

Table 1. Concentrations of K and Rb and K:Rb ratios in some alpine peridotites. NZ, New Zealand; G, Greenland; N, Norway; A, Australia; NF, Newfoundland; V, Venezuela.

Source	K (ppm)	Rb (ppm)	K:Rb
<i>Dunite</i>			
Dun Mtn., NZ	23.9	0.111	215
Papua	61.2	.302	203
Shikoku, Japan	24.2	.099	244
Tulameen, B.C.	26.5	.130	204
Cantwell, Alaska	19.3	.072	268
Siorarsuit, G	643	2.42	266
Konya, Turkey	36.9	0.140	263
Almklovdalen, N	44.2	.131	337
<i>Serpentine</i>			
Kalgoorlie, A	119	.284	419
Bett's Cove, NF	236	1.036	228
<i>Peridotite</i>			
Mt. Albert, Quebec	59.3	0.158	375
Tinaquillo, V	25.8	.093	277

tory basaltic residue from the upper mantle, formed subsequent to the early differentiation.

In this context, the main characteristic of such a differentiation history is the close coupling between the crust and an already differentiated upper mantle whose geochemical characteristics would have been established by the composition of the primitive mantle material and the nature of the first-stage differentiation process. As we have noted, the first-stage differentiation process was such that it caused enrichment of lithophilic and radioactive elements in the upper mantle. If one assumes that the K:Rb ratio of the primitive mantle material was of the order of 1500 or greater (2), the first-stage differentiation process mentioned resulted in lower K:Rb ratios in the upper mantle. In that the ratio is re-

Table 2. Concentrations of K and Rb and K:Rb ratios in some ultramafic inclusions in basalts and kimberlites. A, Austria; M, Mexico; T, Tanganyika; SA, South Africa; NZ, New Zealand; Ant, Antarctica.

	K (ppm)	Rb (ppm)	K:Rb
<i>Peridotite inclusions</i>			
Kerguelen Is.	190	0.420	452
Galapagos Is.	123	.352	349
Kapfenstein, A	31.1	.271	115
Chihuahua, M	152	.413	368
Ludlow, Calif.	77.9	.398	196
Monduli, T	727	3.67	198
Wesselton Pipe, SA	641	4.45	143
Bultfontein Pipe, SA	483	2.03	238
<i>Garnet peridotite inclusion</i>			
Kankanui, NZ	938	1.73	542
<i>Eclogite inclusion</i>			
Visser Pipe, T	716	7.52	95
<i>Dunite inclusion</i>			
Ross Is., Ant	216	1.15	188

lated to the extent of differentiation, one may have in fact variation in ratio values in the mantle, both vertically and laterally.

The alpine-type ultramafic rocks are residual in nature and their alkali elemental concentrations are so low that, for approximation, we can consider that both K and Rb were totally removed from them into the crust. Therefore a general idea of the ratio in the upper mantle regions after the early-stage differentiation is given by the K:Rb ratio of the average continental crust. The ratios in these ultramafic rocks are low primarily because the rocks formed from material of the upper mantle—wherein the ratio had been lowered by the aforementioned first-stage differentiation process. The primitive basalts with high K:Rb ratios are, according to this view, derived from source materials that were less (or not at all) differentiated in this first stage.

If this somewhat oversimplified interpretation were correct, we would expect the alpine ultramafic rocks and the ultramafic inclusions to show more radiogenic Pb and Sr isotopes, as well as relatively more fractionated light rare-earth elements, than the primitive basalts with high K:Rb ratios. Isotopic analyses of lead from these ultramafic rocks are not yet available, but the $\text{Sr}^{87}:\text{Sr}^{86}$ ratios are definitely more radiogenic than those of oceanic tholeiites (8, 10). Similarly, the abundances of rare-earth elements in some of these ultramafic rocks show greater enrichments of the light rare-earth elements than do those of the oceanic tholeiites (11, 12).

The close relation between continental crustal material and the lithophilic element-enriched upper mantle has been mentioned; we suggest that the scatter of the K:Rb ratio, in common igneous rocks, around a value of 300 (13) may result from crustal material forming from an upper-mantle material having approximately the same K:Rb ratios.

Finally we suggest that the K:Rb ratios in ultramafic rocks are consistent with the idea of an early-stage differentiation of the primitive mantle material, during which lithophilic and radioactive elements were concentrated in the regions of the upper mantle (8, 9, 11).

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14. Work supported by NSF grant gp-3448.

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16 May 1966

Mechanism for Intercalation of Kaolinite by Alkali Acetates

Abstract. *The relative strengths of the hydrogen bonds in kaolinite-alkali salt-water systems control kaolinite-salt interactions. A new technique for intercalation results in formation of a kaolinite-salt complex free of excess salt.*

We have achieved intercalation by drying a paste obtained by treating kaolinite with aqueous potassium acetate solutions. This method produces an expanded lattice free from detectable excess salt which is easily and reversibly interconverted to a partially collapsed dehydrated form. Intercalation occurs over a specific range of salt-to-water molecular ratios; this range may be approached from either low or high ratios with samples in equilibrium with controlled relative humidity atmospheres. A mechanism for the interactions between kaolinite, salt, and water is proposed.

Preferential penetration of kaolinite by potassium acetate was first achieved

by dry grinding the clay with excess salt (1). Letting the clay stand in a moist environment after dry grinding assisted complex formation; a 70-percent relative humidity was shown to be most suitable (2). Saturated salt solutions were later found to be equally effective in complex formation, and the reaction is now used in the positive identification (3) and quantitative determination (4) of kaolinite in soil clays. Reproducible results depend on removal of excess salt from the sample, however, and this necessitates the introduction of a laborious washing procedure.

No mechanism for intercalation has been put forward. One-dimensional Fourier projections, based on x-ray diffractograms, suggest that interlayer salt is hydrogen-bonded to the hydroxyl sheet of kaolinite (5). Infrared studies (6) substantiate this interpretation, since the kaolinite hydroxyl stretching frequencies can be shown to decrease through hydrogen bonding to interlayer acetate ion. Weiss *et al.* (5) suggest that intercalation is a function of cation radius and that the acetate carbonyl group is important for reaction.

Intercalated sample mounts free of excess salt are prepared as follows: to a 1-g sample of kaolinite (Ward's No. 5, Lamar Pit, Bath, S.C.) in a 100-ml centrifuge tube is added 25 ml of 4.0M potassium acetate. The stoppered tube is shaken (about 15 minutes) and then centrifuged. The supernatant is decanted; the tubes are inverted and allowed to drain. About 200 mg of the moist surface material is removed from the tube with a thin spatula and spread smoothly onto a petrographic glass slide. The slide mount is allowed to dry in a controlled relative humidity atmosphere prior to irradiation.

Reproducible results are obtained with the 1- to 5- μ (equivalent spherical diameter) particle size fraction. Sample mounts of the 5- to 20- μ fraction buckle upon intercalation; and the <1- μ fraction intercalates more slowly and less completely and exhibits poorer diffraction properties. The degree of intercalation, as determined by the $I_{14.0 \text{ \AA}} / I_{7.1 \text{ \AA}}$ (d_{001} kaolinite-salt complex) to $I_{7.1 \text{ \AA}}$ (d_{001} kaolinite) ratio, is increased by varying the concentration of the potassium acetate solution from 0.3M to 8.1M (Fig. 1). Complex formation is also influenced by the relative humidity over which samples are

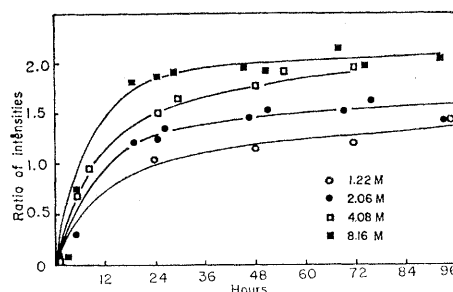


Fig. 1. Intercalation of the 1- to 5- μ size fraction of kaolinite as related to the concentration of potassium acetate in the original suspension. The $I_{14.0 \text{ \AA}} / I_{7.1 \text{ \AA}}$ ratios are used.

equilibrated (Fig. 2). Moisture content and $I_{14.0 \text{ \AA}}$ to $I_{7.1 \text{ \AA}}$ ratios for both wet and dry slide mounts were identical after equilibration with a constant relative humidity (Fig. 3). Dry physical mixtures of kaolinite and salt were prepared by heating freshly prepared wet samples at 110°C for 30 minutes to dispel water. The stability of the interlayer complex is influenced by the partial pressure of water in the external environment. Storage in a relative humidity of greater than 70 percent causes salt to diffuse from the interlayer. This results in a reduction in the intensity of the 14.0- $\text{\AA}$ peak and an increase in the intensity of the peak at 7.1 $\text{\AA}$.

Intercalated samples lose interlayer water rapidly and reversibly upon gentle heating at 60°C or upon storage over a desiccant for 24 hours, to yield a partially collapsed lattice with a d_{001} spacing of 11.8 $\text{\AA}$. Samples of the material evolved during partial collapse of the complex were collected *in vacuo* and shown by mass spectrometric analysis to be water alone. Upon introduction of the dehydrated complex into an atmosphere of high relative

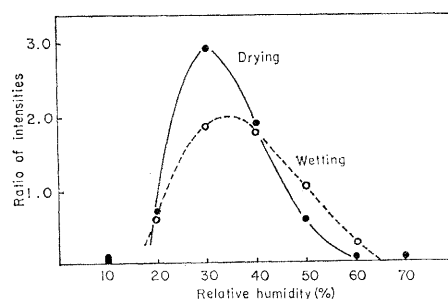


Fig. 2. Intercalation of kaolinite treated with 4.08M potassium acetate as related to the initial moisture content of the kaolinite-salt mixture and to the moisture content of the atmosphere at equilibrium. The $I_{14.0 \text{ \AA}} / I_{7.1 \text{ \AA}}$ ratios are used.

humidity, rehydration occurs quickly as shown by the rapid growth of the 14.0- $\text{\AA}$ peak during constant irradiation ($\text{CuK}\alpha$) at $6.2^\circ 2\theta$. Decay of the 11.8- $\text{\AA}$ diffraction maximum occurs simultaneously and follows the same time dependence. We have tested the hypothesis that a d_{002} diffraction maximum from the hydrated complex is superimposed on the kaolinite d_{001} spacing by dehydrating the complex with immediate irradiation at $12.4^\circ 2\theta$. For the ratio of intercalated complex to kaolinite in our preparations the intensity of the 7.1- $\text{\AA}$ peak remains unchanged on dehydration; consequently, this diffraction maximum may be attributed to unreacted kaolinite alone. The dehydrated kaolinite-potassium acetate complex can be easily and effectively studied by immediately wrapping a slide heated at 110°C with a household plastic. (Union Carbide's Glad-Wrap or Primrose Plastics' Kwik-Wrap was used.) Attempts to replace expelled interlayer water with ammonia, methane, and hydrogen sulfide failed. Differential thermal analysis indicates that cation hydration water is lost at about 60°C and that kaolinite containing interlayer salt dehydroxylates at a lower temperature than untreated kaolinite. Properties similar to those described above obtain with rubidium acetate complexes which have a hydrated d_{001} spacing of 14.4 $\text{\AA}$ and a partially collapsed spacing of 11.8 $\text{\AA}$.

The results of this investigation serve to suggest a mechanism for the intercalation reaction which stresses the role of hydrogen bonding. The lone pair electrons of the carbonyl oxygen in the acetate ion are more available for hydrogen bonding than those of the siloxane groups of kaolinite. Thus, as the water content in the clay-potassium acetate-water system decreases, the carbonyl oxygen of the acetate ion interacts with a hydroxyl group of kaolinite to give a stronger hydrogen bond than had existed between Si-O and Al-OH groups, and intercalation begins. For the interaction to continue, the water content of the system must be sufficiently high to prevent crystallization of the salt; this state is favored by the deliquescent nature of potassium acetate. On the other hand, an increase in the water content following intercalation reverses the process; salt diffuses out of the interlayer and Si-O-Al-OH hydrogen bonds are reformed.

In our procedure excess salt is removed in the supernatant obtained by

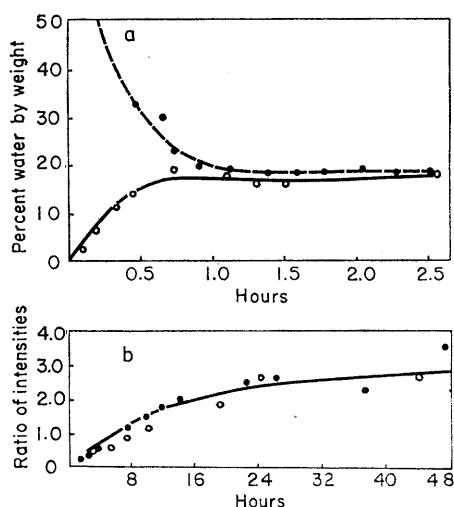
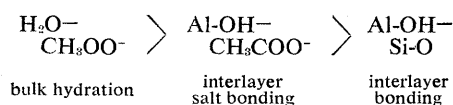


Fig. 3. The equilibrium moisture content, rate of intercalation, and extent of intercalation in wet and dry mixtures of the 1- to 5- μ size fraction of kaolinite with potassium acetate. (Filled circles, wet; open circles, dry.) We used a 4.08M solution of potassium acetate in the original suspension of kaolinite and salt. (a). Rate of equilibration and moisture content at equilibrium in the laboratory. (b). Rate and extent of intercalation in the laboratory. The $I_{14.0 \text{ \AA}}/I_{7.1 \text{ \AA}}$ ratios are used.

centrifugation following mechanical mixing of a clay-intercalating reagent suspension. Drying occurs after preparation of the slide mount, and the salt solution occluded in the sample is concentrated. The cation and anion begin to share water molecules and conditions become favorable for intercalation, which apparently is initiated by the acetate ion. In solution, this ion is hydrogen bonded to water principally through the lone pair electrons of the carbonyl groups. With the sharing of water molecules, however, the interaction of carbonyl groups with other hydrogen bonding sites becomes energetically more favorable. In the salt-kaolinite-water system, the hydroxyl groups at the edge and on the interior octahedral surfaces of the kaolinite are potential sites for hydrogen bonding. Thus, as the water content decreases, the salt ions approach the edges of the kaolinite (the approach of the salt is favored by reduction in steric interference of the hydration spheres), and at some point the acetate carbonyl group begins to interact with hydroxyl groups of the kaolinite. Decreases in the hydroxyl stretching frequencies in the hydroxyl planes have been shown in dehydrated systems (6) where the only suitable hydrogen bonding site is the carbonyl group. The free energy change for this overall process of ex-

change of hydrogen bonding sites is favorable, since (i) the carbonyl oxygen-kaolinite hydroxyl interaction is stronger than that between the oxygen and hydroxyl planes of atoms in kaolinite where the decrease in hydroxyl stretching frequency on intercalation (6) is accounted for through Badger-Bauer rule considerations (7) by an increase in the relative enthalpies of the hydrogen bonds, and (ii) the releasing of water of hydration from the anion and cation and the breaking of the layer structure of the kaolinite undoubtedly contribute to a favorable entropy change in the system. Layers of kaolinite begin to separate at the edges as the exchange of hydrogen bonds occurs. The breaking and making of new hydrogen bonds continues during this process and the expansion caused by the presence of the salt in the interlayer can be followed by x-ray diffraction. When the water content of the external environment is increased the interlayer salt begins to diffuse from between the layers of kaolinite to reform its hydration spheres in the bulk aqueous solution. The apparent order of preference for interaction in the system is:



Intercalation then occurs primarily because of the availability of potential hydrogen bonding sites on some atom of the intercalating species—the carbonyl oxygen in the case of partially dehydrated potassium acetate solutions. Consequently, we expect that other salts or molecules with lone pairs of electrons in directed orbitals might also be effective. This is the case in the reactions observed between kaolinite and rubidium acetate, urea, hydrazine, and formamide (5). The acetates of lithium and sodium, however, do not intercalate directly (1, 5). This lack of activity can best be explained by the observation that these two salts preferentially crystallize as hydrates at a low but adequate water content to satisfy the bonding demands of carbonyl groups, and the water content is never reduced to the point where intercalation can begin. This explanation of the non-intercalation of lithium and sodium acetates differs from that given by Wada (1), who postulates that the lithium and sodium ions are too small for the hexagonal holes of the kaolinite silica-

oxygen sheet, effectively preventing the formation of a stable complex. Wada's explanation presupposes reaction has occurred, while the explanation just presented suggests that no reaction is initiated.

The failure of cesium acetate to intercalate by our method (see 5) appears to be an effect of its extremely high solubility (1345 g/100 ml at 88.5°C). If excess salt is present in the slide mount, its deliquescence prevents the proper reduction in moisture to initiate reaction. If the amount of salt is reduced to allow proper moisture equilibration, the amount present is not sufficient for intercalation. Evidence to support this explanation is derived from consideration of rubidium acetate experiments. A 2.76M rubidium acetate-kaolinite solution did not give a detectable complex, while a 0.84M solution reacted. The solubility of rubidium acetate is intermediate between potassium and cesium acetates and consequently a complex forms at a concentration intermediate between the other two salts.

Interactions between organic molecules and clay minerals have interested scientists for many years. Our mechanism for the intercalation of kaolinite by potassium acetate suggests that many such interactions involve hydrogen bonding between the exposed hydroxyl groups of phyllosilicates and organic compounds containing atoms with lone pair electrons, especially when the water content of the system is minimal.

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7 March 1966