- 18. C. Kuhlemeier, R. Fluhr, P. J. Green, N.-H. Chua, Genes Dev. 1, 247 (1987)
- S. A. Johnston *et al.*, *Cell* **50**, 143 (1987).
 P. K. Sorger and H. Pelham, *ibid.* **54**, 855 (1988).
 H. Fromm, F. Katagiri, N.-H. Chua, *Plant Cell* **1**, *cell* **50**, 143 (1987).
- 977 (1989)
- 22. F. Katagiri, E. Lam, N.-H. Chua, Nature 340, 727 (1989)
- 23. G. Struhl, K. Struhl, P. M. Macdonald, Cell 57,

1259 (1989).

We thank P. Green and P. Benfey for plasmids, H. 24. Williams for photography, B. Niner for expert tech-nical assistance, and P. Gilmartin for critical reading of the manuscript. E.L. was supported by a postdoctoral fellowship from NIH. This work was supported by Monsanto Co

1 November 1989; accepted 8 March 1990

Ostwald Ripening of Clays and Metamorphic Minerals

Dennis D. Eberl,* Jan Środoń, Martin Kralik, Bruce E. Taylor, Zell E. Peterman

Analyses of particle size distributions indicate that clay minerals and other diagenetic and metamorphic minerals commonly undergo recrystallization by Ostwald ripening. The shapes of their particle size distributions can yield the rate law for this process. One consequence of Ostwald ripening is that a record of the recrystallization process is preserved in the various particle sizes. Therefore, one can determine the detailed geologic history of clays and other recrystallized minerals by separating, from a single sample, the various particle sizes for independent chemical, structural, and isotopic analyses.

LAY MINERALS GENERALLY HAVE large surface areas and exhibit a range of particle sizes. These characteristics suggest that clays may undergo Ostwald ripening (1-6) when exposed to fluids such as ground water or hydrothermal solutions, although this process must occur slowly at near-surface temperatures because clays are so insoluble. Recent evidence (7, 8)indicates that illite can recrystallize by Ostwald ripening in some hydrothermal systems. In this report we show that this process also occurs in other minerals and environments, and we discuss the effect that Ostwald ripening has on the crystal chemistry and geology of clays.

Ostwald ripening is a recrystallization process that is characterized by the simultaneous dissolution and growth of a mineral in a single medium. After nonexplosive nucleation, a system contains a great many crystallites of different sizes. Surface free energy then tends toward a minimum by the dissolution of small particles and the growth of large particles as matter is transferred from the former to the latter through solution (4). As ripening proceeds in a closed

8, A-1030 Vienna, Austria. B. E. Taylor, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8. Z. E. Peterman, U.S. Geological Survey, Mail Stop 963, Federal Center, Denver, CO 80225.

system, the mean crystallite size increases, the level of supersaturation in the solution decreases, the particle size distribution spreads out, and the number of particles decreases. As the level of supersaturation in solution decreases with increasing particle size, the mechanism of crystal growth may change from a process with a first-order reaction rate to one with a second-order rate (4, 5). Equilibrium cannot be attained until, by some process, the mineral consists of a single crystal or all the crystallites of a mineral are the same size. A complete record of the recrystallization process will be contained in the largest particle: it will be zoned progressively from an older core, representing the nucleation stage, to a younger rim, because the largest particles in the system never undergo dissolution (4). This history also will be preserved in the various particle sizes because the relative size relation between particles formed in the original nucleation step is maintained during ripening (9).

The occurrence of Ostwald ripening can be detected, and the mechanism that controlled the rate of the ripening process can be determined, from the particle size distribution, as originally suggested by Lifshitz and Slyozov (10) and Wagner (11). This quantitative description of Ostwald ripening is known as the LSW theory (4). Particle thickness distributions for three illites (Fig. 1) from shales from the Glarus Alps (12) show a sequence expected for ripening: mean particle thicknesses increase and particle thickness distributions spread out as metamorphic grade increases. In addition,

the Alpine illites show convergence to a steady-state profile when particle thickness distributions are nondimensionalized (based on the use of reduced coordinates according to LSW theory; Fig. 2A); this is done by dividing by both the mean particle thickness for each distribution and the value for the maximum frequency in each distribution.

The occurrence of similar, reduced profiles (Fig. 2A) that approach a steady-state distribution (a distribution that is independent of the mean particle size and the initial, pre-recrystallization particle size distribution) is indirect proof that the clays have undergone Ostwald ripening (4, 10). Profiles having shapes similar to those found for the Alpine samples, but displaced toward larger reduced radii, also were found for





Fig. 1. Particle thickness distributions for illites from the Glarus Alps (12): metamorphic grade increases from sample MF4 (beginning of the anchizone) via MF23 to sample MF998 (epizone) on the basis of illite "crystallinity." Thickness measurements were made by the Warren-Averbach (W-A) technique (14), with Siemens D500 software, and the 002 and 005 x-ray diffraction peaks for Sr-saturated, <2-µm samples. Particle thicknesses measured by the W-A technique were checked by TEM measurements for five illite samples. The two techniques were found to give nearly identical mean particle thicknesses and particle thickness distributions. Ages are from (12).

D. D. Eberl, U.S. Geological Survey, Mail Stop 404, Federal Center, Denver, CO 80225.

J. Srodoń, Institute of Geological Sciences, Polish Acade-my of Sciences, 31-002 Krakow, Senacka 3, Poland. M. Kralik, Geotechnical Institute, Federal Testing and Research Institute–Arsenal, Faradayg, 3, Post Office Box

^{*}To whom correspondence should be addressed.

hydrothermal illites from the Silverton caldera [Fig. 2B; see also (7, 13)], and similar shapes were found for kaolinites, chlorites, and illites from a variety of other locations (Fig. 2C). Data from different techniques yield similar results: Most of the particle thickness data (parallel to c*, perpendicular to the a-b plane) were obtained with the Warren-Averbach x-ray peak-broadening technique (7, 14). However, one profile in Fig. 2C is for the *a*-*b* crystal plane of an illite (RM30) measured by scanning electron microscopy (SEM) [measurements based on $(\ell w)^{1/2}$, where ℓ is length and w is width], and another is the average profile for illite crystal lengths (8) measured by transmission electron microscopy (TEM) from eight samples.

The near coincidence of the various profiles for clays from a given location (Fig. 2, A and B) indicates that the kinetics of ripening for these clays were controlled by the same process. However, the observed shape does not fit any of the theoretical profiles (Fig. 3) calculated from LSW theory for a specific growth mechanism and rate law [for example, for volume diffusion control or surface control of growth; see (3)]. The profiles do fit log-normal distributions, although the rate law that gives rise to this steady-state curve has not yet been identified. The same process also appears to have controlled ripening for some coarser, metamorphic minerals and for calcite in micritic limestone (Fig. 2D), as well as for many substances that have been ripened artificially. For example, reduced particle size distributions for reagent grade calcite (3), commercially available from Fisher Scientific and from Mallinckrodt Chemical Works, fit closely the calculated log-normal curve for clay sample MF998 (Fig. 2A). The log-normal particle size distribution that we attribute to crystals that have undergone Ostwald ripening also has been found for materials as diverse as annealed Al metal (15) and ripened photographic emulsions composed of AgBr (16).

In order to determine the evolution of illite particle size distributions as a function of mean particle size, we measured particle thickness distributions for a series of mixedlayer illite-smectites (Carboniferous and Silurian metabentonites and one sericite; Fig. 3), using TEM and the Pt-shadowing technique (17). Illite-smectites are considered to be thin illite crystals that have absorbed water on their basal surfaces; these surfaces interact between adjacent illite crystals to form smectite layers by interparticle swelling (18). Reduced profiles for the thinnest illite crystals (mean thicknesses of 1.2 to 1.7 nm; Fig. 3A) fit none of the theoretical or lognormal distributions. Profiles for two illites having thicknesses of 2.7 nm (Fig. 3B)

27 APRIL 1990

approximately fit a theoretical curve expected for ripening by first-order kinetics [a characteristic of crystal growth rate controlled by volume diffusion or by spiral growth at moderate levels of supersaturation; see (5)]. Reduced profiles for illites having mean thicknesses from 2.2 to 3.2 nm (Fig. 3C) fit the theoretical curve expected for second-order kinetics [crystal growth rate controlled by spiral growth at low levels of supersaturation, consistent with results from a separate study of metabentonites (19)]. The overall rate law is (4)

$$r^{n} - r_{0}^{n} = K_{n}(t - t_{0})$$
(1)

where r is the mean particle radius (or thickness) for the particle size distribution after reaction for time t; r_0 and t_0 are the initial mean particle radius and initial time, respectively; and K_n is the coefficient that characterizes the growth rate of the mean radius. Recrystallization follows first-order kinetics when n = 2 and second-order kinetics when n = 3. The thickest illite crystals (2.5 to 5.8 nm; Fig. 3D) generally fit a lognormal distribution, which is the common profile for many of the clays we examined (Fig. 2).

Thus, although there is considerable over-

lap in particle thicknesses between groups (Fig. 3), the rate law for illite recrystallization generally changes as mean crystal thicknesses increase. The pattern for this change can be explained as follows. The thinnest crystals (Fig. 3A) have not ripened sufficiently to establish a steady-state reduced profile. The subsequent progression from first-order to second-order kinetics (Fig. 3, B and C) with generally increasing illite particle thickness is expected for systems in which the level of supersaturation decreases as particle size increases, thereby leading successively to crystal growth by screw dislocation control under linear and then quadratic growth regimes. If this trend in reaction mechanism with particle solubility continues, a log-normal reduced profile (Fig. 3D) apparently results, perhaps when the ripening rates are controlled by dissolution kinetics under very low levels of supersaturation (that is, the fine particles dissolved more slowly than the coarser particles could grow).

If it can be shown that a mineral specimen has undergone Ostwald ripening, then the crystal population will contain information concerning the ripening process. For example, a linear relation between apparent K-Ar



Fig. 2. Particle size distributions for clays and other minerals plotted on reduced coordinates. (**A**) Reduced profiles for illites (particle thicknesses measured by the W-A technique) from the Glarus Alps (12). The solid line is a reduced profile calculated for a log-normal distribution for sample MF998 (Eq. 2). (**B**) Reduced profiles for illites (W-A technique) from the Silverton caldera, Colorado (7, 13). The solid line is a log-normal distribution calculated for sample RM30. (**C**) Reduced profiles for clays measured by the W-A technique, by SEM (RM30, based on 250 SEM measurements) and by TEM (8). The solid lines are those calculated for MF998 and RM30. (**D**) Reduced profiles for metamorphic minerals (24–26) and calcite (27) measured optically. The solid line is that calculated for RM30.

age and particle thickness for illites from the Silverton caldera (Fig. 4A) is consistent with a history of renewed ripening of clays that originally formed during a hydrothermal event at 21 million years ago (Ma) (7, 13) during a subsequent event at 12 Ma: some radiogenic Ar apparently was lost from the older clays during the younger ripening event as the finer crystals dissolved. Volume diffusion driven by the younger heating event also could cause the Ar loss. A similar relation between particle thickness and apparent age has been found for illites (12) from the Glarus Alps (Fig. 4, B and C); the lack of agreement between K-Ar and Rb-Sr ages probably is related to the loss of radiogenic⁴⁰Ar by volume diffusion during early low-grade metamorphism when the illite particles were very thin.

A second consequence of ripening is that clays may expel ions that do not fit well in their crystal structure as recrystallization proceeds through progressively lower levels of supersaturation. This process of recrystallization, a method commonly used by chemists to purify compounds, can account for the decrease in Sr content with particle size (Fig. 5) in sample RM30, which contains pure illite (13). The isotopic data (Fig. 5) demonstrate that the various particle sizes for this sample formed at approximately the same time (20.6 Ma), and the sizes studied were not affected significantly by a younger event at 12 Ma (13). Chemical analysis shows that the amount of Rb⁺, an ion that substitutes readily for K⁺ in the illite structure, is relatively constant for the range of particle sizes analyzed (ppm Rb = 0.0022, 337.0, 343.5, and 329.0 from the leachate through the range of increasing particle sizes). The regular increase in the Rb/Sr ratio with increasing particle size therefore reflects a decrease in Sr in the illite structure.

Oxygen isotopes also were measured as a function of particle size for sample RM30. The δ^{18} O for the size fractions <0.3 μ m, 0.3 to 0.5 μ m, and 0.5 to 2.0 μ m was +0.32, +0.75, and +1.55 per mil (± 0.02 ; duplicate analysis), respectively. These data compare to +1.4 for the bulk sample (13), which represents the average isotope composition of the clay after ripening. This change in δ^{18} O with particle size is consistent with nucleation of illite because of rapid influx of hot water; as the water gradually cooled, ripening proceeded, and the larger particles thereby became progressively enriched in ¹⁸O. The total variation in δ^{18} O of 1.23 among the size fractions is consistent with a minimum decrease in temperature of 25°C during the clay particle ripening, based on illite-water fractionation in the interval from 200° to 150°C (20)

The recognition that clay minerals ripen

has implications for understanding the thermodynamic stability of clay minerals. As long as a clay system has a distribution of particle sizes, surface free energy is not minimized and the clay may continue to react. This tendency of minerals to increase in particle size with time, long known to take place in the metamorphic environment, also apparently extends into the diagenetic and sedimentary environments. The mechanism responsible for this tendency now appears to be Ostwald ripening. Therefore, most clay minerals are on a one-way trip through geologic time toward the formation of coarser crystals. Anything that tends to increase fine particle solubility in the stability field of a clay mineral (for example, an increase in temperature, the presence of mineralizers, increased water flow, and so forth) will increase the rate of clay crystal growth. Conversely, clay recrystallization can be prevented, a desirable goal, for example, in the manufacture of clay catalysts and in the design of clay barriers for radioactive waste disposal, by use of a single particle size (for example, sodium rectorite). Finally, be-

22

20



Apparent K-Ar age (Ma) 18 16 12 10 20 60 в Apparent K-Ar age (Ma) 50 40 30 20 10 -. 30 10 20 40 100 С Apparent Rb-Sr age (Ma) 80 60 40 20 0 20 30 0 10 40 Particle thickness (nm)

Fig. 3. Reduced profiles for a series of mixed-layer illite-smectites having various particle thicknesses. Particle thicknesses, which generally increase from (\mathbf{A}) through (\mathbf{D}) , were measured by the TEM Ptshadowing technique (17) for approximately 100 to 150 measurements per sample. The theoretical first-order profile was extracted from diagrams in (3), and the theoretical second-order profile was calculated from an equation in (3). The calculated curves in (A) and (D) for sample RM8 are for a lognormal distribution and are based on TEM data.

Fig. 4. Apparent radiometric ages plotted against mean particle thicknesses (measured by the W-A technique) for illite samples from (A) the Silverton caldera (7, 13, 22) and (**B** and **C**) the Glarus Alps (12). The equations for the lines are as follows: (A) y = 24.7 - 0.65 x; (B) y = 64.1 - 0.65 x $27.9 \log x$; (C) $y = 122.3 - 69.4 \log x$.

SCIENCE, VOL. 248

A



Fig. 5. A Rb/Sr isochron determined for several particle size fractions for illite sample RM30. Size separations were made by repeated centrifugation. Samples were exchanged with Na+ and NH4⁺ before chemical analysis. The age in millions of years is 20.6 ± 0.8 Ma; the initial 87 Sr/ 86 Sr ratio is 0.7075 ± 0.0003; the mean square of the weighted deviants is 0.9. ISOPLOT (28) was used for regression of the data.

cause fundamental illite particles (18), rather than MacEwan crystallites (that is, stacks of illite particles), participate in the ripening process, it seems most convenient to treat mixed-layer illite-smectite as a single thermodynamic phase, illite, having a range of particle sizes. [For a discussion of this issue see (21, 22)].

Particle size distributions for samples with a log-normal reduced profile can be extracted solely from a measurement of mean particle size. For example, the formula for the log-normal distribution is (23)

$$f(\omega) = \left[\frac{1}{\omega\beta(2\pi)^{1/2}}\right] \\ \times \exp\left\{-\left(\frac{1}{2} \beta^2\right)[\ln(\omega) - \alpha]^2\right\}$$
(2)

where $f(\omega)$ is the frequency of observation ω (that is, the frequency of the thickness, or of the thickness divided by the mean thickness), β^2 describes the variance of the logarithms of the observations and equals $\Sigma[\ln(\omega) - \alpha]^2 f(\omega)$, and α describes the mean of the logarithms of the observations and equals $\Sigma(\ln \omega) f(\omega)$. For RM30, a sample typical of illites from the Silverton caldera (Fig. 2B), $\beta^2 = 0.2107$ and $\alpha = -0.1187$. These parameters, together with Eq. 2 and a knowledge of the mean, can be used to calculate approximately the particle size distributions for many minerals that have undergone ripening (Fig. 2). This approximation is useful because many fewer measurements (for example, by TEM) are required to determine accurately a mean size than a distribution. The parameters for the reduced particle thickness distribution for illite sample MF998 (Fig. 2A), a sample that represents the lower extreme for reduced radii for the illites measured here (that is, it is the farthest left of the profiles in Fig. 2), are β^2

= 0.5639 and α = -0.3963. These parameters also fit reduced profiles for synthetic calcites and some clay minerals (Fig. 2C).

Although the log-normal distribution (which has sometimes been mistaken for the second-order profile in Fig. 3C) closely fits the experimental data, it alone offers little insight into the reaction mechanism because many natural populations are so distributed. However, Ostwald ripening is indicated for this type of distribution by the evolution of illite crystal size distributions, from those predicted for ripening by LSW theory (Fig. 3, B and C), into the log-normal distribution (Fig. 3D) with increasing illite crystal size, and by the observations that many synthetically ripened materials have this distribution and that log-normal reduced plots approach a steady-state shape for many samples (4, 10). The parameters for sample RM30, for example, fit reduced distributions for minerals having crystal sizes that range over several orders of magnitude (Fig. 2, B and D). There are, however, subtle differences in maxima for some of the reduced profiles [compare, for example, the Alpine illites (Fig. 2A) with the Silverton illites (Fig. 2, B and C)]. An explanation for these differences awaits an understanding of the ripening reaction that gives rise to the log-normal particle size distributions.

REFERENCES AND NOTES

- W. Ostwald, Z. Phys. Chem. 34, 495 (1900).
 B. H. T. Chai, Geochemical Transport and Kinetics (Carnegie Institution of Washington, Washington, DC, 1974).
- , thesis, Yale University (1975).
- A. Baronnet, Estud. Geol. (Madrid) 38, 18 (1982).

- 5. B. N. Sun and A. Baronnet, Chem. Geol. 78, 301 (1989)
- 6. J. W. Morse and W. H. Casey, Am. J. Sci. 288, 537 (1988)
- 7. D. D. Eberl and J. Środoń, Am. Mineral. 73, 1335 (1988).8. À. Inoue et al., ibid., p. 1325.
- A. J. Markworth, Metallography 3, 197 (1970).
- 10. I. M. Lifshitz and V. V. Slyozov, Phys. Chem. Solids 15, 35 (1961).
 11. C. Wagner, Z. Elektrochem. 65, 581 (1961).
 12. J. C. Hunziker et al., Contrib. Mineral. Petrol. 92, 157
- (1986).
- 13. D. D. Eberl, J. Środoń, M. Lee, P. H. Nadeau, H. R. Northrop, Am. Mineral. 72, 914 (1987).
 14. B. E. Warren and B. L. Averbach, J. Appl. Phys.
- 21, 595 (1950).
- 21, 333 (1330).
 P. A. Beck, Adv. Phys. 3, 245 (1954).
 R. P. Loveland and P. H. Trivelli, J. Phys. Colloid
- Chem. 51, 1004 (1947
- 17. P. H. Nadeau and J. M. Tait, in A Handbook of Determinative Methods in Clay Mineralogy, M. J. Wil-son, Ed. (Blackie, London, 1987), chap. 6.
- 18. P. H. Nadeau, M. J. Wilson, W. J. McHardy, J. M. Tair, *Science* **225**, 923 (1984). 19. K. E. Tellier, thesis, Dartmouth College (1988). 20. $\delta^{18}O = [({}^{18}O/{}^{16}O_{sample}/{}^{18}O/{}^{16}O_{SMOW}) 1] \cdot 1000;$ SMOW, standard mean ocean water.

- 21. S. P. Altaner and N. Vergo, Am. Mineral. 73, 1472 (1988)
- 22. D. D. Eberl, J. Środoń, M. Lee, P. H. Nadeau, ibid., p. 1475. 23. G. S. Koch, Jr., and R. F. Link, Statistical Analysis of
- Geological Data (Dover, New York, 1971). 24. K. A. Jones and A. K. Galwey, Geol. Mag. 101, 762
- (1964).
- 25. R. Kretz, J. Geol. 74, 147 (1966). R. L. Stanton and H. Gorman, Econ. Geol. 63, 907 26.
- (1969)27. N. Minoura, J. Fac. Sci. Hokkaido Univ. Ser. 4 16,
- 193 (1974).
- K. R. Ludwig, U.S. Geol. Surv. Open-File Rep. 88-557 (revision 3 January 1990). 20
- We thank M. Frey for supplying samples of illites from the Glarus Alps; R. Burtner and M. Distefano for supplying chlorites; A. Baronnet, P. Costanzo, M. Frey, R. Glasmann, H. May, and G. Whitney for reviewing the original manuscript; and M. Reddy for helpful comments. M.K. thanks the Max Kade Foundation, Inc., for supporting 9 months of research at the U.S. Geological Survey.
 - 18 December 1989; accepted 23 February 1990

Phosphorus Uptake by Pigeon Pea and Its Role in Cropping Systems of the Indian Subcontinent

Noriharu Ae,* Joji Arihara,† Kensuke Okada, Teruhiko Yoshihara, Chris Johansen

Pigeon pea was shown to be more efficient at utilizing iron-bound phosphorus (Fe-P) than several other crop species. This ability is attributed to root exudates, in particular piscidic acid and its p-O-methyl derivative, which release phosphorus from Fe-P by chelating Fe³⁺. Pigeon pea is normally intercropped with cereals under low-input conditions in the Indian subcontinent. Although pigeon pea can utilize the relatively insoluble Fe-P, intercropped cereals must rely on the more soluble calcium-bound phosphorus. This finding suggests that cultivation of pigeon pea increases total phosphorus availability in cropping systems with low available phosphorus.

HOSPHORUS IS NORMALLY THE most limiting nutrient for growth of leguminous crops in tropical and subtropical regions. This particularly applies to soils of high iron or aluminum oxide con-

tent, where P is strongly bound and largely unavailable for crop uptake. Pulses have been cultivated as protein sources under low-input agriculture for thousands of years. Among these pulses, pigeon pea [Cajanus