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RATE CONTROL OF MINERAL DISSOLUTION UNDER EARTH SURFACE CONDITIONS*

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ABSTRACT. Simple calculations indicate that increased renewal of water, or flushing, accelerates the dissolution of minerals in water-saturated rocks, soils, and sediments only up to a limiting flushing rate beyond which flushing has virtually no effect and dissolution is controlled solely by mineral reactivity. Actual dissolution rates generally cannot be accurately predicted from laboratory experiments, because experiments ordinarily fail to reproduce the composition and structure of natural mineral surfaces, especially with regard to adsorbed trace inhibitor species, and poorly understood biological factors are usually ignored. Laboratory experiments can be helpful, however, in distinguishing rate-limiting mechanisms, or in other words, whether dissolution is primarily controlled by surface reactions or by transport of ions away from the surface. Discernment of the type of controlling mechanism is useful in that the slowest rate of transport-controlled dissolution, that where transport is by molecular diffusion, can be calculated. Slower measured rates than this are due to surface reaction-control and are dependent upon the chemistry and not upon the hydrodynamic state of the solution.

Evidence based on laboratory experiments, theoretical calculations, and observations of partly dissolved minerals shows that three major dissolution processes, the weathering of feldspar on land and the dissolution of skeletal $CaCO_3$ and biogenic silica in the deep sea, all represent examples of surface reaction controlled dissolution. Correlation of rate controlling mechanism with solubility enables tentative predictions to be made for other minerals whose dissolution kinetics have not yet been studied. On this basis it is probable that many other dissolution processes occurring at low temperatures are also controlled by surface reaction and not by transport through solution nor by retarded diffusion through continuous coatings on mineral grains.

INTRODUCTION

Dissolution of minerals by water is an important Earth surface geochemical process. Notable examples include weathering in soils and dissolution of planktonic tests in the deep sea. Although much work has been done in predicting, from thermodynamic calculations, whether or not dissolution *can* occur, little attempt has been made to elucidate *how* dissolution occurs under natural conditions. The purpose of this paper is to point out some of the factors that control the rate of dissolution of minerals and to give the reader a better idea of the applicability of chemical kinetics to the solution of geochemical problems.

THE ROLE OF FLUSHING IN DISSOLUTION

The following calculation is presented purely for illustrative purposes to show in a simple manner how flushing rate can affect the rate of dissolution of minerals. It does not necessarily apply to any natural situation. Assume that a fixed volume of pore space within a water-saturated rock, soil, or sediment is continually flushed with water and that the volume is sufficiently small or well mixed that the concentration of a dissolved species i within it is spatially uniform (box model). Species i is added to the pore water by dissolution of a sparingly soluble salt

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so that over short time scales the pore volume doesn't increase. Also, let water entering the volume have zero concentration (to insure undersaturation). The expression for the conservation of mass is:

$$\frac{dc}{dt} = R - \frac{F}{V} c \tag{1}$$

where:

c = concentration of dissolved i (mass per unit volume)
t = time
F = inflow = outflow = flushing rate (volume per unit time)
V = fixed volume of water with concentration c
R = rate of dissolution (mass per unit volume of solution per unit time)

Now assume that the rate of dissolution is linearly proportional to the departure of c from the saturation concentration c_{eq}, in other words that $R = k(c_{eq} - c)$, and that the fixed volume element is at steady state $[dc/dt = 0]$. Under these conditions:

$$c = \frac{k\, c_{eq}}{k + k_f} \tag{2}$$

$$R = \frac{k k_f c_{eq}}{k + k_f} \tag{3}$$

where:

k_f = flushing frequency = F/V
k = dissolution rate constant

Note from eqs (2) and (3) that as flushing rate F is increased (at constant k, c_{eq}, and V), c decreases, and R increases. In other words, dissolution rate is accelerated by the flushing because of the drop in c. If flushing rate is sufficiently high that $k_f >> k$, then eqs (2) and (3) reduce to:

$$c \approx (k/k_f)c_{eq} << c_{eq} \tag{4}$$

$$R \approx kc_{eq} \tag{5}$$

In this case the maximum rate of dissolution, kc_{eq}, is attained which is independent of flushing rate.

The opposite situation results if flow is sluggish. As F decreases, c increases, and R decreases. If $k_f << k$, then:

$$c \approx c_{eq} \tag{6}$$

$$R \approx k_f c_{eq} \tag{7}$$

In this case saturation is attained, and the rate of dissolution is controlled solely by the rate of flushing.

These calculation show that, as is generally assumed, increased flushing of a rock, soil, or sediment by water increases the rate of dissolution. However, if flow is continuous and sufficiently high, the calculations also show that a limit can be reached beyond which flushing rate is no longer a controlling factor. Whether or not this limit is reached in a given natural water can be estimated by determining the state of saturation of the water with respect to the dissolving mineral. Langmuir (1971) states that ground waters draining limestones are close to saturation with calcite ($c/c_{eq} > 0.5$); thus, dissolution of the calcite is probably strongly affected by flushing rate. By contrast, waters draining feldspathic terrains are often highly undersaturated with respect to the dissolving feldspars (Garrels and Christ, 1965; Helgeson, Garrels, and Mackenzie, 1969; Droubi and others, 1976). Here dissolution rate, in zones where pore spaces are continually filled with water, is most likely controlled more by the reactivity of the feldspar grains than by flushing rate. (Of course, in the unsaturated zone of a soil, flushing controls the rate of dissolution simply because of the need for water.)

The above discussion shows that one must be careful in assuming that dissolution of minerals is directly proportional to flushing rate. This is true only when waters are sufficiently close to saturation that reactivity of the minerals can be neglected. The main thing to consider is the rate of flushing *relative to the rate of mineral reaction* (as embodied in k) and not simply the flushing rate itself, a point that has also been recently emphasized by Fouillac, Michard, and Bocquier (1977).

KINETICS OF DISSOLUTION

In the above discussion major emphasis is placed on the roles of flushing and mineral reactivity as they affect the degree of undersaturation. Nothing has been said so far about how fast dissolution may occur for a given, fixed degree of undersaturation or how dissolution rate actually varies with varying undersaturation. The purpose of this section is to address these questions by presenting theoretical arguments that limit speculation regarding the rates, mechanisms, and functional dependence of dissolution.

Rate-limiting mechanisms.—Dissolution rate at a fixed degree of undersaturation is limited by the following processes: (1) transport of solute away from the dissolving crystal, (2) detachment of ions or molecules from the surface of the crystal (including desorption, surface diffusion, et cetera), or (3) a combination of transport and detachment. (For further details concerning rate mechanisms consult Nielsen, 1964, and Ohara and Reid, 1973.) In the first case we are dealing with pure "transport-controlled" kinetics, in the second with "surface reaction-controlled" kinetics, and in the third with mixed or partial surface reaction-controlled kinetics. The difference between the three processes can be seen in figure 1 and from the following discussion.

In pure transport-controlled dissolution ions are detached so rapidly from the surface of a crystal that they build up to form a saturated solution adjacent to the surface. Dissolution is then regulated by transport of these ions via advection and diffusion into the surrounding undersaturated solution. The rate of dissolution depends upon flow velocity and the degree of stirring with increased stirring and flow resulting in accelerated transport and, therefore, faster dissolution. (In the special case where crystals are so small that they are carried along with eddies, dissolution is not enhanced by further stirring — see Nielsen, 1964.)

In pure surface reaction-controlled dissolution ion detachment is sufficiently slow that ion buildup at the crystal surface cannot keep pace with advection and diffusion, and the resulting concentration level adjacent to the surface is essentially the same as that in the surrounding solution (see fig. 1). In this case increased flow and stirring have no effect on dissolution rate.

Intermediate cases between pure transport-control and pure surface reaction-control exist where surface detachment is sufficiently fast that the surface concentration builds up to levels greater than the surrounding solution but lower than that expected for saturation. This is also shown in figure 1.

Normally dissolution via surface reaction control is slower than dissolution via transport control because transport control results from more rapid surface detachment. However, for rapidly dissolving substances it is possible (at least in principle) to attain a stirring rate so high that ions are prevented from building up to saturation near the crystal surface, and, as a result, rate control by surface reaction occurs. In this case surface reaction control is faster than transport control. Nevertheless, this situation is normally achieved in the laboratory only at stirring rates greatly exceeding those in natural waters, so that for our purposes we may assume that transport controlled dissolution, for any given substance, is always faster than that for surface reaction control.

The slowest manner by which a crystal can dissolve via transport-controlled kinetics is by pure diffusion without advection due to stirring

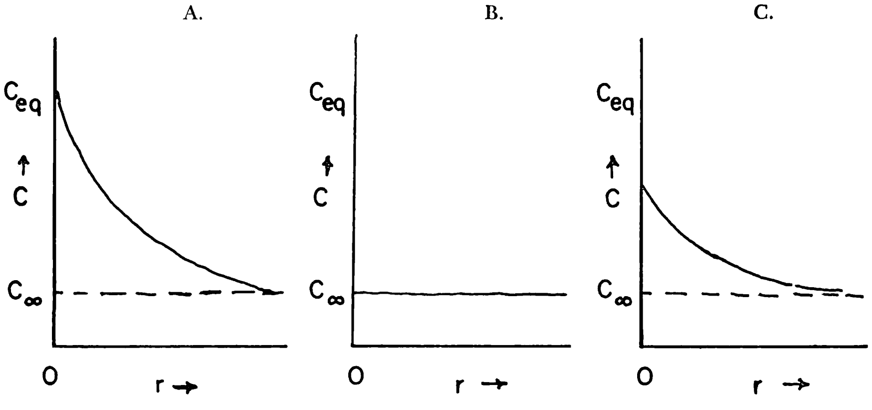


Fig. 1. Concentration C versus distance r from a crystal surface for three rate controlling processes. (C_{eq} = saturation concentration; C_∞ = concentration out in solution).

(A) Transport-control; (B) surface reaction-control; (C) Mixed transport and surface reaction-control.

or flow or in other words in water that is stagnant over the time and distance scales of molecular diffusion. In this case we have "diffusion-controlled" kinetics. The rate of diffusion-controlled dissolution, which can be readily calculated, defines a boundary between more rapid, transport-controlled rates and slower, surface reaction-controlled rates. Consequently, comparison of rates calculated for diffusion control with measured rates enables one to deduce the rate-controlling mechanism and, thereby, decide whether or not dissolution is affected by stirring and flow. Conversely, if no measured rate data are available and the water is reasonably stagnant (or particles are sufficiently small that they are carried along with the eddies), calculation of the diffusion-controlled rate provides a measure of the maximum dissolution rate to be expected.

An appropriate expression for diffusion-controlled dissolution (Frank, 1950; Nielsen, 1964) in natural waters (Berner, 1971) is:

$$R = \frac{D_s \phi \bar{A} \, (c_{eq} - c)}{r} \tag{8}$$

where:

R = rate of dissolution in terms of mass per unit volume per unit time

c = concentration in the outer solution

c_{eq} = equilibrium or saturation concentration

r = spherical radius of the dissolving crystals

D_s = diffusion coefficient in the water, soil, rock, et cetera

ϕ = porosity

$\bar{A}$ = surface area of dissolving crystals per unit volume of solution

Eq (8) is most applicable if the dissolving crystals are equidimensional (ideally spheres), more-or-less uniform in size, and separated by at least five diameters on the average (see Nielsen, 1964).

Eq (8) shows that the rate of diffusion-controlled dissolution is directly proportional to the degree of departure from equilibrium ($c_{eq} - c$). This assumption, which was used in the model of the previous section, is often used in diagenetic models (for example, see Lerman, 1975; Schink, Guinasso, and Fanning, 1975). It is the correct functional representation if dissolution is purely transport controlled, whether by diffusion alone or by stirring (Ohara and Reid, 1973). However, if dissolution rate is controlled by surface reaction, the functional relationship is often not first order and can be exceedingly complex. Some examples of complex and higher order kinetics are provided by the results of Berner and Morse (1974), Sjöberg (1976), and Plummer and Wigley (1976) for calcite dissolution. Since I will show later that several geochemically important dissolution processes are surface reaction-controlled it is likely that the assumption of first order dependence upon the degree of undersaturation is, in general, incorrect. The fact that field data can be fitted to a first order model does not prove the model correct, because the same data can often be just as well fitted by higher order expressions.

Another problem is that at high degrees of undersaturation surface detachment can be so fast (because of a strong functional dependence on undersaturation) that transport-controlled dissolution results, whereas as equilibrium is approached detachment rate drops rapidly so that surface reactions become rate limiting. Thus, the same mineral in the same solution may experience a change in mechanism as equilibrium is approached. This means that one must be careful to determine the state of saturation before undertaking kinetic predictions.

A simpler method for determining the rate-controlling mechanism for dissolution is microscopic examination of the surface morphology of partly dissolved crystals. Crystals dissolved by transport control should exhibit smooth surfaces with a relative absence of crystallographically controlled surface features such as etch pits. This is because ion detachment over the entire crystal surface is so rapid that selective etching does not occur. Rapid detachment results in formation of both a solution layer of laterally uniform equilibrium concentration adjacent to the surface and a smooth, generally rounded surface (see pl. 1-A). (In larger crystals where local convections may enhance local dissolution rates, smooth but irregular shapes may result.)

During surface reaction-controlled dissolution ion detachment is so slow that selective dissolution of the crystal surface occurs. Low energy, flat, defect-free portions of the surface are relatively immune to dissolution whereas regions of excess energy, such as occur at intersections of dislocations with the surface, are places of preferential attack. Also, ion detachment occurs at different rates in different crystallographic directions. As a result of preferential dissolution, a surface results that is angular and shows crystallographically controlled and usually geometrically regular etch pits, ledges, corners, et cetera (see pl. 1-B).

Another method for elucidating the rate controlling mechanism is determination of the temperature dependence of dissolution rate. At constant degree of undersaturation and constant surface area, eq (8) upon differentiation becomes:

$$\frac{\partial \ln \mathrm{R}}{\partial(1/\mathrm{T})} = \frac{\partial \ln \mathrm{D_s}}{\partial(1/\mathrm{T})} = -\mathrm{E_d}/R \tag{9}$$

where:

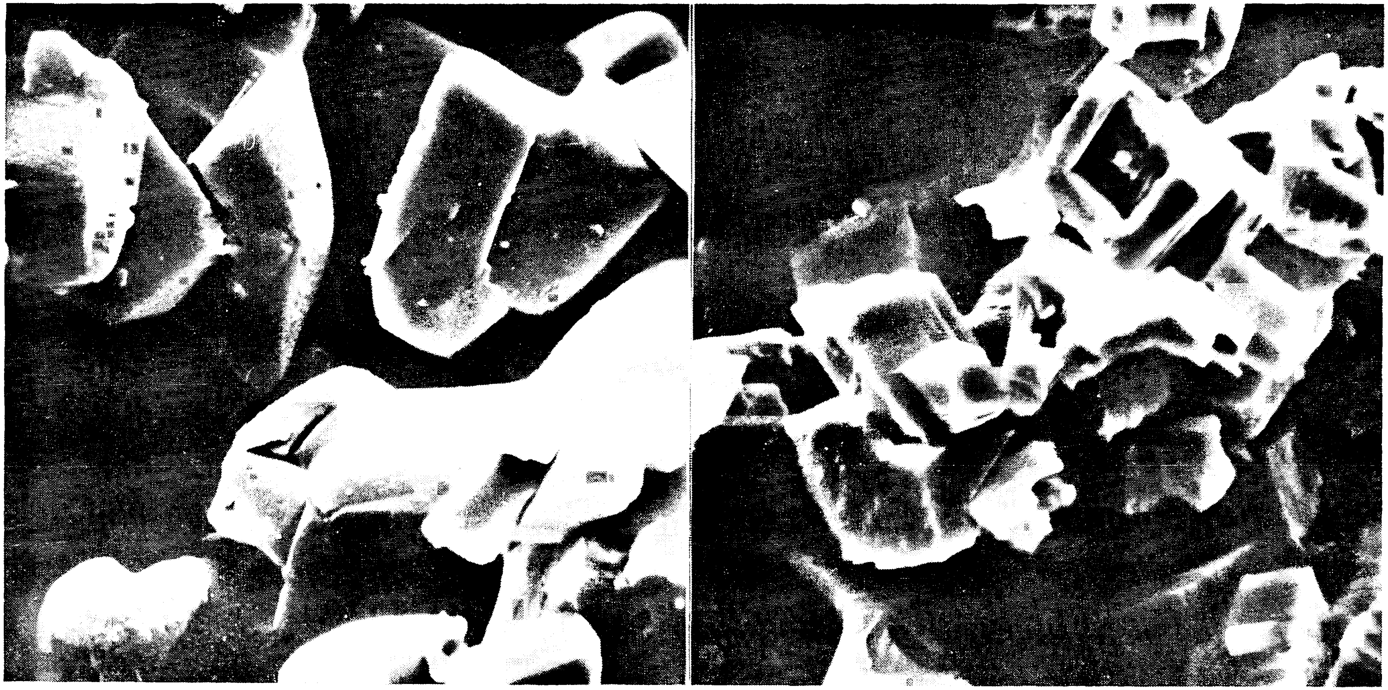
T = absolute temperature

$\mathrm{E_d}$ = activation energy for diffusion

R = gas constant

Values of $\mathrm{E_d}$ for common salts over the interval 0° to 25°C, calculated from the data of Robinson and Stokes (1959), fall in the range 4 to 5 kcal/mole. Thus, for diffusion controlled dissolution a plot of ln(R),

PLATE 1



Scanning electron photomicrographs of reagent grade calcite partially dissolved in seawater (×5000). (After Berner and Morse, 1974.) (A) Diffusion-controlled dissolution at pH = 3.9, $P_{CO_2} = 10^{-2.5}$ (80 percent of original mass removed by dissolution). (B) Surface reaction-controlled dissolution at pH = 6.0, $P_{CO_2} = 10^{-2.5}$ (60 percent of original mass removed by dissolution).

(at a constant degree of undersaturation) versus (1/T) should result in a calculated activation energy equal to E_d, or in other words about 4 to 5 kcal/mole. For surface reaction controlled dissolution, by contrast, such a plot should result in an overall empirical "activation energy" ($= \partial \ln R / \partial (1/T)$) distinctly greater than E_d.

If rate control is by stirring and advective flow, the predicted temperature dependence of dissolution, at constant stirring rate and constant saturation state, is more complex, but one formulation, the Frossling Equation (Ohara and Reid, 1973; Bird, Stewart, and Lightfoot, 1960), upon differentiation gives the following temperature dependence:

$$\frac{\partial \ln R}{\partial (1/T)} = \frac{2}{3} \frac{\partial \ln D_s}{\partial (1/T)} - \frac{1}{6} \frac{\partial \ln \nu}{\partial (1/T)} \tag{10}$$

where ν = kinematic viscosity of the solution.

Evaluation of $\partial \ln \nu / \partial (1/T)$ has been done using the viscosity data of Robinson and Stokes (1959) for pure water and Sverdrup, Johnson, and Fleming (1942) for seawater, and both values are found to be about equal (within 12 percent) to $\partial \ln D_s / \partial (1/T)$ but of opposite sign. Assuming equality, eq (10) reduces to:

$$\frac{\partial \ln R}{\partial (1/T)} \approx \frac{5}{6} \frac{\partial \ln D_s}{\partial (1/T)} = -\frac{5\,E_d}{6\,R} \tag{11}$$

Thus, the expected temperature dependence of dissolution rate, when controlled by transport in a stirred solution, is just slightly less than that predicted for rate control by pure diffusion.

Application of laboratory results to natural processes.—Although it is possible to deduce rate limiting mechanisms of natural dissolution processes, it is extremely difficult to predict accurate absolute rates in nature from laboratory experiments, even when conducted under simulated natural conditions. Laboratory rate measurements, unlike thermodynamic measurements, are not of universal applicability. Major problems arise because of differences between the field and the laboratory with regard to: (1) the surface composition and configuration of the mineral grains, (2) the effects of trace species in solution which absorb onto the mineral surfaces, and (3) the role of organisms in natural waters.

Equivalence of surface area of two samples of the same mineral is no assurance that the two will dissolve at the same rate. Differences in surface defect density, kink and step density (Burton, Cabrera, and Frank, 1951), surface curvature, and the numbers of edges and corners per unit volume can all combine to bring about appreciable differences in reactivity. More important, the presence of adsorbed impurities often acts as a strong inhibitor of crystal dissolution or growth (for example, see Ohara and Reid, 1973). Unless the trace species composition, both organic and inorganic, of laboratory and natural waters is identical, one runs the risk of missing a potentially important rate-controlling inhibitor. In addition, treatment (for example, washing) of natural minerals prior to laboratory study may result in loss of adsorbed inhibitors.

Inhibition can be effective at very low levels as demonstrated by the strong retarding effect on calcite dissolution of sub-micromolar to micromolar concentrations of dissolved Sc^{+4} (Terjesen, Erga, and Ve, 1961) and orthophosphate (Berner and Morse, 1974).

Because of failure to reproduce natural trace inhibitors and because of necessary steps required to prepare mineral samples for study, rates measured in the laboratory are generally higher than the corresponding rates in nature. This has been demonstrated by Hurd (1973) and Lawson and Hurd (1978) for the dissolution of radiolarian silica and by Morse and Berner (in preparation) for the dissolution of pelagic calcareous sediment in seawater.

Ignoring the role of microorganisms in natural dissolution processes often results in incorrect estimates of reaction rate. For example, Singer and Stumm (1970) concluded, after extensive investigations, that the oxidative dissolution of pyrite in the laboratory was slower than it is in nature because of the presence in nature of bacteria which catalyze one or more steps of the overall reaction. Besides microorganisms, various macro-organisms, such as worms and zooplankton, ingest and defecate mineral particles and, as a result, may drastically alter mineral dissolution rates by coating the grains with a layer of organic material (for example, Rhoads, 1974; Honjo, 1977).

RATE CONTROL IN THE DISSOLUTION OF CALCIUM CARBONATE, OPALINE SILICA, AND FELDSPARS

Nielsen (1964) and Berner (1971) make the statement that most crystal dissolution should occur via transport (diffusion)-controlled kinetics. This statement is probably incorrect. In this section it will be shown that several important earth-surface geochemical processes all take place via surface reaction-controlled kinetics.

Calcium carbonate.—In the deep ocean, seawater is distinctly undersaturated with respect to calcium carbonate. As a result, calcite and aragonite in the form of sedimented tests of planktonic foraminifera, coccolithophorids, and pteropods, undergo extensive dissolution, and no $CaCO_3$ is found in bottom sediments below a depth of about 4500 to 5500 m (the carbonate compensation depth). Morse and Berner (1972) by means of eq (8) have shown that the measured rate of dissolution of calcite spheres suspended in deep Pacific seawater by Peterson (1966) is distinctly slower than that expected for rate control by molecular diffusion. In addition, Berner and Morse (1974) and Morse and Berner (in preparation) have shown that reagent grade calcite and foram-coccolith ooze dissolve in seawater in the laboratory at a rate much less than that calculated for molecular diffusion control. This was found for the entire range of saturation states found in the deep ocean.

Two independent observations agree with these findings. First, Sjöberg (1976) has shown that the activation energy for the dissolution of calcite in pure 0.7N KCl solution is distinctly higher (8.4 kcal/mole) than that expected for diffusion or transport control (4-5 kcal/mole).

Since seawater would be expected to contain potential inhibitors not present in the KCl solution, Sjöberg's conclusion of mainly surface reaction control in KCl strongly suggests a similar controlling mechanism in seawater. Secondly, Berner and Morse (1974) have presented scanning electron photomicrographs (reproduced here in pl. 1) of calcite crystals partially dissolved in seawater which show crystallographically controlled etch patterns on crystals dissolved at moderate undersaturation, where surface reaction-control was predicted, and rounding of corners and edges on crystals dissolved at very high degrees of undersaturation (not found in the ocean), where transport-controlled dissolution was expected.

Taken together, the above findings all strongly suggest that the rate of calcite dissolution in the deep sea is controlled by surface processes, a conclusion in agreement with that of Wollast (1975). Slow dissolution by surface control is also in keeping with common observations of calcium carbonate-rich sediment overlain by undersaturated water, the occurrence of dissolution over a rather wide zone extending 1000 to 2000 m above the carbonate compensation depth, and the selective dissolution of certain foram and coccolith species. (For a summary discussion of natural observations, see Berger, 1976.)

Opaline silica.—Opaline silica, in the form of sedimented diatom and radiolarian debris, also undergoes extensive dissolution on the sea floor. Dissolution continues during burial of sediment as evidenced by the buildup of concentrations of dissolved silica in pore waters to values far in excess of those found in the overlying seawater. The profile of dissolved silica versus depth in deep sea pelagic sediments provides the basis upon which the rate controlling mechanism for opaline silica dissolution can be adduced.

Berner (1974) has derived a theoretical expression for the distribution of dissolved silica versus depth in sediments where opaline silica dissolution occurs via diffusion-controlled kinetics. As shown in the appendix, from this expression one can straightforwardly derive an expression for the sediment depth at which dissolved silica has built up to half its saturation (or asymptotic) value. It is:

$$X_{1/2} = \frac{0.69r}{[3F(1-\phi)(\rho_t/\rho_d)]^{1/2}} \qquad (12)$$

where:

$X_{1/2}$ = the half-saturation depth

r = nominal (spherical) radius of dissolving particles (assumed to be constant during equilibration — that is negligible mass is lost while approaching saturation)

F = weight fraction (dry wt) of dissolving solids

ρ_d = density of dissolving particles

ρ_t = average density of total solids

ϕ = porosity

For biogenic silica $\rho_d \approx 2.2$ and a typical value $F = 0.1$ and a maximum value $r << 0.01$ cm can be chosen. (The value for r represents an *extreme maximum* because high contributions to surface area, due to rough surface topography and ubiquitous micropores, are ignored — for example, see Lawson and Hurd, 1978.) Also, $\phi \approx 0.75$, $\rho_t \approx 2.5$. Using the above values:

$$X_{1/2} << 0.02 \text{ cm}$$

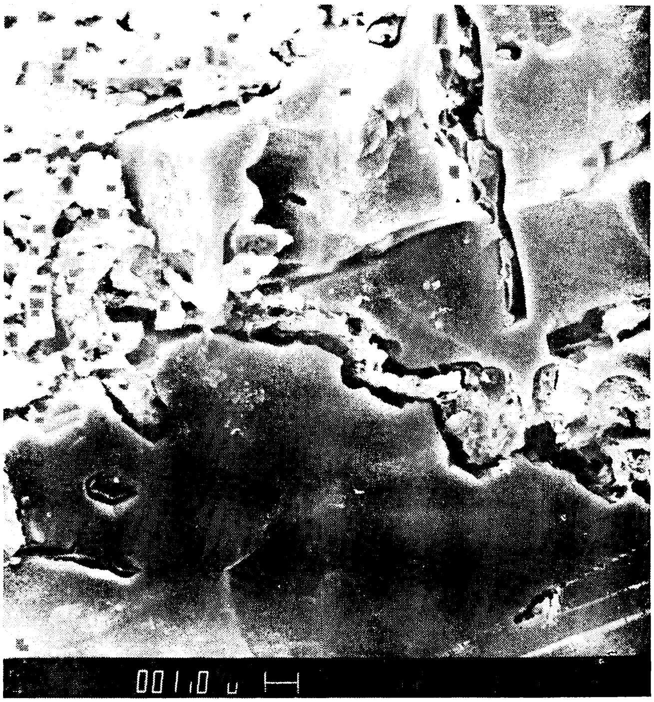
This value means that the pore water silica profile expected for diffusion-controlled dissolution in deep sea sediments should appear simply as a constant "saturation" value right up to the sediment-water interface. Measured profiles for pelagic sediments (for example, Schink, Guinasso, and Fanning, 1975) instead almost always show half-saturation depths on the order of about 10 cm. Thus, the rate of silica dissolution in interstitial seawater is far slower than that expected for diffusion control and must, instead, represent control by surface chemical reaction. Quantitative consideration of bioturbation, according to the model of Schink, Guinasso, and Fanning (1975), does not change this conclusion.

The recent results of Lawson and Hurd (1978) strongly support the above calculation. They determined the activation energy for the dissolution of fresh, untreated siliceous plankton in seawater to be 13.8 kcal/mole, which is far too high to represent diffusion or transport control. In addition, it can be shown using eq (8) that their measured rates are five to nine orders of magnitude lower than that expected for diffusion control. (The exact value depends upon whether their measured specific surface area which reflects microporosity, or the outer dimensions of dissolving particles, is used.)

From the half-saturation calculation and the results of Lawson and Hurd, it appears that opaline silica dissolution in seawater is highly retarded by surface processes. This helps to explain why opaline silica-rich sediments exist. In contrast to the situation for calcium carbonate, where undersaturation occurs only at depth, seawater is everywhere highly undersaturated with respect to opaline silica. Consequently, if dissolution were controlled by transport at the levels of turbulence found in the ocean, it can be readily shown that diatom and radiolarian skeletal debris should be completely dissolved away before burial and, therefore, be absent from bottom sediments. However, sediments highly enriched in opaline silica, such as those found around Antarctica, exist, and this is a direct manifestation that opaline silica dissolution is controlled by surface chemical reaction.

Feldspar weathering.—It has been suggested that the rate of dissolution of feldspar during weathering in soils is controlled by very slow (solid state) diffusion through a protective layer of fine-grained aluminosilicate (clay) weathering product (Correns and von Engelhardt, 1938; Wollast, 1967; Helgeson, 1971; Busenberg and Clemency, 1976) or cation-depleted feldspar (Pačes, 1973). Recent studies have failed to find evidence for such a layer either in laboratory dissolution experiments

PLATE 2

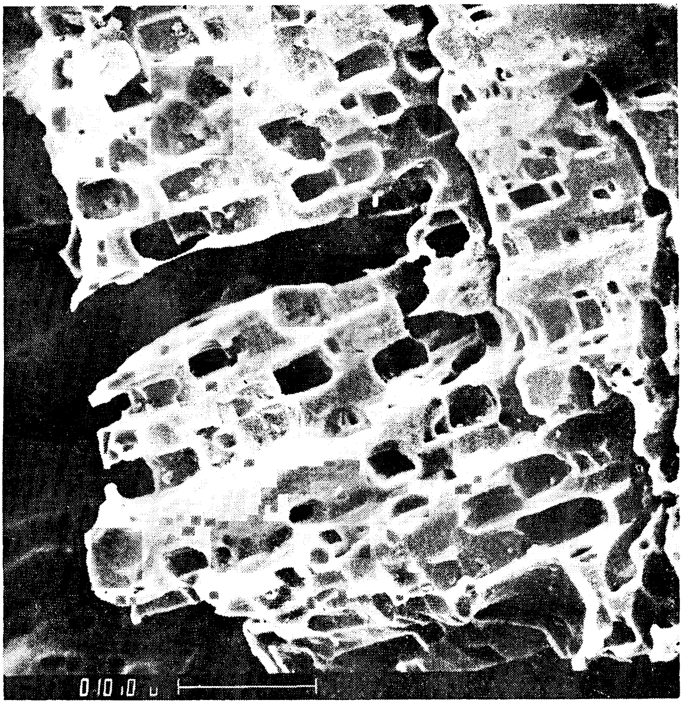


(A) Scanning electron photomicrograph of a soil feldspar grain showing that clay that adheres to the feldspar surface after ultrasonic cleaning has contracted and separated from the surface upon drying (see crack in center of photomicrograph). Sample from a gray-brown podzolic soil, Sangre de Cristo Mountains, New Mexico. (After Berner and Holdren, 1977.)

(Petrovič, Berner, and Goldhaber, 1976) or from studies of feldspars from soils (Berner and Holdren, 1977). The soil studies, using scanning electron microscopy have shown that clay that adheres to feldspar grains after ultrasonic cleaning is patchy, discontinuous, and sufficiently porous and hydrous that shrinkage features, such as micro-mudcracks, appear upon drying (see pl. 2-A). Such a layer should not be protective nor cause diffusion rates to be greatly lowered. Furthermore, the outermost ~ 30 Å of those feldspar grains from which all adhering clay had been ultrasonically removed was found, via X-ray photoelectron spectroscopy, to consist of normal feldspar composition with no signs of appreciable cation depletion.

Instead of finding a protective surface layer, Berner and Holdren found that the bare feldspar surfaces were characterized by the development of well-defined, crystallographically-controlled etch pits (pl. 2-B). From study of hundreds of photomicrographs, a dissolution etch pit sequence was constructed that can be matched by leaching fresh feldspars with HF in the laboratory. The presence of etch pits points to preferential

PLATE 2



(B) Scanning electron photomicrograph of a soil feldspar (ultrasonically cleaned to remove clay) from a lateritic soil near Piedmont, N.C. (USA). Note prominent prismatic etch pits. (After Berner and Holdren, 1977.)

dissolution at regions of excess energy on the feldspar surface, probably dislocations (Lundstrom, 1970). From the reasoning pointed out earlier, these observations strongly suggest that the rate of feldspar dissolution during weathering is controlled by surface chemical reactions and not by diffusion through a protective surface layer. Also, rate control by diffusion through aqueous solution is highly unlikely, because rates calculated on this basis erroneously preclude the existence of feldspar grains in soils (that is, complete dissolution in a few months is predicted).

SOLUBILITY AND RATE CONTROL

The substances discussed in the previous section are all rather insoluble, and all dissolve via surface reaction control. This finding, along with the observation that highly soluble salts dissolve rapidly and with general rounding, suggests that a correlation can be made between solubility and the type of rate-controlling dissolution mechanism. With this in mind a table has been prepared (table 1) listing the rate controlling process for a number of substances along with their solubilities. The term solubility, as used in table 1, refers to the number of moles of the formula given in the table per liter which dissolve in pure water to saturation. For the less soluble substances, solubility is calculated as follows: for 1:1 salts solubility is set equal to the square root of the thermodynamic solubility product K, calculated from the data of either Berner (1971) or Garrels and Christ (1965); for 1:2 or 2:1 salts solubility is equal to $(K/4)^{1/3}$; for the two feldspars solubility is equal to $(K/6912)^{1/9}$. In the latter case this refers to the dissolution reaction:

$$\left.\begin{matrix} KAlSi_3O_8 \\ NaAlSi_3O_8 \end{matrix}\right\} + 8H_2O \;\; \begin{matrix} < \\ > \end{matrix} \;\; \left.\begin{matrix} K^+ \\ Na^+ \end{matrix}\right\} + Al^{+++} + 3H_4SiO_4 + 4OH^-$$

For AgCl, $Ba(IO_3)_2$, and the more soluble substances, solubility values are taken directly from the literature.

Table 1 shows that there is indeed a good correlation between solubility and rate controlling mechanism of dissolution. Below a solubility of about 10^{-4} moles per l surface reaction control dominates. From about 10^{-4} to 10^{-3} either surface-reaction or transport is rate controlling depending on the substance. (Lead sulfate exhibits both rate controlling mechanism depending upon degree of undersaturation and temperature.) Above 2×10^{-3} transport control dominates. The only major exception to this trend is AgCl which is quite insoluble (solubility $= 1 \times 10^{-5}$) but which has been well documented as dissolving by transport control (Jones, 1963). This exceptional behavior of AgCl compared to

TABLE 1

Dissolution mechanism for various substances arranged in order of solubilities in pure water

Substance	Solubility (mole/liter)	Kinetics Reference	Soly. ref. no. (see below)
		Surface reaction control	
$KAlSi_3O_8$	3×10^{-7}	This paper	(1)
$NaAlSi_3O_8$	6×10^{-7}	This paper	(1)
$BaSO_4$	1×10^{-5}	Liu, Nancollas, and Gasiecki (1976)	(1)
$SrCO_3$	3×10^{-5}	Sonderegger, Brower, and LeFebre (1976)	(1)
$CaCO_3$	6×10^{-5}	This paper	(1)
Ag_2CrO_4	1×10^{-4}	Jones, Linge, and Wilson (1975)	(2)
$SrSO_4$	9×10^{-4}	Campbell and Nancollas (1969)	(1)
Opaline SiO_2	2×10^{-3}	This paper	(1)
		Mixed control	
$PbSO_4$	1×10^{-4}	Bovington and Jones (1970)	(2)
		Transport control	
AgCl	1×10^{-5}	Jones (1963)	(3)
$Ba(IO_3)_2$	8×10^{-4}	Jones, Madigan, and Wilson (1973)	(3)
$CaSO_4 \cdot 2H_2O$	5×10^{-3}	Christoffersen, and Christoffersen (1976)	(1)
$Na_2SO_4 \cdot 10H_2O$	2×10^{-1}	Zdanovskii (1956)	(1)
$MgSO_4 \cdot 7H_2O$	3×10^{0}	Zdanovskii (1956)	(4)
$Na_2CO_3 \cdot 10H_2O$	3×10^{0}	Zdanovskii (1956)	(4)
KCl	4×10^{0}	Zdanovskii (1956)	(4)
NaCl	5×10^{0}	Zdanovskii (1956)	(4)
$MgCl_2 \cdot 6H_2O$	5×10^{0}	Zdanovskii (1956)	(4)

(1) Berner (1971)
(2) Garrels and Christ (1965)
(3) Same as kinetics reference
(4) Linke (1965)

other salts has also been noted by Nielsen and Söhnel (1971), who have found a correlation between solubility and specific surface free energy for most salts with silver salts being notable exceptions. The reason for the anomalous behavior of AgCl may be due to photochemical effects during experimentation.

It is tempting to use the results of table 1 to predict the dissolution behavior of other substances. However, the reader is cautioned that the dissolution kinetics of more substances should be studied before one can make accurate predictions based on solubility. Also, it must be emphasized that the results of table 2 are (with the exception of $CaCO_3$, opaline silica, and feldspar) only for pure salt solutions. Foreign ions, as they exist in natural waters, might act as dissolution inhibitors and cause some of the substances listed as dissolving by transport control to dissolve in natural waters instead via a surface-reaction-controlling mechanism, due to surface poisoning. At any rate the results of table 1 do strongly suggest that there are many other relatively insoluble minerals whose rates of dissolution, under Earth surface conditions, are controlled by surface chemical reaction.

CONCLUSIONS

The rates of three major Earth surface processes, the dissolution of biogenic calcium carbonate and opaline silica in the deep sea and the weathering of feldspars on land, are all governed by surface chemical reactions and not by transport either through solution or through protective surface layers. It is probable that this conclusion also applies to many other minerals that so far have not been studied. Thus, currently popular models that treat diagenesis and weathering solely in terms of diffusion, advection, and chemical equilibrium may rest on incorrect assumptions. It is not enough to replace Gibbsian models with Fickian models; what is needed in addition is more studies of surface chemistry.

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APPENDIX

The writer (Berner, 1974) has derived an expression for the distribution of dissolved silica versus depth in surficial marine sediments based on a model that assumes: (1) steady state diagenesis; (2) dissolution of opaline silica (as uniform spherical particles) via molecular diffusion control — see eq (8) of text; (3) negligible mixing via bioturbation; and (4) negligible compaction. If the effects of rapid equilibrium adsorption (Berner, 1976) are included in the model, the resulting expression is:

$$\frac{D_s}{1+K}\frac{\partial^2 C}{\partial x^2} - \omega \frac{\partial C}{\partial x} + \frac{3F\,(1-\phi)D_s\rho_t}{r^2\,(1+K)\rho_d}\,(C - C_s) = 0 \qquad (1A)$$

where:

C = concentration of dissolved silica in the interstitial water

x = depth in sediment below the sediment-water interface

C_s = "saturation" concentration or asymptotic concentration as $x \rightarrow \infty$ (not necessarily the true equilibrium value—for example, see Hurd, 1973)

D_s = diffusion coefficient of dissolved silica in the sediment

K = adsorption constant equal to the ratio of reversibly adsorbed silica to dissolved silica

ω = rate of sedimentation

r = average spherical radius of the dissolving silica particles (assumed essentially constant during dissolution)

ϕ = porosity

F = weight fraction of dissolving particles

ρ_d = density of dissolving particles

ρ_t = average density of total sediment solids

For deep sea sediments of very low sedimentation rate it can be shown (for example, Schink, Guinasso, and Fanning, 1975; Berner, 1976) that the middle term on the left hand side of eq (1A) is negligible compared to the other two terms. On this basis (1A) reduces to:

$$\frac{\partial^2 C}{\partial x^2} + \frac{3F(1-\phi)\rho_t}{r^2\,\rho_d}(C - C_s) = 0 \qquad (2A)$$

With the boundary conditions:

$$x = 0, \quad C = C_o$$
$$x \rightarrow \infty, \quad C \rightarrow C_s$$

the solution of (2A) is:

$$\frac{C - C_s}{C_o - C_s} = \exp\left[-\left(\frac{3F(1-\phi)\rho_t}{r^2\,\rho_d}\right)^{1/2} x\right] \qquad (3A)$$

The depth, $X_{1/2}$, where $(C-C_s) = \frac{1}{2}(C_o-C_s)$ is, thereby, given by:

$$X_{1/2} = \frac{0.69\ r}{[3F(1-\phi)(\rho_t/\rho_d)]^{1/2}} \qquad (4A)$$

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