

The nature, formation, and stability of end-member illite: A hypothesis

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ABSTRACT

The nature and stability of end-member illite (I), $K_{0.88\pm 0.01}/O_{10}(OH)_2$, a K-deficient mica, has been a subject of much controversy. Evidence for the metastability of “illite” with respect to ideal muscovite (Ms) + pyrophyllite (Py) has been discussed in the literature but conflicting evidence from studies of natural and synthetic systems point to the stability of K-deficient micas with respect to Ms below ~ 360 °C. Py coexists with K-deficient micas in natural assemblages thought to have formed between 300 and ~ 360 °C.

Available evidence suggests that end-member illite (I) has an ordered, domain structure. Structural strain due to K-deficiency in micas may be accommodated by the creation of Py domains. The resulting structure could be stable with respect to Ms + Py at low temperatures only if the domains are ordered. Recent FTIR studies have established the presence of local Py domains and molecular water in Al-rich illite. Py stability (~ 360 °C at 1 kbar) limits the stability of the domain structure; Ms coexists with andalusite + water at 400 °C.

The prograde, stepwise transformation of S (smectite) \rightarrow I-S \rightarrow I probably leads to a metastable, compositional end-member (I_w) containing “excess,” interlayer water. Dehydration of I_w results in the formation of a metastable, disordered K-deficient mica (I_d) that may recrystallize to form a stable, ordered, Py domain structure (I_o). I_w may persist metastably but solid-state alteration of Ms can only yield I_o . Fine-scale, Py domains have not been observed in K-deficient micas by TEM as yet, but available evidence suggests that end-member illite (I_o) is a distinct, ordered, domain structure, stable below ~ 360 °C.

INTRODUCTION

Many dioctahedral K-micas exhibit apparent deficiencies in interlayer (alkali) cations (Guidotti and Sassi 1998). Although some of these deficiencies may be accounted for by analyses that neglect the possible presence of cations that may substitute for K (Guidotti and Sassi 1998), interlayer cation deficiencies are commonly interpreted as vacancies, implying at least partial solid solution from muscovite toward pyrophyllite (e.g., Rosenberg 1987; Wang and Banno 1987). Alkali-site deficiencies have also been attributed to the presence of “excess” water in interlayer sites either in the form of H_3O^+ or H_2O (see Guidotti and Sassi 1998), but the nature and effects of these apparent deficiencies have not been resolved.

According to the recent IMA report on the nomenclature of the micas (Rieder et al. 1998), dioctahedral K-micas with 0.85–1.0 total interlayer cations per half cell should be termed muscovite, illite being defined as a “series” with 0.6–0.85 interlayer cations per half cell. However, this definition of muscovite includes the composition of the apparent end-member of the illite series, widely regarded as having 0.88 ± 0.01 interlayer cations per half cell (e.g., Yates and Rosenberg 1997, 1998; Środoń et al. 1992; Meunier and Velde 1989; Ylagan et al. 2000). It is premature, perhaps, to define this composition as either muscovite or illite because little is known about its nature or stability. The general term K-deficient mica may be pref-

erable for dioctahedral micas with compositions close to the system $K_2O-Al_2O_3-SiO_2-H_2O$ until the relationship between illite and muscovite is resolved. Inasmuch as an extensive literature bearing on this problem already exists, a synthesis may provide some insight into its possible solution.

THE COMPOSITION AND STABILITY OF K-DEFICIENT MICAS

The nature and stability of K-deficient micas have been debated for many years. The prograde series from smectite through a mixed-layer illite-smectite (I-S) to end-member illite (Yates and Rosenberg 1997; Środoń et al. 1992), a nonexpandable, K-deficient mica with a composition approximating $K_{0.88}Al_2(Si_{3.12}Al_{0.88})O_{10}(OH)_2$, has been well-documented both from experimental investigations (Yates and Rosenberg 1996, 1997, 1998) and from studies of natural materials (Inoue et al. 1987; Środoń et al. 1992). Direct evidence of the stability of K-deficient micas with respect to muscovite based on experimental investigations (Yates and Rosenberg 1996, 1997, 1998) and studies of natural mineral assemblages (Perry and Hower 1970; McDowell and Elders 1980, 1983) has also been reported in the literature.

In the Salton Sea geothermal field, detrital muscovite reacts directly to form “illite with considerable interlayer vacancies” at temperatures above 275 °C (McDowell and Elders 1980) suggesting the stability of an alkali-deficient mica with respect to ideal muscovite at relatively low temperatures. At temperatures below 200 °C, alteration of muscovite and ka-

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ollinite results in the formation of I-S (R1), which serves as a precursor to end-member illite (Giorgetti et al. 2000) suggesting that the transformation takes place primarily by solution and crystallization within the prograde crystallization sequence at least at lower temperatures. These observations are in accord with experimental results that suggest that the formation of end-member illite from ideal muscovite follows two reaction paths: a prograde, solution and crystallization path from I-S to I predominating at lower temperatures; and a retrograde, solid-state path from Ms to I predominating at higher temperatures (Yates and Rosenberg 1997, 1998). Together, these studies provide compelling evidence that K-deficient micas are stable with respect to ideal muscovite at temperatures below about 300 °C but provide no maximum thermal stability limit.

Primary (magmatic) K-micas lie close to muscovite in composition (Speer 1984; Speer and Becker 1992), whereas hydrothermal or metamorphic K-micas are typically alkali-deficient. None of the primary K-micas from 16 North American and European plutons analyzed by Miller et al. (1981) is significantly alkali-deficient. However, an analysis of K-micas from felsic gneisses in the Canadian shield, including Ca, Ba, and Na as well as K, gave an interlayer occupancy of 0.88 (Snoeyenbos et al. 1995). K-micas from metamorphic zones in the northern Apennines, particularly those coexisting with pyrophyllite, show a clear deficiency in interlayer cations, averaging 0.11 alkali-site vacancies per half-cell (Baldinelli et al. 1989). Based on the presence of sudoite in these assemblages, temperatures and pressures were estimated to be 330 ± 40 °C and <5 kbar (Franceschelli et al. 1989). Furthermore, Franceschelli et al. (1986) observed K-micas with 11% alkali-site vacancies coexisting with pyrophyllite while Frey et al. (1988) reported K-micas with 11.5% vacancies both in low-grade metasediments thought to have equilibrated at 300–350 °C. These K-deficient micas are similar in composition to K-micas that have been referred to as end-member illites (e.g., Środoń et al. 1992). Thus, the compositions of magmatic K-micas approach that of ideal muscovite, whereas metamorphic and hydrothermal K-micas are alkali-deficient and have a composition that approaches that of the end-member of the illite series.

Jiang et al. (1990) reported two examples of fine-grained assemblages of muscovite interlayered with pyrophyllite, both close to ideal composition, which they observed and analyzed by means of HRTEM and AEM, respectively. They concluded, in view of the wide miscibility gap inferred to exist in the binary system muscovite-pyrophyllite, that intermediate compositions (“illites”) are metastable with respect to muscovite. There is no direct evidence to support any assumption of equilibrium at diagenetic temperatures in the case of the sample from northeastern Pennsylvania. However, the second sample from the Witwatersrand is an Al, Si, K-rich pelite subjected to greenschist-facies metamorphism (Phillips 1987). Its simpler mineralogy and higher temperature of metamorphism (300–400 °C) make an assumption of equilibrium easier to justify. Although there is little mutual solid solution between pyrophyllite and muscovite, the muscovite compositions are not ideal. The mean alkali content per half cell reported by Jiang et al. (1990) is 0.94 whereas the value obtained by Phillips (1987; recalculated and normalized to 100 wt% by Jiang et al. 1990)

is 0.91. Furthermore, the alkali-content per half-cell for the fine-grained material is 0.89 (Jiang et al. 1990), essentially the same as that for K-deficient mica and end-member illite.

Thus, it appears that a miscibility gap actually lies between a nearly ideal pyrophyllite and an alkali-deficient mica of an approximate composition, $K_{0.89}/O_{10}(\text{OH})_2$. Experimental replacement of muscovite by illite (Yates and Rosenberg 1997) did not yield compositions intermediate between end-member illite and ideal muscovite suggesting that a miscibility gap also exists between these minerals. Therefore, an alkali-deficient mica of composition $K_{0.88}/O_{10}(\text{OH})_2$ could be a stable phase in the system muscovite-pyrophyllite. This composition closely approximates the compositions of alkali-deficient micas widely regarded as natural end-members of the illite series [e.g. Kaube illite, Środoń and Eberl. 1984; San Juan illite, SG4, Eberl et al. 1987; both $K_{0.87}/O_{10}(\text{OH})_2$].

Dioctahedral K-micas have been synthesized in many experimental studies but far too little attention has been devoted to the chemical composition of the products of these experiments. Characterization of the products of these experiments is usually based only on optical microscopy and/or XRD analysis. Two studies are exceptional in this regard. K-deficient muscovites synthesized by Rosenberg (1987) at 500–700 °C and 2 kbar from pyrophyllite or kaolinite and quartz in the presence of a KOH fluid were found to be Si-rich and alkali-deficient. An average alkali-content of 0.83 ± 0.03 per half-cell was determined using ATEM methods. Similar results were obtained by Velde and Weir (1979) at 320 °C and 2 kbar using gel starting materials and a different analytical procedure. However, chemical equilibrium was probably not attained in either of these investigations. It seems likely that muscovites synthesized in many other experimental studies were also K-deficient. However, in a recent experimental study by Frank et al. (1998), ideal muscovite was found to coexist in assemblages with quartz and andalusite or kyanite in the presence of brines at and above 400 °C suggesting that K-deficient compositions are not stable at these temperatures.

END-MEMBER ILLITE: AN ORDERED DOMAIN STRUCTURE?

Many investigators have attributed alkali deficiencies in muscovite to alkali-site vacancies implying solid solution toward pyrophyllite according to the equation, ${}^{\text{IV}}\text{Al}^{3+} + {}^{\text{XII}}\text{K}^{+} = {}^{\text{IV}}\text{Si}^{4+} + {}^{\text{XII}}\square$ (e.g., Wang and Banno 1987; Rosenberg 1987); thus, K⁺-deficiencies are compensated by increased ${}^{\text{IV}}\text{Si}/{}^{\text{IV}}\text{Al}$ ratios. Random variations in these compositional parameters will result in local charge imbalance, increasing the energy of the structure. Ordering of interlayer occupancy and ${}^{\text{IV}}\text{Si}/{}^{\text{IV}}\text{Al}$ ratios would diminish local charge imbalance by creating regions of muscovite and pyrophyllite composition but would result in structural strain in regions of pyrophyllite composition due to differences between the muscovite and pyrophyllite structures. In order to relieve this strain, regions of pyrophyllite composition may invert to the pyrophyllite structure in which the tetrahedral rings are laterally displaced across the interlayer gap and no mica-like K-sites exist (Guggenheim et al. 1987). The result would be an ordered structure composed of muscovite and pyrophyllite domains which, if it ex-

ists, could be a stable phase in the system muscovite-pyrophyllite (Rosenberg and Yates, 1999). According to Jiang et al. (1990), end-member illite could be stable with respect to assemblages of muscovite + pyrophyllite *only* if the structure is ordered thereby lowering its entropy relative to a mechanical mixture of muscovite and pyrophyllite. Thus, disordered, K-deficient micas are probably metastable whereas the ordered domain structure may be a stable phase.

A pyrophyllite component has long been predicted to exist in K-deficient micas (Loucks 1991 and references therein). Recent FTIR studies have established the presence of local pyrophyllite domains in Al-rich muscovite solid solutions either within layers or as alternate layers (Besson and Drits 1997a, 1997b). Pyrophyllite domains have not, as yet, been observed in alkali-deficient micas using XRD or TEM techniques. However, the absence of superstructure reflections does not rule out the presence of an ordered superstructure, as domains may be too small to be analyzed using AEM techniques (Livi et al. 1997). The loss of alkali cations (particularly Na) from the interlayer site during AEM analysis using finely focused, intense electron beams is a further complicating factor.

Ferrow et al. (1990) observed exsolution on a very fine scale in muscovites from the Lawler Peak granite. Although the lamellae were too small to be analyzed directly, Ferrow et al. (1990) inferred that a second dioctahedral mica unmixed from the muscovite. A possible reaction involving a celadonitic phase was discussed and later confirmed by XRD (Ferrow 1994). Exsolution at scales below the resolution of most TEM studies may be common in muscovites, but difficult to detect (Ferrow et al. 1990), suggesting the possibility that other phases may also exsolve from muscovite. Recently, Ferraris et al. (2000) observed oriented platelets of quartz in white micas formed at high pressures using HRTEM methods and concluded that white micas may not always be homogeneous and should be examined more carefully.

Computer simulations of one-dimensional HRTEM images (Guthrie and Veblen 1989, 1990) may resolve compositional periodicities resulting from the ordering of interlayer cations and reveal structural details on the sequencing and thickness of layers. This approach has been applied with some success to illite/smectite (Guthrie and Veblen 1989, 1990) but not, as yet, to end-member illite. However, such studies may not be conclusive because the absence of superperiodicities does not rule out the presence of compositional ordering.

Some of the mottling commonly observed in TEM images of muscovite may be related to short-range ordering (Noe and Veblen 1999). Fine-scale mixtures of compositionally different domains in the dioctahedral micas often leads to the "mottling" of TEM images (Livi et al. 1997). Although mottling has been observed in end-member illites (Yates and Rosenberg 1998), Type 2 mottling, associated with short-range order (Noe and Veblen 1999), has not, as yet, been distinguished.

"EXCESS" WATER

Many muscovites that exhibit deficiencies in interlayer cations appear to contain "excess" water that cannot be accounted for by the generally accepted structural formula. A hypothesis to account for apparent "excess" water in dioctahedral

phyllosilicates that may be traced back to studies by Brown and Norrish (1952), Foster (1964), Hower and Mowatt (1966), and Loucks (1991) suggests that full interlayer occupancy is achieved by incorporation of H_3O^+ and/or H_2O into interlayer sites. Hervig and Peacock (1989) observed that if excess H is attributed to H_3O^+ , then the alkali-sites are completely filled in all of their samples. The presence of "excess" water has also been inferred in synthetic K-deficient micas (Rosenberg 1987) and "illites" (Velde and Weir 1978). Although the results of these studies suggest the presence of interlayer H_3O^+ and/or H_2O , none have produced definitive results and, thus, the "excess" water problem remains unresolved (Guidotti and Sassi 1998).

The acid conditions necessary for the formation and substitution of H_3O^+ into micas are not compatible with ordinary diagenetic environments and, thus, extensive substitution of H_3O^+ into K-micas is not likely under these conditions (Jiang et al. 1994). Furthermore, most K-deficient micas and illites have a low layer charge relative to muscovite (Hower and Mowatt 1966; Srodoń et al. 1992) and, therefore, the "excess" water must be largely in the form of neutral water molecules. The hydrophilic character of illite (Bantignies et al. 1997) is in accord with this inference.

Structural water is rarely detected in K-deficient micas (e.g., FTIR studies of illite, Eberl et al. 1987) probably because it occupies, at most, only about 0.12 sites per half-cell in alkali-deficient micas. However, IR absorption bands at 3420 and 3260 cm^{-1} , corresponding to structural water molecules, have been observed recently in K-deficient micas after KBr pellets were carefully dried by heating to 120 °C to remove absorbed water (Besson and Drits 1997a, 1997b). Two of these samples, RM4 and RM30, are from the suite of essentially non-phengitic San Juan "illites" characterized by Eberl et al. (1987). The presence of neutral water molecules in interlayer sites may relieve structural strain in disordered, K-deficient micas enhancing their metastable persistence with respect to the ordered domain structure described above.

THE ILLITE/MUSCOVITE TRANSFORMATION: A MODEL

The prograde transformation of illite to a K-deficient mica (i.e., end-member illite) under diagenetic to low-grade metamorphic conditions has recently been described by Gharrabi et al. (1998) based on detailed XRD studies. During diagenesis, the smectite-to-illite reaction appears to progress stepwise with a decreasing proportion of smectitic layers and an increase in the proportion of illitic layers until I-S consists of about 95% illitic layers. This phase may persist but further reaction progress results in the formation of small diffracting domain illite (SDD) containing <5% of a smectitic component but showing no change on glycolation (Gharrabi et al. 1998). At a later stage, the SDD illite appears to dehydrate and large diffracting domain illite that contains no smectitic layers forms at the expense of SDD. This sequence corresponds approximately to the reaction series described by Ylagan et al. (2000).

SDD illite may be a metastable, disordered, K-deficient mica (I_w) stabilized by the presence of "excess" interlayer water derived from the conversion of smectitic to illitic layers. Kodama and Brydon (1968) report a pronounced DTGA peak at about 250–

300 °C in hydrothermal sericite, which may correspond to the loss of structural (interlayer) water (Loucks 1991). If so, then dehydration of SDD would create interlayer vacancies and, thus, promote the conversion of metastable, disordered K-deficient mica (I_d) to a stable, ordered muscovite/pyrophyllite domain structure (I_o). Pyrophyllite becomes a stable phase in the system Al_2O_3 - SiO_2 - H_2O at about 275 °C at 1 kbar (Hemley et al. 1980).

Gharrabi et al. (1998) believe that their proposed recrystallization sequence demonstrates that end-member illite is not a "mica" and suggest that a miscibility gap exists between illite and "K-mica" (muscovite). This conclusion is in accord with the existence of a miscibility gap between I_o and ideal muscovite proposed in this discussion. During diagenesis, the illitization process may end with the formation of SDD illite with some smectite (Gharrabi et al. 1998) (i.e., excess water), a phase which is metastable with respect to end-member illite.

The formation of end-member illite may be accompanied by the transformation of the $1M$ (or $1M_d$) to the $2M_1$ polytype. Inoue et al. (1987) suggested a prograde reaction series between smectite and $2M_1$ illite with a transition from the lath-like $1M$ polytype to the platy, hexagonal $2M_1$ polytype as the final step. According to Inoue et al. (1988), these two polytypes have different interlayer K-contents and expandability ranges in addition to different morphologies. However, both $1M$ and $2M_1$ may exist at apparent 0% expandability. The San Juan illites RM30 and SG4 (Eberl et al. 1987; Rosenberg and Hooper 1996) are both non-expandable, end-member illites, [both $K_{0.87\pm 0.01}/O_{10}(OH)_2$]. RM30 is a $1M$ polytype with lath-like crystals whereas SG4 is a $2M_1$ polytype with platy, hexagonal crystals. Similar conclusions were reached by Ylagan et al. (2000). Lath-like crystals represent a metastable morphology that eventually recrystallizes to form the platy crystals expected under equilibrium conditions (Bauer et al. 2000; Güven 2001). The apparent conversion of the $1M_d$ to the $2M_1$ polytype may be related to a decrease in the number of stacking faults as the proportion of illitic layers increases (Dong and Peacor 1996).

Based on natural occurrences discussed above, K-deficient micas (end-member illites) of composition $K_{0.88}/O_{10}(OH)_2$ appear to be stable to at least 350 °C. This temperature is consistent with the upper thermal stability limit of pyrophyllite with respect to andalusite, quartz, and water (366 °C at 1 kbar) determined experimentally by Hemley et al. (1980). At higher temperatures, pyrophyllite domains in K-deficient micas would be expected to decompose to form andalusite and water coexisting with an ideal muscovite in accord with the observations of Frank et al. (1998). Conversely, alteration of muscovite in the solid state at temperatures below ~360 °C should yield only the ordered, domain structure (I_o). The formation of I-S from ideal muscovite would be possible only by dissolution and crystallization, a transformation mechanism observed by Giorgetti et al. (2000) in sediments of the Salton Sea Geothermal Field.

SUMMARY REMARKS

A hypothesis is proposed herein to account for the nature and stability of end-member illite based on the following observations from the literature. (1) The end-member composition of K-deficient micas and illite is $K_{0.88\pm 0.01}/O_{10}(OH)_2$. Apparent miscibility gaps exist between this composition and

those of pyrophyllite and ideal muscovite. (2) End-member illite appears to be a stable phase below ~360 °C (near the upper thermal stability of pyrophyllite) based on experimental data and studies of natural mineral assemblages whereas ideal muscovite coexists with andalusite and water at and above 400 °C. (3) An ordered, domain structure is required if end-member illite is a stable phase in the system muscovite-pyrophyllite. Pyrophyllite domains have been observed in illites by FTIR. (4) "Excess" water has been shown to be present in many illites (e.g., Besson and Drits 1997a) and may be lost in the temperature range 250–300 °C. (5) Exsolution may be common in muscovites on a scale below the resolution available in most TEM investigations. (6) The detailed XRD studies of Gharrabi et al. (1998) and others provide a framework for a hypothesis on the nature and formation of end-member illite.

The widely accepted sequence of crystallization during prograde illitization is smectite \rightarrow I-S, random \rightarrow I-S, ordered \rightarrow illite, $1M_d \rightarrow$ muscovite, $2M_1$ (e.g., Zhao et al. 1999). The proposed hypothesis modifies the latter part of this sequence to I-S $\rightarrow I_w \rightarrow I_d \rightarrow I_o$, the only stable phase at temperatures below ~360 °C. Some of these steps appear to overlap, resulting in mixtures with varying proportions of phases. Muscovite may be transformed directly to I_o in the solid state or by dissolution and crystallization through all or part of the illite crystallization sequence (Yates and Rosenberg 1998). Both solid-state and dissolution/crystallization reaction mechanisms have been inferred to be operative in natural environments (Altaner and Ylagan 1997).

According to the proposed hypothesis, end-member illite is not a disordered K-deficient muscovite solid solution but a stable, ordered structure consisting of muscovite and pyrophyllite domains and, thus, a distinct mineral. This is not an entirely new idea, results of studies by Środoń et al. (1992) and Meunier and Velde (1989) suggest that illite has a unique chemical composition different from those of muscovite or phengite. Gharrabi et al. (1998, p. 87) concluded that "illite is not a mica and hence not a part of the mica solid solutions" and proposed a miscibility gap between illite and mica.

Direct evidence to support the existence of an ordered domain structure has not been reported in the literature perhaps because it is difficult to observe and has not been the focus of any investigations. The proposed hypothesis accounts for the available evidence but requires testing that could be accomplished by detailed TEM (HRTEM and SAED) studies of end-member illite.

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