1986). Working with an experimental design more used in rock mechanics experiments than in geochemical kinetics studies and using naturally rounded quartz sand, Elias and Hajash (1992) showed a heightened concentration of dissolved silica, above silica solu-bility, that was sustained as long as an effective pressure (defined as the difference between confining and pore pressures) was applied to the sand sample. These experiments were conducted under pressure and temperature conditions typical of late diagenesis; a flexible Teflon jacket enclosing the sand pack allowed the maintenance of effective pressures. When effective pressures were removed, the excess silica above quartz solubility slowly vanished. This suggests that it was the *nonhydrostatic* stress applied at grain boundaries (and not strain effects, such as microfracturing, or production of ultrafine and highly soluble particles, or any crystal plastic deformation) that caused the elevated silica concentration in the pore fluid.

In a series of similar experiments, Dewers and Hajash (1995) showed that reaction kinetics is also enhanced in the presence of effective pressure. This is shown in Fig. 4, and apparently is independent of grain size. This enhanced dissolution rate, the stress-enhanced silica solubility (above no-stress quartz solubility), and the time-dependent compaction rates all shared the same exponential dependence on effective pressure,

$$rates, soly \sim \exp(\alpha P_e) \tag{1}$$

where the coefficient measured was similar in all cases, and P_e is effective pressure. In addition, rates of compaction determined from mechanical data on pore volume loss coincided well with rates of com-paction calculated from the observed stress-enhanced reaction rates. This indicates a direct effect of applied stress on reaction rates, and that the response of stressed grain contacts results in measurable changes in pore fluid chemistry.
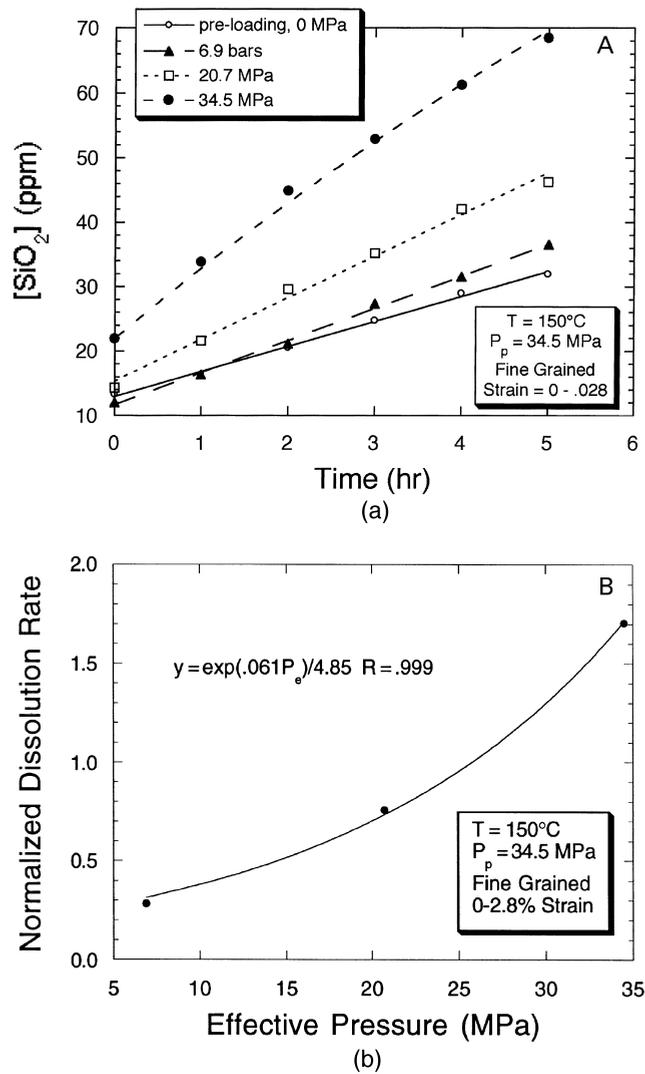
Fig. 4. Pressure solution of quartz sand in a column under different effective pressures from zero to 34.5 MPa at 150°C. At start of experiment, a sudden water flow rate is imposed through the sand. Water samples are removed sequentially at the outlet. Successive water aliquots have gradually longer residence times, thus higher silica concentrations with increasing time (A). From the data in (A), the calculated normalized dissolution rate increases exponentially with effective pressure (B). From Dewers and Hajash (1995).

5. Mass and momentum conservation

Because of the dependence of rates on stress, models of replacement require additional equations describing conservation of momentum. These are a force balance relation, a kinematic condition, and a constitutive law describing the macroscopic rock rheology. Assuming a hydrostatically stressed medium and Newtonian rheology (i.e., constant viscosity), these relations when combined yield a single Navier–Stokes equation coupling rock flow and nonuniform pressure distribution (Dewers and Ortoleva, 1989):

$$-6\eta^{-1}\nabla P^m + 3\nabla^2\vec{u} + \nabla(\nabla\cdot\vec{u}) = 0 \qquad (2)$$

where P^m is the mean stress or pressure, u is the rock flow velocity, and η is the bulk shear viscosity of rock flow. The Newtonian rheology can be replaced by

more realistic expressions for viscous flow. The divergence of the rock flow velocity is not zero (as for an incompressible medium), but is a function of the volumetric growth rates of each reactive solid phase. In other words, the rock is allowed to locally expand or contract by growth or dissolution of minerals.

As the viscosity approaches zero, the rock easily deforms on the time scale of reaction, and Eq. (2) yields

$$\nabla P^m = \vec{0} \qquad (3)$$

which is required in order to keep the first term in Eq. (2) finite. In other words, the mean effective stress or pressure is constant in space. This is the condition implicitly assumed in current geochemical modeling over a range of P, T, and time scales. It means that growth and dissolution of minerals are physically unconstrained.

If on the other hand the viscosity tends to infinity, Eq. (2) yields

$$3\nabla^2 \vec{u} + \nabla(\nabla \cdot \vec{u}) = 0 \qquad (4)$$

If there is no imposed rock flow at the boundaries of the system under consideration, and if the system is closed with respect to solute transport, then Eq. (4) simplifies to

$$\nabla \cdot \vec{u} = 0 \qquad (5)$$

which states that over a system large enough to be considered closed, rock flow is divergence-free, or that volume is constant, and that pressure becomes a *dependent* variable. Petrographically this is recognized as constant-volume replacement. When coupled with continuity equations for the grain-number density and for mineral volumes within a representative volume element (see Eqs. II.3 to II.8 in Ortoleva et al., 1982), Eq. (5) leads to

$$n_A R_A + n_B R_B = 0 \qquad (6)$$

for a two-mineral system of negligible porosity (Dewers and Ortoleva, 1989). (The R_i's are growth rates and the n_i's are number densities, or number of grains per unit rock volume.) That is, growth of mineral A, through the resulting increase in the local mean stress, drives pressure solution of an equal volume of B. This is precisely the same conclusion reached above on the basis of the observed preservation of volume and internal details effected by replacement.
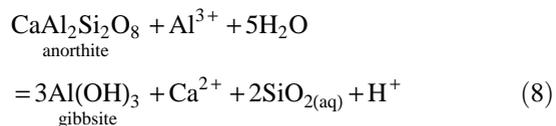
In the case of diffusion control of reaction rates, which is likely for mineral reactions releasing ions into a grain boundary fluid, the volumetric reaction rates could be written

$$R_i = A_i D_i c_{eq}(1 - \Omega_i) \qquad (7)$$

where D_i is the diffusion coefficient, c_{eq} is the equilibrium concentration, A_i is surface area of mineral i per cm^3 of bulk rock, and Ω_i is the saturation state of the intergranular fluid with respect to mineral i. (Although written is terms of concentrations, a similar equation can be derived in the case of transport due to chemical potential gradients, and not concentration gradients, within the grain boundary region. This is discussed by Dewers and Ortoleva, 1990).

6. Some consequences of replacement for modeling

1. Since replacement reactions preserve solid volume, they should be balanced on volume. For instance, replacement of anorthite by gibbsite, very common in laterites, should be written

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + Al^{3+} + 5H_2O$$

$$= \underset{\text{gibbsite}}{3Al(OH)_3} + Ca^{2+} + 2SiO_{2(aq)} + H^+ \qquad (8)$$

where the three gibbsite formulas approximately have the same volume as the anorthite formula (Merino et al., 1993). Exact equality of volumes would warrant a coefficient of (100/32), the ratio of the formula volumes of the two minerals. Microporosity of the gibbsite aggregate, if any, can easily be inserted in the balancing as discussed in Merino et al. (1993, p. 142, Eq. A′). Note that one aqueous aluminum ion ('bare' as shown here or paired with OH$^-$ or other ligands) needs to be supplied for this replacement, underscoring what many diagenetic, weathering and metamorphic cement textures already imply—that Al indeed is mobile. It is the coefficients of this volume-balanced reaction that enter as multipliers into the source terms in mass continuity equations representing the dynamics of the process (Wang et al., 1995).

(The reaction, anorthite + ... = gibbsite + ..., if balanced to conserve for example aluminum between the two minerals, would require a factor of 2 on the gibbsite, would not therefore conserve volume, and would require different inputs and outputs of ions, even, for H^+, on different sides of the reaction, as compared with the reaction described by Eq. (8) above.)

2. The thermodynamics of replacement reactions may have to be revised to take account of the fact that they take place not at constant T and P but at constant temperature and *volume*, with the local stress becoming a dependent function. The revision would involve use of Helmholtz free energies of formation of the minerals involved in the replacement, instead of their Gibbs free energies. See the example of Dockal (1988) for carbonate replacements.

3. Models of water–rock reaction are needed that can predict when and where in the system replacement reactions should take place. That prediction involves calculation of the growth-driven grain/grain stress, and needs to take account of the stress-dependence of mineral dissolution and growth rates in rocks.

4. Beyond (3), water–rock reaction modeling may also tackle cases (possible in rocks of sufficiently low viscosity) where the accommodation of the growth of a guest mineral takes place by both pressure solution and local deformation of the host. One such interdependence has been quantified by Fletcher and Merino (1997b), who link the supersaturation driving the growth of the guest mineral in a rock, the additional stress locally generated, the rock's local viscosity (which can be made Newtonian or non-Newtonian), and the kinetics of both guest growth and host pressure-solution. From their expressions the cases of only-dissolution or only-deformation can be obtained by letting the viscosity tend to infinity or zero, respectively. Experiments quantifying the stress dependence of mineral dissolution rates have been summarized above.

If a particular replacement is independently known to occur in a rock, volume-balancing of it could be included easily in the modeling of water–rock reaction for that rock with existing reaction–transport models; see the example of Wang et al. (1995). The second consequence listed above, use of Helmholz free energies for minerals involved in a replacement, also could be added to existing water–rock models without modifying their basic structure and algorithms. These two changes would be phenomenological (that is, not predictive) additions, both relatively easy to introduce.

But the third implication above—prediction of when and where in the system should replacement take place—would involve significant changes in the structure, equations, and algorithms of existing models, in order to provide for the effect of grain/grain stress on growth and dissolution rates, and for the effect of mineral growth rates on grain/grain stress. Any one of these effects, let alone their interactions, constitutes by itself a difficult problem, even under constant temperature.

The same is true for the fourth implication above—the case where the growth also deforms the local host rock. Here, one would need to add the effect, if any, of strain rates on the local aggregate viscosity of the rock (the so-called non-Newtonian behavior of materials), and the interactions and feedbacks between these effects—growth, pressure solution and deformation (Fletcher and Merino, 1997a, b). If the accommodation by the host rock around a growing mineral grain or grain aggregate can in principle take place by pressure solution, by viscous deformation of the local rock, or perhaps by a mixture of the two mechanisms, how does the rock 'decide' which one, or what mix of them, to adopt in a particular case? This fourth implication is particularly difficult, since it would involve not just interacting mineral pressure–solution and growth kinetics and deformation, but the shape (bulky, flat, or rod-like) of the growing aggregate as well—a shape which has a strong effect on the strain energy added to the host rock (Nabarro, 1940), thus on the stress field, and therefore (via the constraint on space) on mineral kinetics. These feedbacks among growth kinetics, stress field, pressure solution kinetics, and even shape of the crystal aggregate are, we think, aims toward which water–rock modeling should work.

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