

DIFFERENTIAL RELEASE OF POTASSIUM FROM INTERSTRATIFIED MICA CLAY MINERALS AS RELATED TO PROBABLE DIFFERENCES IN THEIR MICA LAYER COMPONENTS*

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Abstract—Release of potassium by extraction with solutions containing sodium tetraphenyl boron or by leaching with 0.1 N barium chloride seemed to be related to the nature of the mica layers in the interstratified minerals studied. The rate of potassium release was lower when the calculated Si/Al^{IV} ratio of the mica component layers resembled muscovite and higher when this ratio was intermediate between muscovite and pyrophyllite. This supported a recent hypothesis that the composition and structure of the mica component layers may vary in different interstratified minerals of similar total chemical composition.

INTRODUCTION

HYDROUS mica complexes (interstratified mica-montmorillonite and/or vermiculite minerals) reported on recently differed considerably in their proportions of mica component layers and their stacking sequence. However, their chemical compositions, except for the interlayer cations, were surprisingly similar (Kodama *et al.*, 1969). The Si/Al^{IV} ratios of the over-all tetrahedral sheets of the minerals studied all fell in a narrow range from 4.0 to 5.6. This range was intermediate between 3.4 for microcrystalline muscovite (Kodama and Brydon, 1968) and 6.7 for beidellite (Weir and Greene-Kelly, 1962). If the rectorite-type materials (Brown and Weir, 1963; Kodama, 1966) were excluded, the Si/Al^{IV} ratios of 4.0-5.6 would be narrowed to ratios of 4.8-5.6. To explain the structural variety, Kodama *et al.* (1969) proposed the hypothesis that the composition and structure of the mica component layers could vary in different interstratified minerals of similar total chemical composition.

This hypothesis is illustrated by a comparison of two samples, 5028 and Yonago, whose characteristics are briefly summarized from the previous paper by Kodama *et al.* (1969) (Table 1). Both samples consist of non-expanding muscovite-type layers interstratified with expanding montmorillonite and/or vermiculite layers, but the proportion of mica component layers is greater in the 5028 than in the Yonago sample. The chemical structure for-

mulae for the two samples are shown in Table 2. The formulae in Case I were obtained on the assumption that the structural formula of mica component layers was identical to that of ideal muscovite. The formulae in Case II were calculated on the basis of the mixing proportion estimated by X-ray analysis. The formulae for the Yonago sample are nearly the same, but there is a considerable difference between the formulae for the 5028 sample. On the basis of X-ray and CEC data, the Case I formula of the 5028 sample should be rejected since a proportion of 61 per cent of mica component is too low. A comparison of the Case II formulae of the two samples shows that the mica component of the 5028 sample has a higher Si/Al^{IV} ratio and therefore a lower charge than the mica component of the Yonago sample. As a result, the potassium in the 5028 sample would be less strongly bonded than that in the Yonago sample (e.g. Schwertmann 1962). Hence, the hypothesis that the composition and structure of the mica components may differ in different interstratified minerals of similar total chemical composition was tested by comparing the rates of potassium release of these two samples. This paper describes the experimental results.

EXPERIMENTAL

The rates of potassium release from the 5028 and Yonago samples were studied by extraction with solutions containing sodium tetraphenyl boron (NaTPB) (Scott *et al.*, 1960) and by leaching with 0.1 N BaCl₂. To avoid possible structural damage

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Table 1. Atomic proportions (basis of 44 oxygens), CEC, mica component proportions and $d(001)$ spacings for 5028 and Yonago samples (Kodama *et al.*, 1969)

		5028*	Yonago†	
Tetrahedral ions	Si	13.26	13.37	
	Al	2.74	2.63	
Ratio	Si/Al	4.83	5.08	
	Al	7.78	7.58	
Octahedral ions	Ti	0.01	0.19	
	Fe ⁺³	0.02	0.03	
	Mg	0.19	0.16	
Interlayer ions	Non-Exch.	K	2.42	1.84
		Na	0.02	0.17
		Ca		0.01
	Exch.	Ca		0.01
		and/or Mg	0.24	0.34
CEC, m-equiv./100 g		20	47	
Proportions of mica-layer (%)		80	55	
$d(001)$ (Å) Ca-form, 45% R.H.		10.2 ~ 10.4	25	

*Collected from the Abeshiro mine, Akita Prefecture, Japan.

†Collected from the Yonago mine, Nagano Prefecture, Japan.

Table 2. Possible chemical formulae of 5028 and Yonago samples

	5028	Yonago
Case I	$0.61[(X)Al_2(Si_3Al)O_{11}]$	$0.51[(X)Al_2(Si_3Al)O_{11}]$
	$0.39[(X^*)_{0.16}(Y)_{2.00}(Si_{3.82}Al_{0.18})O_{11}]$	$0.49[(X^*)_{0.17}(Y)_{1.98}(Si_{3.70}Al_{0.30})O_{11}]$
Case II	$0.80[(X)_{0.75}Al_2(Si_{3.25}Al_{0.75})O_{11}]$	$0.55[(X)_{0.92}Al_2(Si_{3.08}Al_{0.92})O_{11}]$
	$0.20[(X^*)_{0.30}(Y)_{2.00}(Si_{3.58}Al_{0.42})O_{11}]$	$0.45[(X^*)_{0.19}(Y)_{1.98}(Si_{3.76}Al_{0.33})O_{11}]$

X, Non-exchangeable interlayer cations, K, Na and Ca.

X*, Exchangeable interlayer cations, Ca and Mg.

Y, Octahedral cations, Al, Ti, Fe and Mg.

by mechanical grinding, each sample was separated without grinding into two fractions, the $2-1 \mu$ and $< 1 \mu$, by the sedimentation technique. Fractionated samples were concentrated by flocculation with $CaCl_2$ solution, then washed free of chloride with water and ethyl alcohol and freeze-dried. The potassium contents (as K_2O) for the $< 1 \mu$ fractions of both air-dried 5028 and Yonago samples were 7.23 and 5.52 per cent respectively. These values were in good agreement with the corresponding previous data, that is, 7.2 per cent for the $< 2 \mu$ fraction of the 5028 sample and 5.38 per cent for the unfractionated Yonago sample. For these samples the potassium contents were almost invariable with particle size. The sodium content (as Na_2O) for the $< 1 \mu$ fraction of the Yonago sample was 0.57 per cent and for the unfractionated sample 0.49 per cent. Thus the chemical structure formulae

given in Table 1 are still valid for discussion of results from the fractionated samples.

The method used for extracting potassium with NaTPB was essentially the same as that described by Reed and Scott (1966). Fifty mg samples were placed in 50 ml polyethylene centrifuge tubes and 5 ml of a 1 N NaCl-0.2 N NaTPB-0.01 M disodium dihydrogen EDTA solution were added to each sample. These mixtures were swirled and placed in a constant temperature water bath at 25°C without shaking. After specific periods of time the mixtures were transferred to 400 ml 0.05 N NH_4Cl solution also containing 4 m-moles $HgCl_2$, boiled for 20 min, cooled, filtered and washed with 100 ml 0.5 N NH_4Cl . The potassium in the filtrates was determined by atomic absorption spectrometry. To minimize errors due to interference the standards were carried through exactly the same boiling,

filtering and washing procedure as the samples except that instead of the clay a known amount of potassium from a KCl solution was added to the extracting solution.

The rates of potassium release for the 5028 and Yonago sample were determined also by leaching with 0.1 N BaCl₂. Three hundred mg of each sample were mixed with 25 g acid-washed, pure quartz sand. Leaching of this sand with 0.1 N BaCl₂ released no measurable amounts of potassium and sodium. The sand-clay mixture was placed in a polyethylene tube (15 cm long and 3 cm in diameter) and enclosed at each end with a sphere of cotton and a bored rubber stopper. The leaching solution from an 18 l. polyethylene bottle was passed through plastic tubing to and from the contents in the leaching tube and collected into 8 l. polyethylene bottles. The samples were leached in a constant temperature room (24°C), and a leaching rate of 250 ml/hr was maintained using a constant hydraulic head and a valve adjusting the flow of solution into the leaching tube. The rapid leaching rate and small amount of sample were chosen to minimize the amount of potassium in the leaching solution at any moment. These precautions were taken to avoid the inhibition of potassium release from the mica by the potassium in solution. The leachates were collected after every hour for the first three hours and then after every day for a total of 11 days. Aliquots of the leachates were concentrated ten times by evaporation in polycarbonate beakers at about 60°C and potassium and sodium in the 1 N BaCl₂

solutions were determined by atomic absorption spectrometry.

RESULTS

Data for potassium release were expressed by the relationship of fraction extracted (α), which is the amount of extracted potassium/total potassium in the sample, against reaction time in hours.

NaTPB extraction method

For both the 5028 and Yonago samples the rate of potassium released was relatively high in the first hour, then decreased gradually and was almost zero after around 0.7–0.8 fraction was extracted after 5 hr reaction (Figs. 1 and 2). Unlike results obtained by Scott (1968), there were neither "induction" reaction stages nor a high potassium release in the first few minutes. The difference in particle size of the 2–1 μ and the < 1 μ fractions made no appreciable difference in the rates except that the < 1 μ fraction of both samples gave a slightly smaller amount of potassium released over a prolonged time of reaction (Fig. 2). However, for both the 2–1 μ and the < 1 μ fractions, the rate of release of the total potassium extracted was lower for the Yonago than for the 5028 sample.

BaCl₂ leaching method

This method was used to check the results obtained by the NaTPB method and to determine the release of non-exchangeable sodium present in the Yonago sample.

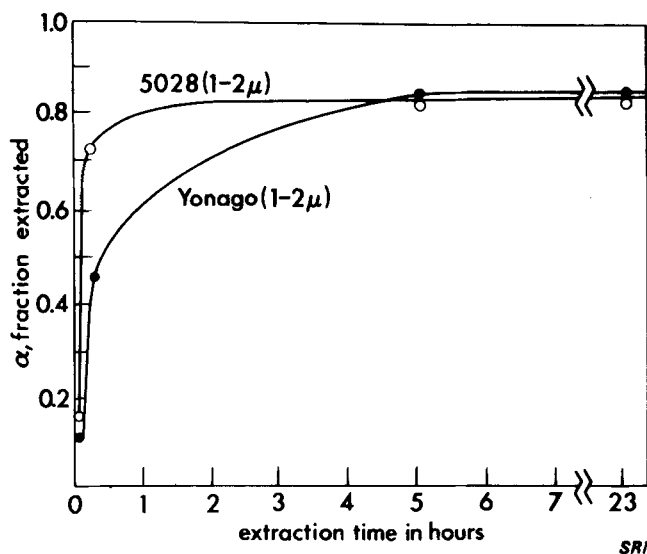


Fig. 1. Potassium extracted from the 1–2 μ fractions of 5028 and Yonago samples with NaTPB solutions.

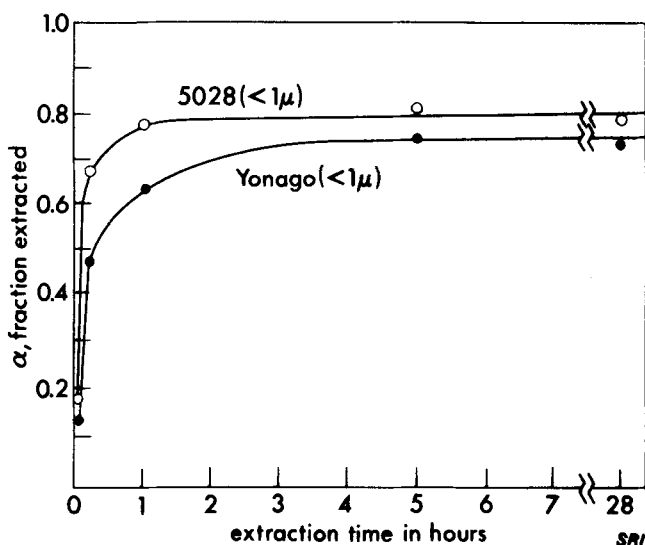


Fig. 2. Potassium extracted from the $< 1 \mu$ fractions of the 5028 and Yonago samples with NaTPB solutions.

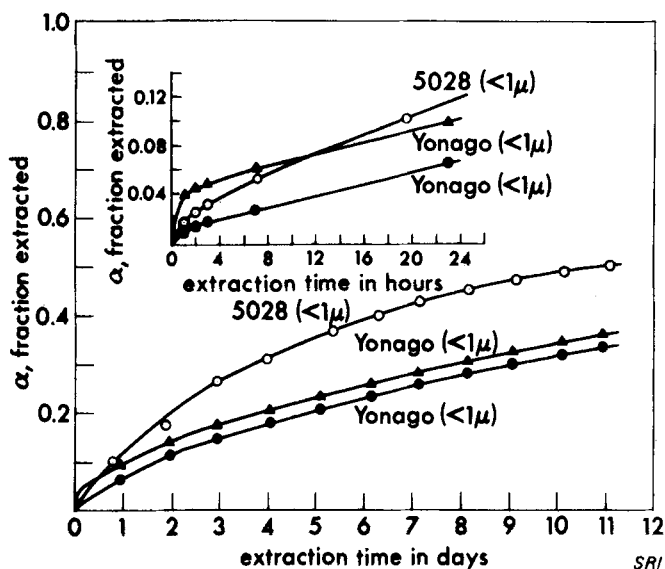


Fig. 3. Potassium and non-exchangeable sodium extracted from the $< 1 \mu$ fractions of the 5028 and Yonago samples by leaching with 0.1 N BaCl₂. Potassium (○) from the 5028 sample, Potassium (●) from the Yonago sample and potassium plus non-exchangeable sodium (▲) from the Yonago sample.

A comparison of the curves in Fig. 3 with those in Figs. 1 and 2 shows that the NaTPB extraction method is by far the more efficient method since more potassium was extracted with NaTPB in the first 15 min than with BaCl₂ in 11 days. As with the NaTPB extraction method, the rate of potassium release was considerably lower for the Yonago than

for the 5028 sample.* With the leaching method, however, the two rates approached each other after 7 days leaching when α was 0.43 for the 5028 and

*Sodium release is neglected in this comparison since the non-exchangeable sodium content in the Yonago sample was less than 10 per cent of its potassium content.

0.26 for the Yonago sample. For the Yonago sample, the initial rate of release of potassium plus sodium was about 4 times that of potassium alone (Fig. 3, inset) since more than 70 per cent of the total sodium was released in the first hour. Another 20 per cent was released gradually so that the two rates were approximately the same during the remainder of the leaching period.

Considering the high rates of potassium extracted with the solutions containing NaTPB and the limited amount of potassium leached out with 0.1 N BaCl₂ and also the recent evidence indicating the complexity of the mechanism governing potassium release in micas (Newman and Brown, 1969), the experimental data were judged inadequate for further kinetic analysis.

DISCUSSION

To justify the selection of a difference in the mica components of the two samples as the factor that controlled the difference in their potassium release, other factors affecting their potassium release should have been small or constant for both samples. Major factors known to affect potassium release from dioctahedral aluminous micas and from interstratified dioctahedral micaceous minerals as well, are particle size, stage of weathering or degradation, structural damage due to grinding, and charge density (e.g. Rich, 1968). The type of interstratification has also been suggested as a factor affecting the release of potassium (Bassett, 1959). Considering these factors in comparing the two samples, particle sizes were similar. Natural degradation was probably not significant in view of the hydrothermal origin of these minerals (Kodama *et al.*, 1969). Induced structural damage was avoided because grinding prior to size fractionation was not necessary for these microcrystalline samples. There was a difference in the type of interstratification and in the calculated Si/Al^{IV} ratios and resultant charge densities of the mica components of the samples. The Yonago sample had a more regular interstratification (Table 1) and a lower Si/Al^{IV} ratio of its mica component (Table 2). These two factors may in fact be related if the regular alternation is considered to arise from structural and/or compositional variations from layer to layer within individual crystals (Sudo *et al.*, 1962). Bassett's (1959) hypothesis implies that the potassium release from a regularly interstratified mineral should be slower than that from a randomly interstratified one. A lower Si/Al^{IV} ratio and resultant higher charge density of the mica component should also decrease the rate of potassium release. With these samples, these two factors can not be clearly differentiated and at this time their effect on potassium release can not be evaluated separately. However, there is

no doubt that the difference in charge densities of the mica components as indicated by the calculated Si/Al^{IV} ratios, if real, was a major factor causing the different rates of potassium release of the two samples.

Regarding the composition of the mica component of the 5028 sample as an intermediate between pyrophyllite and muscovite, three potassium atoms are distributed statistically among four holes of oxygen hexagons of the tetrahedral sheets. These potassium sites may be closely related to the locations of tetrahedral layer charge sites arising from Al-Si substitution. Although at the present stage of knowledge it is difficult to know the state of ordering of the Al-Si substitution, the experimental results obtained in this study clearly suggest certain chemical structural varieties in the mica component layers.

The data concerning the release of sodium as compared to potassium are rather scanty since only one sample contained any measurable amount of non-exchangeable sodium. The results obtained here show a preferential release of sodium relative to potassium and differ from the results obtained by Cook and Rich (1962) showing a non-preferential release of sodium relative to potassium in the weathering of sodium-potassium mica in soils of the Virginia Piedmont. Apparently, further investigation into this problem is necessary to establish firm conclusions.

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Résumé— Dans les minéraux interstratifiés observés, la libération de potassium par extraction avec des solutions contenant du tétraphényl-bore de sodium, ou par lavage avec du chlorure de barium 0,1N semble être en relation avec le nature des couches de mica. Le taux de libération du potassium diminue lorsque le rapport Si/Al^{IV} calculé des couches de mica ressemble à celui de la muscovite, et augmente quand ce rapport est intermédiaire entre celui de la muscovite et de la pyrophyllite. Ceci appuie une récente hypothèse selon laquelle la composition et structure des couches de mica peuvent varier dans des différents minéraux interstratifiés de composition chimique totale similaire.

Kurzreferat— Die Freigabe von Kalium durch Extraktion mit Natriumtetraphenylbor enthaltende Lösungen oder durch Auslaugen mit 0,1N Bariumchlorid stand scheinbar in Beziehung zu der Natur der Glimmerschichten in den zur Untersuchung gelangenden zwischengelagerten Mineralen. Die Geschwindigkeit der Kaliumfreigabe war niedriger wenn das errechnete Si/Al^{IV} Verhältnis der Glimmerbestandteilschichten dem Muskowit ähnelte und höher wenn dieses Verhältnis zwischen Muskowit und Pyrophyllit lag. Das bekräftigt eine vor kurzem aufgestellte Hypothese, wonach die Zusammensetzung und das Gefüge der Glimmerbestandteilschichten in verschiedenen zwischengelagerten Mineralen ähnlicher chemischer Gesamtszusammensetzung veränderlich sein kann.

Резюме — Экстракция калия растворами, содержащими натриевый тетрафенил-бор, или растворами 0,1 N хлорида бария, по-видимому, зависит от природы слюдяных слоев изученных смешаннослойных минералов. Скорость извлечения калия была ниже, если вычисленное отношение Si/Al^{IV} слюдяного компонента было близким к мусковитовому; при значении указанного отношения между мусковитовым и пирофиллитовым скорость извлечения калия была выше. Это подтверждает недавно сформулированную гипотезу, согласно которой состав и структура слюдяного компонента слоев может варьировать в различных смешаннослойных минералах одного и того же валового химического состава.