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INFRARED STUDY OF CO_2 INCORPORATION INTO PYROPHYLLITE [$Al_2Si_4O_{10}(OH)_2$] DURING DEHYDROXYLATION

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Abstract—We report infrared spectroscopic observations of the incorporation of CO_2 into pyrophyllite that has been heated between 200ºC and 1250ºC for periods of 15 min, 1 h and 5 days. The presence of CO_2 is characterized by the ν_3 band of CO_2 near 2347 cm^{-1}, detectable in samples in which dehydroxylation has commenced after heating above 450ºC. With increasing temperature, the CO_2 signal becomes more intense. The signal reaches its maximum intensity near 800ºC with an annealing time of 15 min. Further heating leads to a decrease in the CO_2 signal and the occurrence of an extra signal near 2156 cm^{-1} that implies the presence of CO. The process is characterized by significant time-dependence, indicating its kinetic nature. The peak positions of CO_2 signals show systematic variations with temperature. Our results suggest that the CO_2 molecule is associated with the local structure rather than being present as free gaseous CO_2, and that the local structure of pyrophyllite is gradually modified during high-temperature treatments. However, no signals related to carbonate molecules (CO_3^{2-}) were detected. The results suggest that CO_2 or other carbon-based molecules may diffuse into some clay minerals during dehydroxylation and may become altered due to structural modifications at high temperatures. This may have significance for possible CO_2 sequestration in shales and clay formations.

Key Words—CO_2, CO, Dehydroxylation, Infrared Spectroscopy, Pyrophyllite, Sequestration.

INTRODUCTION

Pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, is an important industrial resource, especially in the manufacture of ceramics, glass, refractory materials and pressure-transfer media. A better understanding of what happens in pyrophyllite at the atomic level in high-temperature environments is of importance and useful for these industrial applications. Furthermore, pyrophyllite may be regarded as a model dioctahedral structure from which one may develop models of the behavior of more complex layer silicates. The process of H_2O-CO_2 exchange can be anticipated as a control in CO_2 sequestration within soils and shale formations. Mineral sequestration has been suggested as a potentially important and permanent sink for anthropogenic CO_2 emissions associated with the use of fossil fuels. The mechanisms by which carbonation processes occur in potential sink minerals remain unclear, although there has been significant recent effort to unravel the reaction processes (Béarat *et al.*, 2002).

Pyrophyllite is a 2:1 aluminosilicate. It has a dioctahedral layer structure in which a sheet of octahedrally coordinated Al ions is sandwiched between two sheets of linked SiO_4 tetrahedra (Bailey, 1966; Rayner and Brown, 1966; Wardle and Brindley, 1972). Heating pyrophyllite to high temperatures results in dehydroxylation and phase transformations. Extensive studies have been performed to investigate the dehydroxylation mechanism (Drits *et al.*, 1995; Fitzgerald *et al.*, 1996; Frost and Barron, 1984; Kloprogge and Frost, 1999; Guggenheim *et al.*, 1987; Heller *et al.*, 1962; MacKenzie *et al.*, 1985; Muller *et al.*, 2000; Wang and Zhang, 1997; Wang *et al.*, 2002), the structure of pyrophyllite dehydroxylate (Fitzgerald *et al.*, 1989; 1996, Frost and Barron, 1984; Wardle and Brindley, 1972), and thermally induced transformations of pyrophyllite dehydroxylate (Heller, 1962; Wang and Zhang, 1997, Wang *et al.*, 2002). In recent IR spectroscopic work, Wang *et al.* (2002) reported data for pyrophyllite treated between 200 and 1500ºC. They observed new OH species at 3690 and 3702 cm^{-1} and their overtones at 7208 and 7234 cm^{-1} in the temperature range 550–900ºC, suggesting that the dehydroxylation of pyrophyllite is a complex process.

While the thermal decomposition of pyrophyllite has been studied extensively, the authors know of no investigation into carbonation of pyrophyllite. The kinetics of simultaneous dehydroxylation and carbonation of other sheet minerals, notably brucite $Mg(OH)_2$, have, however, come under some scrutiny (Butt *et al.*, 1996; Béarat *et al.*, 2002). In these studies it has been suggested that carbonation is enhanced during dehydroxylation, with the two processes being described as "distinct but interrelated" (Béarat *et al.*, 2002). It appears that intermediate oxyhydroxides, which occur during dehydroxylation of brucite, are important for the formation of carbonate from this phase. One might anticipate similar phenomena occurring in the gibbsite-like octahedral sheet of pyrophyllite.

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The incorporation of CO_2 has previously been reported in minerals and glasses as part of studies of CO_2 solubility in melts (*e.g.* Mysen, 1976; Fine and Stolper, 1985; Taylor, 1990). The CO_2 contents and their molecular speciation in minerals can offer information on the formation condition and geological history of the rocks in which they occur. Understanding of the solubility and stability mechanisms of CO_2 in silicate melts, for example, is of great interest because of the important role played by CO_2 in petrogenesis of a wide range of igneous rocks. To our knowledge, there have been no reports on the incorporation of CO_2 and CO into clays like pyrophyllite which has been thermally treated in the laboratory. However, due to the structural rearrangement in partially dehydroxylated pyrophyllite, it is anticipated that molecular exchange could occur in pyrophyllite during its dehydroxylation and structural modifications at high temperatures. In this paper, we report new IR observations and analysis of CO_2 and CO signals in thermally treated pyrophyllite samples. Our results reveal, for the first time, that CO_2 and CO do occur and then disappear in pyrophyllite during thermal treatments in air, implying that diffusion of carbon-related substances during structural modifications (*e.g.* dehydroxylation, recrystallization) of clay minerals at high temperatures may be one of the possible paths for the incorporation of CO_2 or CO. They also indicate that when heating in air, the dehydroxylation process in pyrophyllite can be a complex process: a loss of H_2O accompanied by incorporation of other species (*e.g.* CO_2 or CO).

MATERIALS AND EXPERIMENTAL METHODS

The two pyrophyllite samples used in this study are identical to those investigated previously by Wang *et al.* (2002). Sample EM08 is a pyrophyllite (2*M* + 1*Tc*) from the Emei large pyrophyllite deposit, Fuzhou, China. Sample SK06 is a pyrophyllite (2*M*) from the Shankou large pyrophyllite deposit, Qingtian, China. The chemical compositions of the two samples are almost identical to the ideal formula of $Al_2Si_4O_{10}(OH)_2$ for pyrophyllite (Wang, 1994). Their IR powder absorption spectra between 350 and 11000 cm^{-1} show characteristic bands of pyrophyllite (Wang *et al.*, 2002).

Thin-sections of pyrophyllite were subjected to thermal treatment. Samples were ground and polished to a final thickness of 0.32±0.01 mm. The thermal treatment between 200 and 1250ºC was performed using a one atmosphere vertical tube furnace. Two Pt-PtRh thermocouples were used in the furnace; one was coupled with a Eurotherm temperature controller to control the furnace, and the second was used to measure the sample temperature. The instability of the sample temperature was <5°C. Samples were loaded into preheated furnaces and annealed for periods of 15 min, 1 h or 5 days. The annealed samples were quenched in air and measured after quenching. After measurements, the samples were stepwise annealed at a higher temperature. Powdered pyrophyllite samples used in the study of Wang *et al.* (2002) were pressed with KBr powder (sample: KBr = 1:100) under vacuum and measured to check for the presence of trace CO_2.

A Bruker IFS 66v spectrometer was used for IR measurements in the wavenumber region 2000–13000 cm^{-1} at room temperature. Apertures of 1.0–2.5 mm, a tungsten lamp, a liquid-nitrogen-cooled Hg-Cd-telluride detector and a CaF_2 beam-splitter were used. A total of 350–512 scans with an instrumental resolution of 2 cm^{-1} were collected for each spectrum. All spectra were recorded under vacuum (better than 1 mbar). Commercial software (OPUS-IR II, Bruker) was used for data analysis. Integrated absorbance was obtained by curve fitting or simply by integrating the measured data with linear base lines.

RESULTS

No bands characteristic of CO_2 were observed in untreated pyrophyllite EM08 and SK06, suggesting the absence of CO_2 in the starting materials. Heating pyrophyllite EM08 to high temperatures leads to a systematic development of an absorption feature near 2347 cm^{-1} (Figure 1a,b). This band is attributed to the ν_3 anti-symmetric stretching of molecular CO_2 (Fine and Stolper, 1985; Mysen, 1976). It becomes detectable in samples treated at 450ºC. Pyrophyllite SK06 (2*M*) shows essentially similar thermal behaviors except the clear development of additional absorption signal near 2356 cm^{-1} occurs at temperatures >600°C (Figure 2a,b). The annealing time shows a significant effect on the temperature evolution of this CO_2 signal. Prolonged heating generally shifts the point at which the intensity is greatest to lower temperatures. This can be seen clearly in Figure 3, where the integral absorption coefficient (*i.e.* integral absorbance/sample thickness) of the CO_2 feature is plotted as a function of temperature. The integral absorption coefficient rather than integral absorbance is used in Figure 3, so as to avoid any potential influence resulting from the slight variation of the thin-section thickness (0.32±0.01 mm) among the samples. For the same reason the absorption coefficient is used in Figures 1, 2 and 5. We note that at temperatures between 450 and 600ºC, the spectral feature near 2347 cm^{-1} appears as a single band, similar to the CO_2 features in glasses reported by Fine and Stolper (1985) and Brooker *et al.* (2001). At temperatures above ~700ºC the feature clearly consists of two local maxima at 2345 and 2362 cm^{-1} (*e.g.* Figure 2a).

The concentrations of CO_2 in the thin-sections were estimated using a published calibration for CO_2. According to a study on sodium aluminosilicate glasses (Fine and Stolper, 1985), the CO_2 content can be determined by equation 1,

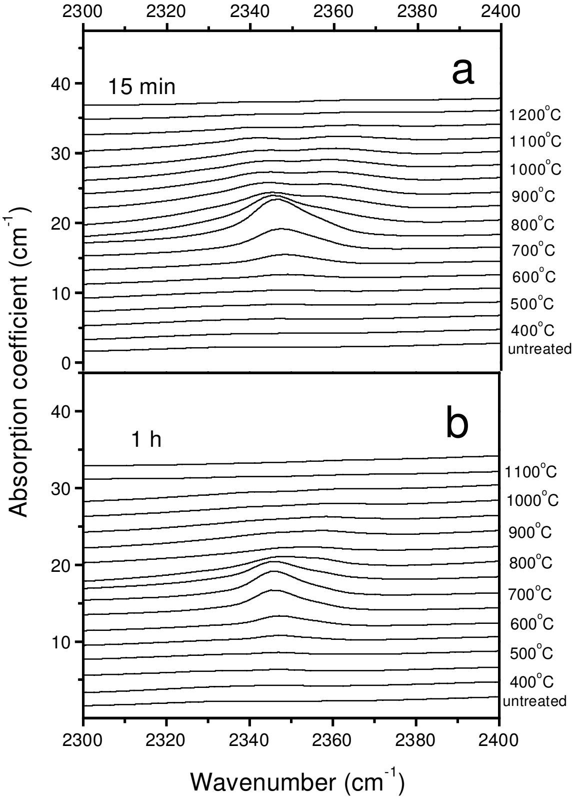

Figure 1. IR spectra of CO_2 in the region 2300–2400 cm^{-1} in pyrophyllite EM08 (Emei, Fuzhou, China) samples (thin-sections) stepwise annealed at 400–1250°C for (a) 15 min, and (b) 1 h. Successive spectra have been offset vertically by 2 cm^{-1} for clarity.

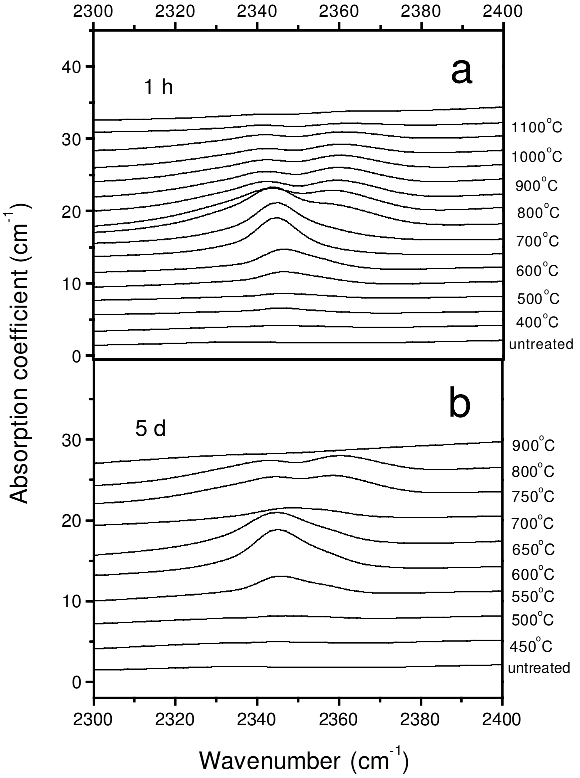

Figure 2. IR spectra of CO_2 in the region 2300–2400 cm^{-1} in pyrophyllite SK06 (Shankou, Qingtian, China) samples (thin-sections) stepwise annealed at 400–1250°C for (a) 1 h, and (b) 5 days. Successive spectra have been offset vertically by 2 cm^{-1} in Figure 2a and by 3 cm^{-1} in Figure 2b for clarity.

$$c = 44.01 \times \frac{\text{integral absorption}}{\text{density} \times \text{thickness} \times \varepsilon} \times 100 = \frac{44.01 \times \text{integral absorption coefficient}}{\text{density} \times \varepsilon}$$

where c (wt.% CO_2) is the concentration of CO_2, 44.01 is the molecular weight of CO_2 in g mol^{-1}, ε is the integral molar absorptivity (25200 ± 1200 L mol^{-1} cm^{-2}) (Fine and Stolper, 1985), and integral absorbance in units of cm^{-1} (or integral absorption coefficient in units of cm^{-2}). A density of 2.845 g cm^{-3} (*i.e.* 2.845×10^3 g L^{-1}) was used for pyrophyllite SK06 (Wang *et al.*, 1984). This estimates a value of 0.01 wt.% CO_2 in the thin-sections heated at 750°C for 1 h. If the incorporation of CO_2 into heated pyrophyllite is considered to be due to a diffusion process, the estimated concentration of CO_2 should be an averaged value across the whole sample. The CO_2 concentrations in the sample surface layers could be much higher than those in the central regions. Because the calibration of Fine and Stolper (1985) was based on the experimental data from glasses and since there is no calibration for pyrophyllite available, we are unable to evaluate further the accuracy of this estimate at this stage.

We did not detect signals between 1300 and 1700 cm^{-1} that would be expected from possible CO_3^{2-} ions. A free undistorted carbonate group (D_{3h} symmetry) gives rise to a ν_3 band (antisymmetric stretching) near 1415 cm^{-1}. According to White (1974) and Nakamoto

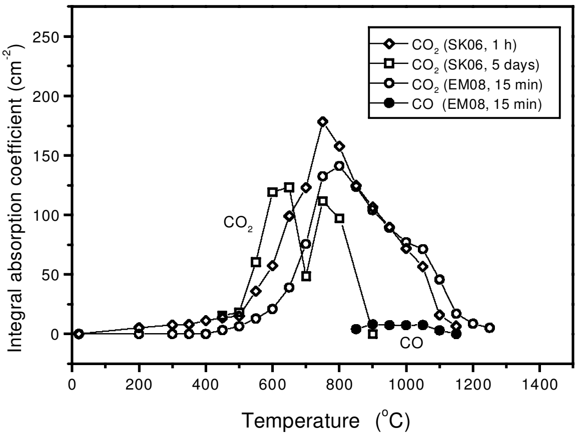

Figure 3. Temperature dependence of integral absorption coefficient (integral absorbance/sample thickness) of CO_2 (open symbols) and CO (filled circles) for different heating conditions (data from thin-sections).

(1978), distortion of the CO_3^{2-} group (C_{2v} symmetry) leads to a loss of the degeneracy and the occurrence of two bands near 1610 and 1375 cm^{-1} with a splitting of 235 cm^{-1}. These absorption lines were not observed in either the untreated or the thermally treated samples. Thus, the incorporation of CO_2 in the heated pyrophyllite did not occur as a result of CO_3^{2-} within the structure, unless the concentration is too low to be detected. This observation supports the idea that the presence of CO_2 was mainly related to diffusion rather than chemical reaction.

In order to understand whether the CO_2 molecules are associated with local environments or local configurations, peak positions of the CO_2 signals observed are plotted as a function of temperature in Figure 4. The absorption peak of the CO_2 is centered near 2347 cm^{-1} at 450°C. With increasing temperature between 600 and 700°C, the peak position starts to decrease weakly and a weak absorption line appears at 2354 cm^{-1}. The 2347 cm^{-1} signal drops further to 2338 cm^{-1} at 1200°C upon annealing for 15 min or at 900°C after annealing for 1 h (Figure 4). The 2354 cm^{-1} band shows a significant increase in wavenumber with increasing temperature, and it lies at 2365 cm^{-1} at 800°C. With further heating, its wavenumber increase becomes weaker. Our observation of the systematic change of the CO_2 peak positions in heated pyrophyllite indicates that the CO_2 molecules are not in a free gaseous state, and they are somehow incorporated within the structure in specific local environments.

Apart from CO_2, CO was observed at temperatures between 800 and 1100°C in both samples (Figure 5). It is characterized by an additional signal near 2156 cm^{-1}. It shows an absorption coefficient (band height) of 0.6 cm^{-1} for sample EM08 annealed at 850°C for 1 h. The integral absorption coefficient of CO (in filled circles) is also plotted as a function of temperature in Figure 3. The CO concentration shows a gradual increase with increasing temperature. The CO signal is also affected by annealing time. It was detected after annealing for 15 min at 850°C, whereas at 700°C it appeared (with a height of 0.9 cm^{-1}) in sample SK06 only after annealing for 5 days. Our data suggest that the formation of CO is at the expense of CO_2, as the signals related to CO_2 show significant decreases starting near 800°C (Figure 3). Unfortunately, we were unable to estimate the CO contents in our samples and to confirm or rule out whether the occurrence of CO is partially or fully responsible for the decrease in the CO_2 signals.

DISCUSSION

It is advantageous to understand the physics behind the incorporation of CO_2 and CO into heated pyrophyllite as this is important in the understanding of where these species are located in the structure. We can be sure that our observations of CO_2 and CO signals in these samples cannot be attributed to artefacts due to any potential errors related to the measurements. Firstly, the data were obtained under vacuum (the pressure was better than 1 mbar). The systematic and reproducible change in peak profiles of CO_2 rule out the possibility that they were caused by improper data acquisition. Secondly, the absence of CO_2 and CO signals in the untreated samples suggests that their presence in heated pyrophyllite is related to the thermal treatments. The potential formation of macro-fractures or cracks during heating may play a certain role (*e.g.* speeding up the diffusion of CO_2 or CO) in the CO_2 incorporation during high-temperature treatments. However, this is unlikely to be the dominant factor, because the treated powdered

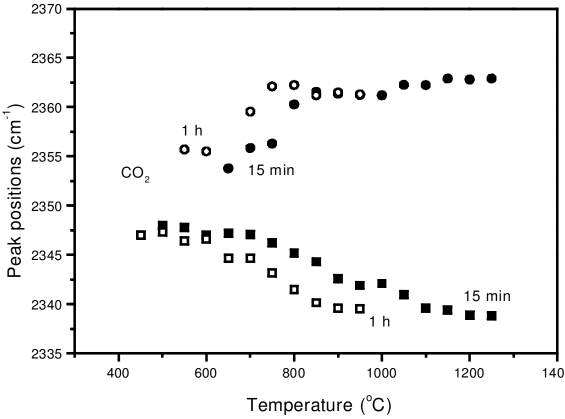

Figure 4. Temperature dependence of peak positions of CO_2. Open symbols represent data from sample SK06 (thick sections) annealed for 1 h and filled symbols from sample EM08 (thick sections) annealed for 15 min. The peak positions were obtained using curve-fitting or the second-derivative method.

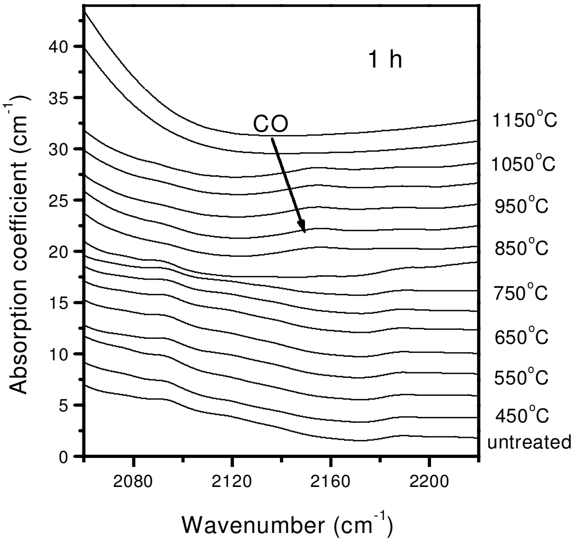

Figure 5. IR spectra of CO in the region 2060–2220 cm^{-1} in pyrophyllite EM08 samples (thin-sections) stepwise annealed for 1 h. Successive spectra have been offset vertically by 2 cm^{-1} for clarity.

samples (with particle sizes of a few µm) prepared in KBr pellets also showed the presence of CO_2, although the averaged concentrations of CO_2 in heated powdered samples and thin-sections were different. In addition, CO_2 in cracks is not expected to give the systematic change of intensity observed in this study. Furthermore, CO_2 trapped in cracks is expected to appear as free gaseous molecules and should show a peak with a constant wavenumber, as well as changes in the spectra associated with out-gassing in the vacuum of the instrument.

We think that the incorporation of CO_2 in pyrophyllite is caused by diffusion of carbon-based substances which were present in the furnace (this is probably simply atmospheric CO_2 or CO). Unlike CO_2 in some silicate glasses and minerals, the presence of the CO_2 species in the heated pyrophyllite is not associated with the dissociation of CO_3^{2-}, since no CO_3^{2-} species were detected in the untreated samples. As the crystal structure of pyrophyllite consists of cages to accommodate OH^- ions, and displays some structural flexibility, the structural modifications of pyrophyllite occurring during dehydroxylation might offer good opportunities for other substances (originally absent from the starting materials) to find their way into the clay. This explanation is further supported by the fact that annealing time significantly affects the peak profiles of the CO_2 signals and prolonged heating leads to the a shift of the temperature at which the maximum in CO_2 absorption intensity is seen to lower temperatures (Figure 3), as more C-bearing substances can diffuse into the material with increasing annealing time. Based on the IR data on samples annealed in the temperature range 450–800ºC, we consider that the molecular CO_2 in the temperature region is dissolved at a molecular scale, probably located in 'cages' formed during the structural modifications during dehydroxylation. Since the particle sizes of the powdered samples in KBr pellets are of the order of µm, the occurrence of CO_2 indicates that the sizes of the cavities must be of the order of nm or sub-micro meter, but certainly larger than 4.96 Å (the diameter of the CO_2 molecule). However, the presence of the 'double' bands suggests the possible existence of both dissolved CO_2 and gaseous CO_2 at higher temperatures. The observations in this study also raise an important question: do other 2:1 phyllosilicate clays show similar behaviors at high temperatures?

Our results from heated phyllosilicate differ from those for brucite carbonation (Butt *et al.*, 1996; Béarat *et al.*, 2002), as we find no evidence for the formation of carbonate. This is, perhaps, unsurprising given the absence of Mg within the structure. It would be interesting to compare the dehydroxylation, and incorporation of CO_2, that we observe for pyrophyllite with what one might anticipate in muscovite, where the formation of magnesite is possible at a local scale. Discussions of mineral sequestration of anthropogenic CO_2 are dominated by carbonate (principally magnesite) formation. It is interesting to note that even when carbonate formation is apparently absent, as in the case of our study of pyrophyllite, CO_2 incorporation may still occur in a mineral dehydroxylate to some limited degree. This underlines the complexity of possible reaction pathways during 'carbonation' of hydroxide minerals, especially at elevated temperatures. It confirms that mineral sequestration of CO_2 is expected to be enhanced at temperatures above which dehydroxylation may occur.

CONCLUSIONS

Our IR spectroscopic evidence shows that CO_2 and CO can be incorporated into the structure of pyrophyllite during dehydroxylation and structural transformations of pyrophyllite at high temperatures. The presence of CO_2 is characterized by the ν_3 band of CO_2 which begins to appear near 450ºC. The CO_2 molecules are associated with the local structure rather than present as free gaseous CO_2. Further heating results in the incorporation of CO, presumably at the expense of CO_2. These observations suggest that carbon-bearing species can easily find their way into pyrophyllite during dehydroxylation.

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REFERENCES

Bailey, S.W. (1966) The status of clay mineral structures. *Clays and Clay Minerals*, **14**, 1–23.

Béarat, H., McKelvy, M.J., Chizmeshya, A.V.G., Sharma, R. and Carpenter, R.W. (2002) Magnesium hydroxide dehydroxylation/carbonation reaction processes: implications for carbon dioxide mineral sequestration. *Journal of the American Ceramic Society*, **85**, 742–748.

Brooker, R.A., Kohn, S.C., Holloway, J.R. and McMillian, P.F. (2001) Structural controls on the solubility of CO_2 in silicate melts Par II: IR characteristics of carbonate groups in silicate glasses. *Chemical Geology*, **174**, 241–254.

Butt, D.P., Lackner, K.S., Wendt, C.H., Conzone, S.D., Kung, H., Lu, Y.C. and Bremser, J.K. (1996) Kinetics of thermal dehydroxylation and carbonation of magnesium hydroxide. *Journal of the American Ceramic Society*, **79**, 1892–1898.

Drits, V.A., Besson, G. and Muller, F. (1995) An improved model for structural transformations of heat-treated aluminous dioctahedral 2:1 layer silicates. *Clays and Clay Minerals*, **43**, 718–731.

Fine, G. and Stolper, E. (1985) The speciation of carbon dioxide in sodium aluminosilicate glasses. *Contributions to Mineralogy and Petrology*, **91**,105–121.

Fitzgerald, J.J., Dec, S.F. and Hamza, A.I. (1989) Observation of five-coordinated Al in prophyllite dehydroxylate by solid-state ^{27}Al NMR spectroscopy at 14 T. *American Mineralogist*, **74**, 1405–1408.

Fitzgerald, J.J., Hamza, A.I., Dec, S.F., and Bronnimann, C.E.

(1996) Solid-state ^{27}Al and ^{29}Si NMR and ^{1}H CRAMPS studies of the 2:1 phyllosilicate pyrophyllite. *Journal of Physical Chemistry*, **100**, 17351–17360.

Frost, R.L. and Barron, P.F. (1984) Solid-state silicon-29 and aluminium-27 nuclear magnetic resonance investigation of the dehydroxylation of pyrophyllite. *Journal of Physical Chemistry*, **88**, 6206–6209.

Guggenheim, M., Chang, Y.H. and Koster van Groos, A.F. (1987) Muscovite dehydroxylation: High-temperature studies. *American Mineralogist,* **72,** 537–550.

Heller, L. (1962) The thermal transformation of pyrophyllite to mullite. *American Mineralogist,* **47**, 156–157.

Heller, L., Farmer, V.C., Mackenzie, R.C., Mitchell, B.D. and Taylor, H.F.W. (1962) The dehydroxylation and rehydroxylation of triphormic dioctahedral clay minerals. *Clay Minerals Bulletin*, **5**, 56–72.

Kloprogge, J.T. and Frost, R.L. (1999) An infrared emission spectroscopic study of synthetic and natural pyrophyllite. *Neues Jahrbuch für Mineralogie Monatshefte*, 62–74.

MacKenzie, K.J.D., Brown, I.W.M., Meinhold, R.H. and Bowden, M.E.J. (1985) Thermal reactions of pyrophyllite studied by high-resolution solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy. *Journal of the American Ceramic Society*, **68**, 266–272.

Muller, F., Drits, V., Plançon, A., and Robert, J.L. (2000) Structural transformation of 2:1 dioctahedral layer silicates during dehydroxylation-rehydroxylation reactions. *Clays and Clay Minerals*, **48**, 572–585.

Mysen, B.O. (1976) The role of volatiles in silicate melts: Solubility of carbon dioxide and water in feldspar, pyroxene and feldspathoid melts to 30 Kb and 1625C. *American Journal of Science*, **276**, 969–996.

Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley and Sons, New York, 448 pp.

Rayner, J.H. and Brown, G. (1966) Structure of pyrophyllite. *Clays and Clay Minerals*, **25**, 73–84.

Taylor, W.R. (1990) The dissolved $(CO_3)^{2-}$ in alumino-silicate melts – Infrared spectroscopic constraints on the cationic environment of dissolved $(CO_3)^{2-}$. *European Journal of Mineralogy*, **2**, 547–563.

Wang, L. (1994) Metallogeny of pyrophyllite in the coastal region of Southeast China and pyrophyllite's thermal stability. PhD thesis, Changsha Institute of Geotectonics, Chinese Academy of Sciences (in Chinese).

Wang, L. and Zhang, Z.Y. (1997) High-temperature phases of pyrophyllite and their evolutionary characteristics. *Chinese Science Bulletin*, **42**, 140–143.

Wang, L., Zhang, M., Redfern, S.A.T. and Zhang, Z.Y. (2002) Dehydroxylation and transformations of the 2:1 phyllosilicate pyrophyllite at elevated temperatures: An infrared spectroscopic study. *Clays and Clay Minerals*, **50**, 272–283.

Wang, P., Pan, Z.L. and Weng, L.B. (1984) *Systematic Mineralogy*. Geological Publishing House, Beijing, 522 pp (in Chinese).

Wardle, R. and Brindley, G.W. (1972) The crystal structures of pyrophyllite, 1Tc, and of its dehydroxylate. *American Mineralogist*, **57**, 732–750.

White, B.W. (1974) The carbonate minerals. Pp. 227–284 in: *The Infrared Spectra of Minerals* (V.C. Farmer editor). Monograph **4**, Mineralogical Society, London.

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