

Synthesis of pyrophyllite polytypes and mixed layers

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Abstract

Monoclinic, triclinic, and disordered pyrophyllites have been synthesized in hydrothermal experiments conducted at 2 kbar between 355° and 450°C. The monoclinic variety formed at the lowest temperature, and the disordered variety formed after a short run time at 360°C. The triclinic polytype formed at higher temperatures. Varying the Al/Si ratio of the system did not greatly affect this pattern of reaction. Mixtures of mixed-layer pyrophyllite/smectite and margarite/smectite were synthesized from a gel which had a composition halfway between Ca-beidellite and pyrophyllite at 375° and 400°C, thereby suggesting that these phases may be found in nature.

Introduction

Pyrophyllite is a geologically important but relatively little-studied mineral that has recently been shown to exist in several polytypic and mixed-layered forms. Natural 2-layer monoclinic and 1-layer triclinic pyrophyllites have been analyzed by Brindley and Wardle (1970). They also described a disordered pyrophyllite which was not amenable to detailed analysis. Randomly interstratified and partly-ordered mixed-layer pyrophyllite/smectites with a range of expandabilities have been synthesized by Eberl (1979) from natural montmorillonite in hydrothermal solutions containing $AlCl_3$. These phases have not yet been found in nature.

The present hydrothermal experiments were undertaken to discover genetic relationships between the polytypes, and to synthesize mixed-layer pyrophyllite/smectite starting from a gel rather than from montmorillonite. It was hoped that the former experiments would prove to be petrologically useful, although there would be the usual problem of applying relationships found in the chemically simple, short-term, experimental system to nature. A synthesis of pyrophyllite/smectite from completely disordered starting material would indicate (although far from prove) that the phase is not simply a metastable reaction product of montmorillonite, and would increase the likelihood that it will one day be found in nature.

Synthesis experiments have revealed that illite polytypes are related in the series $1M_d \rightarrow 1M \rightarrow 2M$

with increasing temperature and pressure (Yoder and Eugster, 1955; Velde, 1965), and that the formation of pseudomonoclinic (*b*-axis disordered) and triclinic (*b*-axis ordered) kaolinite is a function of both temperature and the Al/Si ratio of the system, with synthesis of the triclinic form favored by higher temperature and a greater Al/Si ratio (Eberl and Hower, 1975). Given this experience with illite and kaolinite polytypes, both temperature and the Al/Si ratio were varied in an attempt to synthesize the polytypes of pyrophyllite.

Experimental techniques

Starting compositions included gels with Al/Si ratios corresponding to pyrophyllite (Al:Si = 1:2), pyrophyllite + 2 quartz (Al:Si = 1:3) and pyrophyllite + Ca-beidellite (Al:Si:Ca = 2.33:3.67:0.165). They were prepared by the method of Hamilton and Henderson (1968), with the exception of the gel used in run 8 (Table 1) which was prepared according to Luth and Ingamells (1965). Details of hydrothermal techniques have been described elsewhere (Eberl and Hower, 1976). Briefly, starting compositions were run in welded gold tubes with an equal weight of distilled water at 2 kbar, water pressure. Run products were mounted on glass slides and X-rayed at 1° 2 θ per minute with Ni-filtered $CuK\alpha$ radiation with a Norlco diffractometer. Pyrophyllite polytypes were identified from peak positions and patterns given in Brindley and Wardle (1970) and by comparison with

Table 1. Hydrothermal runs made at 2 kbar

Run no.	Gel composition	Temp. (°C)	Time (days)	Run products
1	pyrophyllite	355	38	monoclinic pyrophyllite
2	pyrophyllite	360	11	disordered pyrophyllite
3	pyrophyllite	375	38	triclinic pyrophyllite
4	pyrophyllite	380	12	triclinic pyrophyllite
5	pyrophyllite	400	38	triclinic pyrophyllite
6	pyrophyllite	430	12	triclinic pyrophyllite
7	pyrophyllite	450	38	triclinic pyrophyllite, quartz
8	pyrophyllite*	380	169	pyrophyllite, quartz
9	pyrophyllite + 2 quartz	355	38	monoclinic pyrophyllite
10	pyrophyllite + 2 quartz	375	38	triclinic pyrophyllite, cristobalite
11	pyrophyllite + 2 quartz	380	12	triclinic pyrophyllite (poor)
12	pyrophyllite + 2 quartz	400	38	triclinic pyrophyllite
13	pyrophyllite + 2 quartz	430	12	triclinic pyrophyllite (poor)
14	pyrophyllite + 2 quartz	450	38	triclinic kaolinite
15	pyrophyllite + Ca-beidellite	375	38	pyrophyllite/smectite (30)**, margarite/smectite (70)
16	pyrophyllite + Ca-beidellite	400	38	pyrophyllite/smectite, margarite/smectite
17	pyrophyllite + Ca-beidellite	450	38	beidellite, kaolinite

*Gel prepared by the method of Luth and Ingamells (1965). All other gels prepared by the method of Hamilton and Henderson (1968).
 **Number in parenthesis refers to percent smectite in the mixed-layer phase.

samples given to our laboratory by Dr. Brindley (Fig. 1). Mixed-layer pyrophyllite/smectite was identified from calculated X-ray patterns computed with a program modified from Reynolds and Hower (1970), and from patterns presented in Eberl (1979).

Experimental results

Both monoclinic and triclinic pyrophyllite were synthesized from the pyrophyllite gel (runs 1 and 3–6 in Table 1; Fig. 2). Monoclinic pyrophyllite formed at the lowest temperature (355°C, run 1), whereas the triclinic variety formed at 375°C and above. A short run at 360°C yielded disordered pyrophyllite (run 2), for which no X-ray reflections appear on the band-head beginning at 4.42Å. The long run at 380°C (run 8, Fig. 3) and the highest-temperature run (run 7) produced pyrophyllite plus quartz, suggesting that these polytypes do not have the ideal composition, as will be discussed. The polytype for run 8 (Fig. 3) could not be determined. If the 4.26Å peak for this sample is entirely due to quartz, then the polytype is the disordered form. A comparison between this peak and the other quartz reflection at 3.34Å, however, suggests that the 4.26Å peak is too intense to be entirely quartz. Thus the peak could also be a triclinic pyrophyllite reflection, except that the other important reflection at 4.06Å is missing.

Decreasing the Al/Si ratio of the system did not change significantly the pattern of reaction (runs 9–13), except for the 450°C run which, surprisingly, formed triclinic kaolinite rather than pyrophyllite. The pyrophyllites formed in runs 9–13 were not as well-crystalline as their lower-silica counterparts.

The pyrophyllite/beidellite gels produced mixtures of mixed-layer pyrophyllite/smectite and margarite/smectite at 375° and 400° (runs 15–16), and beidellite plus kaolinite at 450°C (run 17). The X-ray pattern for the 375°C run is given in Figure 4 with a computer-simulated pattern. The simulated pattern, which was constructed by adding together computed profiles for 70% expandable randomly interstratified margarite/smectite and 30% expandable randomly interstratified pyrophyllite/smectite, is a satisfying match: peak positions correspond exactly with the real pattern, although intensities of the low angle scattering and the peak at 8.90Å are slightly different. In addition, there is a very weak peak at 2.53Å in the real pattern which is not accounted for in the calculated pattern. Basal spacings used in the calculation were: margarite = 9.6Å, pyrophyllite = 9.2Å, and smectite = 16.9Å, with an equally weighted crystallite size of 10 to 15 layers. Expandabilities for run 16 could not be determined due to poor X-ray intensities.

Conclusions

Monoclinic and triclinic pyrophyllite are related through changing temperature in the hydrothermal systems studied here. Monoclinic pyrophyllite is the low-temperature form. Mixtures of monoclinic and triclinic pyrophyllite did not appear in these experiments, although they have been found in nature (Brindley and Wardle, 1970). Disordered pyrophyllite is related to the monoclinic form by reaction time: it formed after a short run time at 360°C. Changing the Al/Si ratio of the system did not

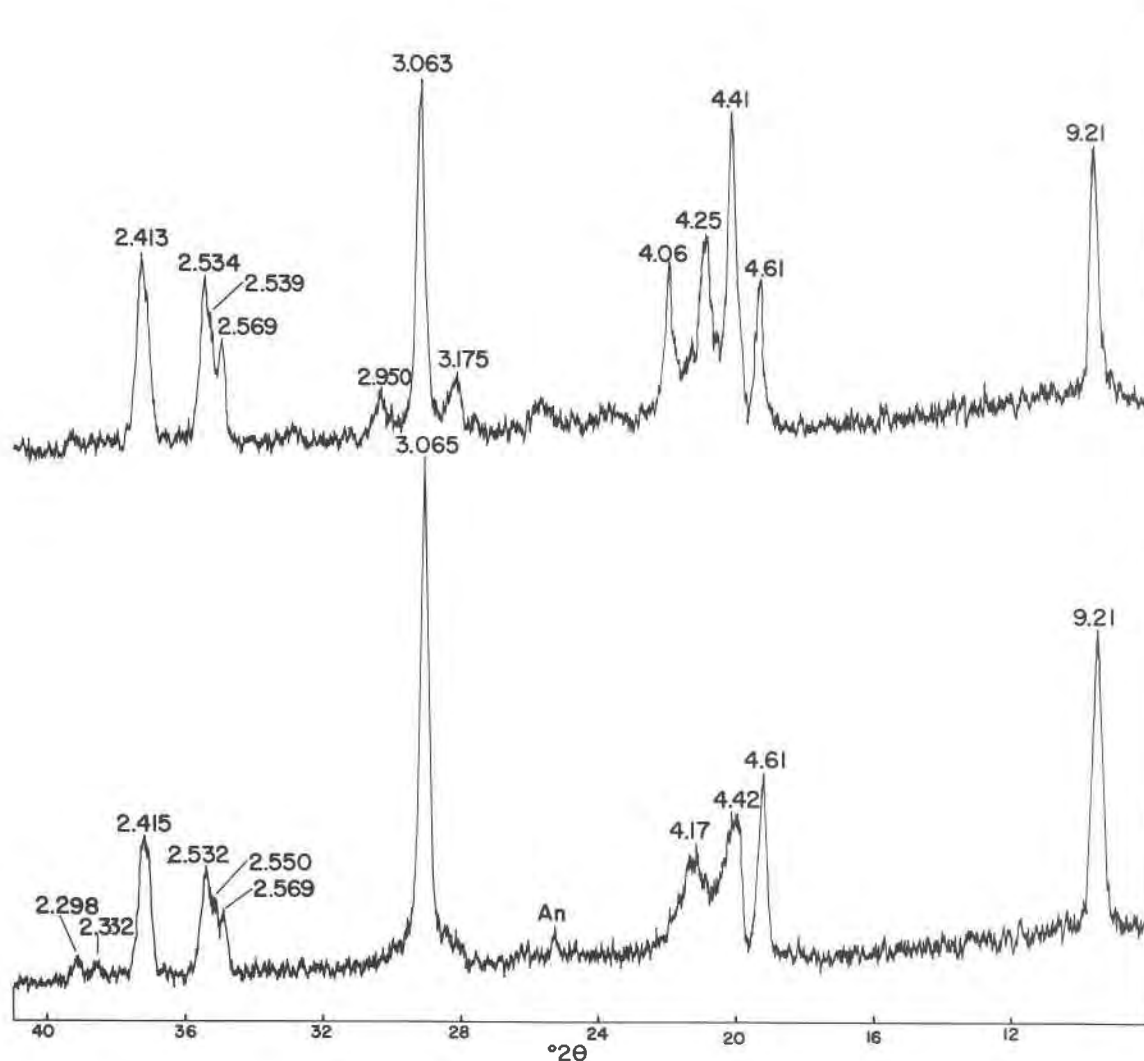


Fig. 1. X-ray diffraction patterns of triclinc pyrophyllite from New Zealand (reference #1 of Brindley and Wardle, 1970) at the top, and monoclinic pyrophyllite (reference #3) from Honami at the bottom. An = anatase.

change the general pattern of reaction, although the pyrophyllite + 2 quartz composition did form kaolinite at 450°C. This product was surprising, since kaolinite was thought to disappear in such a system at 350°C (Eberl and Hower, 1975).

The formation of pyrophyllite plus quartz from pyrophyllite gel in runs 7 and 8 indicates that pyrophyllite in these runs may be richer in aluminum than ideal pyrophyllite. Rosenberg (1974) also suggests that some pyrophyllites have more aluminum than the ideal, and also bases his argument on the crystallization of pyrophyllite plus quartz from pyrophyllite gels. He proposes that this extra Al^{3+} substitutes for Si^{4+} in the tetrahedral sheet and is electrically balanced by H^+ associated with the basal

oxygen plane. Evidence for the $Al^{3+} + (OH)^- = Si^{4+} + O^{2-}$ coupled substitution is given by hydroxyl enrichment for synthetic pyrophyllites as shown by infrared analysis, and by chemical analyses of natural pyrophyllites which show an inverse relationship between Si^{4+} and both R_2O_3 and structural water. He found no evidence for H_3O^+ in the structure. Evidence for the position of the extra H^+ on the basal oxygen plane is founded on enlarged basal spacings for synthetic pyrophyllites; Rosenberg feels that H^+ associated with apical oxygens could not sufficiently increase the basal spacings to give the measured values. Giese (1975), however, has shown that an imbalance in charge in the tetrahedral sheet of pyrophyllite would result in a strong electrostatic repulsion be-

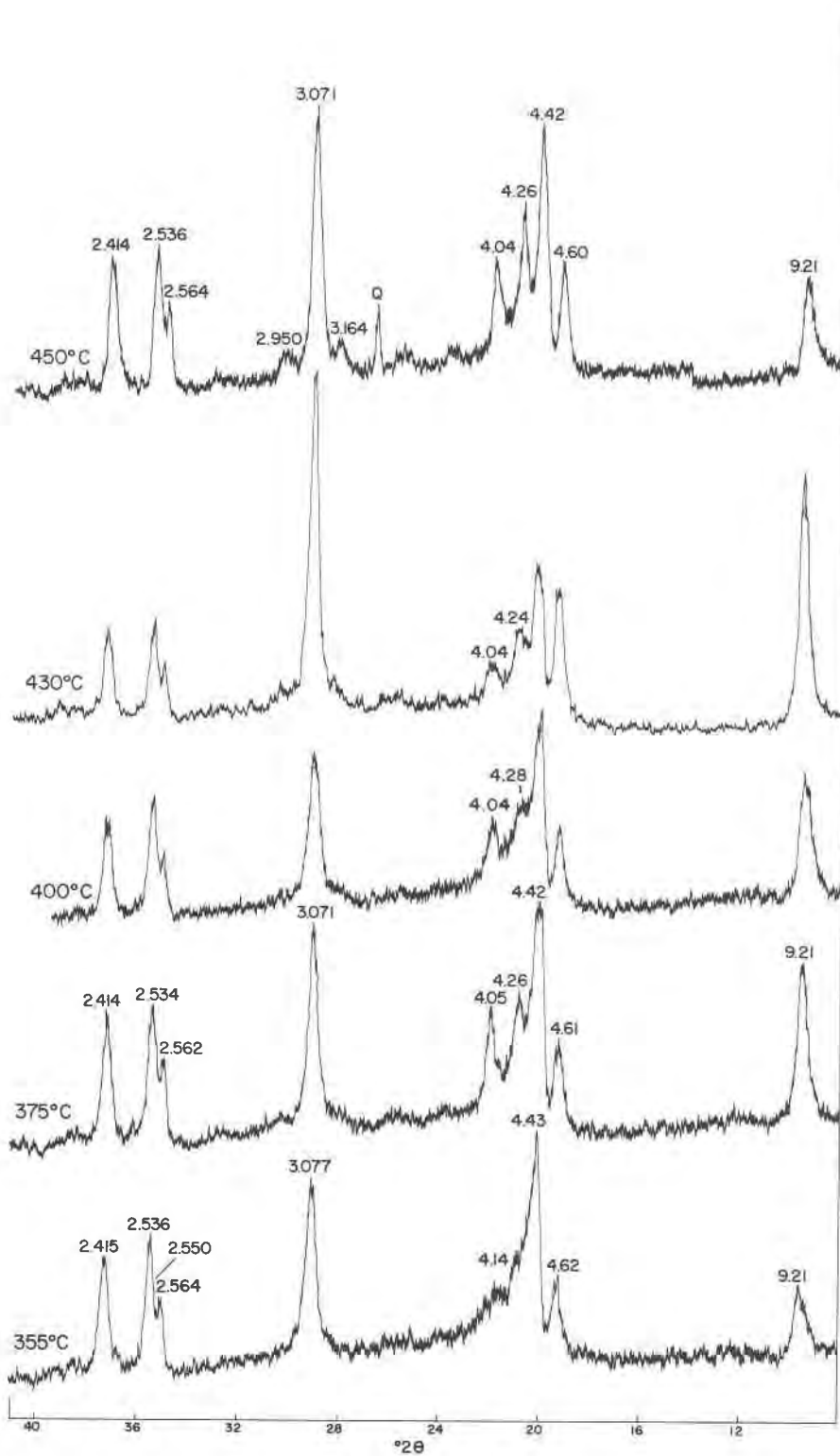


Fig. 2. X-ray diffraction patterns of synthetic pyrophyllites. From bottom to top, products are from runs 1, 3, 5, 6, and 7 (see Table 1).

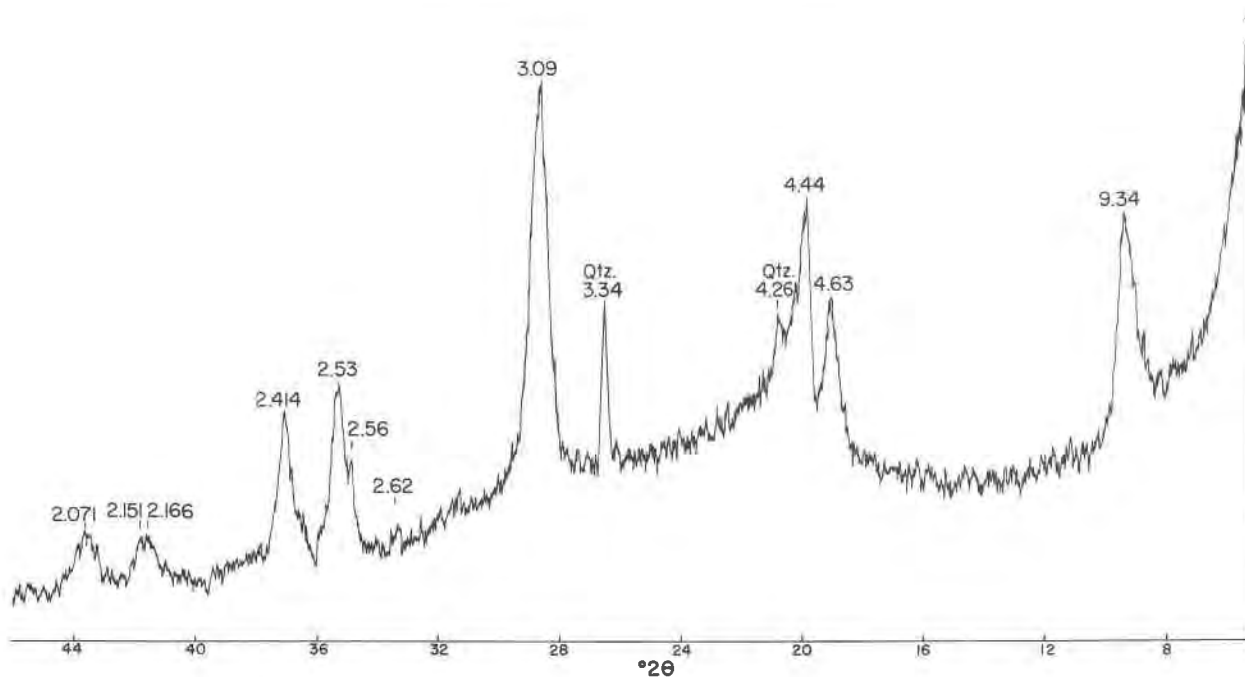


Fig. 3. Pyrophyllite and quartz formed in run 8.

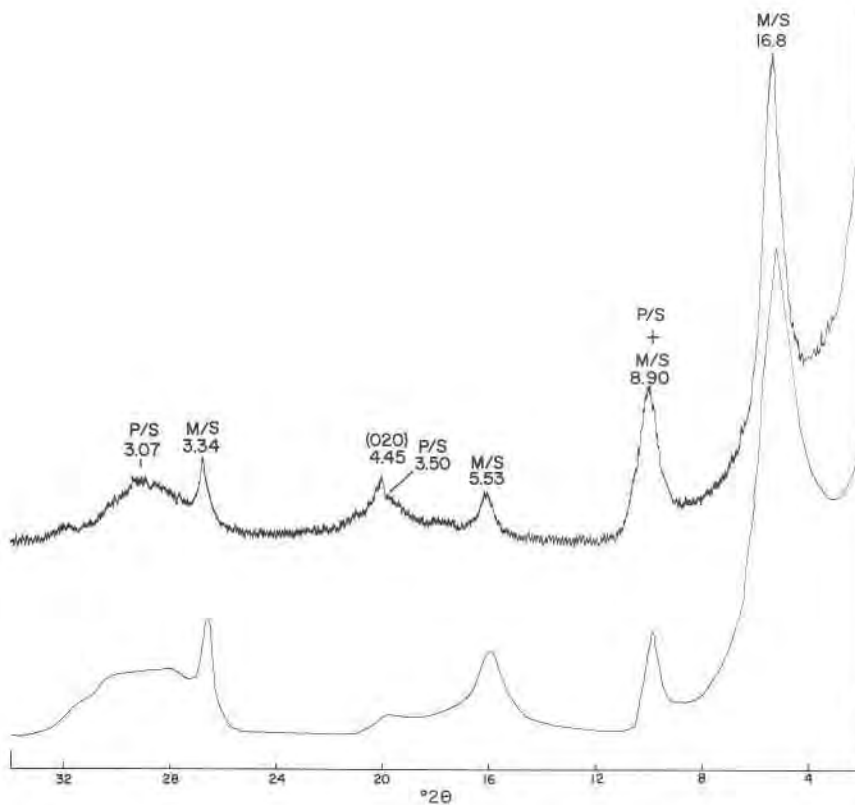


Fig. 4. X-ray diffraction pattern of a mixture of randomly interstratified pyrophyllite/smectite (P/S) and randomly interstratified margarite/smectite (M/S) formed in run 15, with its calculated profile beneath.

tween layers. Presumably this repulsion could also yield an enlarged spacing even though the extra H⁺ was associated with apical oxygens. An enlarged basal spacing was seen in one of the present runs which formed quartz (run 8, Fig. 3).

The present experiments further demonstrate that mixed-layer pyrophyllite/smectite can be synthesized directly from the gel. The formation of margarite/smectite in addition to pyrophyllite/smectite in these runs from a 50:50 pyrophyllite:Ca-beidellite gel makes sense chemically, since the run composition lies on a chemical join between pyrophyllite and margarite.

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