KINETIC MODEL OF ZEOLITE PARAGENESIS
IN TUFFACEOUS SEDIMENTS

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Abstract—The sequence of mineral reactions involving zeolites and other authigenic phases in tuffaceous sedimentary rocks can be explained by growth- and dissolution-reaction kinetics. Kinetic factors may determine the specific authigenic phases which form and the temporal and spatial constraints on the solution composition during irreversible dissolution and growth reactions in glass-bearing rocks. The glass phase generates a high level of supersaturation with respect to a variety of aluminosilicates in the pore fluid. The sequence of assemblages formed during a series of metastable reactions resembles an Ostwald step sequence. Metastable reactions occur because formation of less stable phases such as gels, clays, and disordered zeolites may lower the total free energy of the glass-bearing system faster than the growth of the stable assemblage including ordered feldspars, quartz, and micas. Eventually, after a series of steps, the most stable silicate assemblage for the bulk composition, temperature, and pressure may form. However, the formation of intermediate metastable phases can delay the attainment of equilibrium by as much as tens of millions of years.

Key Words—Dissolution, Kinetics, Potassium feldspar, Thermodynamics, Tuffaceous sediments, Volcanic glass, Zeolites.

INTRODUCTION

Of all geochemical systems, chemical equilibrium between fluids and mineral phases is least likely to be attained in sedimentary rocks containing volcanic glass. Observations of mineral parageneses in glass-bearing sediments provide an excellent example of the effects of nonequilibrium conditions on the chemical evolution of rocks undergoing diagenesis and burial metamorphism. Once the effects of reaction kinetics on the mineral assemblage are determined for glass-bearing rocks, conclusions about rate processes for other water/rock interactions may be reached.

Zeolites are some of the most common authigenic and metamorphic minerals formed in glass-bearing rocks. The paragenesis of zeolites in tuffaceous sediments deposited in saline, alkaline lakes has received the most detailed attention (Hay, 1977; Surdam and Sheppard, 1978). Concern about whether zeolites in these rocks represent metastable phases formed under nonequilibrium conditions or stable assemblages in equilibrium with pore solution has been paramount (Hay, 1966; Surdam and Parker, 1972; Surdam and Sheppard, 1978).

In this paper, we briefly examine the general thermodynamic and kinetic constraints that influence glass dissolution and mineral-growth reactions. Observations of natural systems are used to illustrate the nonequilibrium processes that influence reaction paths in glass-bearing systems. The controls of dissolution and growth kinetics on reaction paths are examined, and a general kinetic model for zeolite and clay mineral paragenesis in tuffaceous rocks is proposed. The kinetic model accounts for the general decrease in abundance of zeolites and clay minerals and the increase in feldspars in sedimentary rocks with time.

THE IRREVERSIBLE REACTION COUPLE

A fundamental principle relating to solid/fluid reactions is that no bulk thermodynamic equilibrium state can be attained *during* the process of crystallization of one phase coupled with the dissolution of another (Dibble and Tiller, 1981). The total driving force or departure from equilibrium necessary for the growth of one solid at the expense of another, ΔG_{rxn}, is related to the difference in solubilities of the two solid phases. The real activities of components in solution at both the solid/fluid interface and in the bulk solution will depend on the magnitudes of driving forces for the following: interface-detachment or -attachment kinetics, ΔG_K; solution transfer, ΔG_s; and surface processes not related to detachment or attachment, ΔG_E (Dibble and Tiller, 1981).

Without an understanding of interface-controlled reaction kinetics, it is not possible to predict accurately the activities of components in the bulk solution *during* silicate alteration reactions, or to determine precisely the control the bulk solution composition has on the phases that form (Dibble and Tiller, 1981). For exam-

ple, if solute transport controls the irreversible dissolution of an unstable phase such as glass (fast kinetics) but the growth of the alteration products is controlled by interface attachment (slow kinetics), then the solution composition will reflect mainly the solubility of the glass for equal areas of glass and alteration products. On the other hand, if the relative order of reaction rates were reversed such that alteration products grow much faster than host phases dissolve, the bulk solution composition will be determined chiefly by the solubilities of the alteration products (Berner, 1980). An intermediate, general case is illustrated in Figure 1.[1]

Reactant and product phases constitute a reaction couple as shown in Figure 1. The source phase dissolves supplying components which diffuse down the free energy gradient in the reactant–solute diffusion boundary layer (δ_s^r) *to* the bulk solution. The product phase is a sink of components which diffuse down the free energy gradient in the product–solute diffusion boundary layer (δ_s^p) *from* the bulk solution. The quantities K_{sp}^r and K_{sp}^p represent the equilibrium solubility products for reactants and products, respectively. The quantities Q_{int} and Q are the real activity products in the fluid at the interface and in the bulk fluid, respectively.

The values of Q_{int} and Q for both reactant and product phases depend on many factors such as flow rates and interface-attachment or -detachment parameters. Many details of each dissolution and growth reaction must be known to predict the composition of the bulk fluid (Figure 1) accurately during the dissolution of unstable phases coupled with the growth of more stable minerals. Changing the thermodynamic and/or kinetic constraints on either one or both halves of the reaction couple can affect the overall reaction path. However, for a mathematically linear system, a simple superposition of the effects for many different reactant and product phases following the formulations of Dibble and Tiller (1981) is sufficient to describe the time-varying dissolution and growth velocities of the phases plus the concentration excursions of the fluid.

The thermodynamic constraints on mineral-growth reactions (right side of Figure 1) during the irreversible dissolution of unstable phases (left side of Figure 1) are limited to the values of ΔG_{rxn} for all possible reactions involving any reaction couple. Any mineral may form if the solution is supersaturated with respect to it. Reactions forming many metastable phases may occur within the limits of RT ln K_{sp} imposed by equilibrium thermodynamics shown in Figure 1. The larger the difference between K_{sp}^r and K_{sp}^p, the greater the number of metastable reactions that can occur. For example, if the net rate of glass dissolution is high relative to the
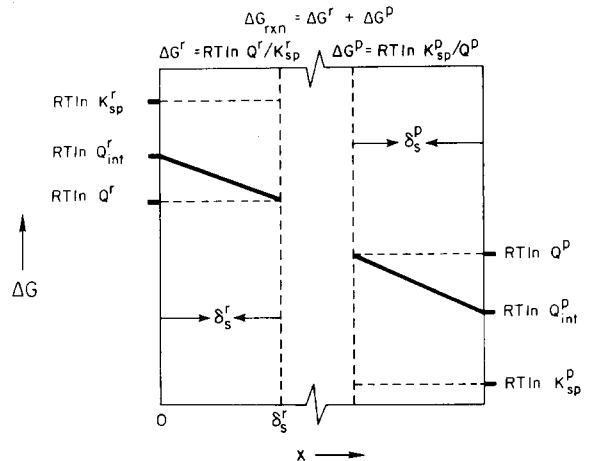

Figure 1. The free energy driving each dissolution reaction, ΔG^r, and each growth reaction, ΔG^p, during the irreversible formation of products from reactants is a function of the thickness of the diffusion boundary for the reactant, δ_s^r, and product, δ_s^p, phases, respectively. The free energy of the system decreases with increasing distance, x, from the reactant/solution interface (see Dibble and Tiller, 1981). K_{sp} is the equilibrium solubility product for reactant, r, or product, p. Q_{int} and Q are the ion-activity products in the fluid at the interface and in the bulk fluid, respectively. The bulk solution is represented between the solute diffusion boundary layers, δ_s, which can range from tens to thousands of micrometers thick depending on flow rates.

net growth rate of alteration products, the bulk solution may become supersaturated with respect to many aluminosilicates because of the high glass solubility relative to stable products. The thermodynamic constraints, in this case, require a *large* departure from equilibrium in glass-bearing systems. Whether or not the *most stable* aluminosilicates grow under conditions of high supersaturation caused by irreversible glass dissolution is a problem of interface-controlled reaction kinetics.

Thus, the qualitative thermodynamic constraints on glass/water interactions suggest that glass dissolution may generate large supersaturations with respect to many phases. Alteration products formed during glass dissolution constitute one half of a reaction couple and, therefore, indicate the relative levels of supersaturation that are generated by the other half of the couple. For example, formation of aluminosilicate gels (Eugster and Jones, 1968; Mariner and Surdam, 1970) indicate that high general levels of supersaturation relative to stable phyllosilicates and perhaps ordered feldspars may be generated by glass dissolution. Likewise, precipitation of noncrystalline silica or opal signifies that a high supersaturation with respect to quartz is produced and may reflect generally high supersaturation with respect to other stable silicates. The specific phases and the temporal and spatial constraints on the solution composition which result from steady-state, ir-

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[1] Figure 1 shows a general case where Q^r does not equal Q^p; and, consequently, ΔG_{rxn} cannot be equated simply to the difference between RT ln K_{sp}^p and RT ln K_{sp}^r.

reversible dissolution and growth reactions are determined by kinetic factors to be discussed below.

NONEQUILIBRIUM AUTHIGENESIS

Figure 1 illustrates that the local, interface-solution composition may determine the nature of precipitated minerals rather than the bulk solution composition. The bulk solution composition affects the phases formed during glass dissolution only if the bulk pore solution is a source or sink of components. Assuming that the source of components is glass and that the sink is the immediate surrounding product with a fluid phase between them, the bulk pore solution *outside* the source glass/reaction-product couple need not influence the reaction path because the subsystem containing the reaction couple and *local* fluid phase may be effectively closed. The mineral assemblage formed will be affected if the bulk pore solution *outside* the reaction couple is a sink (open system, high flow rates) or source of components. Examples are the crystallization of abundant smectite from glass in an open system (Hay and Sheppard, 1977) or the crystallization of analcime from other zeolites in an NaCl solution of high ionic strength (Surdam and Sheppard, 1978). In the former system, the bulk solution is a sink for components which can be transported away if the flow rates are much greater than rates of reaction forming stable or metastable products. In the latter example, the pore fluid may be a source of Na for analcime crystallization.

Figure 1 illustrates a case where the diffusion-boundary layers of reactant and product phases do not overlap. Where the diffusion-boundary layers overlap, higher supersaturation with respect to all possible products results (Dibble and Tiller, 1981). Thus, the proximity of alteration products to glass surfaces can indicate which phases grow consistently under conditions of highest supersaturation with respect to stable phases. Also, alteration-mineral parageneses and regional zoning patterns can indicate the general level of supersaturation with respect to stable products as a function of both time and distance.

Small-scale zoning of secondary phases around glass shards is common in altered tuffs (Sheppard and Gude, 1973, p. 30). Typically, clay minerals (or, less commonly, gels) form early around glass shards in closed systems. Early-formed clays consistently occur at the innermost zone near the glass, whereas later-formed zeolites may fill shard cavities farther from the glass surface (Sheppard and Gude, 1968, 1969, 1973).

In well-flushed, open systems, the supersaturation of components relative to many phases, ΔG_{rxn}, could be small or even less than zero some distance from the glass/solution interface. In such environments, mobility of several components is possible, and production of abundant zeolites is unlikely far from glass surfaces. However, supersaturation with respect to several product phases may still be large close to the glass surface.

In fact, because of the proximity of growth to glass surfaces, clay minerals commonly form pseudomorphs of glass shards even in open systems (Khoury and Eberl, 1979).

Similar observations of a close spatial association between clay minerals and glass have been made in glass/water interaction experiments at elevated temperature and pressure (Guillemette *et al.*, 1980; Potter, 1981). Under a variety of conditions in glass-bearing systems, clay minerals tend to occupy a geochemical "niche" located close to glass surfaces; whereas, zeolites commonly occur farther from the glass/solution interface. Observations of fine-scale zoning of smectite and zeolites around glass shards (Sheppard and Gude, 1973) suggest that clay minerals form early in regions of maximum supersaturation with respect to stable phases, and nonanalcimic zeolites crystallize in regions of lower supersaturation and probably later in time.

The regional zoning of clays, zeolites, and feldspars in tuffs follows a pattern similar to the fine-scale zoning sequence discussed above. Similar zonal distributions of zeolites and clays repeatedly occur in tuffs deposited in saline, alkaline lakes, in hydrothermally altered tuffs, and in tuffaceous sediments subjected to burial metamorphism (Hay, 1977). In glass-bearing rocks near lake margins, authigenic reaction products are commonly clays and nonanalcimic zeolites (Surdam and Sheppard, 1978). Abrupt changes in zeolite parageneses occur farther from lake margins and have been attributed to the disappearance of the glass phase. For example, the transition from alkali zeolite assemblages to analcime- and/or feldspar-bearing assemblages seems to occur in a zone where the glass shards have been totally dissolved (Sheppard and Gude, 1968, 1969, 1973). At Shoshone, California, chabazite and phillipsite occur near the fresh glass-zeolite zone boundary in the Pleistocene Lake Tecopa beds and are associated with abundant relict glass. Analcime, however, occurs near the zeolite–potassium feldspar zone boundary where glass does not exist. Petrographic studies of Sheppard and Gude (1968) indicate that the potassium feldspar and searlesite formed from a zeolite precursor rather than directly from glass.

Similar zonal patterns and parageneses in tuffs of the Big Sandy Formation led Sheppard and Gude (1973) to conclude that dissolution of silicate glass by pore solution provided the materials necessary for authigenic zeolite crystallization with the exception of analcime. Analcime formed later from the dissolution of pre-existing zeolites after glass dissolution was completed. Feldspars forming from analcime or other zeolites near the centers of hydrographically closed lake basins or after long time periods have been noted by Sheppard and Gude (1968, 1969) and Surdam and Parker (1972). Feldspars have *never* been found to co-exist with glass (Surdam and Sheppard, 1978).

The observations summarized above suggest that the

overall process of tuff alteration involves reactions of metastable phases with solutions which occur in a series of irreversible steps. Clays and gels form in regions and during times of maximum supersaturation with respect to more stable phases generated by relatively rapid glass dissolution. Alkali zeolites, on the other hand, crystallize in regions of intermediate to high supersaturation possibly after glass dissolution rates have diminished. Analcime and feldspars grow in regions of lowest supersaturation, after all glass has disappeared, and at the expense of previously formed clays and zeolites.

The pore-fluid composition influences both the thermodynamic stability of alteration minerals and the rates of reaction. However, as illustrated in Figure 1, in the presence of glass, the pore solution may become supersaturated with respect to many product minerals regardless of the initial pH and ionic strength. The effect of pore-solution chemistry on reaction rates is critical for glass-bearing systems.

The increase in rates of alteration of tuff with increase in pH and ionic strength is well known (Hay, 1966; Mariner, 1971). Pore-fluid compositions in sediments in closed, alkaline, saline-lake basins commonly vary from near-neutral pH and low ionic strength at the lake margins to higher pH and ionic strength near the center (Surdam and Sheppard, 1978). Therefore, glass will persist for longer times at the periphery of lake basins where reaction rates tend to be lowest (Surdam and Sheppard, 1978). As a result, minerals which form preferentially near glass such as clays and nonanalcimic zeolites can dominate the alteration assemblage near lake margins. On the other hand, near the centers of lake basins in regions of high pH and ionic strength, glass-alteration reactions will proceed more rapidly leading to lower levels of supersaturation after shorter times. Complete dissolution of glass will also occur after shorter times, and, consequently, analcime and feldspars can crystallize earlier. Thus, the zonal patterns of alteration assemblages observed in vitric tuffs may result predominantly from the effect of pore-solution chemistry on reaction rates.

In summary, the alteration of glass may produce metastable phases owing to high levels of supersaturation with respect to the most stable minerals. Postulated metastable phases include aluminosilicate gels, smectites, and open-structure, disordered,[2] alkali zeolites. Early-formed phases are later transformed via dissolution and growth reactions to more stable tectosilicates (ordered analcime and feldspars) and phyllosilicates (illite and chlorite, see Tank, 1972; Milton, 1971). As reaction rates increase, due to changes in solution chemistry, temperature, and pressure, the more

stable phases may be produced in less time. The question remains why more stable phases do not grow initially, whereas metastable phases precipitate ubiquitously. An answer to this question requires an understanding of some aspects of dissolution and growth kinetics.

DISSOLUTION AND GROWTH KINETICS

The most thermodynamically stable phases may not nucleate and grow, hence, they may not appear in authigenic assemblages under conditions of high supersaturation created by glass dissolution. In systems supersaturated with respect to several aluminosilicates, reactions tend to occur that lead to the most rapid decrease in the supersaturation or total free energy of the system, and most phases that form early are those with high growth rates. Thus, under conditions which thermodynamically favor the growth of several minerals, only those having high growth rates may dominate the initial mineral assemblage. Therefore, the crystallization sequence during tuff diagenesis will probably be controlled by growth kinetics.

The minerals with inherently sluggish growth kinetics may not occur in early-formed assemblages. From the observations of natural parageneses, the phases with high growth rates seem to be the least stable thermodynamically. For example, early-formed phases are noncrystalline aluminosilicates, noncrystalline silica, disordered smectites, and disordered zeolites (all nonanalcimic, alkali zeolites in saline lake environments are disordered according to Gottardi, 1978). The phases growing under conditions of reduced supersaturation after the glass disappeared are commonly more ordered (analcime, feldspars, illite, chlorite). The irreversible series of reactions forming more-stable, ordered minerals from less-stable, disordered phases strongly resembles an Ostwald step sequence. Such a series of metastable reactions in the formation of illite has been noted by Eberl and Hower (1977).

The Ostwald step rule states that the most likely phase to form may not be the most stable thermodynamically (Fyfe and Verhoogen, 1958) and that equilibrium will be gradually approached through a series of irreversible steps. The step rule is probably better defined in terms of growth kinetics. In a system supersaturated with respect to many solids, the phase which dominates the initially-formed assemblage will be the one which grows the most rapidly at a given temperature and pressure. This does not imply that other solids cannot grow as well. The fastest growing silicate contains the largest mass of network-forming components (SiO_2, Al_2O_3) after a given reaction duration. Other phases with the same components but with slower growth rates may simply not be observed in the same interval of time. In addition, by rapidly removing network-forming components from solution, possibly close to the reactant surface, the phase with the fastest

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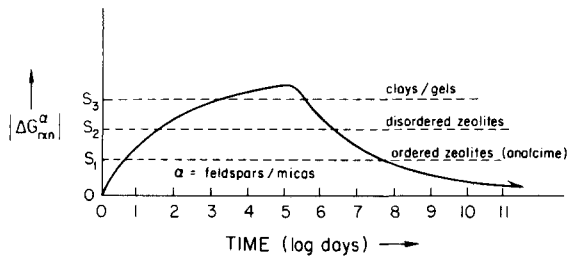[2] For a discussion of order/disorder in zeolites, see Gottardi (1978).

Figure 2. Absolute value of the departure from equilibrium, $|\Delta G^{\alpha}_{rxn}|$, vs. time of reaction forming stable phase α in tuffaceous rocks. Phase α may be a fully ordered feldspar, mica, or quartz. The duration of crystallization of authigenic assemblages is determined by the intersection of supersaturation levels (S_1, S_2, and S_3) indicated below each assemblage with the curve representing the time dependence of reaction-driving force. The formation of phases other than α also requires supersaturation with respect to them and is based on observations discussed in the text.

growth may suppress the formation of other, more stable silicates.

The key to explaining the Ostwald sequences of reactions is an understanding of the differences in interface-reaction kinetics between soluble and much less soluble solids (Dibble and Tiller, 1981). For example, soluble salts such as most evaporite minerals are characterized by rapid interface-attachment kinetics (Berner, 1980). Because interface reactions are so rapid for soluble salts, growth and dissolution rates are commonly controlled by solute-transport kinetics. On the other hand, the dissolution of most sparingly soluble minerals is controlled by interface-detachment kinetics (Dibble and Tiller, 1981), and the reaction rates of most silicate/water interactions are, consequently, significantly lower.

The growth rate controlled by interface reactions is given by an expression based on a kink-site attachment model (Dibble and Tiller, 1981):

$$V_g = k(1 - e^{-\Delta G_k RT}), \qquad (1)$$

where V_g is the growth velocity, k is a rate constant, R is the gas constant, and T is the temperature. The quantity ΔG_k is that part of the total free energy for growth, ΔG^p, which drives the process of attachment of molecules to the interface. The rate constant, k, is an exponential function of the free energy of formation of the activated kink-site complex, ΔG_A^* (activation free energy), and is inversely related to some surface-attachment parameters such as the distance between kink sites (kink spacing), x_0,

$$k \propto (e^{-\Delta G_A^*/RT})/x_0. \qquad (2)$$

Inasmuch as the growth velocity, V_g, is inversely related to the kink spacing, a large x_0 value given by the following relation (Dibble and Tiller, 1981) means the V_g value of Eq. (1) will be small:

$$x_0 = \lambda e^{\Delta H_k/RT}, \qquad (3)$$

where ΔH_k is the enthalpy of formation of a kink site and λ is the lattice spacing in the direction of kink-site motion. The quantity, ΔH_k, depends on the magnitude of the broken-bond energy, ϵ_1, in the direction parallel to the ledge; and ϵ_1, in turn, is a fraction of the enthalpy of solution, ΔH_s. Qualitatively, the ratio $\epsilon_1/\Delta H_s$ is proportional to the area of the kink molecule exposed to the solution in a direction parallel to the edge compared to the total area of the molecule if it were completely surrounded by solution. For example, if a simple cubic crystal has nearest-neighbor bonds only and each molecule can be considered a small cube with 6 equal faces, then a kink would present $1/6$ of its maximum possible contact area to the fluid in a direction parallel to the ledge. In this simple case, $\Delta H_k \sim \Delta H_s/6$. Therefore, the smaller the solubility, the larger is ΔH_s and, consequently, ΔH_k. Thus, the least soluble minerals probably have the smallest rate constants on the basis of kink spacing, and this may be an explanation of the Ostwald step rule.

Other parameters, such as ΔG_A^*, ΔG_k, and nucleation kinetics, may also vary depending on the solubility of the solid but have not been thoroughly evaluated. Consequently, the step rule is still an empirical, albeit useful, observation for the purpose of the kinetic model discussed. For example, a model for the paragenesis of zeolites and other authigenic minerals forming in glass-bearing rocks can be constructed based on a series of reactions resembling a classic Ostwald sequence.

KINETIC MODEL OF ZEOLITE PARAGENESIS

A kinetic model for the paragenesis of authigenic silicates in tuffaceous sediments is summarized schematically in Figure 2, which illustrates qualitatively the relationship between the departure from equilibrium and the reaction time. The quantity $|\Delta G^{\alpha}_{rxn}|$ can be correlated with the supersaturation with respect to the most stable authigenic aluminosilicates. The shape of the curve indicates the postulated integrated effects of the stepwise series of metastable reactions on the driving force leading to the formation of phase α. The real functional relationship between the reaction driving force and time is unknown, although it could be estimated for a well-defined set of conditions and parameters. Figure 2 presents graphically the premise that no state of thermodynamic equilibrium ($\Delta G^{\alpha}_{rxn} = 0$) can be attained during the coupled irreversible reaction between unstable phases and solids of greater stability. Metastable phases of greatest solubility generate the largest supersaturations with respect to the most stable minerals containing the same components. The supersaturation depicted in Figure 2 becomes zero only after all metastable phases disappear and equilibrium with bulk solution is attained.

As indicated by Figure 2, glass dissolution may maintain $|\Delta G^\alpha_{rxn}|$ above S_2 and several nonanalcimic zeolites may form. At very high levels of supersaturation (greater than S_3 in Figure 2) with respect to the most stable phases such as α, the solution may become supersaturated with respect to smectites or even aluminosilicate gels. Below $|\Delta G^\alpha_{rxn}|$ values represented by S_2 but above S_1 (glass absent), analcime may crystallize at the expense of pre-existing metastable phases. Feldspars and/or phyllosilicates may crystallize at the expense of all pre-existing phases after $|\Delta G^\alpha_{rxn}|$ values drop below S_1. Crystallization ceases after equilibrium with pore solution is attained. Figure 2 is consistent with an Ostwald step sequence in which least stable phases form first at the highest supersaturation with respect to the most stable phases, and the stable phases crystallize last. The model is also consistent with the relative levels of supersaturation deduced from observations described above.

The time scale in Figure 2 is consistent with the ages of tuffaceous rocks containing the various authigenic assemblages (Sheppard and Gude, 1968, 1969, 1973; Surdam and Parker, 1972). However, the time scale must be adjusted depending on the initial pH and salinity of the pore fluid in a closed system. For higher pH and higher salinity pore fluids, the overall time scale must be adjusted to account for higher dissolution and growth rates. An assumption regarding constant temperature and pressure is inherent to the model; however, higher temperatures will increase the reaction rate, and the time scale can be adjusted.

In this model, the dissolution of glass at rates much greater than the growth rates for authigenic minerals such as feldspars and analcime causes the pore solution to attain supersaturation with respect to less stable phases such as one or more of a variety of disordered alkali zeolites (mordenite, clinoptilolite, chabazite, erionite, phillipsite). Early in the process of glass alteration, even the growth of siliceous, alkali zeolites is probably not sufficient to decrease $|\Delta G^\alpha_{rxn}|$ values, and smectites and gels may form at the highest levels of supersaturation close to the glass/solution interface. The first observable phases to form around glass shards are clay minerals (or, rarely, aluminosilicate gels, Mariner and Surdam, 1970) which evidently grow at rates greater than or equal to maximum glass dissolution rates.

Once highly unstable sols, gels, and disordered smectites have precipitated, the supersaturation, $|\Delta G^\alpha_{rxn}|$, may drop when the growth rate of these phases exceeds glass dissolution rates. As indicated in Figure 2, the growth duration of the least stable phases may be short, i.e., hundreds of years. The later growth of siliceous, alkali zeolites may cause further reduction in supersaturation. However, both clay minerals and zeolites tend to form and persist in the presence of glass (Sheppard and Gude, 1968, 1969, 1973). The nonanal-

cimic zeolites can persist for tens of thousands of years or more depending on reaction rates limited by initial pore-solution chemistry.

The complete dissolution of glass causes a fundamental change in the authigenic mineral assemblage. High supersaturation cannot be maintained, and the early-formed, least-stable phases may dissolve. However, the dissolution of each metastable phase provides the source of components for the growth of another. In the systems considered, analcime commonly crystallizes at the expense of all previously-formed phases, but it may require hundreds of thousands of years to crystallize in sedimentary environments.

After nucleation and growth of feldspars, the supersaturation decreases further, and analcime may become unstable. The feldspar-growth range of Figure 2 can be divided into ordered and disordered regions having ordered feldspars forming at lower supersaturation and at longer times. It is probable that disordered feldspars form under conditions of higher supersaturations associated with dissolution of unstable phases such as alkalic zeolites and/or analcime. As indicated in the figure, the formation of ordered feldspars, particularly albite, may require a reaction duration of up to tens of millions of years (Surdam and Parker, 1972) even though the system may have been greatly supersaturated with respect to feldspars during this period. As implied by the high level of supersaturation with respect to feldspars maintained by glass dissolution and subsequently-formed alkalic zeolites, feldspar crystallization may be suppressed over a very long time. The extremely sluggish growth kinetics of stable aluminosilicates at low temperatures becomes evident when considering this model and the empirical evidence.

SUMMARY AND CONCLUSIONS

The model for the formation of authigenic silicates in tuffaceous rocks presented in this paper is consistent with an Ostwald series of metastable reactions resulting from high supersaturations generated by glass dissolution. The kinetic controls operate to delay the attainment of equilibrium by imposing a series of metastable reactions on the overall reaction path. Such metastable reactions occur because formation of less stable phases can lower the total free energy of the system faster than growth of the stable phase assemblage. The relative rates of growth of different authigenic silicates are determined by as yet poorly understood aspects of interface-attachment kinetics.

The model accounts for the decrease in abundance of zeolites and clays and increase in feldspars in sedimentary rocks with time. The sequence of reactions described implies that clay and zeolite minerals may not be the most stable thermodynamically in many tuffaceous rocks in agreement with the study of Kastner and Siever (1979) and the conclusions of Hay (1966). The model also has important implications for diagenetic

and low-temperature metamorphic reactions. Attainment of equilibrium at constant temperature and pressure may be significantly delayed by the growth of intermediate, metastable minerals. The time to reach equilibrium may be increased drastically, perhaps from a few thousands of years in the system where the most stable assemblage forms directly, to tens of millions of years in the system where the growth of intermediate metastable minerals prevails.

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Резюме—Порядок минералогических реакций, включающих цеолиты и другие аутигенные фазы в туфовых осадочных породах, можно объяснить кинетикой реакций роста и растворения. Кинетические факторы могут определять образующиеся специфические аутигенные фазы, а также временные и пространственные ограничения, влияющие на состав раствора во время необратимых реакций растворения и роста в породах, содержащих стекло. Стеклянные фазы создают высокий уровень пересыщения различными алюмосиликатами в поровой жидкости. Порядок формаций, образующихся в течение серии метастабильных реакций, напоминает ступенчатый порядок Оствальда. Метастабильные реакции происходят, так как образование таких менее стабильных фаз, как гелей, глин, и неупорядоченных цеолитов, может снизить общую свободную энергию систем, включающих стекло, быстрее, чем рост стабильных формаций, содержащих упорядоченные фельдшпаты, кварц, и слюду. В конечном итоге по серии стадий может образоваться формация силиката наиболее стабильная для общего состава, температуры и давления. Однако образование промежуточных метастабильных фаз может задержать достижение равновесия до 10 миллионов лет. [Е.С.]

Resümee—Die Abfolge von Mineralreaktionen, die Zeolithe und andere authigene Phasen in tuffhaltigen sedimentären Gesteinen mit umfaßt, kann durch Wachstums- und Lösungskinetik erklärt werden. Kinetische Faktoren können die sich bildenden spezifischen authigenen Phasen erklären sowie die zeitlichen und räumlichen Auswirkungen auf die Lösungszusammensetzung während irreversibler Lösungs- und Wachstumsreaktionen in glashaltigen Gesteinen. Die Glasphase verursacht einen hohen Grad von Übersättigung im Hinblick auf eine Reihe von Alumosilikaten in der Porenlösung. Die Abfolge von Mineralkombinationen, die sich während einer Reihe von metastabilen Reaktionen bildet, ähnelt einer Ostwald'schen Stufenregel. Metastabile Reaktionen treten auf, da die Bildung von weniger stabilen Phasen, wie Gelen, Tonen, schlecht geordneten Zeolithen, die gesamte freie Energie des glashaltigen Systems schneller verringern können als das Wachstum stabiler Paragenesen, die geordnete Feldspäte, Quarz, und Glimmer enthalten. Gelegentlich kann sich dann, nach einer Reihe von Schritten, die im Hinblick auf den Gesamtchemismus, die Temperatur und den Druck stabilste Silikatparagenese bilden. Die Bildung von metastabilen Übergangsphasen kann jedoch die Einstellung des Gleichgewichtes um Zehner von Millionen von Jahren verzögern. [U.W.]

Résumé—La séquence de réactions minérales impliquant des zéolites et d'autres phases authigéniques dans des roches tufacées sédimentaires peut être expliquée par la cinétique de réactions de croissance et de dissolution. Des facteurs cinétiques peuvent déterminer les phases authigéniques spécifiques qui se forment, et les contraintes temporelles et spatiales sur la composition de la solution pendant les réactions irréversibles de dissolution et de croissance dans des roches contenant du verre. La phase verre génère un niveau élevé de supersaturation respectivement à une variété d'aluminosilicates dans le fluide des pores. La séquence d'assemblages formés pendant une série de réactions métastables ressemble à une séquence par étapes d'Ostwald. Des réactions métastables sont produites parceque la formation de phases moins stables comme des gels, des argiles, et des zéolites désordonnés peut abaisser l'énergie totale libre du système contenant le verre plus rapidement que la croissance de l'assemblage stable impliquant des feldspaths, du quartz, et des micas ordonnés. Eventuellement, après une série d'étapes, l'assemblage silicate le plus stable pour la composition en masse, la température, et la pression, peut être formée. La formation de phases intermédiaires métastables peut cependant retarder l'obtention de cet équilibre pendant des dizaines de millions d'années. [D.J.]