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Mineral replacement and dynamics of metasomatism: The blind spot of geochemists as illustrated by the brucite-for-periclase replacement in magnesian marbles

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Abstract

Mineral replacements reveal new insights into the dynamics of metasomatism from weathering to metamorphism, but only if the properties and physics of replacement are understood. The insights have remained hidden for decades because geochemists confuse replacement for dissolution-precipitation, which leads them to adjust the relevant mass balances by conserving a component, which violates petrographic evidence of volume conservation. In fact, replacement happens not by dissolution-precipitation but by its converse, precipitation-dissolution, in which guest growth within rigid rock drives – via induced stress – the pressure-dissolution of the host. Only this explains how guest growth and host dissolution are simultaneous and equal-rate, and why volume is preserved, three crucial properties of replacement already known by Bastin 1931, but unknown to geochemists today.

New insights for the brucite-for-periclase replacement in marbles include: (a) This replacement is self-accelerating. (b) The self-acceleration, combined with the strain-rate-softening nature of the carbonate matrix, triggers a kinetic-rheological feedback that causes the replacive growth to transition to *displacive* growth. (c) Only when the mass balance is adjusted on volume do we understand why the brucite-for-periclase replacement releases Mg^{++} which simultaneously drives formation of a dolomite rim. These and other insights are confirmed by petrographic evidence until now undetected. Similar insights have been gained for replacements in weathering and dolomitization.

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“We must unlearn what we have learned” (Yoda, Star Wars)

1. Introduction

All types of rock metasomatism (metamorphism, weathering, burial dolomitization, ore-deposit genesis, serpentinization) primarily involve *replacement* of a host mineral by a new one, the “guest,” a phenomenon only

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detectable petrographically which is characterized because the guest preserves both some morphological details, or “ghosts,” of the host as well as its volume. For decades, however, geochemists of metasomatism have been convinced that replacement is produced by so-called dissolution-precipitation, which leads them to adjust replacement mass balances by conserving a component among the minerals involved. They are apparently unaware that such component-adjusted mass balances often violate the observed conservation of mineral volume that is characteristic of replacement, and fail to account for other properties of genuine replacement. They are also unaware that they are missing a host of dynamic insights hidden in their conceptual blind spot.

Here, I work out the new dynamic insights that can be gained for one specific case, the brucite-for-periclase replacement typical in magnesian marbles, and present the petrographic evidence that confirms the new insights. First I review what replacement is, what its petrographic and kinetic properties are, why these properties cannot be accounted for by dissolution-precipitation, and what the actual mechanism of replacement is.

2. Mineral Replacement: Properties and Mechanism

Properties, visual and kinetic. As noted, the characteristic petrographic property of replacement is that the new mineral, the guest, preserves both morphological details, or “ghosts,” and the volume of the host mineral.^{1,2, 23, 24, 3,4} This double preservation, of “ghosts” and volume, is known as the pseudomorphic property of replacement. It must be grasped visually. In the example of FIG. 1, a euhedral crystal of dolomite, at center, has replaced the right end of the calcitic oölite at left, preserving *in situ* its ring of black inclusions, thus preserving the calcite volume, since the ring has not been swollen or shrunk upon growth of the dolomite. If this replacement had taken place by so-called

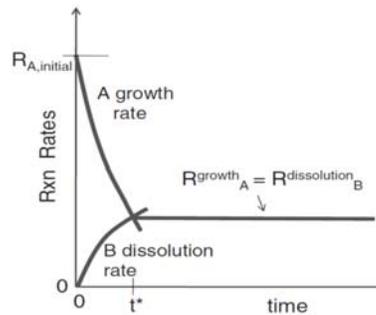


FIG. 1, left: The idiomorphic dolomite crystal at center replaces portions of three oörites at once, preserving *in situ* and undeformed their rings of black inclusions. These features preclude a dissolution-precipitation mechanism for the replacement. (Photo Murray, in ref 22)

FIG. 2, right: Graph shows how the volumetric rates of guest mineral growth and of host pressure-dissolution become automatically equalized by the local induced stress, explaining why replacement preserves mineral volume.^{16,4} As guest A grows, it exerts an induced stress on both itself and the adjacent host B. The induced stress, calculated in ref. 13, increases the equilibrium constants of the two minerals, which results automatically in decreasing the A growth rate and simultaneously increasing the B dissolution rate, until the two become equal to each other, at time t^* .

“dissolution (of calcite)-precipitation (of dolomite)” as geochemists generally believe, the black inclusions of the oölite ring would have been scattered before the dolomite rhomb could have grown and preserved them *in situ*; also, the calcitic oölite could not have dissolved leaving a hollow having precisely the preferred growth form, i.e., rhombohedral, of the future dolomite idiomorph. Each of these two visual criteria (plus a third one, omitted here for brevity) independently precludes formation of this replacement by dissolution-precipitation.

In addition, dissolution-precipitation also cannot explain the remarkable *kinetic* properties of replacement implied by the preservation of “ghosts” and volume. The preservation of ghosts requires that the growth of the new dolomite and the dissolution of the calcite were *simultaneous*. And if the two half-reactions were simultaneous and volume is conserved, then their *volumetric rates must have been mutually equal*, for which they must have been somehow *strongly coupled*. These two crucial kinetic properties, simultaneity and equal-rate, are unknown to geochemists of metasomatism (refs ^{5,6,7,8,9} and many more), though they were deduced – petrographically – already by Bastin.²

Mechanism of replacement.^{3,4,16,18,20} If dissolution-precipitation cannot work, then the correct replacement mechanism must be the converse, precipitation-dissolution, in which it is the growth of the guest mineral which, *via* the growth-generated induced stress, drives the *pressure*-dissolution of the host. The induced stress^{23,13} is the instantaneous, strong coupling needed to *always* equalize the volumetric rates of guest growth and host dissolution regardless of whether host and guest have a component in common or are isostructural, and of which has the higher density or the faster kinetics, FIG 2.

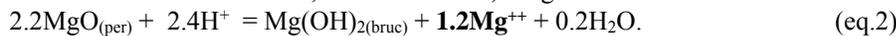
3. New Dynamic Insights Into the Brucite-for-Periclase Replacement in Marbles

FIG. 3¹⁰ shows a typical instance of brucite-for-periclase replacement common in magnesian marbles. The new brucite (black) is described as a pseudomorph¹⁰ implying it conserves the volume and the blocky shape and size of the original periclase crystal. Petrologists (for ex, refs ^{15,11,12,10}) have attributed this replacement to the mass balance



overlooking that it unrealistically conserves Mg between the two minerals and more-than-doubles mineral volume, violating the observed conservation of mineral volume. The traditional, component-adjusted eq.(1) follows from implicitly assuming that replacement takes place by dissolution-precipitation – which we saw cannot work.

However, if we rewrite the mass balance to conserve mineral volume (ref 3), using formula volumes of periclase and brucite of ~11 and 25 cm³, and 25/11 ≈ 2.2, we get:



Only now do we see that Mg⁺⁺, far from being conserved between the two minerals as assumed in eq.(1), is actually released to the interstitial fluid as the replacement takes place. This realization leads to two new insights:

- (1) We immediately grasp why the brucite pseudomorph in FIG. 3 is surrounded by a rim of a Mg-bearing mineral, i.e., dolomite (medium gray), which replaces the calcitic matrix. It is suddenly obvious that this second replacement, dolomite-for-calcite, is a simultaneous consequence of the first, brucite-for-periclase, driven by the released Mg⁺⁺.
- (2) We see that the second replacement takes place at *the same time and rate* as the brucite-for-periclase, and *at the same T, P*. This invalidates reactions petrologists have proposed, i.e., bruc + calc+CO₂=dolo + H₂O, which are assumed to happen *after* the brucite-for-periclase, and *at different T,P*.

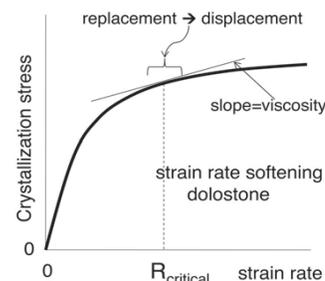
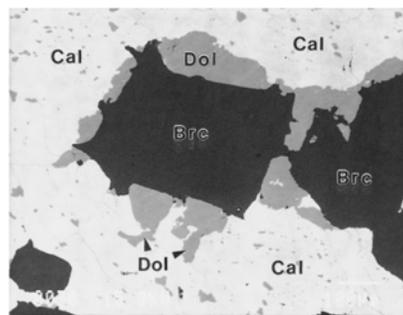
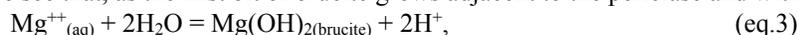


FIG. 3, left. Photomicrograph from ref 10. Brucite completely replaces a blocky periclase crystal, preserving its outline and volume. The brucite is surrounded by a rim of dolomite replacing calcite. The rim is cross-cut by tiny wedges of brucite “shooting out” from the corners of the brucite. FIG. 4, right. Induced stress-versus-strain rate for strain-rate-softening materials, such as crystalline carbonates. The brucite-for-periclase replacement is self-accelerating. The self-accelerating growth – equivalent to increasing strain rate – lowers local rock viscosity (= slope of the tangent to the curve) as the replacement progresses, until it becomes low enough for the replacive growth of the guest mineral to transition to *displacive* growth. Evidence for this displacive growth is the small wedges of brucite at the corners of the brucite, FIG. 3. See text.⁴

Focusing now on the actual mechanism of the brucite-for-periclase replacement, namely precipitation-dissolution, we see that, as the first bit of brucite grows adjacent to the periclase and within rigid marble, *via*



it pressure-dissolves an equal volume of periclase *via* the local induced stress¹³ it exerts on it (and on itself). Thus:

(3) We realize that brucite-for-periclase *is self-accelerating*: the Mg⁺⁺ released by each increment of replacement by eq.(2) increases the ion-activity product for brucite and accelerates the rate of brucite growth, eq.(3), and also the rate at which brucite replaces a new increment of periclase, releasing yet more Mg⁺⁺. The more periclase is replaced, the faster it continues being replaced – until the periclase runs out. No periclase crystal can be left only *half*-replaced by brucite. Indeed, in all reported cases, every periclase is always *completely* replaced by brucite.

(4) The fourth dynamic insight is even more dramatic. Through a surprising kinetic-rheological feedback⁴, the self-accelerating brucite-for-periclase replacement should end up modifying the rheological response of the carbonate matrix to the induced stress¹³ generated by the brucite growth. The property that allows this feedback to happen is the strain-rate-*softening* nature of crystalline carbonates,¹⁴ depicted in FIG. 4, by which their local viscosity decreases as the imposed strain rate increases. Since the strain rate imposed by brucite on the periclase is the same thing as its self-accelerating growth rate, when the replacement becomes fast enough, the local viscosity will decrease sufficiently for the replacive growth to transform itself – gradually – into *displacive growth*. Indeed, the predicted displacive growths can be seen as tiny wedges “shooting out” from the corners of the large brucite-for-periclase pseudomorph in FIG. 3, and cutting across the dolomite rim! This latter detail proves that the rim was indeed simultaneous with the replacement of the periclase crystal – as predicted in the first two insights.

4. Discussion

Replacement lies at the intersection of petrography and physics.⁴ Petrography involves using the right side of the brain. The insights found for the brucite-for-periclase replacement in marbles are *dynamic* – they involve time, rates, feedbacks. Their consequences are independently verified. Yet, the insights have remained hidden for decades in a blind spot that geochemists are unaware of having. The demonstration that mineral replacement in rocks happens not by dissolution-precipitation but by its opposite, precipitation-dissolution, has so far led to breakthroughs in understanding the dynamics of lateritic weathering^{16,18,19}, terra rossa formation^{20,21}, and burial dolomitization.^{4,17}

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