Characterization of 2M pyrophyllite associated with argillic alteration in steam-heated environment, Solo, Mabini, Philippines

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Localized deposit of Fe-rich pyrophyllite was encountered in the kaolinite-dominated alteration halo in Solo, Mabini, Philippines. The environment of formation of this dioctahedral mineral is related to low-temperature advanced argillic alteration found in shallow volcanic region. The pyrophyllite crystallizes as a two-layer monoclinic (2M) structure with the following unit cells, $a=5.16\text{ \AA}$, $b=8.95\text{ \AA}$, $c=18.70\text{ \AA}$, $\beta=99.87^\circ$ while its dehydroxylate form yields a slightly different unit cell parameters with $a=5.17\text{ \AA}$, $b=9.02\text{ \AA}$, $c=18.76\text{ \AA}$, $\beta=99.80^\circ$. The expansion of b on dehydroxylation arises largely from the rearrangement of the Al ions in the octahedral layer and the insertions of oxygen ions in the Al planes. The obtained tetrahedral rotation (twisting of SiO_4 groups) of $11^\circ 52'$ in pyrophyllite is closely comparable to the $9^\circ 40'$ angle of twist in the dehydroxylate. This strongly suggests that the tetrahedral networks of the original pyrophyllite are almost similarly twisted in the dehydroxylate phase. X-ray powder data demonstrate that the dehydroxylation process is accompanied by a significant enlargement of basal spacing with an observed expansion of about 1.99%. Thermal decomposition of pyrophyllite shows a single dehydration event, which takes place over a temperature range of 500–700°C with its peak at 604°C. The occurrence of this low-temperature dehydroxylation can be regarded as a consequence of significant replacement of Al by Fe in the octahedral layer and the presence of some impurities. Chemical data of pyrophyllite obtained from EDX analysis give an average structural formula of $\text{Ca}_{0.01}\text{K}_{0.10}(\text{Al}_{1.81}\text{Fe}^{3+}_{0.16}\text{Ti}_{0.01})(\text{Si}_{3.88}\text{Al}_{0.12})\text{O}_{10}(\text{OH})_2$ with an average $\text{Si}/(\text{Al}^{3+} + \text{Fe}^{3+})$ ratio of 1.86. Analyses of representative samples indicate that the octahedral site is filled with 1.76 to 1.84 Al cations, which is relatively lower than the 1.90 to 1.95 Al cations exhibited by ordinary pyrophyllite. This significant deficiency of Al is believed to be compensated by considerably high Fe^{3+} occupancy in the octahedral site. The source of Fe can be correlated to the previous decomposition of minor amount of pyrite associated with argillic alteration. SEM observations show common disoriented stacks of pyrophyllite plates, but the most visible component of the samples are the loosely compacted stacks in which thin elongated blade-like particles are randomly dispersed in the form of relatively porous aggregates.

The coexistence of pyrophyllite and kaolinite in this environment is a consequence of sluggish crystallization of quartz caused by local variation of silica activity, which explains the crystallization of pyrophyllite instead of stable kaolinite at low temperature ($<300^\circ\text{C}$).

Introduction

Some sizeable nodes of pyrophyllite in Solo, Mabini, Philippines were earlier reported by Mojares et al. (2000) when they examined the surficial distribution of clay minerals in the hydrothermally altered ground of central Calumpan Peninsula (Fig. 1).

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Figure 1. Alteration zone map showing the relative distribution of pyrophyllite and other major clay minerals in Solo alteration halo (after Mojares et al., 2000).

Initial published paper on this undertaking focused solely on the formation of illite/smectite mixed-layer minerals in the alteration zone with brief discussions on other clay mineral assemblages. The present paper is a continuation report of the previous work and deals exclusively with low-temperature pyrophyllite and its allied minerals found in the same alteration zone.

The observed deposit of pyrophyllite occurs in patches in the kaolinite-dominated alteration formed by hydrothermal argillization of andesite rock. The altered zone resembles a halo and is an excellent example of hydrothermal alteration formed under steam-heated environment. The mapped halo extends over an area of about 1300 by 1200 meters and is considered to be the largest exposure of altered ground reconnoitered in the entire peninsula. The mineralogy is suggestive of alumina-rich environment with characteristic features of both argillic and low-temperature advanced-argillic

alterations. Kaolinite and quartz occur ubiquitously in the entire volume of the altered rock with significant association of other clay minerals such as smectite, illite, chlorite, mixed-layer clays, and pyrophyllite.

The hydrothermal process encountered in Solo involves hot convecting solutions that persist at shallow level with attendant preferential escape of acid volatiles and their condensation and reaction immediately above. During this process, sulphate component is added to the system and alunite becomes an important associated phase in the alteration zone. This environment, however, differs from a common solfatara field, where altered rock undergoes extreme acid leaching due to abundance of highly sulfurous materials. A more detailed discussion on the mineralization and geology of the whole Calumpan Peninsula and its relationship to hydrothermal alteration are provided in Mojares et al. (1999).

In order to ascertain the characteristics of Solo

pyrophyllite formed under argillic to low-temperature advanced argillic alteration, several representative samples of this mineral were subjected to various laboratory analyses and treatments. This paper aims to describe the mineralogical features and chemistry of pyrophyllite deposit.

Samples and Experimental

The samples were collected from the delineated pyrophyllite zone previously described by Mojares et al. (2000). The material tested comprised five non-homogeneous samples of pyrophyllite from various surface locations within the delineated pyrophyllite zone. All samples are massive, soft, off-white to light cream in color and can be crushed or ground easily. The proportion of pyrophyllite in the bulk samples varies between 70 to 85% based on semi-quantitative analysis of mixture by X-ray diffraction (XRD) using internal standard method. The remaining percent is assigned to kaolinite, quartz and sulfide impurities.

Sample preparation includes disaggregation of the original samples (partly powder) with a rubber hammer, and dry sieving them using 100-mesh screen. The obtained <100 mesh fraction samples were prepared for mineral identification and analyses. The preparation of fine clay samples involves the segregation of <10 μm fraction from coarser fraction by dispersion, sedimentation, and centrifugation in distilled water.

Powders for XRD analysis were packed on an aluminum sample holder for randomly oriented samples. The X-ray diffractograms were obtained using a Rigaku (Geigerflex) X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. XRD measurement also involved pyrophyllite dehydroxylates obtained from heating the samples at 850°C for 94 hours. The diffraction data for pyrophyllite and its dehydroxylate were indexed for detailed structural analysis. Subsequent refinement of unit cell parameters was undertaken using the LCLSQ program of Burnham (1991). Scanning electron microscopy (SEM) studies were carried out on original bulk aggregate specimens and on <10 μm clay materials using Hitachi S-4100H scanning electron microscope equipped with energy dispersive X-ray (EDX) facilities. The surfaces of specimens were lightly sputtered with a thin film of gold and palladium to carry away any excess charge from the electron beam. Chemical analyses were performed mainly on single crystals of pyrophyllite using EDX analyzer on <10 μm fraction samples under 15 kV accelerating voltage and 10 μA current condition. Powder sample for EDX analysis was slightly pressed on a carbon adhesive tape stuck on the surface of a small

carbon disk to make it oriented. The prepared specimen was later coated with carbon using carbon-sputtering machine. Single crystal analysis was preferred over bulk analysis in an attempt to decrease or eliminate the effect of impurities. This procedure involves determination of chemical composition of some single crystals of pyrophyllite randomly selected from fine-grained material. Under EDX quantification technique, the corrected weight percent of measurable elements were determined and the compound percent of each of these elements were calculated. The percent of error is <1%. Differential thermal analysis (DTA) and Thermogravimetric (TG) curves were recorded on a Rigaku micro DTA-TG apparatus using about 30 mg of fine (<10 μm) and bulk sample materials. Heating was carried out from room temperature to 1100°C at a rate of 10°C per minute. Infrared (IR) spectra of fine fractions of pyrophyllite and its dehydroxylate, incorporated in about 160 mg, 12-mm diameter KBr disks, were recorded over the range of 4000–350 cm^{-1} frequency.

Results of Analysis

X-ray Powder Data and Unit Cell Parameters

The pyrophyllite samples from Solo, Mabini exhibit the characteristic diffraction features of 2 layer monoclinic (2M) structure with the following unit cell parameters: $a=5.16\text{ \AA}$, $b=8.95\text{ \AA}$, $c=18.70\text{ \AA}$, $\beta=99.87^\circ$. The value of b is significantly less than the ideal value calculated for a hexagonal silicon-oxygen sheet (with regular $\text{Si-O}=1.62\text{ \AA}$), which is $4\sqrt{2}\times 1.62=9.15\text{ \AA}$ (Brindley and Wardle, 1970). The twisting of the tetrahedral SiO_4 groups through angles of $\pm 10^\circ$ away from the ideal hexagonal arrangement is related approximately to the observed value of b by the relation $\alpha=\cos^{-1}[b(\text{obs})/b(\text{ideal})]$ (Wardle and Brindley, 1972). Hence, the obtained b parameter, 8.95 $\text{\AA}$, corresponds to silicon-oxygen sheet with an angle of twist (tetrahedral rotation) of $\cos^{-1}(8.95\text{ \AA}/9.15\text{ \AA})=11^\circ 54'$.

The monoclinic structure of the samples was confirmed in the X-ray diagram (Fig. 2) by the remarkable absence of reflections at 3.18 $\text{\AA}$, 2.95 $\text{\AA}$, 3.764 $\text{\AA}$, 3.492 $\text{\AA}$ and 3.454 $\text{\AA}$ of the typical one layer triclinic (1Tc) variety (Wardle and Brindley, 1972). The observed powder diffraction pattern shows three strong reflections at spacings 9.21 $\text{\AA}$, 4.62 $\text{\AA}$, and 3.07 $\text{\AA}$, and associated weak peaks with d -spacings between 2.57 $\text{\AA}$ and 1.37 $\text{\AA}$. Other minor reflections in the diffractogram are assigned to kaolinite, quartz, and pyrite impurities. The obtained X-ray powder diffraction data for Solo 2M pyrophyllite and its dehydroxylate form are

Figure 2. Representative X-ray diffraction patterns of the 2-layer monoclinic (2M) pyrophyllite and its dehydroxylate from Solo alteration halo, and the 1-layer triclinic (ITc) variety from New Zealand (Brindley and Wardle, 1970). P, pyrophyllite; K, kaolinite; Q, quartz; Pyr, pyrite. See text about the explanation on the 3.17 Å and 2.95 Å reflections in the ITc pyrophyllite.

listed in Table 1. The corresponding lattice parameters are summarized in Table 2.

The similarity of the powder diffraction pattern of pyrophyllite and of its dehydroxylate indicates that dehydroxylation produces only small structural changes. The only obvious discrepancy between them lies in the d-spacing and intensity of the 001 reflection. X-ray powder data demonstrate that the dehydroxylation process is accompanied by a significant enlargement of basal spacing. An expansion of $d(001)$ by about 1.99% on dehydroxylation is detected in most samples analyzed. This expansion of basal spacing can be ascribed to the formation of OH on the basal surface as a result of the coupled substitution of Al^{3+} and $(\text{OH})^-$ for Si^{4+} and O^{2-} during rehydroxylation of dehydroxylated pyrophyllite (Rosenberg, 1974). Based on X-ray powder data in Table 1, other XRD reflections of the dehy-

droxylate nearly coincide with that of original monoclinic pyrophyllite with the former exhibiting more characteristic weak reflections.

The observed powder diagrams for the dehydroxylate phase are indexed from the following unit cells: $a = 5.17 \text{ \AA}$, $b = 9.02 \text{ \AA}$, $c = 18.76 \text{ \AA}$, $\beta = 99.80^\circ$. The increase of parameter b to $9.02 \text{ \AA}$ is still significantly less than the ideal calculated value of $9.15 \text{ \AA}$ for a hexagonal silicon-oxygen sheet. The observed expansion of b by 0.75% may arise largely from the rearrangement of the Al ions in the octahedral layer and the insertion of oxygen ions in the Al planes (Wardle and Brindley, 1972). The calculated angle of twist in the dehydroxylate is $\cos^{-1}(9.02 \text{ \AA} / 9.15 \text{ \AA}) = 9^\circ 40'$, which is closely comparable to the $11^\circ 52'$ tetrahedral rotation of the original (unheated) pyrophyllite. This result implies that the twisted tetrahedral networks of pyrophyllite are almost similarly

Table 1. X-ray powder data for Solo 2M pyrophyllite and its dehydroxylate form

2M Pyrophyllite				2M Pyrophyllite (Dehydroxylate)			
hkl	d(obs) Å	d(calc) Å	I(obs)	hkl	d(obs) Å	d(calc) Å	I(obs)
0 0 2	9.204	9.216	100	0 0 2	9.388	9.248	80
0 0 4	4.622	4.608	60	0 0 4	4.685	4.624	50
0 2 0	4.461	4.477	40	0 2 1	4.396	4.382	80
0 0 6	3.068	3.072	100	0 2 2	4.152	4.054	40
1 3 0	2.571	2.574	25	0 0 6	3.119	3.083	100
1 3 2	2.535	2.537	25	1 3 0	2.585	2.589	10
0 2 6	2.535	2.533	25	1 3 2	2.552	2.551	10
1 3 2	2.417	2.425	30	0 2 6	2.552	2.545	8
2 0 4	2.417	2.407	30	1 3 2	2.439	2.439	8
1 3 4	2.332	2.335	4	2 0 4	2.439	2.411	2
0 0 8	2.299	2.304	6	1 3 4	2.383	2.348	8
1 3 4	2.166	2.168	10	0 0 8	2.284	2.312	5
2 0 6	2.156	2.147	9	2 2 0	2.208	2.218	4
1 3 6	2.058	2.063	20	2 2 2	2.088	2.088	4
0 2 8	2.058	2.049	20	2 0 8	1.871	1.878	2
1 3 6	1.895	1.894	5	3 1 2	1.689 *	1.692	10
3 1 2	1.686 *	1.689	12	1 5 0	1.689 *	1.701	10
1 5 0	1.686 *	1.689	12	2 4 2	1.689 *	1.695	10
2 4 2	1.686 *	1.687	12	2 4 0	1.689 *	1.688	10
2 4 0	1.686 *	1.680	12	3 1 0	1.673 *	1.669	1
3 1 6	1.573 *	1.580	3	3 1 4	1.673 *	1.661	2
2 0 8	1.573 *	1.578	3	1 5 2	1.663	1.656	2
0 6 0	1.494	1.492	20	1 5 6	1.454	1.454	4
3 3 4	1.471	1.468	10	3 3 6	1.408	1.417	4
1 1 12	1.384	1.386	20	1 1 12	1.382	1.385	15
3 1 6	1.373	1.370	30	3 1 6	1.374	1.374	15

*not completely resolved (following the 2M pyrophyllite Indexing by Brindley and Wardle, 1970)

Table 2. Lattice parameters of Solo 2M pyrophyllite and its dehydroxylate form

	Normal	Dehydroxylate	% expansion
a	5.16 Å	5.17 Å	0.19
b	8.95 Å	9.02 Å	0.75
c	18.71 Å	18.76 Å	0.27
α	90.00°	90.00°	—
β	99.87°	99.80°	—
γ	90.00°	90.00°	—
d (001)	18.40 Å	18.77 Å	1.99

twisted in the dehydroxylate phase. Apparently, no relaxation (untwisting) of Si–O networks can be recognized since there is no significant expansion of b to near 9.15 Å (Brindley and Wardle, 1970). On the contrary, the parameter a does not show the same expansion as b does and this indicates that the octahedral sheet still exerts a constraint in the a direction.

Structural reorganization involving transformation of Al from 6-fold to 5-fold coordination following dehydroxylation (Guggenheim et al., 1987) has not been validated because a full refinement of the structure is unattainable due to the absence of single crystals of well crystallized 2M pyrophyllite from Solo.

Chemical Analysis and Structural Formula

Structural formulae of 3 samples were calculated using the average chemical compositions of Solo pyrophyllite ($<10\ \mu\text{m}$) as determined by EDX analyzer using single crystal analyses. Structural formulae calculated on the basis of $\text{O}_{10}(\text{OH})_2$ anion framework show a small but ubiquitous substitution of Al for silicon with tetrahedral Al in the range of 0.05 to 0.17 atoms (Table 3). The total octahedral cation is between 1.97 and 1.99 in which Al ions make up about 85% to 95%. The obtained average structural formula of $\text{Ca}_{0.01}\text{K}_{0.10}(\text{Al}_{1.81}\text{Fe}^{3+}_{0.16}\text{Ti}_{0.01})(\text{Si}_{3.88}\text{Al}_{0.12})\text{O}_{10}(\text{OH})_2$ shows a significant deviation from the ideal pyrophyllite composition of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. Most analyses show octahedral Al in the range of 1.76 to 1.84 atoms, which is relatively lower than the usual value of 1.90–1.99 atoms for common pyrophyllite (Newman, 1987). This conspicuous deficiency in Al is believed to be compensated by substantial Fe^{3+} occupancy in the octahedral site, where considerable Fe^{3+} replaces Al^{3+} . Such octahedral substitution frequently causes an over-all negative charge on the layers, which is ordinarily compensated by interlayer cations. The occurrence of Ti on the other hand, appears to have only minimal contribution in the octahedral substitution since the number of calculated Ti ions barely exceeds 0.01. No traces of octahedral Mg

can be detected in all samples analyzed. Among the interlayer cations, K is the most abundant. It persists in all pyrophyllite analyses up to a maximum of 0.11 ions which is comparable to pyrophyllite analyses reported by Newman (1987) with a maximum of 0.2 cations and 0.25 equivalents per formula unit. Ca content, on the other hand, is scarce with only <0.02 ions. The average $\text{Si}/(\text{Al}^{3+} + \text{Fe}^{3+})$ ratio of 1.86, with values ranging from 1.78 to 1.96, is comparatively lower than the ideal ratio of 2.00 for common pyrophyllite. The 1.72 ratio according to Rossenberg and Cliff (1980) seems to be the minimum ratio found in the pyrophyllite structure. The presence of significant amount of octahedral Fe^{3+} in pyrophyllite varying from 0.12 to 0.21 atoms can be correlated to earlier decomposition of minor aggregates of pyrite (FeS_2) associated with argillic alteration. Based on TG-DTA data, the estimated percent of H_2O in pyrophyllite samples ($<10\ \mu\text{m}$ fraction) ranges from 3.9 to 4.2%.

Thermal Decomposition

Dehydroxylation process for nearly all fine ($<10\ \mu\text{m}$) pyrophyllite samples take place over a temperature range of 500°C to 700°C (Fig. 3a), which is slightly lower than the usual range of 650°C to 850°C for common pyrophyllite. The obtained endotherm with its peak at 604°C is characteristically broad and shallow, and suggestive of single dehydration event. This abnormal low-temperature dehydroxylation is due mainly to significant replacement of Al by Fe in the octahedral layer which causes a reduction in the temperature of endothermic reaction (Grim, 1953; Shimoda and Sudo, 1969). The appearance of the main dehydroxylation curve seems to be associated with weak exothermic peak at 997°C . Low-temperature endothermic effect associated with loss of hygroscopic moisture at about 120°C is nearly absent in all samples investigated. The observed thermogravimetric (TG) curve indicates a very significant weight loss of about 4.2% near the 600°C temperature region, which is due mainly to the loss of hydroxyl water in pyrophyllite.

In all bulk samples, the overlapping of the pyrophyllite endothermic peak at 608°C and the kaolinite endotherm at 571°C is notable (Fig. 3b). This is accompanied by a sharp exothermic effect at 462°C and a weak exothermic peak at 997°C . The former can be ascribed to the presence of pyrite (FeS_2), which is known to be highly sensitive to thermal treatment while the latter is related to crystallization of $\gamma\text{-Al}_2\text{O}_3$ from kaolinite or from amorphous alumina (Insley and Ewell, 1935). Also, two low-temperature endothermic effects

Table 3. Structural formula of 2M pyrophyllite from Solo, Mabini

	Sample 1	Sample 2	Sample 3
Number of ions calculated on the basis of $\text{O}_{10}(\text{OH})_2$			
Si	3.95	3.87	3.83
Al	0.05	0.13	0.17
Total Tet.	4.00	4.00	4.00
Al	1.84	1.84	1.76
Ti	0.01	0.01	0.02
Fe^{3+}	0.12	0.14	0.21
Total Oct.	1.97	1.99	1.99
Ca	0.01	0.01	0.02
K	0.09	0.11	0.02
Interlayer charge	0.25	0.29	0.39
$\text{Si}/(\text{Al} + \text{Fe}^{3+})$	1.96	1.83	1.78

AVERAGE STRUCTURAL FORMULA:

$\text{Ca}_{0.01}\text{K}_{0.10}(\text{Al}_{1.81}\text{Fe}^{3+}_{0.16}\text{Ti}_{0.01})(\text{Si}_{3.88}\text{Al}_{0.12})\text{O}_{10}(\text{OH})_2$

Figure 3. DTA-TG curves for <10 μm fraction (a) and bulk (b) samples of pyrophyllite from Solo, Mabini.

were observed below 120°C and these are due to dehydration of adsorbed water on the surface of the crystals. The accompanying TG curve of the bulk sample indicates a relatively sharp weight loss of about 9.4% between the 450°C and the 800°C temperature regions. This is most likely the combined effect of hydroxyl water loss and decomposition of FeS_2 .

As dehydroxylation temperature reached 850°C, the pyrophyllite sample transforms to the dehydroxylate phase by the reaction of $2(\text{OH}) \rightarrow \text{H}_2\text{O}(\uparrow) + \text{O}$, where the residual oxygen is greatly undersaturated. The undersaturation of the residual oxygen and the four

oversaturated oxygens around the aluminum account for the metastable nature of the dehydroxylate form (Guggenheim et al., 1987).

Infrared Spectra

The octahedral substitution of Fe^{3+} for Al^{3+} in pyrophyllite is more or less evident in the IR spectra in Figure 4. The replacement of Al^{3+} by Fe^{3+} in dioctahedral minerals gave rise to increased negative charges on apical oxygens (Farmer, 1974), which account for the Al_2OH vibration to occur at lower frequency, i.e., 3660

Figure 4. Infrared (IR) spectra of $<10\ \mu\text{m}$ fraction sample of Solo 2M pyrophyllite and its dehydroxylate in the $5000\ \text{cm}^{-1}$ to $330\ \text{cm}^{-1}$ region.

cm^{-1} for pyrophyllite instead of the usual 3675 to $3680\ \text{cm}^{-1}$. This strong $3660\ \text{cm}^{-1}$ absorption is accompanied with a weak but distinct absorption band, which occurs as a shoulder near $3640\ \text{cm}^{-1}$, and can be assigned to OH groups ($\text{AlFe}^{3+}\text{OH}$) shared between Al and Fe ions (Farmer and Russel, 1964). Its intensity, which appears to be related to Fe content, is stronger than those exhibited by ordinary pyrophyllite. Likewise, the weak $730\ \text{cm}^{-1}$ band associated with $\text{Fe}^{3+}\text{-O}$ is slightly lower than those involving Al, which exhibit $740\text{--}745\ \text{cm}^{-1}$ frequency. Also, weak OH vibration band at $660\ \text{cm}^{-1}$ differs slightly from the $690\ \text{cm}^{-1}$ band given by pyrophyllite containing high octahedral Al. The shift from $690\ \text{cm}^{-1}$ to $660\ \text{cm}^{-1}$ seems to be the effect of Fe substitutions for Al in the octahedral layer. Other frequency bands in the spectra are consistent with the infrared diagram for natural pyrophyllite proposed by Russell et al. (1970). These include weak vibration bands at $800\text{--}900\ \text{cm}^{-1}$ region, the sharp OH vibration band at $950\ \text{cm}^{-1}$, which is an indicator of Al-rich composition of the octahedral site, the 1070 and $1121\ \text{cm}^{-1}$ in-plane vibrations common in dioctahedral minerals, and the octahedral cation-related bands at $400\text{--}600\ \text{cm}^{-1}$. Generally, the Si-O stretching vibra-

tions in the $700\text{--}1200\ \text{cm}^{-1}$ only weakly affect other vibrations, whereas the Si-O bending vibrations below the $600\ \text{cm}^{-1}$ region are strongly coupled with vibrations of the octahedral cation and with the translatory vibrations of the hydroxyl groups (Farmer, 1974).

Infrared spectra also reveal that the strong OH-related bands at $950\ \text{cm}^{-1}$ (in plane OH vibrations) and the $3660\ \text{cm}^{-1}$ (OH stretching) in pyrophyllite are absent in the dehydroxylate form. This means that infrared absorption is especially sensitive to the coordination between OH groups and nearest cation neighbors during dehydroxylation. Moreover, the bands at 578 , 540 , and $517\ \text{cm}^{-1}$ in pyrophyllite seem to be replaced by a broad band at $565\ \text{cm}^{-1}$ in the dehydroxylate. Such results coincide with the infrared data sets presented by Heller et al. (1962) and Anton (1969) on pyrophyllite and pyrophyllite dehydroxylate.

In this study, all the observed IR data for pyrophyllite and its dehydroxylate are nearly similar in all samples investigated.

Morphological Features

SEM observations on raw powder samples show that

Figure 5. SEM photos showing the relatively coarse elongated plates of pyrophyllite in poorly developed stacks (a and b); and many loosely compacted stacks of pyrophyllite in which thin elongated blade-like particles are randomly dispersed in the form a relatively porous aggregates (c and d). Bar scale = $10\ \mu\text{m}$.

stacks and aggregates of pyrophyllite are the only obvious visible components of the samples. Although visual assessments are not quantitative, the natural size distribution of this clay appears to be more or less bimodal. Each pyrophyllite sample is composed of relatively coarse stacks of elongated plates (about $10\ \mu\text{m}$) (Fig. 5a, b), and loosely compacted assemblages of randomly oriented blade-like particles about $5\ \mu\text{m}$ in size (Fig. 5c, d).

The observed stackings of coarse plates are not uniformly oriented and consists of mostly subhedral particles in poorly developed stacks. Only few coexisting pyrophyllite plates are euhedral. Disorientation

among the stacks is prevalent and well-ordered stacking of plates cannot be observed. A very common morphological feature in all samples is the preponderance of loosely compacted stacks in which thin elongated blades of pyrophyllite are randomly dispersed in the form of relatively porous aggregates. The occurrence of individual blades is believed to be a consequence of weak cohesion between plates. This morphological feature is frequently found in loosely compacted stacks where many thin plates of pyrophyllite break into small elongated blade-like particles. Single blades and randomly dispersed plates usually dominate the $<10\ \mu\text{m}$ fraction and show different morphologies with respect to compo-

nents in the coarser fractions. The observed morphological variations may be related to the natural texture of the material or may be due to mechanical grinding.

Discussions and Conclusions

The relationships between pyrophyllite and other minerals found in the alteration zone can be understood in terms of the activities of species in an aqueous fluid and various saturation conditions. The coexistence of pyrophyllite and kaolinite in the argillized ground of Solo might be a consequence of sluggish crystallization of quartz caused by localized variation of silica activity, which explains the localized crystallization of pyrophyllite instead of stable kaolinite. This particular case arises when high concentrations of aqueous silica do not readily crystallize to quartz at low temperatures, especially in acid solutions. In most cases, the pyrophyllite-kaolinite assemblage persists at high aqueous silica condition in the low temperature environment below 300°C (Hemley et al., 1980). This is very evident in situations of vigorous acid attack on silicic and intermediate rocks, e.g. hydrothermal alteration in volcanic systems, which tends to drive silica rapidly and metastably into solution to produce a fluid supersaturated in quartz with pyrophyllite as a common product.

With the observed style of hydrothermal alteration in Solo, the most obvious control for pyrophyllite formation is the concentration of aqueous silica in the system. The selective crystallization of pyrophyllite, as indicated by its patchy distribution, plausibly takes place as a result of high aqueous silica activity under low temperature (<300°C) condition in acid solutions. Hypothetically, the distribution of Solo pyrophyllite could have been more extensive if vigorous acid leaching activity and high temperature (300°C to 500°C) hydrothermal process are involved.

On the chemical viewpoint, the noticeable enrichment of Fe and K cations in pyrophyllite can be attributed to some mineral reactions in the hydrothermal system. The Fe is probably derived from the chemical breakdown of pyrite while K cation is supplied from the circulating hydrothermal fluid and from the dissolution of original minerals in the host rock. Fe ions are believed to have been preferentially concentrated in pyrophyllite and this reaction takes place at the same time as K ions are fixed during pyrophyllite crystallization.

The absence of major structural changes in pyrophyllite and the non-appearance of other high temperature Al-minerals in the argillic zone strongly suggest

low-temperature environment and weak hydrolytic alteration. This is supported by the scarcity of thermal manifestations in the area and the widespread occurrence of kaolinite relative to pyrophyllite in the alteration halo.

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