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Pyrophyllite Solid Solutions in the System Al_2O_3-SiO_2-H_2O

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Abstract

Pyrophyllite solid solutions have been synthesized in the system Al_2O_3-SiO_2-H_2O between 400° and 565°C at 2 kbar from a variety of starting materials using sealed gold tubes and conventional hydrothermal techniques. The duration of experiments was 3–9 weeks. Products were characterized by X-ray measurements and by infrared spectroscopy.

Appreciably larger basal spacings were observed for pyrophyllite synthesized from gels than for natural pyrophyllite; small amounts of quartz were present in these samples. Basal spacings of pyrophyllite synthesized from mixtures of kaolinite and quartz approach but do not equal those of natural pyrophyllite.

Rehydroxylation of dehydroxylated pyrophyllite under hydrothermal conditions suggests that enlargement of basal spacings cannot be due to dehydroxylation. Substitution of the type $Al^{3+} + H^+ = Si^{4+}$ is proposed to explain the observed variations. The coupled substitution of Al^{3+} and $(OH)^-$ for Si^{4+} and O^{2-} results in expanded basal spacings due largely to the formation of OH on the basal surface and in increased thermal stability due to the formation of H-bonds between oxygens in adjacent silica sheets. Analyses of natural pyrophyllite also suggest limited substitution of this type.

Failure to recognize these substitutions in synthetic samples accounts, in part, for discrepancies in the reported thermal stability of pyrophyllite. Phase characterization, often lacking, is essential in experimental studies of mineral stabilities.

Introduction

Since natural pyrophyllite is commonly believed to deviate only slightly from end-member composition (Deer, Howie, and Zussman, 1962), previous investigators have tacitly assumed that the theoretical end-member was present in the products of their experiments.

During the course of an experimental investigation of compositional variations in topaz (Rosenberg, 1972), inconsistencies were observed in the F/OH ratios of topaz coexisting with pyrophyllite which were thought to be related to variations in the composition of pyrophyllite. Simple substitution of F for OH could not account for the basal spacings of these pyrophyllites, and, therefore, compositional variations in the system without fluorine were suspected.

An investigation of pyrophyllite compositions in the system Al_2O_3-SiO_2-H_2O was clearly prerequisite to an understanding of fluorine substitution. Furthermore, compositional variability might account, in part, for the discrepancies in the upper thermal stability of pyrophyllite reported in the literature (Haas and Holdaway, 1973). Pyrophyllite, synthesized in the ternary system between 400° and 565°C at pressure of 2 kbar, has been characterized by X-ray and infrared techniques in an effort to resolve this problem (see Rosenberg, 1971).

Experimental Details

Conventional hydrothermal equipment and techniques were used throughout this study. All experiments were carried out in sealed, gold tubes and cold-seal pressure vessels.

Starting materials were natural pyrophyllite (Glendon, Moore County, North Carolina), pyrophyllite gels (Luth and Ingamells, 1965) and mechanical mixtures of pyrophyllite composition prepared using kaolinite (API No. 9, Mesa Alta, New Mexico) plus quartz (Minas Gerais, Brazil) and recrystallized $Al(OH)_3$ plus Cab-O-Sil (amorphous silica, dried). Natural pyrophyllite was ground to less than 200 mesh (<74 μm) under alcohol in an agate mortar; average grain size was on the order of 50 μm with only a small fraction less than 10 μm. Constituents of the mechanical mixtures were ground separately to less than 200 mesh under

alcohol in an agate mortar and then mixed together in the required proportions by grinding in a vibratory mill for 15 minutes. Grain size of the resulting mixtures varied from <1 μm to 73 μm; average grain size appeared to be about 10 μm, but was not uniform for different constituents of any given mixture (*e.g.*, quartz coarser than kaolinite).

The natural pyrophyllite used in this study is probably monoclinic (2*M*) according to the criteria of Brindley and Wardle (1970); it was found to contain small amounts of quartz and traces of kaolinite by X-ray diffractometry and optical microscopy. Portions of this specimen having X-ray diffraction maxima corresponding only to pyrophyllite were selected for chemical analysis. Although H_2O^+ was not determined, major-element chemistry (SiO_2, Al_2O_3, Fe_2O_3) was found to be virtually identical to that of a specimen from the same locality reported by Hendricks (1938; see also Deer, Howie, and Zussman, 1962, p. 118), and shown in Figure 2 (No. 4). Other constituents, determined by semi-quantitative spectro-chemical analysis, were present in trace amounts only.

Samples of these mixtures were sealed along with excess water (solid/water ratio ≅ 2/1 by weight) into gold capsules and subjected to temperatures between 400° and 575°C at 2 kbar for periods of 3 to 9 weeks. After quenching, products were identified by X-ray powder diffractometry and by optical microscopy.

Basal spacings of pyrophyllite were determined by measurement of the X-ray reflection at approximately 29.1° 2θ Cu*Kα* [2*M*(006) or 1*Tc*(003); Brindley and Wardle, 1970; Wardle and Brindley, 1972] against annealed, internal standards CaF_2 or CdF_2 which have conveniently located reflections at 28.30°(2θ) and 28.70°(2θ) respectively. Δ2θ values, which are all reported as measurements with respect to CaF_2, were obtained by averaging at least two measurements (scan rate, 1/4° min) per reflection and are known to within 0.01°(2θ). A precision of ± 0.005°(2θ) was attained for well-crystallized pyrophyllites by averaging four or more measurements.

Natural pyrophyllite from Glendon, Moore County, North Carolina, used as a starting material in this study, was found to have a Δ2θ of 0.860 ± 0.005°. Samples from two other localities in North Carolina were also measured (Δ2θ = 0.853 ± 0.005° and 0.856 ± 0.005°) to provide some assurance that this starting material was not unusual; Δ2θ values were the same within the limits of error of these measurements.

Identification of pyrophyllite polymorphs (Brindley and Wardle, 1970) was difficult because of interference caused by coexisting phases and because of the weakness of diagnostic X-ray reflections due to orientation effects and poor crystallinity of many synthetic samples. However, the polymorphic forms of several samples synthesized from each starting mixture are known with reasonable certainty.

Infrared spectrophotometry was used to study the OH-stretching bands of natural and synthetic pyrophyllite. Samples were prepared using conventional KBr pellet techniques (Lyon, 1967) and run on a Beckman IR-8 infrared spectrophotometer with a blank KBr pellet in the reference beam. Since individual crystals of synthetic pyrophyllite could not be resolved under the microscope, measurements of optical properties were not possible.

Experimental Results

Synthesis

The basal spacings and polymorphic form of natural pyrophyllite are essentially unchanged after hydrothermal treatment for periods of 3–4 weeks. (Fig. 1, open squares). All Δ2θ values are slightly less than that of the starting material but the apparent change is very small and may not be real. However, a somewhat larger change in basal spacings was observed in an experiment of 60 days duration at 475°C (Fig. 1, filled square). Δ2θ for this sample (0.831° ± 0.005°) is significantly lower than that of the starting material (0.860° ± 0.005°), suggesting that natural pyrophyllite does undergo an expansion of basal spacings under the conditions of these experiments.

Basal spacings of pyrophyllites synthesized from kaolinite, quartz mixtures (Fig. 1, triangles) at and above 500°C very closely approximate those of the natural material. Below this temperature Δ2θ values obtained for pyrophyllite synthesized in experiments of 3–4 weeks duration (Fig. 1, open triangles) approach but do not equal the value for natural pyrophyllite; basal spacings undergo relatively little change in experiments of longer duration (Fig. 1, filled triangles) and remain larger than for natural pyrophyllite. Several of these synthetic pyrophyllites were found to be monoclinic or a mixture of monoclinic and triclinic forms. Decomposition

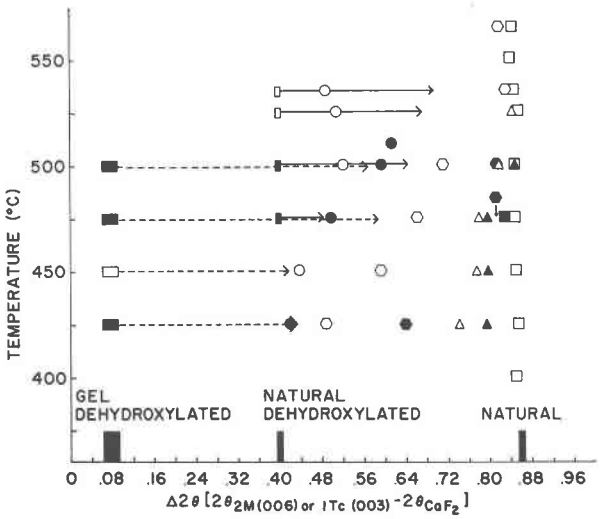

FIG. 1. Variation in $\Delta 2\theta$ ($2\theta_{2M(006)}$ or $_{1Tc(003)}$-$2\theta_{CaF_2}$) of synthetic pyrophyllite with temperature. Starting materials: Squares, natural pyrophyllite; triangles, kaolinite and quartz; hexagons, gibbsite and Cab-O-Sil; circles, gels; rectangles, dehydroxylated pyrophyllite. Rehydroxylation experiments: Solid arrows, natural pyrophyllite; dashed arrows, gel pyrophyllite. Duration of experiments: Open symbols, 3–4 weeks; filled symbols, 8–9 weeks. Width of symbols approximates precision of measurements.

products of pyrophyllite [a synthetic andalusite-like phase called X-andalusite by Carr and Fyfe (1960) and/or mullite] appear in experiments with natural pyrophyllite and mixtures of kaolinite and quartz at and above 500°C.

Considerably larger basal spacings were recorded for pyrophyllite synthesized from gels (Fig. 1, circles). Small amounts of quartz were detected in these samples by X-ray diffraction and/or under the microscope. Although basal spacings were found to decrease somewhat with increased temperature and duration of experiments (Fig. 1, filled circles), $\Delta 2\theta$ values do not approach those of natural pyrophyllite. Gel pyrophyllites, which are invariably triclinic, undergo no further change in basal spacings when used as starting materials in experiments of 3–4 weeks duration at temperatures below 550°C. At or above 550°, pyrophyllite X-ray reflections become very weak, basal spacings are abruptly further enlarged, and X-andalusite (and additional quartz) appears in the products of some experiments. Precise measurements were not possible for these weak reflections, but $\Delta 2\theta$ values were estimated to be in the range $-0.40°$ to $-0.48°$ (not shown in Fig. 1). This abrupt expansion of basal spacings has been reversed by using the solid products of an experiment at 560°C as the starting material for an experiment at 425°C. After 65 days the products were indistinguishable from those of experiments with gels at 425°C.

Pyrophyllite has also been synthesized from a mixture of gibbsite and Cab-O-Sil (Fig. 1, hexagons). Pyrophyllite and quartz were the only products of experiments above 450°C, but at lower temperatures boehmite and traces of diaspore were also present. $\Delta 2\theta$ values at higher temperatures closely approach those of natural pyrophyllites. Considerably larger basal spacings were recorded at lower temperatures, but their rapid decrease with increased duration of experiments (Fig. 1, filled hexagons) suggests that given sufficient time $\Delta 2\theta$ values would approach those obtained for mixtures of kaolinite and quartz (Fig. 1, triangles). The triclinic polymorph was identified in two samples synthesized at high temperatures.

It appears that end-member pyrophyllite cannot be synthesized under the *P-T* conditions of this study in experiments of 8–9 weeks duration. Differences in basal spacings imply compositional variations which are dependent on the nature of starting materials as well as on temperature and duration of experiments. Pyrophyllites synthesized from mechanical mixtures are believed to be unstable at and above 500°C and metastable below 500°C, while gel pyrophyllites appear to be unstable at or above 550°C and metastable below 550°C. Furthermore, the expansion of the basal spacings of natural pyrophyllite with time, particularly at 475°C, suggests that the end-member composition may not be stable in the temperature range of this study.

Dehydroxylation and Rehydroxylation

According to Brindley and Wardle (1970), dehydroxylation of pyrophyllite is accompanied by an enlargement of basal spacings. In order to test dehydroxylation as a possible explanation for the enlarged basal spacings recorded in this study, $\Delta 2\theta$ values of the natural material were measured after heating to 850°C for 2–3 hours at 1 atm. Basal spacings ($\Delta 2\theta = 0.40° \pm 0.005°$) approximately equal to those of gel pyrophyllites at 425°C were observed (Fig. 1). However, it was found that the basal spacings of dehydroxylated pyrophyllite contract after hydrothermal treatment (Fig. 1, solid arrows), suggesting partial rehydroxylation.

Gel pyrophyllites may also be dehydroxylated

under similar conditions with a like enlargement of basal spacings ($\Delta 2\theta = 0.05°–0.09°$) and then fully rehydroxylated hydrothermally (Fig. 1, dashed arrows). Thus, gel pyrophyllites are hydroxylated, and dehydroxylated gel pyrophyllites are not stable under hydrothermal conditions.

Infrared spectroscopy was used to confirm these inferences. Dehydroxylated pyrophyllites show no OH-stretching band while both natural and gel pyrophyllites have strong OH-stretching bands and are presumably fully hydroxylated. OH-stretching band intensities of natural pyrophyllite are unchanged by hydrothermal treatment. Therefore, dehydroxylation cannot account for observed variations in basal spacing. Gel pyrophyllites and their rehydroxylated equivalents consistently show more intense OH-stretching bands than does natural pyrophyllite and thus appear to be OH-rich. In accord with partial rehydroxylation, "rehydroxylated" natural pyrophyllites have weaker OH-stretching bands than natural pyrophyllite and the intensities of these bands are proportional to the measured $\Delta 2\theta$ values. No evidence has been found to suggest the presence of hydronium (H_3O^+) in any of these samples.

Interpretation

Enlarged basal spacings, apparent OH-enrichment, and coexistence of quartz with pyrophyllite synthesized from gels suggest the crystallization of pyrophyllite solid solutions involving the coupled substitution of Al^{3+} and $(OH)^-$ for Si^{4+} and O^{2-} respectively. Other starting materials apparently result in less extensive solid solutions of the same nature, each having the structural formula $Al_2Si_{4-x}Al_xO_{10-x}(OH)_x(OH)_2$.

It has been suggested that Al^{3+} tends to enter tetrahedral sites during the crystallization of pyrophyllite gels (Roy and Osborn, 1954). Entrapment of Al^{3+} in these sites during the crystallization of fine-grained or amorphous starting materials under hydrothermal conditions could result in the formation of Al-,OH-rich pyrophyllite solid solutions having larger unit-cell dimensions than those of end-member pyrophyllite. Abrupt expansion of the basal spacings of gel pyrophyllites at or just above 550°C, which is accompanied by a large increase in the proportion of quartz, seems to be caused by the exsolution of silica from pyrophyllite solid solutions leaving small amounts of an unstable Al-rich pyrophyllite which decomposes to X-andalusite.

In a study of the effect of iron substitution on the unit-cell dimensions of talc, Forbes (1969) observed the enlargement of basal spacings and the presence of excess quartz. He proposed substitution of the type $Fe^{3+} + H^+ = Si^{4+}$ and accounted for the significantly enlarged basal spacings of talc solid solutions by suggesting that protons are added to oxygen atoms bridging Si^{4+} and Fe^{3+} tetrahedra. Overbonding would then increase electrostatic bond lengths resulting in the elevation of bridging $(OH)^-$. Neglecting the probable lateral displacement of Fe^{3+} and Si^{4+} parallel to the basal sheets, the predicted increase in bond length (0.12 Å) for an overbonding of 0.75 would result in a maximum increase in hydroxyl elevation of 0.30 Å (Forbes, 1969).

The observations and implications in the talc study are clearly qualitatively analogous to those for pyrophyllite. Furthermore, the maximum Δd_{001} reported by Forbes (~0.12 Å) is only slightly smaller than that observed for pyrophyllite (~0.14 Å). However, in pyrophyllite, as in other dioctahedral sheet structures, apical oxygen atoms adjacent to octahedral voids are considerably underbonded (0.5), thus providing an alternate site for hydroxyl formation (Forbes, 1972). The enlargement of basal spacings due to hydroxyl formation at apical sites should be quite small as compared with that produced by hydroxyl formation at basal sites and cannot account for the observed variations in basal spacings. Therefore, hydroxyl formation must take place at least partially at basal sites.

The thermal stability of pyrophyllite solid solutions should be higher than that of end-member pyrophyllite as a consequence of hydroxyl formation on the basal surface. In end-member pyrophyllite, bonding between adjacent silica sheets is limited to very weak van der Waals forces between basal oxygens. Hydroxyl formation on the basal surface should result in the formation of hydrogen bonds between basal oxygens, thus strengthening the weakest bonds in the structure which determine its thermal stability.

Natural Pyrophyllite Solid Solutions

Ten analyses of natural pyrophyllite have been selected from the relatively small number reported in the literature on the basis of their apparent reliability and their close approach to the system Al_2O_3-SiO_2-H_2O. Analyses with an alkali-content $(Na_2O + K_2O) \geq 0.5$ wt percent were arbitrarily rejected. An inverse relationship appears to exist

between SiO_2 and both R_2O_3 and H_2O^+ in these samples (Fig. 2) suggesting that the coupled substitution proposed for synthetic pyrophyllite occurs in natural materials. Although the extent of this substitution is small, most natural pyrophyllites may be solid solutions.

Small replacements of Si^{4+} by Al^{3+} have been recognized previously (*e.g.*, Deer, Howie, and Zussman, 1962). Moreover, Swindale and Hughes (1968) concluded that small excesses of alumina and water are present in a pyrophyllite from New Zealand (Fig. 2, S) and that Al^{3+} substitutes for Si^{4+} in this material, which is triclinic (Brindley and Wardle, 1970) and has a $\Delta 2\theta$ of approximately 0.805 [calculated from refined unit-cell dimensions (*ibid.*)].

Discussion

Despite differing experimental procedures and the inadequacies of individual studies (Haas and Holdaway, 1973), it has been difficult to account for the wide range of results obtained in earlier studies concerned with the upper thermal stability of pyrophyllite—namely, 565°C at 2 kbar (Aramaki and Roy, 1963), and 378°C at 2.4 kbar (Haas and Holdaway, 1973). The previously unsuspected deviations from end-member composition described in this paper are believed to partially explain these discrepancies.

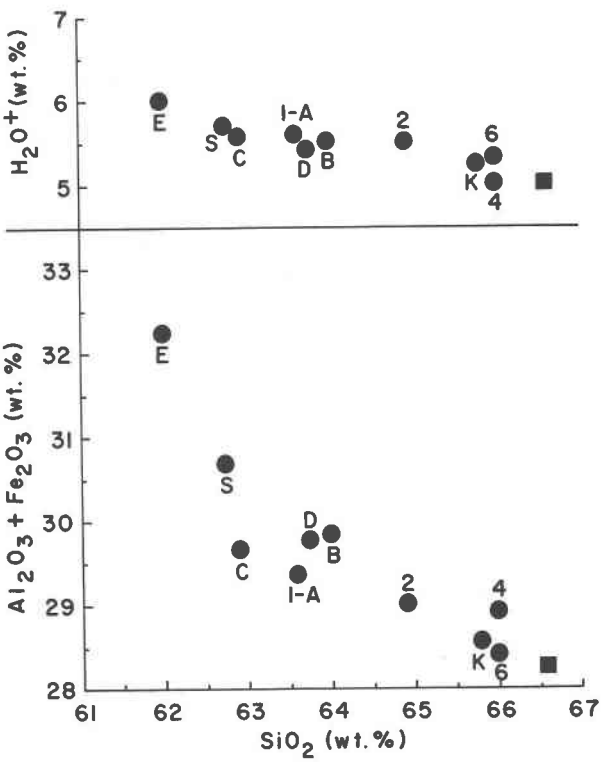

FIG. 2. Variation of R_2O_3 ($Al_2O_3 + Fe_2O_3$) and H_2O^+ with SiO_2 in natural pyrophyllite. Circles, analyses from the literature: 1, 2, 4, 6, Deer, Howie, and Zussman, 1962; A-E, Kodama, 1958; S, Swindale and Hughes 1968; K, King and Weller, 1970. Squares, theoretical end-member.

A correlation seems to exist between the nature of starting materials and the isobaric decomposition temperature obtained for the reaction

pyrophyllite = andalusite + 3 quartz + water.

Pyrophyllites synthesized from fine-grained or amorphous starting materials appear stable up to higher temperatures than those synthesized from coarser-grained crystalline materials. Pyrophyllite solid solutions may have been produced in these experiments (and in nature) during the hydrothermal crystallization of very fine-grained or amorphous starting materials due to the entrapment of Al^{3+} in tetrahedral sites. The extent of solid solution would then be dependent on the proportion of these materials present in the starting mixtures. Thermal stability should increase with the extent of solid solution due to the formation of H-bonds between oxygens in adjacent silica sheets.

In this light, the decomposition temperature (565°C at 2 kbar) obtained by Aramaki and Roy (1963) is readily explained. Using gels as starting materials, they unknowingly produced extensive solid solutions similar in composition and in apparent thermal stability to those synthesized from gels in this study.

Starting materials (mixtures of natural minerals) used by Althaus (1969) were subject to extreme grinding which reduced grain size to the micron or sub-micron range. Velde and Kornprobst (1969) used mixtures of natural and synthetic minerals, presumably finely ground, as well as gels to study the decomposition reaction. In the present investigation, finely ground mixtures of kaolinite + quartz and Cab-O-Sil + gibbsite produced pyrophyllite solid solutions with apparent thermal stabilities comparable to those reported by Althaus (1969) and by Velde and Kornprobst (1969) (~490°C at 2 kbar). Degradation of crystal structures by grinding, particularly by dry grinding of OH-bearing minerals, is well-known. Disordered or amorphous material produced by grinding may contribute an Al-,OH-rich component to pyrophyllite crystallized under hydrothermal conditions.

Investigators using the more sensitive single crystal (crystal-growth) method have observed much lower decomposition temperatures—namely, 410°C ± 15° at 1.8 kbar (Kerrick, 1968) and 370°–393°C at 2.4 kbar (Haas and Holdaway, 1973)—than those obtained by the synthesis method. A direct comparison of the results obtained using these two methods is not possible because factors other than the nature of starting materials may be involved. However, the fact that the lowest decomposition temperatures reported to date (Haas and Holdaway, 1973) were obtained using materials which were subjected to moderate grinding and then elutriated to remove the finest particles is considered to be significant. Since lower decomposition temperatures imply compositions closer to that of the end-member, it seems likely that end-member pyrophyllite is not a stable phase under the conditions of the present investigation. Reversals of the decomposition reaction at higher temperatures (*e.g.*, Kerrick, 1968) probably involve pyrophyllite solid solutions.

Haas and Holdaway (1973) report spurious weight gains of andalusite crystals within the stability field of pyrophyllite which they attribute to "a reaction of unknown nature." The unknown reaction could be the formation of pyrophyllite solid solutions according to the equation,

$$Al_2Si_4O_{10}(OH)_2 = Al_{2x}Si_{4-3x}Al_xO_{10-6x}(OH)_x(OH)_{2-x} + 3XSiO_2.$$

Observed weight gains of andalusite may have been due to the growth of quartz on these crystals. Kerrick (1968) has carefully documented an example of quartz growth on andalusite. The fact that the spurious weight gains are observed only at lower pressures (*e.g.*, 2.4 kbar, Haas and Holdaway, 1973) is in accord with the formation of solid solutions having larger molar volumes than the end-member. Furthermore, the frequency and magnitude of these weight gains seems to be slightly greater in the presence of excess Al^{3+} (PDAW reaction, Haas and Holdaway, 1973) than in the absence of excess Al^{3+} (PAQW reaction, *ibid.*). This is also consistent with the explanation offered. Small weight gains due to the formation of pyrophyllite solid solutions would be observable only within the stability field of pyrophyllite close to its decomposition temperature where andalusite would otherwise be expected to lose weight very slowly. Pyrophyllite solid solutions, if actually formed in this study, could be stable or metastable with respect to the end-member; sufficient amounts of disordered material may have been present in starting mixtures, despite careful treatment, to produce limited solid solution.

The effect of compositional variations on the thermal stability of pyrophyllite is probably not large within the range of natural compositions. Haas and Holdaway (1973) have shown that the natural triclinic pyrophyllite solid solution from New Zealand, analyzed by Swindale and Hughes (1968, Fig. 2, S) and studied by Brindley and Wardle (1970), undergoes apparent decomposition at about 410°C and 4.8 kbar. Andalusite weight gains are approximately the same as for the monoclinic pyrophyllite from Indian Gulch, California, under similar conditions. Unfortunately, this pyrophyllite, which was used as a starting material by Haas and Holdaway (1973) and by Kerrick (1968), has not been adequately characterized. A chemical analysis (Haas and Holdaway, 1973) suggests that it may be a solid soltuion, but the analysis appears to be in error. If the Indian Gulch pyrophyllite is a solid solution, then the stability limit of the end-member should lie at even lower temperatures than those reported by Haas and Holdaway (1973).

Pyrophyllite solid solutions have been shown to exist in this study, but their formation mechanism and stability with respect to the end-member have not yet been firmly established. While a *P-T* stability field for compositions close to that of the end-member is possible in the light of the present study, the apparent dependence of the extent of solid solution on the nature of starting materials implies metastability and it seems more likely that all solid solutions are metastable with respect to the end-member. Experiments are now underway to test these inferences.

Conclusions

In experimental mineralogy it is usually assumed that, if an end-member mineral composition is used as a starting material and products appear to contain only that mineral, then the composition of the synthetic mineral is that of the end-member. The results of this study should serve to caution against such assumptions.

Starting with end-member composition, it has proved to be difficult or impossible to synthesize theoretical pyrophyllite even in experiments of rela-

tively long duration, due to the intervention of substitutions of the type $Al^{3+} + H^{+} = Si^{4+}$. The enlarged basal spacings observed for the resulting pyrophyllite solid solutions are believed to be due mainly to the formation of $(OH)^{-}$ on the basal surface; increased thermal stability probably results from the formation of H-bonds between oxygens in adjacent silica sheets. Solid solutions are believed to form metastably from fine-grained or amorphous starting materials due to the entrapment of Al^{3+} in tetrahedral sites. Many natural pyrophyllites also deviate significantly from end-member composition.

The existence of previously unsuspected pyrophyllite solid solutions can account for discrepancies in the reported thermal stability of pyrophyllite in a general manner. Unfortunately, it is not possible to reevaluate previous experimental investigations at present because starting materials and/or products have not, as a rule, been adequately characterized. Reexamination of the natural and synthetic pyrophyllites of previous investigations, in the light of the present study, might prove to be very instructive. However, a definitive study will probably be necessary to resolve this long-standing problem.

Acknowledgments

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