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# Formation and modification of metastable intermediate sodium potassium mica, paragonite, and muscovite in hydrothermally altered metabasites from northern Wales

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## ABSTRACT

Metastable intermediate sodium potassium mica ($Mu_{47}Pa_{52}Ma_{1}$) is intergrown with paragonite ($Mu_{6}Pa_{91}Ma_{3}$) and muscovite ($Mu_{88}Pa_{12}$), forming aggregates of randomly oriented crystals in the margin of the Ordovician Caradoc metabasites, northern Wales. The cross sections of the mica aggregates resemble the morphology of euhedral plagioclase. Muscovite is the dominant phase with paragonite and intermediate sodium potassium mica being irregularly distributed within mica aggregates. The proportion of the intermediate sodium potassium mica increases as the distance from the sedimentary contact increases.

TEM data show that the intermediate sodium potassium mica occurs as chemically homogeneous, thick stacks of layers that give only one set of 00*l* reflections, with ~9.8 Å periodicity in electron diffraction patterns. All micas are two-layer polytypes. Mixed layering of micas is not observed. The X-ray mapping and lattice-fringe images imply that some interfaces between Na- and K-rich micas obliquely transect basal planes. Intergrowths of subparallel stacks are also present with straight interfaces parallel to the basal planes of one of the adjacent crystals. Both types of interfaces are common. XRD patterns display a second-order reflection having $d = 10.02$ Å, with prominent tailing at high values of $2\theta$ and fourth-order reflections of 5.01, 4.93, and 4.82 Å, consistent with muscovite, intermediate sodium potassium mica, and paragonite. The peak positions of the intermediate sodium potassium mica are nearly identical to those of so-called 6:4 regular mixed-layer paragonite-muscovite reported as occurring in slates from other localities, implying that micas that have XRD patterns lacking superlattice reflections have been misidentified.

The data imply that the intermediate sodium potassium mica formed as hydrothermally derived pseudomorphs after plagioclase microphenocrysts. Subsequent interactions between the intermediate sodium potassium mica and hydrothermal fluids resulted in the redistribution of Na and K in micas and formation of paragonite and muscovite. The $a_{K^+}/a_{Na^+}$ and $a_{K^+}/a_{H^+}$ ratios of the fluids increased during formation, presumably because of interactions with pelites, giving partial replacement of the early formed micas by muscovite and potassium feldspar. Redistribution of Na and K of the micas occurred in two ways: (1) dissolution of the intermediate sodium potassium mica and crystallization of muscovite and paragonite, resulting in lamellar intergrowths of parallel or subparallel packets of micas, (2) alkali exchange between fluids and micas and diffusion within micas without significant dissolution and crystallization, giving rise to inclined irregular interfaces between micas. The breakdown of the intermediate sodium potassium mica represents a stepwise kinetic approach to equilibrium, analogous to the prograde transition of metastable illite to muscovite + pyrophyllite in low-grade rocks.

## INTRODUCTION

Paragonite + phengite (or + muscovite) assemblages are common in anchizonal to epizonal metapelites and in prehnite-pumpellyite to amphibolite or eclogite facies metabasic rocks (Guidotti, 1984; Frey, 1987; Shau et al., 1991, and references therein). The existence of a miscibility gap in the muscovite-paragonite system has been well documented, based on many natural and experimental paragonite + muscovite pairs. Relations among micas whose compositions approximately correspond to the paragonite-muscovite join have been utilized as a geothermometer in spite of uncertainties arising from the possible effects of pressure, interlayer compositions, and phengitic and celadonitic substitutions (Essene, 1989). Maximum solid solutions of paragonite and muscovite that have been observed in natural assemblages are approximately $Mu_{20}Pa_{80}$ and $Mu_{60}Pa_{40}$, typically occurring in single-mica assemblages of high-grade metamorphic rocks (Guidotti, 1984). Apparent compositions intermediate between paragonite and muscovite may have three possible origins, however: (1) averaging of very fine-scale intergrowths of paragonite with muscovite (e.g., Shau et al., 1991), (2) averaging of mixed-layer paragonite-muscovite (Frey, 1969), or (3) a homogeneous metastable solid solution, as implied by phase segregations (Livi et al., 1988) involving diffusion.

The presence of very fine-scale lamellar intergrowths of paragonite and muscovite (or phengite) has been documented by Ahn et al. (1985) and Shau et al. (1991) with transmission electron microscopy (TEM). Shau et al. (1991) showed that compositions of sodium potassium micas consistent with considerable solid solutions are actually due to intergrowths unresolved by electron microprobe analyses, whereas those that approach Na- or K-rich end-members, as analyzed by analytical electron microscopy (AEM), represent the true limits of solid solution. Based on the *d* values of mica 00*l* reflections in X-ray powder diffraction (XRD) patterns, many authors have inferred the presence of 6:4 regular mixed-layer paragonite-muscovite (or paragonite-phengite) in low-grade anchizonal to low-grade epizonal pelitic rocks (equivalent to prehnite-pumpellyite facies through low greenschist facies for mafic rocks) (for reviews, see Kisch, 1983; Frey, 1987). Such materials have never been directly observed or analyzed, however, because they are too fine-grained for conventional methods. Livi et al. (1990) observed paragonite that has significant interlayer vacancies in several low-grade metamorphic slates from the Alps that were determined to contain mixed-layer paragonite-muscovite based on XRD data. They were not able to make direct correlation between XRD data and TEM observations, however. Livi et al. (1988) showed segregation boundaries between paragonite and illite in Alpine black shales that imply either the prior existence of phases with intermediate solid solution between Na- and K-rich micas or replacement across 001 layers. Li (1991) briefly described the occurrence of an intermediate sodium potassium mica ($Mu_{60}Pa_{40}$) in relation to chlorite-mica stacks in an anchizonal slate from central Wales. To our knowledge, homogeneous intermediate solid solutions ($Mu_{60}Pa_{40}$-$Mu_{20}Pa_{80}$) have not been described in detail.

Dioctahedral sodium potassium micas have recently been identified in the margin of metabasites of Caradoc age that intruded a sequence of Ordovician pelitic rocks at Tremadoc, northern Wales, U.K. The micas have wide variations in Na and K contents, ranging from that of muscovite to paragonite. XRD patterns show features indicative of intermediate sodium potassium mica that are similar to those of so-called 6:4 regular mixed-layer paragonite-muscovite, in addition to those of paragonite and muscovite. Although the micas are relatively coarse-grained compared with those in low-grade rocks, they exhibit complex intergrowths. TEM and AEM therefore have been used to characterize them, demonstrating the existence of metastable intermediate solid solutions and showing that such material corresponds to much or all of the so-called 6:4 regular mixed-layer paragonite-muscovite described by others.

## EXPERIMENTAL TECHNIQUES

XRD patterns of bulk rock samples were obtained with Cu*Kα* radiation at 35 kV and 15 mA on a Philips XRG 3100 X-ray generator. A step size of only 0.005° $\Delta 2\theta$ and a long counting time of ~6 s per step were used to resolve the details of 00*l* reflections of micas. Quartz was used as an internal standard. Thin sections of the samples were examined with backscattered electron imaging (BEI) techniques on a Hitachi S-570 scanning electron microscope operated at 15 kV to determine textural relations between micas and other phases and to select areas for TEM observations. Ion-milled TEM specimens were prepared following the method described in Jiang et al. (1990). A Philips CM12 scanning transmission electron microscope was operated at a voltage of 120 kV and a beam current of ~10 μA to obtain TEM images and selected-area electron diffraction (SAED) patterns. Crystals were frequently rotated so as to eliminate the effects of dynamic diffraction and to determine the absence or presence of mixed layering. Lattice-fringe images were obtained with 00*l* reflections ($d \geq 4.7$ Å) included in the objective aperture. X-ray energy-dispersive spectra were obtained from thin edges of the specimens using a low-angle Kevex Quantum detector (X-ray take-off angle ~34°). A raster of ~200 × 200 nm in scanning mode was used to minimize alkali diffusion and volatilization. Ion-milled standards of paragonite, muscovite, albite, clinochlore, fayalite, rhodonite, and titanite were used in the thin film approximation (Lorimer and Cliff, 1976) for quantitative analyses of elements Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe from X-ray energy-dispersive spectra.

## OCCURRENCE OF INTERMEDIATE DIOCTAHEDRAL SODIUM POTASSIUM MICA

The samples are metabasites collected from the Ordovician dolerite sills in a suite of metamorphosed pelites near Tremadoc, northern Wales. Studies of the regional geology suggest that the Ordovician igneous and sedimentary rocks in northern Wales have been tectonically deformed and affected by prehnite-pumpellyite to low greenschist facies metamorphism (or anchizone to epizone for pelitic rocks) during the early Devonian Acadian orogeny (Roberts, 1979, 1981; Bevins et al., 1984; Kokelaar et al., 1984; Merriman and Roberts, 1985; Bevins and Merriman, 1988). The petrology of the sampled dolerite sills has not been studied in detail, but the nearby Tal y Fan metabasite intrusion, emplaced in felsic and mafic tuffs, has similar mineral assemblages and has been investigated by Bevins and Merriman (1988).

The metabasites consist of white micas, chlorite, titanite, bytownite, albite, calcite, potassium feldspar, rutile, quartz, and minor actinolite, pyrite, and Cu-bearing sul-

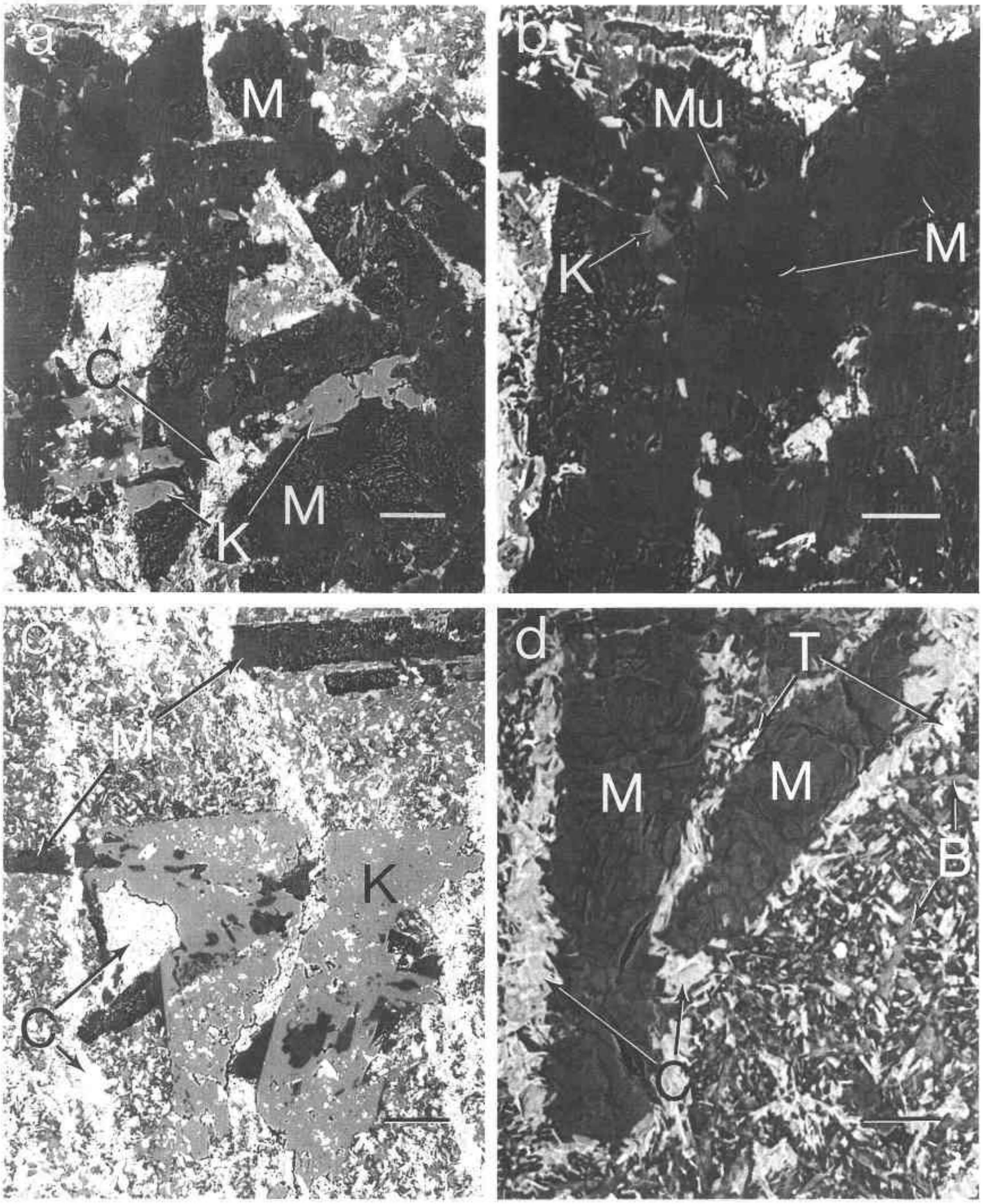

Fig. 1. Backscattered electron images of a metabasite from the margin of the metabasite intrusion near Tremadoc, northern Wales. (**a**) Aggregates (M; elongated, dark gray) of white micas (mainly muscovite) formed as pseudomorphs after plagioclase microphenocrysts, coexisting with potassium feldspar (K; medium gray) and chlorite (C) near the sedimentary contact. Scale bar = 20 $\mu$m. (**b**) Close-up view of a part of **a** showing boundaries (inclined to the mica cleavage) that separate muscovite (Mu) and Na-rich mica (M) displaying different contrasts. Scale bar = 40 $\mu$m. (**c**) Partial replacement of white micas (M) by potassium feldspar (K) that are crosscut by chlorite (C) veinlets. The matrix is also mainly potassium feldspar. Scale bar = 20 $\mu$m. (**d**) Aggregates (ion-milled specimen) of white micas (M) approximately 1.5 cm from the sedimentary contact showing corroded edges in contact with chlorite (C) and titanite (T). The matrix contains corroded lathlike bytownite (B, medium gray). Potassium feldspar is not present. Scale bar = 50 $\mu$m.

fides, with textures implying virtually complete replacement of primary igneous minerals in the margin of the sills near Tremadoc. In the interior of the dolerite sills, clinopyroxene, actinolite, ilmenite, bytownite, albite, titanite, rutile, chlorite, calcite, prehnite, and epidote-group minerals are present with relict ophitic textures, locally with the presence of very small amounts of white micas.

One of the metabasite samples was collected from the lower contact of a dolerite sill approximately 1 km northwest of Tremadoc (National grid reference SH 554409). The sample contains a relatively high proportion of white micas and is the focus of this study. Paragonite, muscovite, and mica that has compositions intermediate between those of muscovite and paragonite are intergrown, forming aggregates (80–250 μm in length; 15–100 μm in width) of randomly oriented crystals (Fig. 1). Such aggregates of micas have well-defined outlines that resemble typical euhedral crystals of plagioclase. Concentrations of mica aggregates are locally present, with or without the presence of potassium feldspar (e.g., Fig. 1a). It was not possible to determine if the third mica is a true intermediate solid solution or a mixture of paragonite and muscovite with BEI techniques, but the TEM results described below demonstrate the presence of a true intermediate sodium potassium mica, and it is therefore referred to as such hereafter. Although some mineral boundaries in mica aggregates are obscured by possible overlaps of two or three micas, some of the interfaces appear oblique to the cleavage planes of adjacent micas (Fig. 1b).

Muscovite is the dominant phase in mica aggregates. Subordinate paragonite and intermediate sodium potassium mica are irregularly distributed in mica aggregates (e.g., Fig. 1a and 1b). The proportion of the intermediate sodium potassium mica increases as the distance from the sedimentary contact increases. In some cases, it appears that mica aggregates consist solely of intermediate sodium potassium mica. In samples from the interior of the sill, very small amounts of irregular aggregates of micas are present, with ragged contacts with clinozoisite and partially albitized bytownite.

Potassium feldspar predominates in the fine-grained matrix and also occurs as large lathlike or irregular grains that partially replace mica aggregates (Fig. 1c) in areas $< \sim 1$ cm from the sedimentary contact (designated as the contact zone). No Na was detected in the potassium feldspar. Chlorite, albite, quartz, and titanite are also major phases composing the matrix. Fine veinlets of chlorite cut across some of the potassium feldspar grains and mica aggregates (e.g., Fig. 1c) and extend into the interior of the sill subnormal to the sedimentary contact. Mica aggregates commonly display corroded edges in contact with chlorite and titanite outside the contact zone of the metabasite (Fig. 1d), where corroded lathlike bytownite is abundant and potassium feldspar is rarely present in the matrix. The bytownite is surrounded mainly by albite, calcite, chlorite, and quartz. Albitization of plagioclase is ubiquitous in both marginal and interior samples of the metabasites. The albitization is likely a result of regional metamorphism in the prehnite-pumpellyite or prehnite-actinolite facies, with the decomposition of bytownite and formation of calcite and albite. Similar processes were also inferred to have occurred in the Tal y Fan metabasites (Bevins and Merriman, 1988).

## X-RAY POWDER DIFFRACTION

XRD patterns of the bulk rock sample display prominent splitting of the basal reflections of micas, indicating the presence of multiple micaceous phases (Fig. 2). Because our electron diffraction data show that these micaceous phases are invariably two-layer polytypes (see below), XRD patterns were indexed on the basis of a two-layer polytype for all of the micas.

The strong 002 peak ($d$ = 10.02 Å) displays a broad high-angle tail having a range of °2$\theta$, corresponding to $d$ values from 10.02 to ~9.60 Å (Fig. 2a). The spacing of 10.02 Å implies a dominant K-rich micaceous phase, as consistent with the observation of muscovite in BEI images. The $d(00l)$ values of micas are strongly dependent on interlayer composition (Guidotti, 1984), for example, $d \cong 10.0$ Å for muscovite and 9.6 Å for paragonite. The spacing of the high-angle tail suggests overlap of the basal reflections of sodium potassium micas of different interlayer compositions, e.g., admixtures of intermediate sodium potassium mica, paragonite, and muscovite.

Three principal fourth-order basal reflections with $d$ = 5.01, 4.93, and 4.82 Å were observed (Fig. 2b), implying the presence of three dominant micas and possibly minor amounts of phases of intermediate compositions. The fourth-order $d$ values of the three micas correspond to muscovite, intermediate sodium potassium mica, and paragonite, respectively. Similar features were also observed for the much weaker tenth-order basal reflections ($d \cong 2.00$ Å). The sixth- and eighth-order basal reflections overlap the peaks of other phases (not shown). The basal reflections of the intermediate sodium potassium mica, however, are also consistent with the observations for so-called 6:4 regular mixed-layer paragonite-muscovite that has been identified in clay separates of many low-grade metamorphic pelites, for example, shales or slates from the Alps (Frey, 1970, 1978), northern Wales (Merriman and Roberts, 1985), and the southern Appalachians (Weaver and Broekstra, 1984). No first-order basal reflection or superlattice reflections (Fig. 2c) were observed for the micas, and none has been recorded from sodium potassium micas elsewhere, except the poorly defined reflection with $d \cong 50$ Å reported by Frey (1969).

## COMPOSITIONS OF SODIUM POTASSIUM MICAS

Table 1 shows representative formulae of the intermediate sodium potassium mica, paragonite, and muscovite normalized on the basis of 12 total tetrahedral and octahedral cations. The analyses presented here were obtained only from areas that were characterized by electron diffraction and lattice-fringe images and shown to be single phases. All of the micas have nearly the same Al

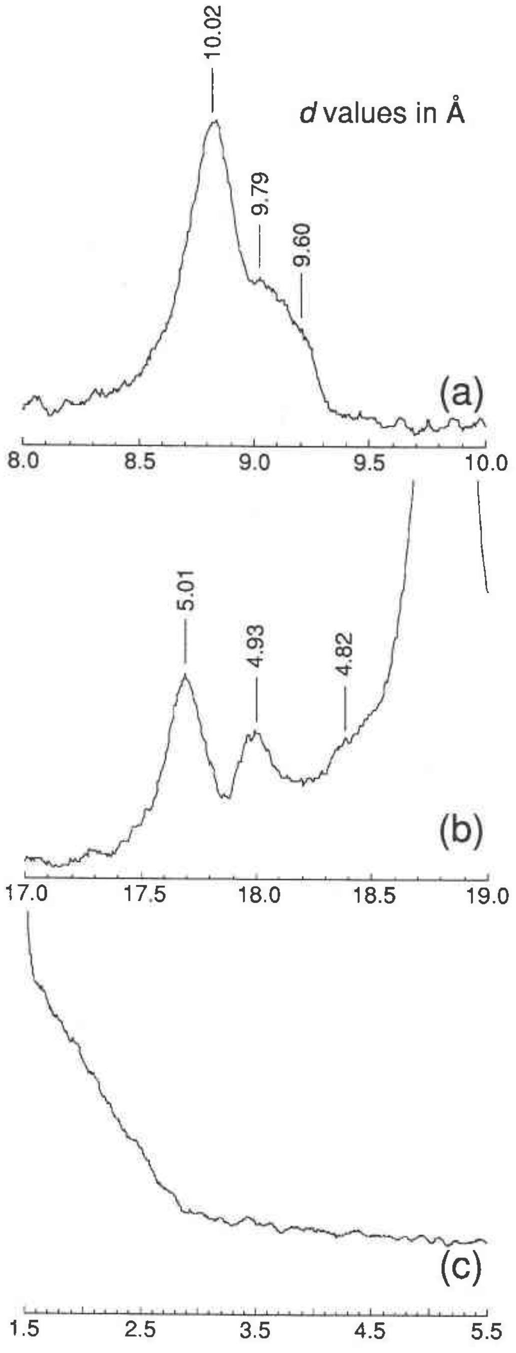

Fig. 2. X-ray powder diffraction pattern (Cu*K*α radiation) of the bulk rock sample of a metabasite collected from the lower contact of a dolerite sill near Tremadoc, northern Wales, showing (**a**) the second-order basal reflections, (**b**) the fourth-order basal reflections, and (**c**) the absence of low-2θ superlattice reflections of micas.

**Table 1.** Representative structural formulae of the intermediate sodium potassium mica, paragonite, and muscovite in the margin of the metabasite intrusion near Tremadoc, northern Wales

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Si | 5.97 | 6.03 | 6.10 | 5.90 | 6.08 | 6.04 |
| Al | 5.93 | 5.86 | 5.85 | 6.02 | 5.80 | 5.85 |
| Ti | 0 | 0.02 | 0 | 0 | 0.02 | 0 |
| Fe | 0.06 | 0.06 | 0.05 | 0.06 | 0.07 | 0.07 |
| Mg | 0.04 | 0.03 | 0 | 0.02 | 0.03 | 0.04 |
| Ca | 0.04 | 0 | 0.04 | 0.06 | 0 | 0.02 |
| Na | 1.03 | 1.03 | 1.75 | 1.81 | 0.24 | 0.23 |
| K | 0.93 | 0.97 | 0.12 | 0.13 | 1.75 | 1.73 |

*Note:* Normalization is based on 12 tetrahedral and octahedral cations total. All Fe is assumed to be $Fe^{2+}$. Formulae 1–2 = intermediate sodium potassium mica, 3–4 = paragonite, 5–6 = muscovite. Two sd on the basis of counting statistics are 0.08–0.14 pfu for Si, 0.10–0.15 pfu for Al, ≤0.01 pfu for Ti, Fe, Mg, and Ca in all analyses, and 0.05–0.08 and 0.01–0.03 pfu for K and 0.02–0.04 and 0.08–0.12 pfu for Na in muscovite and paragonite, respectively.

and Si compositions and minor Mg and Fe contents. The intermediate sodium potassium mica has Na/K atomic ratios spanning the range from 0.5 to 2 (not shown). However, most analyses of the intermediate sodium potassium mica have nearly equal amounts of interlayer Na and K, as typified by those shown in Table 1. The micas that do not have atomic ratios of Na/K ≅ 1 commonly occur in areas with irregular interfaces inclined to mica basal planes. In stacks of parallel or subparallel packets of micas, each packet is homogeneous in composition, consisting solely of intermediate sodium potassium mica (Na/K ≅ 1), paragonite, or muscovite. The compositions of paragonite or muscovite vary slightly in alkali and Ca contents from crystal to crystal but are homogeneous within each individual crystal. Most of the paragonite analyses give Na ≅ 1.80, K ≤ 0.15, and Ca ≤ 0.05 pfu, but some with Ca as high as ~0.20 pfu were also obtained. Most of the muscovite compositions have Na/K ratios nearly equal to 1/7 with or without minor Ca contents.

## TRANSMISSION ELECTRON MICROSCOPE OBSERVATIONS

Aggregates of micas such as those shown in the BEI images were examined by TEM to affirm the identification of the intermediate sodium potassium mica and to determine the intergrowth relations between different micas.

### Intermediate sodium potassium mica

The intermediate sodium potassium mica commonly occurs as thick stacks that are occasionally interleaved with parallel thin packets of paragonite or muscovite. Interstratification of thin packets of layers within thick packets of muscovite is also present. Figure 3 shows a lattice-fringe image and SAED pattern of the intermediate sodium potassium mica. The mica is relatively easily damaged by the electron beam, compared with musco-

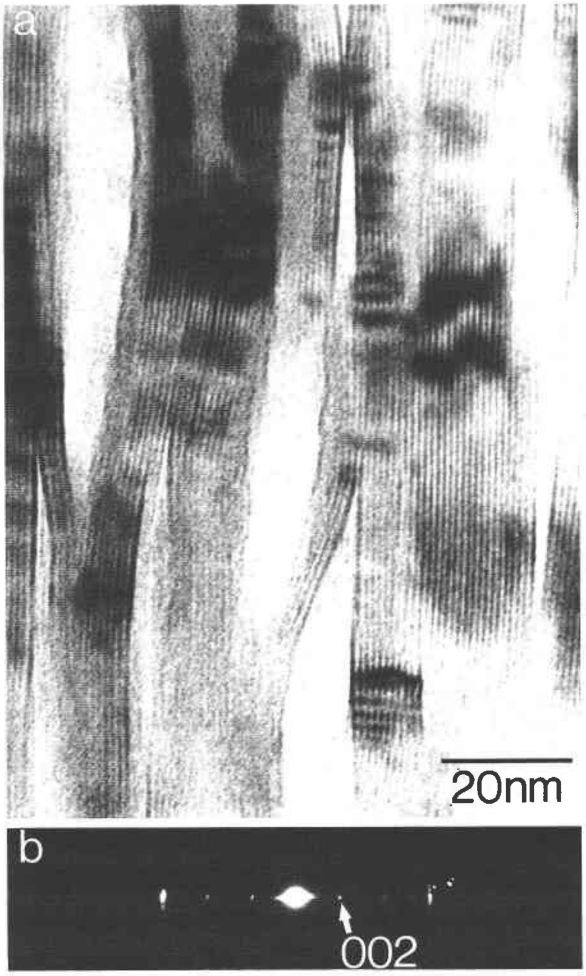

Fig. 3. (**a**) Lattice-fringe image of intermediate sodium potassium mica displaying lenticular pores typical of Na-rich white micas; (**b**) electron diffraction pattern of **a** showing sharp 00*l* reflections that are consistent with a single mica.

vite, giving rise to lenticular pores and a slight distortion of layers. The SAED pattern shows that the 00*l* reflections have slight spreading normal to **c*** but are sharp and have no splitting along **c***, suggesting the presence of several crystals of a single micaceous phase with slightly different orientations. Where the intermediate sodium potassium mica is directly adjacent to muscovite or paragonite, electron diffraction patterns display split pairs of 00*l* reflections, with the split distance approximately half of the separation between corresponding 00*l* reflections of paragonite and muscovite (e.g., Fig. 4), implying a periodicity of ~9.8 Å along **c***, which is consistent with the XRD results.

### Intergrowth relations

Two principal types of interfaces between micas were observed in the sample: (1) straight interfaces that are parallel to basal planes (parallel interfaces), and (2) irregular interfaces that are inclined to the basal planes of parallel or subparallel packets of adjacent micas (inclined interfaces).

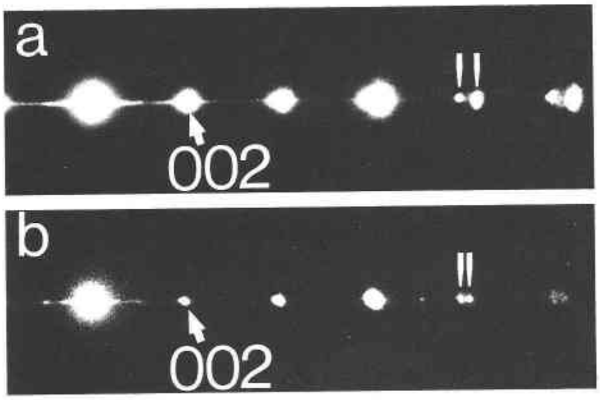

Fig. 4. Electron diffraction patterns of (**a**) muscovite + paragonite and (**b**) muscovite + intermediate sodium potassium mica showing the differences in the separations in their corresponding 00*l* reflections.

**Parallel interfaces.** Figure 5 shows a TEM image of coexisting muscovite and intermediate sodium potassium mica with parallel or subparallel basal planes. The interfaces are parallel to the basal planes of one or both of the adjacent micas. The SAED pattern clearly displays split pairs of 00*l* reflections corresponding to two sets of basal reflections with periodicities of ~10.0 and ~9.8 Å, respectively. The 02*l* reflections have periodicities of ~20.0 and ~19.6 Å along **c*** for the respective phases, suggesting that the intermediate sodium potassium mica and muscovite are two-layer polytypes. No other mica polytypes or mixed layering were observed in the sample. Similar relations also occur between paragonite and muscovite, analogous to those observed by Ahn et al. (1985) and Shau et al. (1991).

**Inclined interfaces.** Figure 6 illustrates interfaces that obliquely transect the basal planes of adjacent domains of paragonite and muscovite. Most lattice fringes are continuous across the interfaces. Terminations of layers and strain contrast commonly occur at such interfaces, implying partial coherency. Figure 7 shows energy-dispersive X-ray maps of elements Na and K of an intergrowth of micas, demonstrating mineral boundaries that are subnormal to the cleavage and separate K-rich and Na-rich areas. Quantitative analyses and electron diffraction data (not shown) suggest that the micas are muscovite and paragonite, respectively, with compositions similar to those listed in Table 1. Such relations are not observed between intermediate sodium potassium mica (Na/K ≅ 1) and paragonite or muscovite. However, some K- or Na-rich micas that have slightly more Na or K than the muscovite or paragonite are observed to have inclined irregular interfaces in relation to paragonite or muscovite. Figure 8 shows interfaces that are inclined to the basal planes of muscovite and relatively Na-rich muscovite

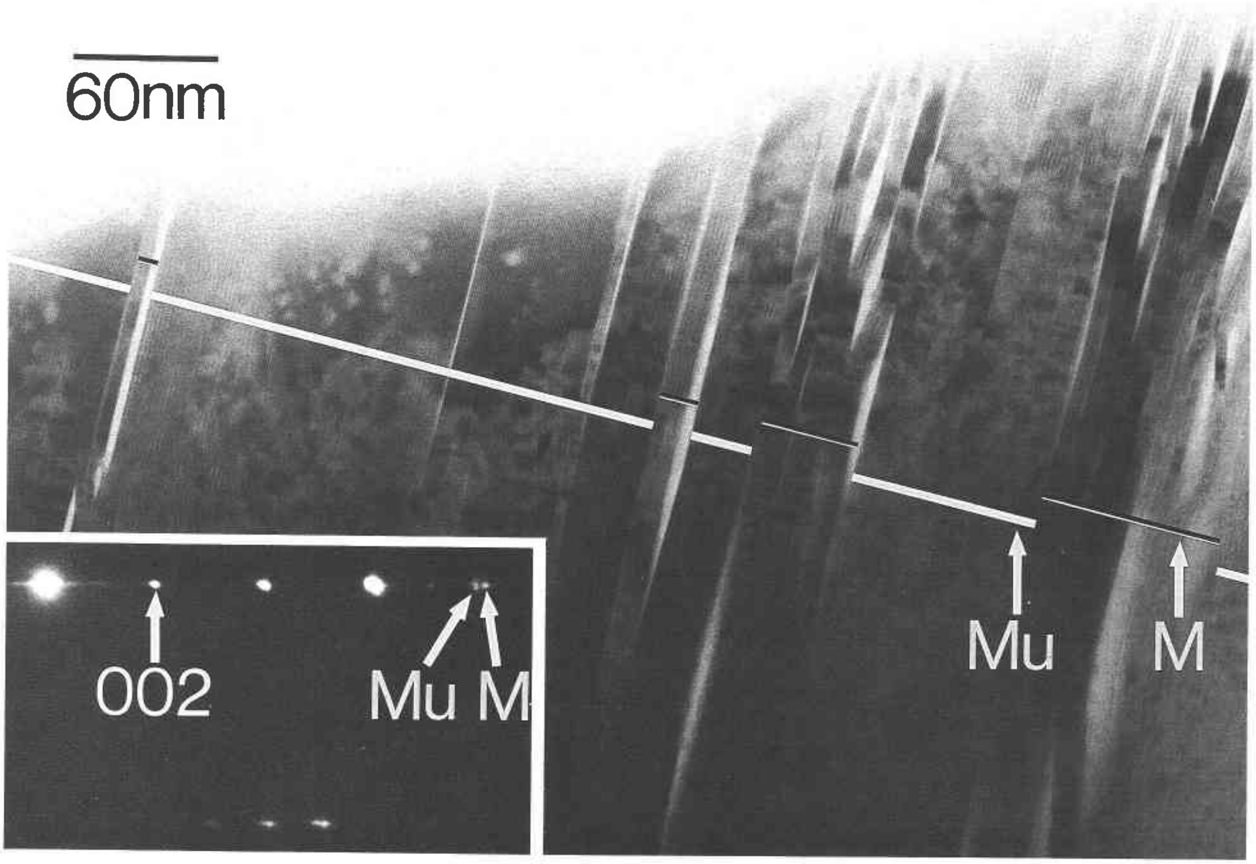

Fig. 5. Transmission electron microscope image of interstratified packets of muscovite (Mu) and intermediate sodium potassium mica (M). The interfaces are parallel to the basal planes of the micas. The splitting of the 00*l* reflections along **c*** of the inset SAED pattern reflects the differences in *d* values. Both of the micas are two-layer polytypes, as suggested by the ~20-Å periodicity of the 02*l* reflections.

($Mu_{75}Pa_{25}$). Portions of the interfaces are defined by lines with light contrast, but with no apparent strain contrast, probably simply reflecting a slight inclination of phase boundaries from 90° to the imaged plane. A layer termination (upper middle) and a parallel interface (lower middle) are also present. Although the difference in the spacings of different mica layers is very small, the SAED pattern clearly shows a slight splitting of the 00*l* reflections. The split distance corresponds to a difference of ~0.1 Å between the periodicities of the micas in the **c*** direction. The 11*l* (or $1\bar{1}l$) reflections suggest that both of the micas are two-layer polytypes.

## DISCUSSION

### Hydrothermal formation of intermediate sodium potassium mica

The similarity between the cross sections of mica aggregates and the morphology of euhedral plagioclase crystals suggests that the mica aggregates are pseudomorphs after plagioclase microphenocrysts. The Na may have been derived from the decomposition of plagioclase, but such a reaction requires significant K input. The fact that the micas and potassium feldspar are concentrated in the margin of the dolerite sill suggests that $K^+$ must have been leached out of the pelitic sedimentary rocks and transported by the convecting fluids during emplacement. Alt and Honnorez (1984) and Böhlke et al. (1984) reported the occurrence of potassium feldspar in response to low-temperature reactions with sea water in altered oceanic mafic rocks. Bevins and Merriman (1988) suggested that potassium feldspar is an early hydrothermal alteration product of plagioclase microphenocrysts in the contact zone of the Tal y Fan metabasite. Sodium potassium micas were not reported in that study. Nevertheless, those authors demonstrated that K-rich phases may occur in altered mafic rocks when affected by fluids of appropriate composition. The micas in the studied metabasites are therefore inferred to be a result of reactions with hydrothermal fluids that interacted with pelitic country rocks and had relatively low $a_{SiO_2}$ and high $a_{K^+}/a_{H^+}$ compared with the Tal y Fan intrusion, which was emplaced within volcanic tuffs. Such replacement of feldspars by micas is common in hydrothermal or deu-

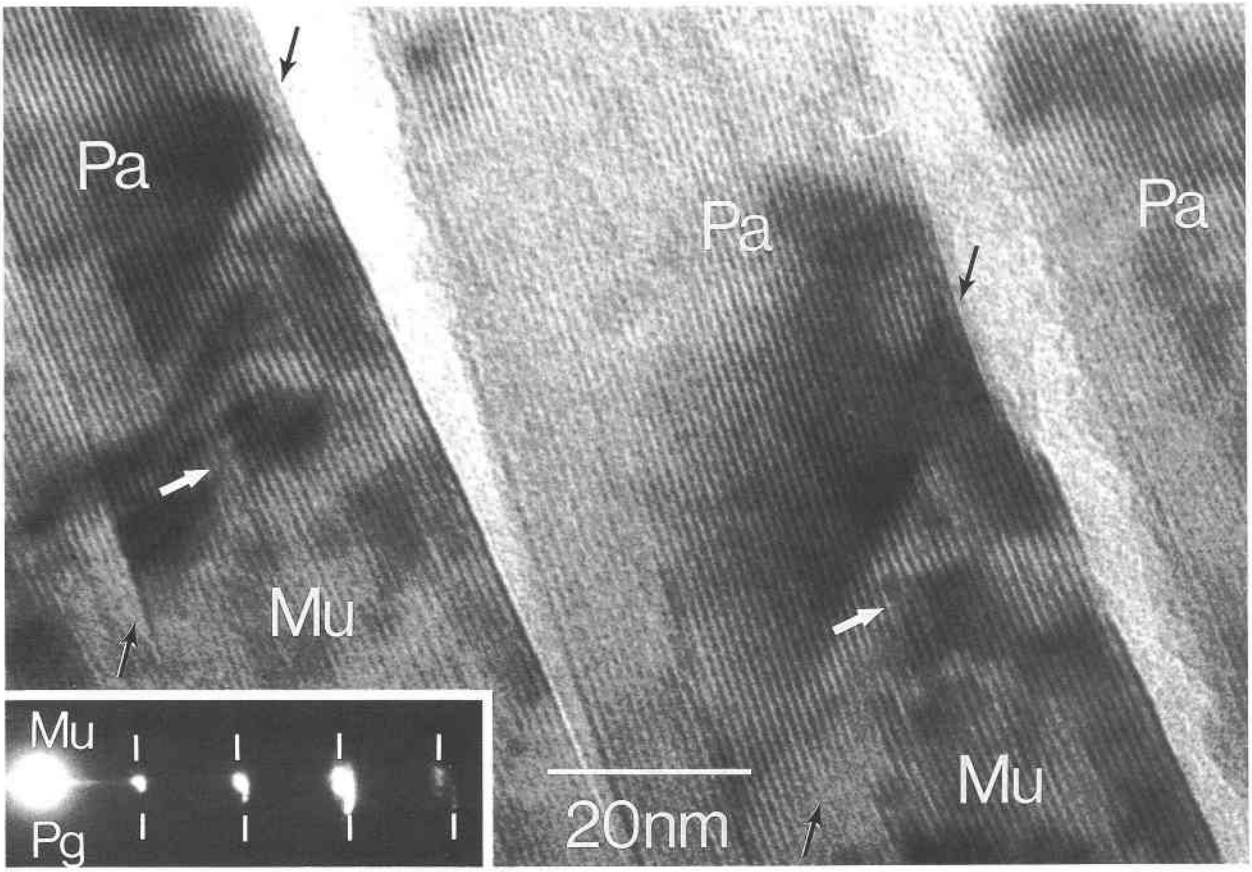

Fig. 6. Lattice-fringe image and electron diffraction pattern of coexisting paragonite (Pa) and muscovite (Mu). Paragonite and muscovite layers are continuous across the inclined interfaces (highlighted with black arrows). The interfaces are associated with strain contrast and layer terminations (marked by white arrows).

teric alteration of granitic and pegmatitic igneous rocks (London and Burt, 1982; Monier et al., 1984; Speer et al., 1980).

The presence of wide variations in mica compositions may be attributed to the superimposed effects of different hydrothermal events or to changing conditions of a single hydrothermal event. The intermediate sodium potassium mica is inferred to have formed during early interactions between K-rich hydrothermal fluids and plagioclase, perhaps metastably at temperatures below the ~550 °C required for equilibrium conditions. The well-constrained occurrence of white micas as pseudomorphs of plagioclase and the high Na contents of the white micas suggest preferential alteration of plagioclase microphenocrysts in early stages of hydrothermal alteration. Supersaturation with respect to the intermediate sodium potassium mica may have occurred because of abrupt changes of fluid chemistry and temperatures during the emplacement and rapid cooling of the dolerite intrusion. Speer et al. (1980) studied igneous and secondary muscovite in granitoid plutons of the southern Appalachian piedmont. The secondary muscovite that occurred as saussuritization products of plagioclase contains more Na than the hydrothermal and magmatic muscovite in the matrix. The composition of that secondary muscovite is apparently affected by the composition of parent plagioclase. Similar relations may also prevail in the metabasites at Tremadoc; i.e., local composition as modified by hydrothermal fluids, rather than bulk rock composition, controls the composition of white micas.

### Metastability of intermediate sodium potassium mica in relation to the formation of paragonite and muscovite

The solvus between paragonite and muscovite has been documented by many authors using experimental and natural paragonite-muscovite pairs (for reviews, see Guidotti, 1984). The solvus closes with increasing temperature and is asymmetric toward paragonite (greater solid solution of Na in muscovite than of K in paragonite) but is truncated by the formation of alkali feldspars and aluminosilicates at high temperatures. The paragonite field becomes smaller, and the miscibility of paragonite in muscovite decreases above the temperature at which alkali feldspar first appears. In rocks, sodium potassium

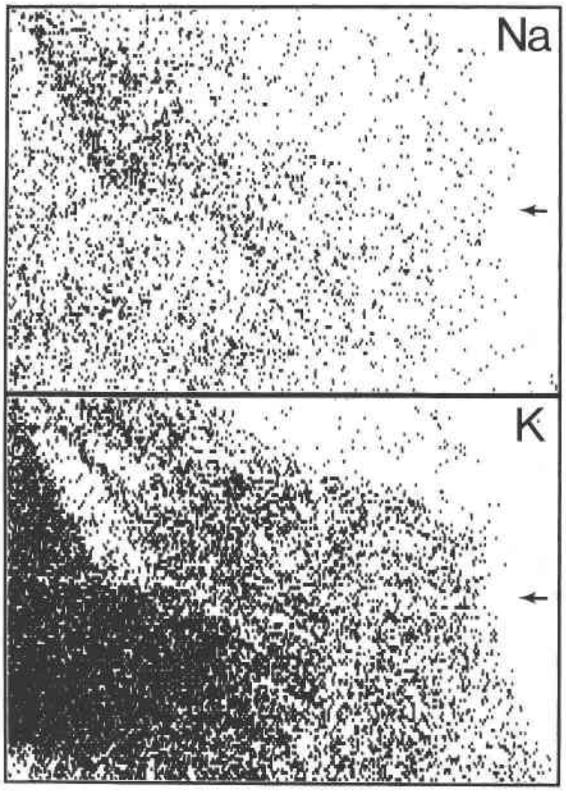

Fig. 7. X-ray maps of Na and K from a paragonite-muscovite intergrowth displaying interfaces oblique to the cleavage; the {001} cleavage direction is indicated by black arrows. Frame width = 3 $\mu$m.

micas that have significant solid solutions occur only in single-mica assemblages that have been buffered by alkali feldspars, but the mica compositions are severely limited by the solvus. These relations collectively show that the intermediate sodium potassium mica in the Tremadoc intrusion is metastable or unstable with respect to paragonite + muscovite.

As consistent with the Ostwald step rule, metastable phases commonly form prior to the formation of stable phases, especially in short-lived and low-temperature alteration or formation processes. The mineralogical, textural, and chemical heterogeneity in the studied samples clearly reflects a lack of equilibrium wherein the intermediate sodium potassium mica is a metastable precursor of muscovite + paragonite. The intimate intergrowths of muscovite, paragonite, and intermediate sodium potassium mica suggest that simultaneous primary formation of the micas due, say, to local variations in composition and kinetic factors did not occur. Instead, the inclined interfaces between muscovite and paragonite imply secondary interactions between fluids and micas and diffusion within some originally homogeneous micas, giving rise to the formation of paragonite + muscovite, as discussed below. In addition, the replacement of the micas by potassium feldspar and the dominance of muscovite near the sedimentary contact imply an increase of K activity, consistent with muscovite being a later phase formed during the same or a second alteration event. The compositions of the coexisting paragonite and muscovite do not represent a paragenetic pair of Na- and K-rich micas that formed under equilibrium conditions. That implies that most of the muscovite has been formed by the alteration of intermediate sodium potassium mica or that the alteration was not homogeneous but involved partial replacement and local chemistry.

Although we do not have data regarding the specific compositions and temperature of hydrothermal fluids, the general trend of the changes in fluids can be inferred. The $a_{K^+}/a_{H^+}$ and $a_{K^+}/a_{Na^+}$ ratios of the hydrothermal fluids are likely to have increased in the early stages of hydrothermal activity because of increasing reaction with the pelitic country rocks at high temperatures. Such conditions resulted in partial decomposition of the intermediate sodium potassium mica, forming muscovite and paragonite. The low proportion of intermediate sodium potassium mica, the high proportion of muscovite in the contact zone, and the irregular distribution of micas in mica aggregates are consistent with such a process. In addition, the amount of muscovite is far in excess of that required to combine with the available paragonite to form the intermediate sodium potassium mica; a source of K is therefore necessary in excess of that required for the intermediate sodium potassium mica. The progressive increase of $a_{K^+}/a_{H^+}$ and $a_{K^+}/a_{Na^+}$ in hydrothermal fluids is also evidenced by the presence of potassium feldspar in the contact zone. Partial replacement of the micas by potassium feldspar in later stages of hydrothermal alteration is consistent with the hypothesis. Such chemical gradients may have been in part due to different degrees of physical infiltration of fluids at different distances from the sedimentary contact.

### Alkali redistribution of sodium potassium mica

There are two types of intergrowths among the micas in the metabasites: (1) lamellar intergrowths of parallel or subparallel packets of micas with interfaces that are parallel to one of the adjacent crystals, and (2) domains of micas with interfaces obliquely transecting their largely continuous basal planes. These two textures are inferred to have formed through dissolution and crystallization and alkali exchange and diffusion, respectively, each of which is discussed below.

**Dissolution and crystallization.** Lamellar intergrowths of parallel or subparallel packets of phyllosilicates are very common in low-grade metamorphic and hydrothermally altered rocks (e.g., Franceschelli et al., 1986; Jiang and Peacor, 1991; Shau et al., 1991). In such rocks, dissolution and crystallization processes prevail in part because solid-state diffusion is sluggish and because the compositional changes of minerals require significant destruction and reconstruction of bonds. Dissolution and crystallization processes are particularly important in low-tem-

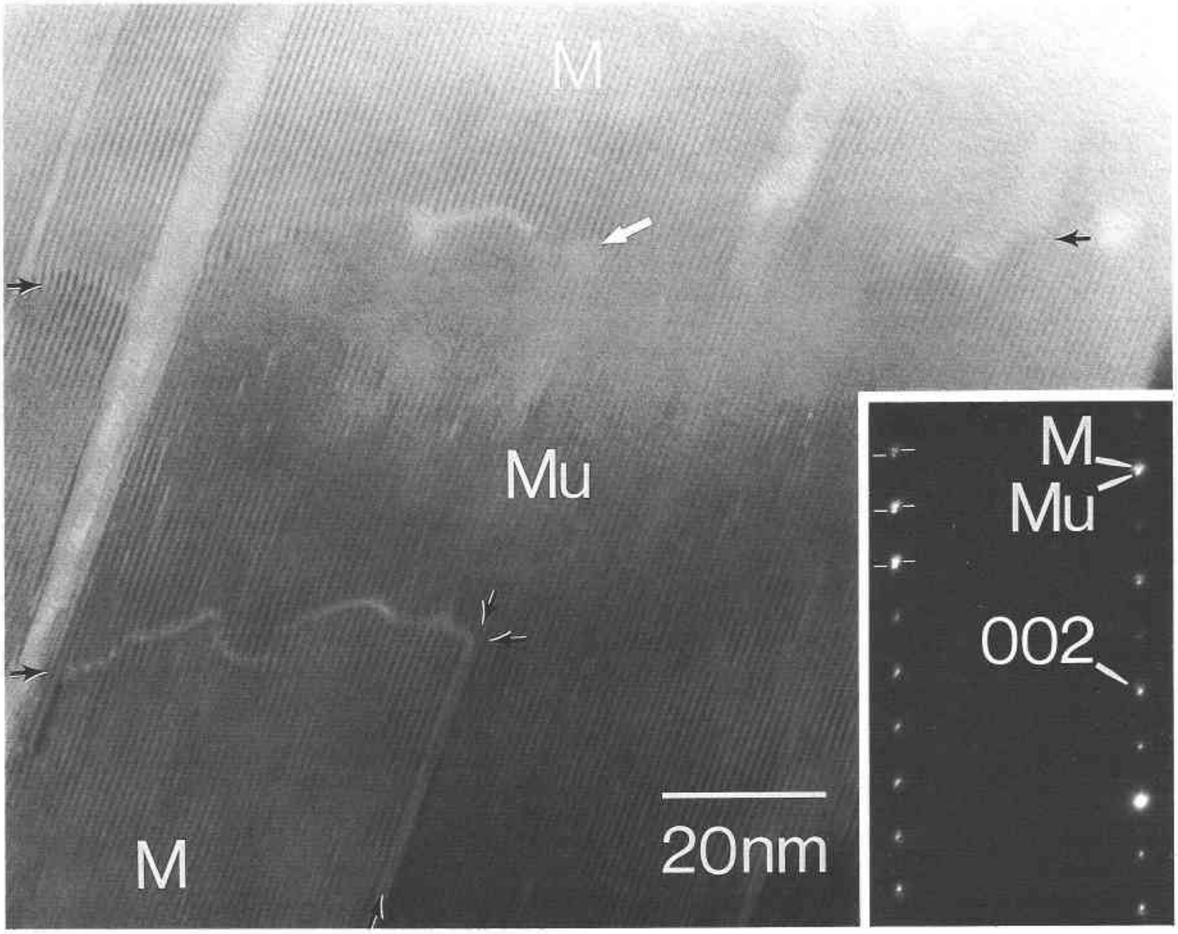

Fig. 8. Lattice-fringe image of domains of muscovite (Mu) and relatively Na-rich muscovite (M). The curved interfaces (indicated in part by black arrows) are subnormal to the basal planes. A layer termination is present in the upper middle (marked with a white arrow). The electron diffraction pattern shows two sets of $00l$ reflections corresponding to ~10.0 and ~9.9 Å periodicities. The $11l$ (or $1\bar{1}l$) reflections imply that the micas are two-layer polytypes.

perature hydrothermal alteration of phyllosilicates because of high $H_2O$ activities, which promote the replacement of individual layers or packets of layers of one phyllosilicate by another (e.g., Jiang and Peacor, 1991; Sharp et al., 1990). Development of lamellar intergrowths of micas by solid-state diffusion requires the transport of large alkali ions across the layer structures of the micas. Such a process is highly unlikely relative to diffusion along layers; it has never been observed, whereas replacement relations along layers are common. In addition, solid-state diffusion implies the retention of original structures and at least partial coherency between resultant phases, which generates significant strain for interfaces parallel to basal planes (Veblen, 1983). Each mica packet in the lamellar mica intergrowths is homogeneous, with interfaces that are free of strain contrast, except for lenticular pores caused by beam damage. Furthermore, packets of muscovite or paragonite are directly adjacent to or interstratified with packets of intermediate sodium potassium mica. These data collectively imply that alteration of an originally homogeneous mica proceeded in part through dissolution, with the subsequent crystallization of paragonite and muscovite. As the period of alteration was short-lived, rapidly changing nonequilibrium conditions are inferred to have given rise to incomplete reaction, with some original homogeneous Na-K packets being unaffected.

**Alkali exchange and diffusion.** As discussed above, dissolution and crystallization processes would generate lamellar intergrowths with straight interfaces parallel to basal planes and with minimal structural coherency. The mica packets that have interfaces inclined to basal planes have individual layers that are largely continuous across the interfaces, with some layer terminations with or without strain contrast. They must therefore have formed by a different process.

The occurrence of inclined interfaces that separate two micas having layers that are largely continuous across the interface is consistent with the diffusion of alkali ions along layers of an originally homogeneous sodium potassium mica. The presence of wide variations in interlayer Na and K contents with compositions for octahedral and tetrahedral cations that are equal within error is consistent with such a mechanism. Inclined interfaces were also observed to occur between paragonite and illite in metamorphosed shales from the Swiss Alps (Livi et al., 1988, 1990), but no firm conclusions were reached regarding their origin. There are two reasons why diffusion in the Tremadoc micas is inferred to have been driven by interaction with Na-K fluids rather than by simple exsolution: (1) No regular patterns of phase or composition distribution such as those observed by Veblen (1983) for exsolution of wonesite to talc and sodium biotite are present, although they are normally observed for products of exsolution in all such cases. (2) The compositions and the large differences in the amounts of paragonite and muscovite within individual stacks are incompatible with exsolution from the intermediate sodium potassium mica. K input is required for the development of muscovite plus subordinate nonparagenetic paragonite from initially homogeneous intermediate sodium potassium mica.

Overgrowth mechanisms have been reported to occur for phyllosilicates with inclined interfaces, e.g., antigorite-talc interfaces observed by Worden et al. (1991). Such interfaces commonly are straight and occur between simple, homogeneous micas with rim-core relations. The irregular patterns of distribution of Tremadoc mica aggregates are not compatible with overgrowth, especially in the case of the curved, inclined mica interfaces.

### Intermediate sodium potassium mica vs. mixed-layer paragonite-muscovite

This study demonstrates the existence of metastable, homogeneous intermediate sodium potassium mica. This mica gave XRD patterns nearly identical to those of so-called 6:4 regular mixed-layer paragonite-muscovite (or paragonite-phengite) (Frey, 1969), except for the absence of a reflection of $d \cong 50$ Å. Although the identification of 6:4 regular mixed-layer paragonite-phengite based on a very ill-defined low $2\theta$ reflection is questionable, many researchers have reported the presence of mixed-layer paragonite-muscovite in low-grade metapelites, based on one or two characteristic peaks that include intermediate basal reflections but no superlattice reflections (for references, see Kisch, 1983; Frey, 1987). However, the intermediate mica of this study satisfactorily is consistent with indexing of all peaks in all such published patterns.

Identification of an ordered interlayered sodium potassium mica is based in part on the assumption that the alternative phase, homogeneous intermediate sodium potassium mica, is not thermodynamically stable in low-grade metamorphic rocks. However, Li (1991) recently has also observed homogeneous intermediate sodium potassium mica ($Mu_{60}Pa_{40}$) in a low-grade slate from central Wales; it is inferred to have originated from smectite and developed in early stages of diagenesis through anchizonal metamorphism (Li et al., 1992), discrete paragonite and muscovite occurring at higher grades, analogous to muscovite and paragonite in pelites from northern Wales reported by Merriman and Roberts (1985). The occurrence of intermediate sodium potassium mica demonstrates the existence of this phase even in low-grade metapelites occurring in ordinary prograde sequences. Indeed, it may be an early metastable phase in a stepwise kinetic sequence, much as illite and mixed-layer illite/smectite (Jiang et al., 1990) precede muscovite in prograde sequences.

We therefore conclude that many of the published XRD patterns of so-called mixed-layer paragonite-muscovite actually correspond to homogeneous sodium potassium mica of intermediate composition or random mixed-layer paragonite-muscovite. Unless well-defined superlattice reflections are observed in XRD or SAED patterns, as indicative of ordering of Na and K at the scale of individual layers, reports of such ordering should be viewed with caution.

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