

## The formation of pyrophyllite solid solutions

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### Abstract

Pyrophyllite solid solutions,  $\text{Al}_2\text{Si}_{4-x}\text{Al}_x\text{O}_{10-x}(\text{OH}_{2+x})$ , have been synthesized from a gel and from lightly ground and milled natural materials. Solid solutions crystallize from structurally degraded or amorphous starting materials due to the tendency for  $\text{Al}^{3+}$  to enter tetrahedral sites. The extent of solid solution is small; synthesis from a gel yielded pyrophyllite with the formula  $\text{Al}_{2.0}(\text{Si}_{3.8}\text{Al}_{0.2})\text{O}_{9.8}(\text{OH})_{2.2}$ .

### Introduction

Pyrophyllite which departs from the ideal formula,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , has recently been synthesized in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  from very fine-grained or amorphous starting materials (Rosenberg, 1974). Synthetic pyrophyllites were characterized by enlarged basal spacings which were attributed to formation of (OH) on basal surfaces accompanying substitutions of the type  $\text{Al}^{3+} + \text{H} = \text{Si}^{4+}$ . These solid solutions have the structural formula  $\text{Al}_2(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10-x}(\text{OH})_{2+x}$  (Rosenberg, 1974). Although comparison with natural samples suggested that the extent of substitution is small, in the absence of chemical analyses the compositions of synthetic pyrophyllite solid solutions were unknown. However, the extent of substitution appeared to be dependent on the structural state of starting materials.

A brief investigation of the effect of structural state of starting materials on the composition of synthetic pyrophyllite solid solutions was attempted to confirm these inferences.

### Experimental details

Natural pyrophyllite from Glendon, Moore County, North Carolina, and pyrophyllite gel (Luth and Ingamells, 1965), both described in Rosenberg (1974), were used in the present investigation. The natural material was crushed and ground lightly under alcohol in an agate mortar for about 30 minutes.

A sample was taken before further grinding, sieved to separate coarser fragments ( $> 74 \mu\text{m}$ ), elutriated to remove the finest particles, and used as one of the starting materials. The remainder of the pyrophyllite was ground in a vibratory mill for 60 minutes before it was used as a starting material. The pyrophyllite structure is rapidly degraded by milling; X-ray reflections began to deteriorate almost immediately and completely disappeared after 60 minutes.

Lightly ground (unmilled) natural pyrophyllite, milled natural pyrophyllite, and pyrophyllite gel were sealed along with excess water (solid/water ratio  $\sim 2/1$  by weight) in gold capsules, which were simultaneously subjected to a temperature of  $472^\circ\text{C} \pm 5^\circ$  at 2 kbar for 72 days in the same cold-seal pressure vessel with water as the pressure medium. After quenching, samples were examined by X-ray powder diffractometry. Unfortunately it was not possible to obtain electron microprobe analyses, due to the small size and aggregation of pyrophyllite crystals coupled with the presence of minor amounts of quartz. However, analytical data were obtained by means of an AEI electron microscope microprobe analyzer (EMMA-4) equipped with a Kevex energy-dispersive analysis system, which permits quantitative determination of elemental ratios (Cliff and Lorimer, 1975; Lorimer and Cliff, 1976). Nine random point analyses of well-formed, thin, plate-like crystals were averaged to obtain count-rate data for  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Relative percentages of  $\text{Al}_2\text{O}_3$  and

SiO<sub>2</sub> were calculated using the natural material as a standard (Rosenberg, 1974) and assuming direct proportionality of the ratio percent oxide/average counts per unit time between sample and standard (Table 1). Because the thickness of crystals in the samples and standard was not known, only relative percentages of the oxides in the samples could be obtained. This limitation is inherent in EMMA analyses.

Basal spacings were determined by measurement of the X-ray reflection at approximately 29.1° 2θ CuKα 2M(006) or ITc(003), (Brindley and Wardle, 1970; Wardle and Brindley, 1972) against an internal standard, CaF<sub>2</sub> (annealed), which has a conveniently located reflection at 28.30° 2θ. Δ2θ values were obtained by averaging at least four measurements (scan rate 1/4°/min) per reflection and are known to within 0.005° 2θ.

The effect of structural state of starting materials on the chemical composition and basal spacings of pyrophyllite after hydrothermal treatment is shown in Figure 1. Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>) ratios are based on chemical data given in Table 1. Because the Fe<sub>2</sub>O<sub>3</sub> content of the natural starting material is small and appears to diminish in the products of the experiments, it has been neglected in the calculation of mole ratios (Fig. 1). The basal spacing and Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>) ratio of unmilled natural pyrophyllite starting material remains essentially unchanged by hydrothermal treatment. However, milling of natural pyrophyllite for 60 minutes to produce an amorphous-to-X-rays starting material results in the crystallization of pyrophyllite with enlarged basal spacings and a higher Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>) ratio. Pyrophyllite crystallized from the gel exhibits even more enlarged basal spacings and a still higher Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>) ratio. Although both the milled pyrophyllite and the pyrophyllite gel are amorphous

Table 1. Chemical data (mole %); partial compositions recalculated to 100%

	Natural Pyrophyllite*	Products		
		Unmilled	Milled	Gel
SiO <sub>2</sub>	79.6	79.2	78.3	77.5
Al <sub>2</sub> O <sub>3</sub>	20.1	20.8	21.7	22.5
Fe <sub>2</sub> O <sub>3</sub>	0.3	Tr	Tr	-

\* Rosenberg (1974) ≡ natural before hydrothermal treatment.

Tr: trace.

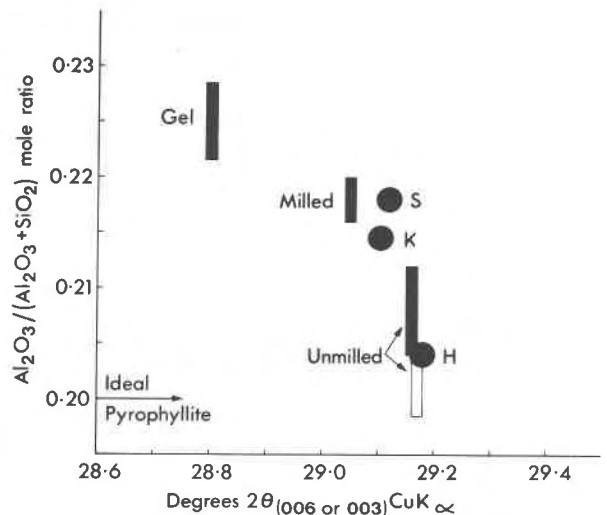


Fig. 1. The effect of the structural state of starting materials on pyrophyllite after hydrothermal treatment. Open bar, before hydrothermal treatment; solid bar, after hydrothermal treatment; length of bar approximates compositional range within one standard deviation; width of bar approximates precision of X-ray measurements. Circles, natural samples; H, Heller *et al.* (1962) chemical analysis, Raynor and Brown (1966), X-ray data; S, Swindale and Hughes (1968), chemical analysis, Wardle and Brindley (1972), X-ray data; K, Kodama (1958) chemical analysis, Brindley and Wardle (1970), X-ray data.

to X-rays, the latter, which is probably in a more disordered state, produces more extensive solid solution.

### Discussion

Broad X-ray reflection at low 2θ angles may be appreciably displaced toward larger *d*-spacings due to variations in the Lorenz-polarization factor. However, this factor changes only about 2 percent across the width (half-height) of the reflections measured. The resulting distortion is very slight and its effect on peak positions is assumed to be negligible.

Apparent displacements in X-ray diffraction maxima might be attributed to the effect of particle size; however, higher-order basal spacings are only slightly affected by particle size (Ross, 1968; Reynolds, 1968). Furthermore, if the effect of particle size on apparent lattice spacings is the same in pyrophyllite as in muscovite, then the reduction in the thickness of coherent scattering domains below 30 layers (~0.03 μm) should result in an apparent contraction rather than the observed expansion of (003) or (006) spacings (Ross, 1968; Reynolds, 1968). Thus, the observed enlargement of basal spacings and its relationship to chemical composition are believed to be real.

Experimental data confirm both the existence of

pyrophyllite solid solutions implied from the basal spacings of pyrophyllite synthesized in the previous study (Rosenberg, 1974) and the inference that the extent of solid solution is dependent on the structural state of starting materials. However, pyrophyllites synthesized in this study do not depart greatly from end-member composition. The structural formula of the gel pyrophyllite, the most extensive solid solution synthesized, calculated assuming that  $(Al + Si) = 6.0$ , is  $Al_{2.0}(Si_{3.8}Al_{0.2})O_{9.8}(OH)_{2.2}$ .

Basal spacings and  $Al_2O_3/(Al_2O_3 + SiO_2)$  ratios of three natural pyrophyllites are shown in Figure 1 for purposes of comparison. These samples are characterized by chemical data and calculated basal spacings from the literature (Fig. 1, S, K) or basal spacings calculated from cell dimensions given in the literature (Fig. 1, H). Small amounts of  $Fe^{3+}$  which may be due to the presence of traces of iron oxides (e.g. Fig. 1, S), have been neglected. Unfortunately few natural pyrophyllites have been adequately characterized. These three samples conform closely with the synthetic pyrophyllites produced in this study. Synthetic solid solutions crystallized from pyrophyllite composition are probably metastable (Rosenberg, 1974), whereas solid solutions from New Zealand (Fig. 1, S) and Japan (Fig. 1, K) which coexist with Al-rich minerals (e.g. kaolinite and diaspore; Swindale and Hughes, 1968) may be stable with respect to end-member pyrophyllite; this has yet to be established.

### Conclusions

Slightly non-stoichiometric pyrophyllite is believed to crystallize metastably from fine-grained or amorphous starting materials of pyrophyllite composition due to the entrapment of  $Al^{3+}$  in tetrahedral sites, charge balance being maintained by hydroxyl formation (Rosenberg, 1974). Ideally,  $Al^{3+}$  is entirely in octahedral coordination in pyrophyllite but it is free to enter tetrahedral sites during the hydrothermal recrystallization of structurally disordered or amorphous starting materials. Although both the milled pyrophyllite and the pyrophyllite gel are

amorphous to X-rays, the latter, which is probably in a more disordered state, produces more extensive solid solution. Thus, the structural state of starting materials appears to control the formation and extent of pyrophyllite solid solutions crystallized from pyrophyllite composition.

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