Implications of pseudomorphic replacement for reaction-transport modeling in rocks

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Introduction

In reaction-transport models of petrological processes in rocks exhibiting replacement, reactions should be balanced on volume, and mineral reaction rate laws should contain a crucial dependence on stress. Existing models neglect this (e.g., Steefel and Lasaga, 1992); they ought to be improved to take account of authigenic textures. Widespread pseudomorphic replacement in rocks of all types follows from the facts that space in rocks is limited, that growth of new mineral grains would develop huge stress if adjacent grains did not simultaneously dissolve under the pressure developed by the growing grains, and that viscosity of rocks is probably enormous on the time scales of replacement reactions. Available experimental mineral rates of dissolution and growth miss the stress-dependence of rates that operates in mineral reactions *in rocks*. This may underlie the apparent disagreement (Brantley, 1992) between laboratory rates and field-derived rates.

Pseudomorphic replacement: properties and recognition

Replacement of grain A by mineral B is the simultaneous dissolution of A and growth of B such that B occupies the space before occupied by A. Preservation of original shape and volume requires that the two reactions proceed at the same volumetric rate. Preservation of internal details of A indicates that the two reactions proceed simultaneously, through a sequence of many, very small, linked increments. The two rates are kept equal to each other by grain-grain pressure (Merino *et al.*, 1993). Supersaturation with respect to B drives B growth; B then presses against A, from within or without, and raises its free energy, solubility, and dissolution rate. Grain A recedes as fast as B pushes. The phenomenon is self-adjusting, because pressure also increases the free energy of B, making it grow *less* fast. Recognition

of replacement is petrographic — see criteria in Lufkin (1983), Maliva and Siever (1988).

Evidence of Pseudomorphic Replacement in Rocks

Replacement is widespread in rocks of all types. It is extensive in weathering: for example, Millot (1964), Nahon (1976, 1991), and Beauvais *et al.* (1987) report it in laterites. In burial diagenesis Coombs (1956) first identified the progressive albitization of plagioclase later found in other deep sedimentary basins (e.g. Boles, 1982). Mutual replacements of diagenetic illite and kaolinite were reported by Millot (1964). Feldspar can be replaced by diagenetic quartz (Wallace, 1976), diagenetic laumontite (Merino, 1975), or many other minerals. Replacement between quartz and calcite is reported or referenced by Maliva and Siever (1988) and many others. In metamorphic rocks every mineral grain present replaces earlier ones; see for example Sicard *et al.* (1986) and Carmichael (1986), who cites outstanding early articles by Lindgren. Reaction rims in igneous rocks are replacements too (e.g. Potdevin *et al.*, 1989). For replacement in ores see Lufkin (1983). There are countless other examples.

Consequences for reaction-transport in rocks

Replacement reactions must be balanced *on volume* (Merino *et al.*, 1993). For example, the replacement of plagioclase by gibbsite, common in laterites, would be

$$CaAl_2Si_2O_{8(an)} + Al^{3+} + 5H_2O = 3Al(OH)_{3(gib)}$$
$$+ 2SiO_2 + Ca^{2+} + H^+ \qquad (1)$$
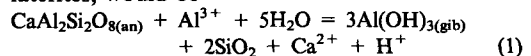
where the 3 formulas of gibbsite approximately impose solid volume conservation. Thus, replacement (except by coincidence or by anomalously large microporosity of B) *requires* mobility and transport of *any* element involved (here, Al). Efforts at finding an element that is 'immobile' during mineral reactions that lead to replacement seem to us misplaced and unnecessary. Various

elements assumed to be immobile are Al (Garrels and Mackenzie, 1967), Zr (Brimhall *et al.*, 1992), Fe, and Ti. All are mobile, at least some times (e.g., for Zr, Colin *et al.*, 1993; Braun *et al.*, 1993).

Replacement also warrants introducing the stress dependence of the rate law into the solubility (as done, roughly, by Merino *et al.*, 1983 and 1993) or, better, taking account of mechano-chemical coupling (Dewers and Ortoleva, 1989). In the weathering example below we replace this step with the more artificial (and simpler) one of establishing 'switches' to let the algorithm decide when and where in the system a mineral reaction takes place.

Example: Pseudomorphic replacement in modeling lateritization. We have modeled quantitatively (Wang *et al*, 1994) the simple case of the weathering of plagioclase explicitly including replacement (but here without calculating and coupling the grain-grain average stress). Characteristic of weathering is to produce, for each mineral in the parent rock, a horizon of congruent dissolution represented by

anorthite + $8H^+$ =
$$2Al^{3+} + Ca^{2+} + 2SiO_2 + 4H_2O \qquad (2)$$
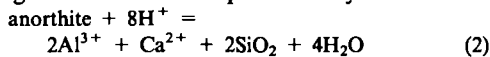
associated with, and overlying, one of pseudomorphic replacement (Merino *et al.*, 1993), represented by reaction (1), which itself overlies the fresh mineral. The Al released by the dissolution (2) travels down and drives replacement (1), coupling the two reactions — *and* the two textures they produce. Continuity equations for aqueous $Al^{3+}_{(tot)}$ and H^+ are

$$\frac{\partial Al}{\partial t} = -\frac{\partial(\text{transport})}{\partial z} - R_r + 2R_d \qquad (3)$$

$$\frac{\partial H}{\partial t} = -\frac{\partial(\text{transport})}{\partial z} + R_r - 8R_d \qquad (4)$$

where transport includes diffusion and advection, and R_r, R_d are the rate laws of anorthite replacement and dissolution, respectively, for which we adopt expressions in terms of anorthite surface area and aqueous concentrations. Replacement imposes its stoichiometry in equations (3,4). For the boundary conditions given in one solution to the system of equations is shown at three times in the evolution of the laterite. Note how the coupled dissolution and replacement fronts (which come out in the correct spatial arrangement) progressively 'sink' a few millimeters in 192 years into the parent rock, at its expense.

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