

Mass transport in sandstones around dissolving plagioclase grains

R. K. Stoessell

Department of Geology and Geophysics, University of New Orleans
New Orleans, Louisiana 70148

ABSTRACT

The dissolution of plagioclase and precipitation of kaolinite is a common late diagenetic process in sandstones. The common occurrence on a thin-section scale of patchy kaolinite adjacent to a dissolving plagioclase grain is consistent with diffusional transport of dissolved constituents combined with precipitation on a favorable nucleation site. The absence in thin-section view of a diffusional related halo of kaolinite around a dissolving grain can be explained by a lack of a halo of favorable nucleation sites.

Numerical modeling results are presented for the transport of aqueous Al by diffusion coupled with fluid flow in sandstones at 100 °C. Within a few months the Al in the anorthite component of plagioclase grains can be removed by diffusion during diagenesis. Fluid velocities needed to overcome diffusion to prevent precipitation on the upstream side of a dissolving grain depend on the *unknown* minimum supersaturation needed for precipitation. These velocities are less than those predicted by the Peclet number but are of the order of metres per year at a distance of a few tenths of a millimetre from the dissolving grain. The *nonlinear* inverse relation of these velocities to the distance from the dissolving grain implies that mass transport to precipitation sites is dominated by fluid flow at distances greater than 1 cm.

INTRODUCTION

Dissolution and/or replacement of feldspars commonly occur during sandstone diagenesis in the Gulf Coast and elsewhere (e.g., Land and Milliken, 1981; Boles, 1982, 1984). This study examines diffusion vs. fluid flow as the transport mechanism for moving aqueous Al away from dissolving plagioclase grains. Al transport is modeled by using coupled diffusion and fluid flow in a two-dimensional finite difference scheme. The results are interpreted in terms of reasonable subsurface fluid velocities and precipitation patterns of kaolinite in the vicinity of dissolving grains.

Authigenic kaolinite commonly occurs near partially dissolved plagioclases (Boles, 1984). The spatial correlation is assumed *in this study* to represent the transport of aqueous Al between the dissolving and precipitating grains. Commonly, the kaolinite forms as a patch on one side of the dissolving grain (e.g., Siebert et al., 1984, Fig. 5). Notably absent are circular halos of kaolinite around dissolving plagioclase grains within the two-dimensional view of a single thin section.

CHEMICAL CONSIDERATIONS

Unlike the albite component in plagioclase, the anorthite component is generally unstable in reservoir fluids at quartz saturation. However, without leaching by large volumes of meteoric water, a critical temperature is needed to initiate

significant dissolution and/or albitization of the anorthite component (Boles, 1982). This temperature depends upon fluid compositions and burial history and varies from about 90 to 120 °C for plagioclase in Gulf Coast sediments (Milliken, 1985).

Feldspar dissolution will locally increase Al and silica concentrations and thus will produce a fluid supersaturated with reference to Al-silicate minerals such as kaolinite, albite, illite, and chlorite. Removal of the aqueous Al from the

vicinity of the grain becomes a race between the transport mechanisms and the *unknown* kinetics of precipitation reactions. Precipitation occurs on favorable nucleation sites in the presence of significant supersaturation.

Total Al activities and approximate concentrations in equilibrium with different aluminum silicates at quartz saturation are plotted in Figure 1 at 100 °C and 300 bar. This figure is limited to the Na₂O-CaO-Al₂O₃-SiO₂-H₂O-HCl system in which the pressure corresponds to a hydro-

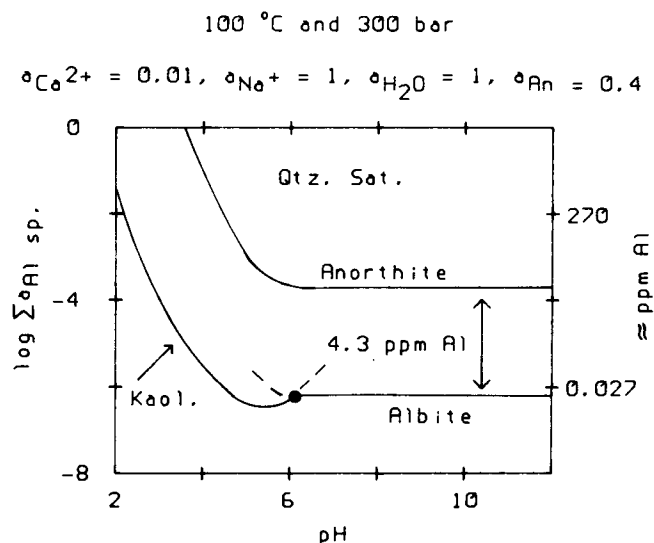


Figure 1. Maximum sum of aluminum activities resulting from anorthite dissolution and minimum sum resulting from precipitation of kaolinite and/or ordered albite for system Na₂O-CaO-Al₂O₃-SiO₂-H₂O-HCl.

static pressure-temperature (P - T) gradient of 25 °C/km. The solubilities of the minerals were computed by using standard thermodynamic P - T algorithms with standard-state data for minerals (Helgeson et al., 1978) and the equations of state for water (Helgeson and Kirkham, 1974) and for aqueous species (Helgeson et al., 1981). Constants for Al-hydroxy complexes were taken from a compilation by Reed (1982; 1985, personal commun.). Anorthite activity was set to 0.4 for An₃₀ (Boles, 1984), and certain activities of aqueous components were held constant at the typical reservoir values indicated in Figure 1.

At quartz saturation, plagioclase dissolution will cause kaolinite to precipitate in acidic solutions with low activities of Na⁺. A Na equivalent of illite forming in sandstones during diagenesis is lacking. Na smectites are presumed unstable because they rarely precipitate except near the earth's surface. In solutions with a higher pH and/or higher activities of Na⁺, ordered albite will precipitate.

The upper curve in Figure 1 follows the log sum of total Al activities as a function of pH in equilibrium with anorthite. The lower curve represents equilibrium with more stable Al-silicate minerals. The 4-ppm difference in Al concentrations between the upper and lower curves can drive diffusion away from a dissolving grain. The presence of additional aluminum complexes, postulated by Surdam et al. (1984) and not considered in Figure 1, will increase the total Al concentration and reduce the time necessary to transport aluminum.

DIFFUSION PARAMETERS

Molecular diffusion in a fluid-saturated sediment takes place in the aqueous phase along a tortuous path. The diffusion coefficient in a fluid medium (lacking sediment), D_{aq} , can be used to estimate D_{sed} , the effective diffusion coefficient for the sediment.

$$D_{sed} = D_{aq} \left[\frac{\phi}{\theta^2} \right] \beta, \quad (1)$$

where ϕ is the porosity fraction, θ is the tortuosity (the ratio of the actual path length, z , to the shortest distance, x , between two points), and β is a random frequency factor discussed below. The term in brackets corrects for the volume of solid matrix, the increased path length, and the pore area perpendicular to the flux in the pore pathways.

Bear (1972, p. 114) used a fluid-saturated, electrically nonconductive, porous solid medium with inclined pores to show

$$F = \frac{\theta^2}{\phi}, \quad (2)$$

where F is the ratio of the electrical resistivity of a cube of fluid-saturated porous solid to that of a

cube of fluid of the same geometric dimensions. In consolidated sandstones, F can be approximated by the empirical relation (Archie, 1942)

$$F = \frac{1}{\phi^2}. \quad (3)$$

In equation 1, β was set to 0.5 to correct for the random movement of aqueous species into branching pores with dead ends at cemented grains, reducing the expected diffusive flux. Stoessel and Hanor (1974) measured diffusion coefficients in an artificially cemented sand having a ϕ of 0.28 and an average grain diameter of 0.2 mm. Their measured coefficients were defined in terms of flux per unit area of pore fluid, equivalent to D_{sed}/ϕ . McDuff and Ellis (1979) used the same procedure to measure diffusion coefficients in unconsolidated sediments. Comparisons of the measured values with calculated estimates by equations 1 and 2 imply that β decreased from near unity in the unconsolidated sediments to 0.5 in the cemented sand.

Mackin and Aller (1983) reported D_{aq} for Al(OH)₄⁻ is 1.04×10^{-5} cm²/s at 25 °C at infinite dilution. I am not aware of other measurements of the aqueous diffusion coefficient for Al³⁺ or for other Al complexes. Calculations of aqueous speciation of Al indicate that under probable reservoir pH conditions (between 4 and 8), most of the Al will be complexed with inorganic or organic anions. Tabulated 25 °C values of diffusion coefficients of aqueous species generally fall between 1×10^{-5} and 2×10^{-5} cm²/s (Harned and Owen, 1958). An average value of D_{aq} for Al has been assumed to be 1.5×10^{-5} cm²/s at 25 °C.

Estimates of the increase in D_{aq} for Al with temperature can be made by using the Stokes-Einstein relation for diffusion of spherical particles and by the Arrhenius equation. An increase by a factor of 3.13 between 25 and 100 °C is predicted by the former, if a decrease in viscosity by a factor of 2.5 for NaCl-rich fluids typical of formation waters (Craft and Hawkins, 1959, p. 264) is assumed. An increase by a factor of 3.45 is predicted from the latter by Manheim (1970) over the same temperature range. Averaging the two increases gives D_{aq} for Al of about 5×10^{-5} cm²/s at 100 °C. The effect of pressure is negligible on D_{aq} (Manheim, 1970).

FLUID FLOW AND DIFFUSION

A wide range of subsurface fluid velocities is expected in sandstones in sedimentary basins. Compaction of sediments in subsiding intracratonic basins will generate fluid velocities below 0.3 cm/yr (Bethke, 1985). Higher velocities would be expected from compaction in a rapidly subsiding basin such as the Gulf Coast. Wood and Hewett (1982) computed fluid velocities of 1 m/yr in convection cells within porous, thick,

permeable, medium- to coarse-grained sandstones. Fluid flow of about 1 m/yr or more occurs in gravity-driven groundwater systems (Bethke, 1986) and hydrothermal systems (Cathles, 1977).

The dimensionless Peclet number, Pe, computed for a particular distance, d , "can be interpreted as the ratio of the effectiveness of mass transfer by fluid flow to that of diffusion" (Wood and Hewett, 1982)

$$Pe = V/(D_{sed}/d), \quad (4)$$

where V is the fluid velocity and d is an appropriate distance observed around a dissolving grain in thin section, 0.2 to 5 mm. D_{sed} can be estimated from equations 1–3 by using the porosity and the procedure previously discussed.

If Pe is unity, diffusive transport of constituents away from a dissolving grain may be effectively canceled on the upstream side by fluid flow. If we assume a sandstone porosity of 15% at 100 °C, V decreases from 900 to 35 cm/yr as d increases from 0.2 to 5 mm. In this study, V is called V_p , the Peclet velocity, when Pe is unity.

Diffusive transport will still exist locally on the upstream side of the dissolved grain if $V \geq V_p$. However, the Al concentrations will be much lower, reducing the supersaturation of Al-silicate minerals and lowering the probability of precipitation during the time span of dissolution. Numerical modeling is used below to delineate the concentration distribution of aqueous Al around the grain as a function of dissolution time, fluid velocity, and diffusional flux.

NUMERICAL MODELING

A Fortran computer program for a Zenith 150 personal computer, involving an implicit alternating-direction finite difference method (Carnahan et al., 1969, p. 452), was used to model two-dimensional diffusion coupled with one-dimensional fluid flow parallel to the x axis. A constant aqueous Al composition was maintained at the surface of the dissolving grain, corresponding to transport control of the rate of dissolution. Qualitative effects on the modeling results due to assuming transport control rather than surface-reaction controlled dissolution are discussed later.

An (x,y) grid of 401 by 100 points was set up with an Al point source at the (201, 1) position. The equations governing transport, initial, and boundary conditions are given below. C is the Al concentration (g/cm³), t is the time in seconds, and C^0 is C at the surface of the dissolving grain. Diffusive flux was not allowed to cross the exterior grid boundaries.

$$\frac{\partial C}{\partial t} = D_{sed} \left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right] - V \left(\frac{\partial C}{\partial x} \right)$$

for $t > 0$, and for all (x, y) except along boundaries; $C = 0$ for all (x, y) except $(201, 1)$ at $t = 0$; $C = C^0$ at $(201, 1)$ at $t \geq 0$ until the grain is dissolved; $\partial C/\partial x = 0$ at $x = 1$ and $x = 401$ and $\partial C/\partial y = 0$ at $y = 1$ and $y = 100$, for $t \geq 0$.

Equal grid point distances of 0.05 cm were used to set up a 20 by 5 cm area. Boundary conditions for the grid size prevented using smaller grid point distances. D_{sed} was derived from equations 1-3 by assuming a sandstone of 15% porosity. Excess Al concentrations of 4 ppm were used at the point source to simulate the dissolution of the anorthite component of an An_{30} plagioclase grain. Fluid velocities ranged

from 0 to 126 cm/yr, with 0.5 daytime steps during total times of up to 60 days.

Excess Al concentrations of 1 ppm are contoured in Figure 2 as a function of time around a point source, simulating Al movement by diffusion away from a dissolving plagioclase cube with 0.1-mm edges. The contour lines move 0.5 cm outward in 27 days before diffusion depletes the Al in the anorthite component. Within 4 days, the excess Al concentrations around the point source decay to below 1 ppm. The time to move the Al is inversely proportional to the concentration gradient; hence, additional Al complexing agents will increase the effectiveness of diffusion (as well as fluid flow).

The effects of coupled diffusion and fluid flow on the location of the 1-ppm excess Al contours after a time period of 30 days are shown in Figure 3. The point source was not allowed to become Al-depleted. The contour locations reflect quasi-steady-state conditions, achieved within weeks and lasting for months until the boundary conditions began to affect the results. Fluid flow spreads the released Al over a wide area downstream, allowing diffusion to rapidly dissipate the excess concentrations. Increasing the fluid velocity decreases the total area within the 1-ppm excess Al contours.

The modeling results are based on transport control of the dissolution rate rather than surface-reaction control. Petrographic examination of partially dissolved plagioclase grains suggests that dissolution is controlled by the latter rather than the former (Boles, 1984). The effect of surface-reaction control would be to lower the Al concentration at the surface of the grain, moving the excess Al contours closer to the

grain surface shown in Figures 2 and 3 and extending the total dissolution time as shown in Figure 2.

The presence of additional Al complexes, not considered in Figure 1, will increase the total Al concentration by a given factor at the surface of the plagioclase grain. Multiplying the 1-ppm contours in Figures 2 and 3 by this factor will correct the figures to this situation. However, the uncomplexed Al concentration is set by the activity product of the anorthite component (assuming quartz saturation and constant pH and Ca^{2+} activity) at the plagioclase grain surface. Consequently, the uncomplexed Al concentration at the contours shown in Figures 2 and 3, to a first-order approximation, can be independent of the total Al concentration represented by the contour.

The dissolution and precipitation reactions depend on the uncomplexed Al^{3+} concentration. Precipitation will occur at favorable nucleation sites in the presence of an unknown minimum supersaturation. To prevent precipitation at a particular distance on the upstream side of a dissolving grain, fluid flow must only prevent the accumulation of aqueous uncomplexed Al concentrations equal to or greater than the minimum supersaturation.

For the sake of discussion, let us assume that the position of the 1-ppm contour of excess Al shown in Figure 3 represents the conditions for minimum supersaturation for precipitation. The distance d upstream of this contour from the dissolving grain would be the maximum distance that precipitation would occur for V , the corresponding fluid velocity. V is compared with V_p in Table 1 by using the appropriate d values from Figure 3. The ratio of $V:V_p$ increases from 0 to 0.46 as d decreases from 0.54 to 0.06 cm.

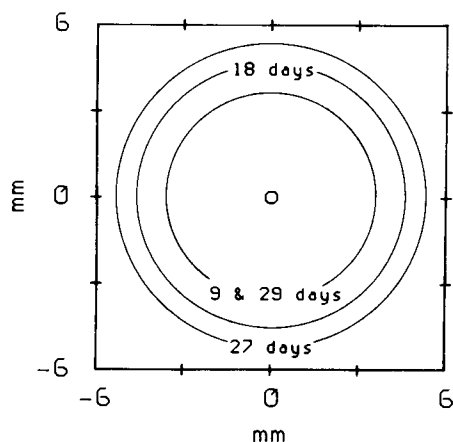


Figure 2. Contours of 1-ppm excess Al resulting from diffusion away from dissolving An_{30} plagioclase cube measuring 0.1 mm on an edge. See text for further explanation.

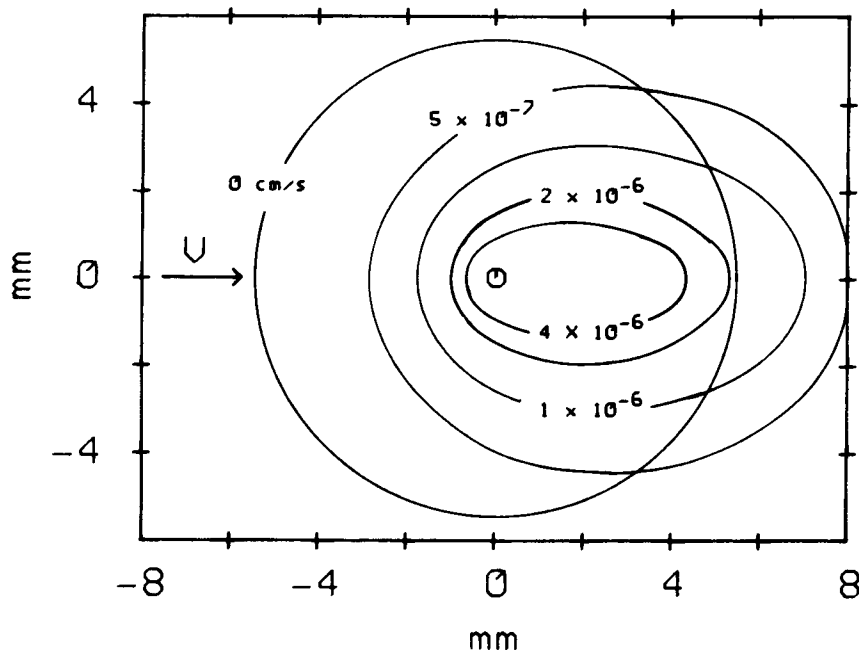


TABLE 1. $\frac{V}{V_p}$ VERSUS $\frac{d}{V}$ FROM FIGURE 3

$\frac{d}{V}$ (cm)	$\frac{V}{V_p}$ (cm/yr)	$\frac{V}{V_p}$ (cm/yr)
0.540	0	32
0.275	16	65
0.170	32	104
0.100	63	177
0.065	126	273

* Distances upstream from the source to the 1 ppm contour.

Figure 3. Contours of 1-ppm excess Al resulting from coupled diffusion (away from point source) and fluid flow (V is parallel to x axis). See text for further explanation. Note that 0.5, 1, 2, and 4×10^{-6} cm/s correspond to 16, 32, 63, and 126 cm/yr, respectively.

This ratio approaches unity near the surface of the grain. If the position of a contour for a larger excess Al concentration were used for the necessary supersaturation, the smaller d value would increase V_p , making V/V_p a smaller number.

DISCUSSION

Fluid flow will reduce mass transfer by diffusion on the upstream side of a dissolving plagioclase grain. The fluid velocity V needed to prevent precipitation of kaolinite (at quartz saturation) at a distance d from the grain is less than that predicted from V_p , the Peclet velocity. V depends upon the *unknown* minimum supersaturation needed to initiate precipitation; however, V/V_p approaches unity as the supersaturation required for precipitation decreases and as d goes to zero.

Interpretation of the modeling results depends on the assumption of the solution conditions necessary for precipitation. In addition, D_{sed} used in the modeling will vary with temperature, formation porosity, and tortuosity, and the modeling results reflect the use of transport control rather than surface-reaction control of the dissolution rate. Nonetheless, some general conclusions can be stated for sandstones undergoing diagenesis. At upstream distances within a few tenths of a millimetre from a grain surface, fluid velocities on the order of metres per year are needed to overcome mass transport by diffusion. Fluid velocities of this magnitude are not expected in deeply buried sandstones. At distances greater than 1 cm, mass transfer from fluid velocities on the order of 1 cm/yr and less will dominate over diffusional transfer. These are reasonable fluid velocities in subsurface sandstones. In addition, the dispersal nature of diffusional transport may reduce concentrations below those needed to initiate precipitation.

In thin-section view, patchy kaolinite is commonly observed within a few tenths of a millimetre from plagioclase grains that have undergone dissolution (Thomson and Stoessell, 1985). These occurrences are consistent with diffusional transport of dissolved constituents coupled with the location of favorable nucleation sites. The absence of halos of kaolinite around a dissolving plagioclase grain in thin section can be due to the absence of a halo of favorable nucleation sites.

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Reviewer's comment

Gives a nice explanation for a texture seen in some sandstones. Moreover, the hypothesis may help in the evaluation of ancient fluid velocities.

Ronald Surdam