Dynamic model of the genesis of calcretes replacing silicate rocks in semi-arid regions

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(Received July 13, 1993; accepted in revised form July 13, 1994)

Abstract—In both pedogenic and groundwater calcretes, calcium carbonate precipitates in voids, or displacing other grains, or replacing underlying parent silicates. Replacement textures are widespread in pedogenic calcrete. Many calcretes also contain magnesium layer silicates and minor chert.

We present a reaction-transport model that accounts for the genesis of replacement in calcretes and for their mineralogy. Replacement is difficult to account for geochemically because it requires simultaneous removal of large amounts of silicates and import of also large amounts of CaCO3. In the model the genesis of replacement is directly related to seasonally alternating dry-wet climates and to appropriate groundwater (or circulating soil water) compositions. In a dry season, water evaporation causes CaCO3 and sepiolite (or attapulgite) to precipitate. If groundwater contains enough Mg2+, sepiolite precipitation by the chemical-divide mechanism depilates SiO2(aq.), resulting in the dissolution of parent silicates. In the following wet season, sepiolite dissolves fast, and silica and cations are flushed away by rainwater, making room for CaCO3 precipitation in the next dry season. As climate cycles repeat, CaCO3 is accumulated and silicates are removed. The sepiolite (or attapulgite, or Mg-smectite) serves as a temporary reservoir for the efficiency of replacement in removing silicates.

Calcrete formation involves import of CaCO3, whose source is considered to be eolian or the parent rock or upstream Ca-bearing rocks. In all cases, water is implicitly essential in dissolving and transporting the CaCO3. The calcium carbonate is thought to be eolian in calcretes of the southwestern USA (e.g., MACHETTE, 1985; MARION et al., 1985; MAYER et al., 1988) and in some calcretes of South Australia and Victoria (QUADE et al., 1994). But the eolian contribution is negligible in west African calcretes (NAHON and RUELLAN, 1972; BOULET, 1974; NAHON, 1976, 1977; MILLOT et al., 1984). In western Senegal, calcretes are well developed on marls and limestone but not on kaolinitic sandstones, especially not on sandstones by the ocean (NAHON, 1976). In the Sahara, the 87Sr/86Sr ratio of calcretes indicates a calcium source from parent schists (NAHON, 1976, p. 183).

Two types of calcrete are distinguished, pedogenic and groundwater calcretes (WRIGHT and TUCKER, 1991). The latter are formed at or near water tables. Calcretes display void-filling, displacive, and replacive textures (WATTS, 1978; CHADWICK and NETTLETON, 1990; NAHON, 1976). As we show below, the replacive texture poses the hardest problem from a geochemical standpoint.

Calcrete accumulation in soils has been simulated with compartment models by MCFADDEN and TINSLEY (1985), MARION et al. (1985), and MAYER et al. (1988). These...
models take account of onlyolian dust source of calcium carbonate and only calcite growth, and thus they fail to account for some of the mineralogical and textural changes observed in calcrete profiles.

Our purpose in this paper is to propose a geochemical model of the genesis of calcretes replacing underlying silicate rocks. In the model, calcrete formation is driven by the wet/dry seasonal alternations of semi-arid climates. The model allows us to estimate rates of calcrete formation and, by numerical simulation, to predict the response of calcrete formation to climatic and groundwater-composition changes. The model incorporates both short and long timescales. We observed in calcrete profiles.

Calcretes may reach several meters in thickness, form in arid zones with 400–600 (or less) mm annual rainfall, and tend to develop preferentially on low-angle fans and pediments or glacis (Goudie, 1983). They can form on rocks with little or no calcium (Gile et al., 1966; Ruellan, 1971) in semi-arid areas, but, in more humid areas, they develop only on Ca-bearing parent rocks (Nahon and Ruellan, 1972; Duco lux et al., 1984). Calcretes usually display well-defined vertical and lateral sequences. From bottom to top, and also from uphill to downhill, the calcium carbonate occurs successively as diffuse patches, unindurated nodular accumulations, indurated nodules, plates, and a hard crust; the general sequence is always from nodular accumulations toward the bottom (or uphill) to planar precipitates toward the top (or downhill). See, e.g., Reeves (1970) for the calcretes near Lubbock, Texas, USA, Ruellan (1971) for the calcretes of northeast Morocco, Hay and Reeder (1978) for the calcretes of Olduvai Gorge and Ndolanya Beds in Tanzania, and Nahon (1991, p. 166) for calcretes from Mauritania. Contacts between adjacent horizons in the sequence are gradual. The orientation of the bunched and plates may be controlled by the texture of the host rock, especially if the latter is a schist (Wieder and Yaalon, 1974; Wieder, 1977) or if it is fractured (Milot et al., 1977).

MINERALOGY OF CALCRETES

Calcretes consist of authigenic carbonates, which are dominant. Mg clays, and chert, plus relict minerals of the parent rock. The proportion of the latter decreases from bottom to top (or downhill). The main carbonate is calcite. The earliest carbonates are disordered, hydrated, or organic-matter-bearing calcite (Duc loux et al., 1984; Dupois et al., 1984), and they may include aragonite, but all of them quickly recrystallize into the ordered calcite that makes up most of the calcrete. The transition occurs over tens of micrometers, and has been reproduced experimentally (Dupois et al., 1984). Aragonite has been identified in calcretes from South Africa, the Mediterranean region, and West Africa (Goudie, 1973; Nahon et al., 1980). Magnesian calcite is rarer (Milot et al., 1977). Both aragonite and magnesian calcite are always minor relative to well crystallized calcite.

Silicopetalite [Mg,Al,Si_2O_5(OH)_4, H_2O] and attapulgite (= palgorskite) [(Mg,Al,Fe)_2Si_2O_5(OH)_4, nH_2O] are common in calcretes (e.g., Watts, 1980; Hay and Wiggins, 1980, Arakel, 1986; Jones and Galán, 1988; Monger and Daugherty, 1991b). Progressive growth of calcite is accompanied by increasing attapulgite, which reaches its peak toward the top of the nodular horizon, from where it decreases in amount and disappears upwards (Milot et al., 1989; Goudie, 1983, in Fig. 4.2). In more humid areas smectite grows rather than attapulgite, and it also disappears in the platy and crust horizons at the top (Nahon et al., 1975; Mil lot et al., 1977). Petrographic, microprobe, and X-ray diffraction work (Milot et al., 1977) shows that clay growth proceeds as host mineral grains dissolve.

Minor amorphous silica or chalcedony occur in calcretes, toward their base (Nahon, 1976). Microscopically, the chert occurs adjacent to partly dissolved parent quartz grains (Ducloux et al., 1990, photo 3a). The chert described by Duc loux and Laouina (1988) contains minor magnesium. In central Australia dolomitic and chalcedonic replacements of calcrete generally coincide with present drainage channels in washout areas (Arakel, 1986).
Many calcretes, particularly pedogenic ones in semi-arid countries, display replacement of parent silicate rocks by calcite (NAGTEGAAL, 1969; ARISTARAIN, 1971; BOULET, 1974; CHAPMAN, 1974; NAHON et al., 1975; NAHON, 1976; MILLOT et al., 1977; DURAND, 1979; BECH et al., 1980; REHEIS, 1988; DUCLOUX et al., 1990; MONGER and DAUGHERTY, 1991a,b). Microscopic and macroscopic observations show conclusively that the replacement is pseudomorphic, regardless of the nature of the parent rock (granite, basalt, sandstone, argillite, shale, schist, quartzite). Textures and structures of the parent rock are preserved.

Because of its importance and solidity, we summarize here some evidence. In a Precambrian greenschist of southern Morocco, a calcite develops progressively upward along the joints and schistosity (Fig. 1) (MILLOT et al., 1977). The calcite occurs as a millimeter-thick "grid," discontinuous at bottom, continuous higher up. The "bars" of the grid separate volumes of greenschist of progressively smaller size upward. The schistosity planes and quartz veins can be traced from volume to neighboring volume. The calcite making up the bars of the grid contains innumerable tiny relics of greenschist that preserve the original orientation, a detail which precludes the interpretation that the calcite is a fracture filling. The evidence is conclusive, and the complete description should be studied in Millot et al. (1977): the progressive calcitization took place without disturbing the original schistosity or the original bulk volume. Similarly compelling observations also demonstrating pseudomorphic replacement by calcium carbonate have been carried out on other schists in Mauritania (NAHON, 1976) and on granites, shales, and quartzites in Morocco (MILLOT et al., 1977).

Microscopic evidence also shows pseudomorphic replacement conclusively. In the coarse-grained Ifni granite of southern Morocco (MILLOT et al., 1977) calcite microcrystals grow first along grain contacts and cleavage planes (Fig. 2C). With progressive growth higher in the profile, the microcrystals form a microgrid that cuts up each grain of feldspar or quartz into small islands. These islands display optical continuity, and twin planes can be traced from island to island (Fig. 2D, F). Biotite grains are replaced by micritic calcite and some calcium carbonate have been carried out on other schists in Mauritania (NAHON, 1976) and on granites, shales, and quartzites in Morocco (MILLOT et al., 1977).

We propose here a dynamic model of calcrete formation that solves the problems listed above. In the model the process is driven by the alternation of dry and wet seasons, the mechanism of chemical divides (driven by evaporation) plays a crucial role, and the major geochemical problem involved is that of supplying and precipitating calcium carbonate while dissolving and removing silicates. To see how the model works, consider the replacement of quartzite by calcrite. Assume that the groundwater (or circulating soil water) brings in dissolved Ca, Mg, and SiO2(aq). In a dry season, evaporation of water concentrates all solutes in the porewater at the drying front. Calcite and sepiolite begin to precipitate. If the solubility ratio of Mg to SiO2 in the incoming water is greater than 2/3, the precipitation of sepiolite depletes SiO2 in porewater while Mg continues to be concentrated as evaporation proceeds (this works as in the chemical divides of HARDIE and EUGSTER, 1970). Eventually, SiO2(aq) concentration becomes so low that quartz starts to dissolve. Dissolved silica contributes to form more sepiolite. Note that quartz dissolution here is unavoidable even if the initial water was saturated with quartz. In the following wet season, downward percolating rainwater dissolves sepiolite rapidly, thus massively removing silica from the system (although minor amorphous silica or chalcedony may still precipitate locally due to the high concentration of SiO2). The net effect of one year's climate cycle is that some silica is evacuated and some calcium carbonate accumulates. After hundreds of yearly climate cycles, a calcrite forms.

Because only a tiny volume of the parent rock is removed in each climate cycle and the space left is immediately filled by calcite, in the next dry season, the original rock textures and structures are preserved and kept from being altered during calcitization. Note, however, that this pseudomorphic replacement is different from that caused by crystallization force, a mechanism that forces the dissolution rate of the replaced mineral to be exactly equal to the growth rate of the replacing mineral (MALIVA and SIEVER, 1988; MERINO et al., 1993). During calcrite formation, the two rates are certainly not equal on the seasonal scale, but they are roughly equal over the time span of a year.
Furthermore, sepiolite precipitated in a dry season may be completely dissolved in the following wet season near the top of the profile, where the porewater is close to rainwater in composition and therefore very undersaturated with sepiolite. As a result, parent rocks appear to be directly replaced by calcite toward the top of profile, even though the absent sepiolite still plays a key role there in removing silica.

The proposed mechanism also works for a calcrete replacing aluminosilicate rocks, and then attapulgite (or even smectite if climates are more humid), which contains Al, would play the same role as sepiolite does in the chemical divide. In addition, the eolian source of calcium carbonates is not excluded in the mechanism. As long as eolian sourced calcium carbonate undergoes dissolution and reprecipitation in forming calcretes, and if Mg concentration is high enough in porewater, the proposed mechanism still works. The scenario described above is simulated below with a transport-reaction model, in order to further clarify the effect of climate, hydrology, and chemical kinetics on calcrete formation.

**TRANSPORT-REACTION MODEL OF CALCRETE FORMATION**

**Chemical Reactions**

For simplicity, we only consider a calcrete replacing quartzite. The following chemical reactions take place:

\[
\begin{align*}
SiO_2 (quartz) + 2H_2O &\rightarrow H_2SiO_4 \\
CaCO_3 (calcite) + H^+ &\rightarrow Ca^{2+} + HCO_3^- \\
MgSi_1.5O_3\cdot(OH)_{0.5} (H_2O)_{0.5} &\rightarrow Mg^{2+} + 1.5 H_2SiO_4 \\
SiO_2 (amorphous silica) + 2H_2O &\equiv Ca^{2+} + HCO_3^- \\
CO_2 + H_2O &\equiv H^+ + CO_3^- \\
HCO_3^- &\equiv H^+ + CO_3^- \\
H_2O &\equiv H^+ + OH^- \\
H_2SiO_4 &\equiv H^+ + H_2SiO_4.
\end{align*}
\]

Note that reaction 1 only proceeds to the right, but reaction 4 may go either way. For the heterogeneous reactions 1-4, we adopt kinetic laws as follows:

\[
R_i = \begin{cases} 
\frac{k_1 \theta}{\theta_0 + \theta} (1 - \frac{a_{H_2SiO_4}}{K_i}) & \text{for } a_{H_2SiO_4} < K_i \\
0 & \text{otherwise}
\end{cases}
\]

\[
R_2 = k_2 \frac{\theta}{\theta_0 + \theta} (1 - \frac{a_{Ca^{2+}} a_{HCO_3^-}}{K_2})
\]

\[
R_3 = k_3 \frac{\theta}{\theta_0 + \theta} (1 - \frac{a_{Mg^{2+}} a_{H_2SiO_4}}{K_3})
\]

\[
R_4 = k_4 \frac{\theta}{\theta_0 + \theta} (1 - \frac{a_{H_2SiO_4}}{K_4})
\]

and they must satisfy

\[
R_i < 0 \text{ when } V_i = \theta, \quad i = 1-4,
\]

where \( R_i \) is the rate of reaction \( i \) (mol/cm\(^3\) s); \( k_i \) and \( K_i \) are, respectively, the rate and equilibrium constants of reaction \( i \); \( \theta \) is the activity of chemical species \( j \); \( \theta_0 \) is the saturation degree, the fraction of pore space occupied by liquid water; \( \theta_0 \) is a small positive constant; \( V_i \) is the volume fraction of mineral \( i \).

The reactive surface area of a mineral may not necessarily decrease as the mineral dissolves, because new reactive surface area may be created by disaggregating large aggregates into small pieces (Figs. 1F and 2D). Secondary minerals, usually forming coatings around parent mineral aggregates, may have large reactive surface areas even where a small amount of them is present. For simplicity, reactive surface areas are taken to be constant in Eqs. 9-12 and are buried in \( \theta_0 \) values. Equation 13 simply means that no dissolution is allowed for a mineral which is not present. The factor \( \frac{\theta}{\theta_0 + \theta} \) (with \( \theta_0 \) = fraction of pore space occupied by liquid water) in Eqs. 9-12 represents the degree of contact between liquid water and minerals. This factor is needed because minerals can only dissolve or grow to the extent that there is liquid water in the pores.

According to the Ostwald ripening rule (e.g., Morse and Casey, 1988), an unstable phase is more favored to form than a stable one from solution in a low-temperature environment. If the latter grows too slowly compared to the former. Therefore, in our model quartz precipitation is not

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**Fig. 1.** (A) Calcrete replacing a Precambrian greenschist (Anzi Series, 30 km east of Tiznit, southern Morocco). Schistosity dips 15° off the vertical. The rock is densely jointed across the schistosity. The calcrete develops progressively from bottom to top of a 5-m profile. In the lower part of the profile, the original schistosity is preserved by a "grid" of calcium carbonate (light), and the relict islands (dark) of greenschist retain their original orientation, indicating that the replacement is macroscopically pseudomorphic. (See Plate I-1, Millet et al., 1977.) (B) Detail of the top of the calcrete profile (hard crust): in the indurated calcrete (c), the original structure of greenschist (gs) is still preserved. Relicts of greenschist are "floating" on massive calcite matrix and still keep the original orientation, with no displacement. (C) Base of the calcrete profile on greenschists. Early stage of pseudomorphic replacement of the greenschist (gs) by attapulgite (a) from microfissures (f); (crossed nicols). (See Plate II-7, Millet et al., 1977.) (D) Detail of Fig. 1C. Attapulgite (a) is in turn replaced by a small amount of calcite (c) along microfissures. (See Plate II-7, Millet et al., 1977.) (E) Higher in the same calcrete profile, calcite increases and attapulgite decreases in amount. But still the greenschist (gs) is first replaced by attapulgite (a), which is then replaced by calcite; (crossed nicols). (See Plate II-9, Millet et al., 1977.) (F) Top portion of the calcrete profile (hard crust). The greenschist (gs) is "directly" replaced by calcite (c); (crossed nicols). (See Plate II-10, Millet et al., 1977.)
FIG. 2. (A) Calcrete developed on the Messi granite, 5 km from Ifni, southern Morocco. At the base of the profile, calcrete (c) replaces granite (g); note the apparently sharp reaction front. (B) The calcite formed by replacement, not by fracture filling, as shown by the preservation of the crystalline-granular granite texture in the (white) calcrete. Also, note that the front is not as sharp as it looks in (a). (See Plate I-3, MILLOT et al., 1977.) (C) Incipient replacement of a plagioclase (pf) by calcite (c) with no displacement of the twins. (See Plate III-11, MILLOT et al., 1977.) (D) Advanced stage of pseudomorphic replacement of a plagioclase by calcite, with no displacement of twin planes. (See Plate III-12, MILLOT et al., 1977.) (E) Pseudomorphic replacement of biotite (b); ghosts of cleavages are still preserved (arrow) near the reaction front. (F) The fragments of the original grain still maintain optical continuity, indicating that the replacement took place without any displacement. (MILLOT et al., 1977).
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allowed, as is implied in Eqn. 9, whereas amorphous silica can precipitate or dissolve.

The dependence of quartz reaction rates on concentrations is based on DOVE and CRERAR (1990) and RIMSTIDT and BARNES (1980); calcite rates are based on MORSE (1983) and INSKEEP and BLOOM (1985). Because of the lack of appropriate kinetic data, the exponents on concentrations in the rate law of sepiolite dissolution are chosen to equal stoichiometric coefficients in reaction 3.

Reactions 5-8 are assumed to be fast and thus in equilibrium. The equilibrium condition is imposed by

\[ a_{\text{H}_2\text{SiO}_3} + a_{\text{HCO}_3^-} = K_2 \text{PCO}_2 \] (14)

\[ a_{\text{H}_2\text{SiO}_3} + a_{\text{CO}_2} = K_6 a_{\text{HCO}_3^-} \] (15)

\[ a_{\text{H}_2\text{SiO}_3} + a_{\text{OH}^-} = K_7 \] (16)

\[ a_{\text{H}_2\text{SiO}_3} + a_{\text{SO}_4^{2-}} = K_9 a_{\text{H}_2\text{SiO}_4^-} \] (17)

where \( K_i \) is the equilibrium constant of the \( i \)th reaction; \( \text{PCO}_2 \) is the partial pressure of CO\(_2\), which is assumed to be constant in the whole system.

Continuity Equations for Water

The one-dimensional system to be modelled is shown in Fig. 3. The coordinate is located at the Earth surface, with positive direction downward. Water movement in the profile is governed by Darcy’s law (RICHTER, 1987):

\[ Q = -\phi K(\theta) \left( \frac{\partial \Psi}{\partial Z} - 1 \right) \] (18)

\[ \frac{\partial (\phi \Psi)}{\partial t} = \frac{\partial}{\partial Z} \left[ \phi K(\theta) \left( \frac{\partial \Psi}{\partial Z} - 1 \right) \right] \] (19)

where \( Q \) is water flux (cm/s); \( \Psi \) is hydraulic head (cm); \( \phi \) is porosity; \( \theta \) is the relative saturation degree, defined as \( (\theta - \Theta) / (1 - \Theta) \), where \( \Theta \) is residual moisture; \( K(\theta) \) is the effective permeability (cm/second), which is a function of \( \theta \); \( Z \) is the distance from the Earth surface (cm); \( t \) is time (s). The effective permeability \( K \) and hydraulic head \( \Psi \) are related to the relative moisture \( \theta \) by (VAN GENUCHTEN, 1980)

\[ K(\theta) = K(1) \theta^{2[(1 - (1 - \theta^{m_1})^m_1]^2 \) (20)

\[ \theta = \begin{cases} 
1 + (h/\Psi)^{1/m} & \text{for } \Psi \leq 0 \\
1 & \text{for } \Psi > 0
\end{cases} \] (21)

with \( m = 1 - 1/n \). Here \( K(1) \) is the effective permeability for saturated rock; \( n \) and \( h \) are two constants characterizing rock capillarity.

Continuity Equations for Solute

Solute concentrations in porewater satisfy the following mass continuity equations:

\[ \frac{\partial M_{\text{Ca}^{2+}}}{\partial t} = \frac{\partial}{\partial Z} \left( \phi D \frac{\partial M_{\text{Ca}^{2+}}}{\partial Z} \right) - \frac{\partial (Q M_{\text{Ca}^{2+}})}{\partial Z} + \frac{R_2}{\rho_w} \] (22)

\[ \frac{\partial M_{\text{Mg}^{2+}}}{\partial t} = \frac{\partial}{\partial Z} \left( \phi D \frac{\partial M_{\text{Mg}^{2+}}}{\partial Z} \right) - \frac{\partial (Q M_{\text{Mg}^{2+}})}{\partial Z} + \frac{R_3}{\rho_w} \] (23)

\[ \frac{\partial M_{\text{SiO}_4^{2-}}}{\partial t} = \frac{\partial}{\partial Z} \left( \phi D \frac{\partial M_{\text{SiO}_4^{2-}}}{\partial Z} \right) - \frac{\partial (Q M_{\text{SiO}_4^{2-}})}{\partial Z} + \frac{R_1 + 1.5R_3 + R_4}{\rho_w} \] (24)

where \( \rho_w \) denotes the density of water (10\(^{-3}\) kg/cm\(^3\)); \( M_j \) is the molality of the subscripted chemical component; \( D \) denotes dispersion coefficient (cm\(^2\)/s), which is taken to be constant for all aqueous species in our model:

\[ M_{\text{SiO}_4^{2-}} = M_{\text{SiO}_4^{2-}} + M_{\text{H}_2\text{SiO}_4} \] (26)

\[ M_\Delta = M_{\text{HCO}_3^-} + 2M_{\text{CO}_2} + M_{\text{OH}^-} + m_{\text{H}_2\text{SiO}_4} \]

\[ -2M_{\text{Mg}^{2+}} - 2M_{\text{Ca}^{2+}} - M_{\text{H}^+} \] (27)

\( M_\Delta \) takes account of the effect of the other ions, which are not explicitly considered in the model, in maintaining electroneutrality of solution (HARDIE and EUGSTER, 1970). The first terms on the right sides of Eqns. 22–25 represent the dispersion effect, and the second terms characterize the solute transport by water advection due to infiltration or evaporation.

Alternating Boundary Conditions

One of the key elements in the model is that the seasonal alternation of dry-wet climate changes in semi-arid regions is explicitly incorporated as upper boundary (\( Z = 0 \)) conditions. The lower boundary (\( Z = L \)) is set at water table. The boundary conditions are imposed as follows:

at \( Z = 0 \):

in dry seasons:

\[ O = -O_\circ \] (28)

\[ \phi D \frac{\partial M_j}{\partial Z} + Q M_j = 0 \quad (j = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{SiO}_4^{2-}, \Delta) \] (29)
in wet seasons:

$$Q = Q_{\text{inf}}$$  \hspace{1cm} (30)

$$M_i = M_i^0 \quad (j = \text{Ca}^{2+}, \text{Mg}^{2+}, \Sigma \text{Si}, \Delta)$$  \hspace{1cm} (31)

at \( Z = L \):

in dry seasons:

$$\Psi = 0$$  \hspace{1cm} (32)

$$M_i = M_i^f \quad (j = \text{Ca}^{2+}, \text{Mg}^{2+}, \Sigma \text{Si}, \Delta)$$  \hspace{1cm} (33)

in wet seasons:

$$\Psi = 0$$  \hspace{1cm} (34)

$$\frac{\partial M_i}{\partial Z} = 0 \quad (j = \text{Ca}^{2+}, \text{Mg}^{2+}, \Sigma \text{Si}, \Delta).$$  \hspace{1cm} (35)

where \( Q_e \) is evaporation rate in dry seasons; \( Q_{\text{inf}} \) is infiltration rate in wet seasons; \( M_i \) represents rainwater composition; \( M_i^f \) represents groundwater composition.

MINERAL VOLUME CHANGES

Let \( V_i \) \((i = 1-4)\) denote the volume fractions of quartz, calcite, sepiolite, and amorphous silica, respectively. The changes in mineral volume are described by

$$\frac{dV_i}{dt} = -v_{im} R_i,$$  \hspace{1cm} (36)

where \( v_{im} \) is molar volume of mineral \( i \). The initial conditions for Eqn. 36 are

$$t = 0: \quad V_1 = V_1^0, \quad V_2 = 0, \quad V_3 = 0, \quad V_4 = 0,$$  \hspace{1cm} (37)

where \( V_1^0 \) is the volume fraction of quartz in fresh quartzite. Rock porosity \( \phi \) is related to mineral volume fractions by

$$\phi + \Sigma V_i = 1.$$  \hspace{1cm} (38)

QUASI-STATIONARY STATE APPROXIMATION

Assuming that transient periods of the system are much shorter than season duration (i.e., assuming that Eqs. 19 and 22-25 approach steady state much faster than seasonal climate changes), we can drop off all terms on the left sides of those equations, and we then obtain

$$\frac{\partial}{\partial Z} \left( \phi K(\theta) \left[ \frac{\partial \Psi}{\partial Z} - 1 \right] \right) = 0,$$  \hspace{1cm} (39)

$$\frac{\partial}{\partial Z} \left( \phi D \frac{\partial \text{MCa}^{2+}}{\partial Z} \right) - \frac{\partial (\phi \text{MCa}^{2+})}{\partial Z} + \frac{R_3}{\rho_w} = 0,$$  \hspace{1cm} (40)

$$\frac{\partial}{\partial Z} \left( \phi D \frac{\partial \text{M}^{2+}}{\partial Z} \right) - \frac{\partial (\phi \text{M}^{2+})}{\partial Z} + \frac{R_1}{\rho_w} = 0,$$  \hspace{1cm} (41)

$$\frac{\partial}{\partial Z} \left( \phi D \frac{\partial \text{MSi}}{\partial Z} \right) - \frac{\partial (\phi \text{MSi})}{\partial Z} + \frac{R_1 + 1.5 R_4 + R_6}{\rho_w} = 0,$$  \hspace{1cm} (42)

and

$$\frac{\partial}{\partial Z} \left( \phi D \frac{\partial \Delta}{\partial Z} \right) - \frac{\partial (\phi \Delta)}{\partial Z} = 0.$$  \hspace{1cm} (43)

Because they are a set of steady-state equations, Eqs. 39-43 do not require initial conditions. We should, however, be aware that \( \Psi \) and \( M_i \) in those equations still vary with time because the boundary conditions and mineral volume fractions change with time. So Eqs. 39-43 are not steady-state equations in a strict sense. The approximation employed is called quasistationary state approximation (Lichtner, 1988).

DIMENSIONLESS PARAMETERS AND DUAL TIMESCALES

The parameters in the model can be grouped into a least number of independent and dimensionless parameters. To achieve this, first insert the following scaled dimensionless variables into Eqns. 9-12 and 18-25:

$$q = \frac{Q}{K(1)}, \quad m_j = \frac{M_j}{M}, \quad \psi = \frac{\Psi}{I}, \quad k' = \frac{K}{K(1)};$$  \hspace{1cm} (44)

and then group factors so as to end up with as few coefficients as possible in each equation. \( M \) is the typical concentration of aqueous species. The resulting independent dimensionless parameters are

$$u = \frac{K(1)L}{D}, \quad k' = \frac{L^2}{\rho_w MD} k; \quad h' = hL.$$  \hspace{1cm} (45)

where \( u \) is Peclet number, characterizing the relative importance of water advection to hydrodynamic dispersion; and \( k' \) is the rate constant of chemical reaction scaled relative to the dispersion coefficient.

According to the proposed mechanism, the replacement of a quartzite by a calcrete is limited by the dissolution of quartz. Thus, we can estimate, from the kinetic data of quartz dissolution, the rate of the calcrete formation. Let us first scale Eqn. 36 for quartz into

$$\frac{dV_i}{d\tau} = -\frac{\Theta}{\Theta_0 + \Theta (1 - \Omega_i)}, \quad \tau = \frac{t}{T},$$  \hspace{1cm} (46)

with

$$T = \frac{1}{v_{im} k_i},$$  \hspace{1cm} (47)

where \( T \) is a typical time scale for calcrete formation; it is only on this scale that significant changes in mineral-volume fractions can take place.

From Dove and Crear (1990, Fig. 8), the rate constant of quartz dissolution in 25°C electrolyte solutions is \( 10^{-11} \) mol/m² s. By choosing a specific surface area of 60 cm²/cm³ (which corresponds to grain sizes of 1 mm), \( k_i \) is \( 6 \times 10^{-14} \) mol/cm² s. Since molar volume of quartz, \( v_m \), is 22.45 cm³/mol, the timescale of calcrete formation is estimated from Eqn. 47 to be 0.75 \times 10^{12} \text{ s}, i.e., 24,000 years. Also from dove and crear (1990), the rate constant of quartz dissolution in pure water at 25°C is \( 10^{-12} \) mol/m² s, and for the same specific surface as before, \( k_i \) is \( 2.4 \times 10^{-15} \) mol/cm³ s, which again with Eqn. 47 yields a timescale of 560,000 years. According to the proposed mechanism, quartz dissolution takes place in dry seasons, when cations are concen-
trated in porewater by evaporation. Therefore, we think that the actual timescale of calcrete formation falls between the two estimates and probably is closer to the shorter one.

The estimated timescale seems comparable with measured timescales for various calcretes, including calcic soils: HAY and REEDER (1978) found that the Olduvai calcrete in Tanzania formed rapidly, perhaps over several thousand years. HAWLEY et al. (1976) have claimed that at least 100,000 years are required to form the calcrete of the Jornada surface in New Mexico, USA. CARLISLE (1983) inferred that valley calcretes formation began less than 0.5 myr ago, perhaps during a major arid phase starting 25,000 myr ago. The U-Th dating carried out by SZABO et al. (1981) shows that the age of calcretes in southern Nevada, USA, ranges from 5,000 to 345,000 years.

In contrast to the timescale of mineral-volume changes, the concentrations of aqueous species ($M_i$), water flow ($Q$), and reaction rates ($R_i$) vary seasonally, on a timescale of months or even less. That is, calcrete formation inherently involves dual timescales. The long-term mineral-volume changes are directed controlled by the short-term variation of climates. This dual timescale brings about a difficulty for numerical modeling, because it would be very time consuming to simulate a geochemical process of $10^5$ years with a time resolution less than a month. To overcome this difficulty, we design an averaging technique to solve the model on the two timescales but still in a modest computing time.

**NUMERICAL SIMULATION**

The model is solved by a finite difference method and Newton-Raphson iteration (HUYAKORN and PINDE, 1983). The model is solved on two different timescales by using the following strategy: Let $\Delta t$ denote the time increment to solve for mineral volume changes on the large timescale; thus $\Delta t$ can be 100 years. And let $\Delta t$ represent the time increment to solve for the seasonal variation of the system; $\Delta t$ must be less than a month, say, a half month. The long-term variation of mineral volume is calculated by

$$V_i' (t + \Delta t) = V_i(t) + \Delta t \sum_{r=1}^{1 \text{year}} V_i' \Delta t.$$  \hspace{1cm} (48)

Equation 48 is based on the assumption that annual mineral-volume changes vary smoothly over the large timescale $\tau$. In the numerical simulations presented here, as a first order approximation, activity coefficients are taken to be 1. Numerical simulations show that calcrites can form near the Earth's surface well above the water table (Fig. 4a,b,c). Figure 4a,b show that sepiolite accumulates below a calcite-rich horizon, the upper part of which is almost exclusively pure calcite. At the bottom of the quartz dissolution zone, quartz is replaced only by sepiolite. Higher in the profile, both calcite and sepiolite accumulate. Sepiolite grows at expense of quartz through the chemical divide mechanism in the dry season (Fig. 4d,e); some of the precipitated sepiolite in turn dissolves in the following wet season (Fig. 4f,g), making room for calcite accumulation. Thus, this zone would display a texture of parent rocks replaced by sepiolite, which is in turn partly replaced by calcite. Near the top of the calcrete, because there is no net sepiolite accumulated over each climate cycle, parent rocks appear to be "directly" replaced by calcite: the sepiolite, though all gone, still has played a key role in removing silica. Furthermore, Fig. 4a,b show that the porosity in the calcrete reaches its minimum value over most of the profile. We set this minimum value at 0.15 to avoid unrealistic zero porosity. This implies that in these intervals of the profile the total (tiny) volume of quartz dissolved can be effectively refilled with calcite and sepiolite over each climate cycle, leaving the original textures and structures preserved. That is, the replacement is pseudomorphic. Also, the porosity decrease may contribute to calcrete induration. All these predicted details just nicely coincide with the observations summarized above. In addition, the model suggest that a high porosity zone could be developed just under the pure calcite zone.

Figures 4 and 5 show that the spatial sequence of calcite and sepiolite accumulation is insensitive to the reaction-rate constant ratio of sepiolite to calcite, provided that the rate constants ($k_2$ and $k_5$) of the two minerals are high enough relative to that ($k_1$) of quartz. Experimental data do show that the reaction rates for both calcite and sepiolite are higher than that for quartz (DOVE and CRERAR, 1990; RIMSTIDT and BARNES, 1980; MORSE, 1983; INSKEEP and BLOOM, 1985; BRADY, 1992). This insensitivity results from the asymmetry of reaction rate laws for dissolution vs. growth and from the proposed chemical reaction path. The reaction rate of a mineral, $R$, is roughly related to the saturation index, $\Omega$, by $R = k(1 - \Omega)$, where $k$ is a rate constant ($R > 0$ means dissolution and $R < 0$ means precipitation). $R$ is not a symmetric function of $\Omega$ around $\Omega = 1$. As $\Omega$ approaches 0, $R$ reaches its maximum value, $k$. That is, there is a upper limit on mineral dissolution rate. In contrast, if mass transport is fast enough, there is no upper limit on the precipitation rate. As a result, the amount of calcite that can be dissolved in a wet season is limited, but calcite can in principle precipitate in any amount during a dry season, if the groundwater contains enough Ca and evaporation is strong enough. It is this asymmetry that causes calcite to accumulate in most of the profile over each climate cycle. This is, however, not the case for sepiolite. If the concentration ratio of silica to Mg is low in groundwater, most of the silica needed for sepiolite precipitation is supplied by quartz dissolution, and thus sepiolite precipitation in a dry season is limited by slow dissolution of quartz. As a result, near the top of the profile, sepiolite precipitated in a dry season would be effectively removed by its fast dissolution in the following wet season. This is why sepiolite accumulates below the calcite-rich zone.

The chemical divide effect (HARDIE and EUGSTER, 1970) between Mg and SiO$_2$ can be seen clearly in Fig. 4d. It is caused by sepiolite precipitation and driven by evaporation. It requires the mole concentration ratio of Mg to SiO$_2$ in the groundwater water to be greater than 2/3 in the case simulated here. Otherwise, the evaporation cannot deplete silica.
Fig. 4. Simulated profile of a calcrete replacing quartzite. (a) Mineral volume fractions and porosity vs. scaled depth at 10^3 years after the calcrete started to form. Quartz has dissolved in the upper half of the profile; both sepiolite and calcite have accumulated. Sepiolite accumulates below the calcite-rich zone. (b) Mineral volume fractions and porosity versus scaled depth at 2 x 10^5 years. (c) Saturation degree θ (moisture) profile at 2 x 10^5 years. Water table is located at the bottom of the profile. (d) Concentration profile of aqueous species at the end of the dry season at 2 x 10^5 years. Because of the chemical divide imposed by growth of sepiolite, Mg^{2+} concentration increases while SiO_2 (aq) concentration decreases toward the top of the profile. It is this SiO_2 depletion that forces quartz to dissolve. (e) Mineral dissolution
rates vs. depth at the end of the dry season at $2 \times 10^5$ years; negative values represent growth rates. (f) Concentration profile of aqueous species at the beginning of the wet season at $2 \times 10^5$ years. (g) Mineral dissolution rates vs. depth at the beginning of the wet season at $2 \times 10^5$ years. Parameter values in this simulation are chosen as follows: dry season duration = 0.8 years, $M = 10^{-4}$ molality, $m_{Ca} = 3$, $m_{Mg} = 3$, $m_{Al} = 1$, $m_{Si} = -1.5$, $m_{Na} = 0$, $m_{K} = 0$, $m_{HCO}_3 = 0$, $m_{SO}_4 = 0$, $p_{CO}_2 = 10^{-3}$ atm, $u = 10$, $q_e = 0.01$, $q_{inf} = 0.01$, $P_{Quarts} = 0.85$, $k_{Quarts} = 5$, $k_{Calcite} = 30$, $k_{Sepiolite} = 80$, $k_{Amorphous~Silica} = 5$, $h' = 2$, $n = 2$. 
in water, and quartz can not dissolve in dry seasons. Calcite then grows mainly in the original pore space, and no replacement takes place, as shown in Fig. 6. The requirement of a high concentration of Mg relative to Si in groundwater is consistent with reported water compositions in calcrete regions (Arakel, 1986, Table 1; Goudie, 1971, Table 5) and the occurrence of dolomite and Mg-rich calcite in calcretes (Arakel, 1986; Watts, 1980; Hay and Reeder, 1978). Some textures indicate that the low-Mg calcite in calcretes may be transformed from original high-Mg calcite (Watts, 1980). Arakel (1986) reports for the water from the calcrete area in central Australia that SiO2(aq) becomes depleted as water salinity increases. Also, Mann and Deutscher (1978) report concurrent Mg increase and Si decrease with Cl− in a calcrete aquifer in Western Australia. In this aquifer the water is supersaturated with sepiolite but undersaturated with amorphous silica. All this evidence supports the idea that the chemical-divide mechanism operates in calcrete formation.

Furthermore, Figs. 4 and 6 demonstrate the effect of Mg/Si ratio in groundwater on the intensity of calcitization. If the upstream groundwater contains high enough Mg, water evaporation causes Mg and Mg/Si in groundwater to become higher downstream, and therefore increases the intensity of calcitization. Thus, our model predicts that calcretes would increase in their thickness and Mg content downslope. The prediction agrees with observations (Nahon, 1976; Carlisle, 1983; Arakel, 1986; Fig. 7c; Wright and Tucker, 1991, Fig. 6b).

Increasing wet season duration or infiltration rate shifts sepiolite accumulation downward and significantly reduces the thickness of the calcite zone at the top of the profile (Figs. 7, 8). If wet season duration is long enough and infiltration rate is high, rainwater can leach away any calcite accumulated in dry seasons, and then calcretes cannot form. On the other hand, if wet season duration is too short and infiltration rate is too low, there is not enough rainwater to dissolve sepiolite (or attapulgite) and to flush away the dissolved components effectively, and then little space is created for calcite precipitation by removing parent rocks. Therefore, under certain climate conditions, the replacement of silicate rocks by calcretes would proceed most effectively.

Figures 8 and 9 demonstrate that an increase in Pco2 in calcrete profiles dramatically reduces both calcite and sepiolite accumulation. This is consistent with the idea suggested by Salomons and Mook (1986) that the degassing of CO2 is another factor causing calcite precipitation.

CONCLUSIONS

In the model herein the genesis of replacement is directly related to seasonally alternating dry-wet climates and to appropriate groundwater (or circulating soil water) compositions. In a dry season, water evaporation causes CaCO3 and sepiolite (or attapulgite) to precipitate. If groundwater contains enough Mg2+, the sepiolite precipitation by the chemical-divide mechanism depletes SiO2(aq), resulting in the dissolution of parent silicates. In the following wet season, sepiolite dissolves fast, silica and cations are flushed away by
Calcrete replacement of silicate rocks

We simulate the replacement of quartzite by calcrete with a transport-reaction model, which consists of nonlinear partial differential equations taking account of mass conservation, dispersion, advection, evaporation, and the kinetics of mineral reactions. The hydrodynamics of unsaturated medium is applied in determining water flow in calcrete profiles. Seasonal climate changes are explicitly incorporated as boundary conditions. The model is solved numerically on two different timescales, one of 1 month, the other 1000 years, both of which are essential for the overall phenomenon. The model successfully produces the mineral and textural zonation observed in many calcretes (namely, at the bottom of the profile the parent rock is first replaced by sepiolite, only part of which is in turn replaced by calcite, whereas at the top of the calcrete the sepiolite is itself completely replaced by the calcite, which appears to "directly" replace the parent rock). The model can produce calcrete near the Earth's surface well above the water table. Low $P_{CO_2}$, intensive evaporation, and long dry seasons all are predicted to produce thicker calcretes.

Calcretes constitute an effective geochemical tool that, via replacement, removes parent silicate rocks and shapes the landscape of semi-arid countries. Our model provides a mechanism that accounts for the high efficiency of replacement in removing silicates. This high efficiency is attributed to two factors. First, quartz (the most resistant silicate) dissolution in dry seasons is accelerated by high cation concentrations in porewater. Second, in dry seasons, by the chemical-divide mechanism, water evaporation (through the precipitation of attapulgite or sepiolite) makes porewater very undersaturated with silicates, thus also accelerating silicate dissolutions.

In the numerical simulations shown here, silica concentrations are high enough for chaledony or opal-CT to form (Fig. 4f). This coincides with the occurrence of minor chaledony in calcretes (Goudie, 1971; Nahon, 1976; Arakel, 1986). Because the precipitated silica directly comes from the dissolution of sepiolite, the predicted rock texture would show that sepiolite is replaced by the precipitated silica. This texture is indeed observed in the calcretes of central Australia (Arakel, 1986) and in the Argus Range of California, USA (Hay and Wiggins, 1980). Furthermore, also because this precipitated silica is derived from Mg-phyllosilicates, they should contain traces of Mg as was reported by Ducloux and Laouina (1988). Silicification is often associated with calcretization in semi-arid regions (Goudie, 1971; Watts, 1980). The proposed model thus gives a genetic explanation for the association of sepiolite-palygorskite with silica (e.g., Jones and Galán, 1988). In addition, because the dissolved silica is carried downward or downslope in the rainy seasons, silicification is thus most likely to occur at the bottom of the profile (Reeves, 1970; Watts, 1980) or far down-dip (Arakel, 1986). As calcretization proceeds further, this authigenic silica may also be removed.

Rainwater, making room for CaCO$_3$ precipitation in the next dry season. As climate cycles repeat, CaCO$_3$ is accumulated and silicates are removed. The sepiolite (or attapulgite, or Mg-smectite) serves as a temporary storage of silica between seasons. If the groundwater contains too little aqueous Mg then the model predicts growth of calcium carbonate without removing silicates, thus producing void filling and or displacive textures instead of replacement.

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Fig. 7. Calcrete profiles at $2 \times 10^7$ years. All parameter values used here are the same as those in Fig. 4 except for $q_{inr} = 0.03$ and dry season duration = 0.73 year. Compared with Fig. 8, this figure shows that increasing wet season duration or infiltration rate shifts sepiolite accumulation downward and significantly reduces the thickness of the calcite zone at the top of the profile.

Fig. 8. Calcrete profile at $2 \times 10^7$ years with longer dry season duration ($= 0.8$ year) and lower infiltration rate ($q_{inr} = 0.01$). All other parameter values are as in Fig. 7.
According to the model, high-Mg carbonates are expected to precipitate in dry seasons, because Mg$^{2+}$ is concentrated by evaporation. In the rainy seasons, porewater becomes diluted, and the high-Mg carbonate may transform into low-Mg calcite, as some textures indicate (Watts, 1980). This transformation should take place more completely at the top of a calcrete than at the base, because Mg$^{2+}$ concentration in rainy seasons is increased downward by the dissolution of Mg-phyllosilicates. Therefore, the amount of high-Mg carbonates such as dolomite may increase toward the base of a calcrete, just as observed by Phillips and Milnes (1988).

Figure 2A indicates that the reaction front of calcretization is rather sharp. This sharp front may be caused by the reduction of the mass-transport rate in the water unsaturated zone, where dispersion can be significantly reduced as water saturation degree decreases, so that the whole chemical process may become transport-limited, and the thickness of the reaction front approaches 0 (Ortoleva et al., 1987).

The results presented here demonstrate the importance of short-term climate variations to long-term Earth surface processes. Actual climates may be of multiple timescales ranging from as little as hours to thousand years. We think that realistic geochemical models for the Earth surface processes should take into account this inherent timescale variability of climates. The approach we employ here may have an implication on geochemical modeling of other weathering processes.

Acknowledgments—We are grateful to the U.S. NSF (grants EAR 9003633 and EAR 9104198) and the CNRS of France (grant MRT90L0712) for partial support of this research. We thank Fred M. Phillips as associate editor, J. Ouade, A. White, and anonymous reviewer for their constructive suggestions, and Quade and Phillips for unpublished manuscripts. We also thank R. Dassule, J.-J. Motte, J.-P. Ambrosi, and Marc Benedetti, all of Marseille, and Lorie Canada of Bloomington, for their help.

Editorial handling: F. M. Phillips

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