

## INFRARED STUDY OF CO<sub>2</sub> INCORPORATION INTO PYROPHYLLITE [Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] DURING DEHYDROXYLATION

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**Abstract**—We report infrared spectroscopic observations of the incorporation of CO<sub>2</sub> into pyrophyllite that has been heated between 200°C and 1250°C for periods of 15 min, 1 h and 5 days. The presence of CO<sub>2</sub> is characterized by the ν<sub>3</sub> band of CO<sub>2</sub> near 2347 cm<sup>-1</sup>, detectable in samples in which dehydroxylation has commenced after heating above 450°C. With increasing temperature, the CO<sub>2</sub> signal becomes more intense. The signal reaches its maximum intensity near 800°C with an annealing time of 15 min. Further heating leads to a decrease in the CO<sub>2</sub> signal and the occurrence of an extra signal near 2156 cm<sup>-1</sup> that implies the presence of CO. The process is characterized by significant time-dependence, indicating its kinetic nature. The peak positions of CO<sub>2</sub> signals show systematic variations with temperature. Our results suggest that the CO<sub>2</sub> molecule is associated with the local structure rather than being present as free gaseous CO<sub>2</sub>, and that the local structure of pyrophyllite is gradually modified during high-temperature treatments. However, no signals related to carbonate molecules (CO<sub>3</sub><sup>2-</sup>) were detected. The results suggest that CO<sub>2</sub> 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<sub>2</sub> sequestration in shales and clay formations.

**Key Words**—CO<sub>2</sub>, CO, Dehydroxylation, Infrared Spectroscopy, Pyrophyllite, Sequestration.

### INTRODUCTION

Pyrophyllite, Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>, 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<sub>2</sub>O-CO<sub>2</sub> exchange can be anticipated as a control in CO<sub>2</sub> sequestration within soils and shale formations. Mineral sequestration has been suggested as a potentially important and permanent sink for anthropogenic CO<sub>2</sub> 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<sub>4</sub> 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; Klopogge 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 1500°C. They observed new OH species at 3690 and 3702 cm<sup>-1</sup> and their overtones at 7208 and 7234 cm<sup>-1</sup> in the temperature range 550–900°C, 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)<sub>2</sub>, 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<sub>2</sub> has previously been reported in minerals and glasses as part of studies of CO<sub>2</sub> solubility in melts (*e.g.* Mysen, 1976; Fine and Stolper, 1985; Taylor, 1990). The CO<sub>2</sub> 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<sub>2</sub> in silicate melts, for example, is of great interest because of the important role played by CO<sub>2</sub> in petrogenesis of a wide range of igneous rocks. To our knowledge, there have been no reports on the incorporation of CO<sub>2</sub> 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<sub>2</sub> and CO signals in thermally treated pyrophyllite samples. Our results reveal, for the first time, that CO<sub>2</sub> 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<sub>2</sub> or CO. They also indicate that when heating in air, the dehydroxylation process in pyrophyllite can be a complex process: a loss of H<sub>2</sub>O accompanied by incorporation of other species (*e.g.* CO<sub>2</sub> 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 (2M + 1Tc) from the Emei large pyrophyllite deposit, Fuzhou, China. Sample SK06 is a pyrophyllite (2M) from the Shankou large pyrophyllite deposit, Qingtian, China. The chemical compositions of the two samples are almost identical to the ideal formula of Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> for pyrophyllite (Wang, 1994). Their IR powder absorption spectra between 350 and 11000 cm<sup>-1</sup> 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 1250°C 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<sub>2</sub>.

A Bruker IFS 66v spectrometer was used for IR measurements in the wavenumber region 2000–13000 cm<sup>-1</sup> at room temperature. Apertures of 1.0–2.5 mm, a tungsten lamp, a liquid-nitrogen-cooled Hg-Cd-telluride detector and a CaF<sub>2</sub> beam-splitter were used. A total of 350–512 scans with an instrumental resolution of 2 cm<sup>-1</sup> 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<sub>2</sub> were observed in untreated pyrophyllite EM08 and SK06, suggesting the absence of CO<sub>2</sub> in the starting materials. Heating pyrophyllite EM08 to high temperatures leads to a systematic development of an absorption feature near 2347 cm<sup>-1</sup> (Figure 1a,b). This band is attributed to the ν<sub>3</sub> anti-symmetric stretching of molecular CO<sub>2</sub> (Fine and Stolper, 1985; Mysen, 1976). It becomes detectable in samples treated at 450°C. Pyrophyllite SK06 (2M) shows essentially similar thermal behaviors except the clear development of additional absorption signal near 2356 cm<sup>-1</sup> occurs at temperatures >600°C (Figure 2a,b). The annealing time shows a significant effect on the temperature evolution of this CO<sub>2</sub> 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<sub>2</sub> 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 600°C, the spectral feature near 2347 cm<sup>-1</sup> appears as a single band, similar to the CO<sub>2</sub> features in glasses reported by Fine and Stolper (1985) and Brooker *et al.* (2001). At temperatures above ~700°C the feature clearly consists of two local maxima at 2345 and 2362 cm<sup>-1</sup> (*e.g.* Figure 2a).

The concentrations of CO<sub>2</sub> in the thin-sections were estimated using a published calibration for CO<sub>2</sub>. According to a study on sodium aluminosilicate glasses (Fine and Stolper, 1985), the CO<sub>2</sub> content can be determined by equation 1,

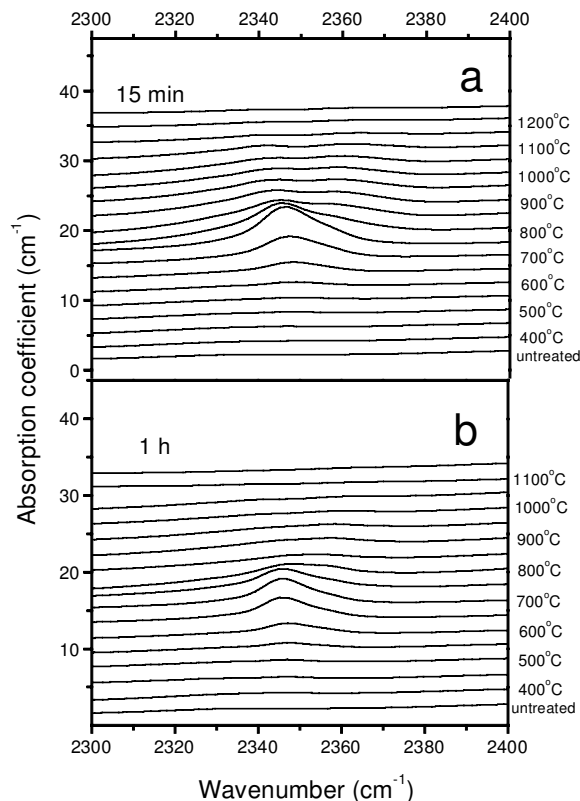


Figure 1. IR spectra of CO<sub>2</sub> in the region 2300–2400 cm<sup>-1</sup> in pyrophyllite EM08 (Emei, Fuzhou, China) samples (thin-sections) stepwise annealed at 400–1250°C for (a) 15 min, and (b) 1 h. Successive spectra have been offset vertically by 2 cm<sup>-1</sup> for clarity.

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

where  $c$  (wt.% CO<sub>2</sub>) is the concentration of CO<sub>2</sub>, 44.01 is the molecular weight of CO<sub>2</sub> in g mol<sup>-1</sup>,  $\varepsilon$  is the integral molar absorptivity (25200±1200 L mol<sup>-1</sup> cm<sup>-2</sup>) (Fine and Stolper, 1985), and integral absorbance in units of cm<sup>-1</sup> (or integral absorption coefficient in units of cm<sup>-2</sup>). A density of 2.845 g cm<sup>-3</sup> (*i.e.* 2.845 × 10<sup>3</sup> g L<sup>-1</sup>) was used for pyrophyllite SK06 (Wang *et al.*, 1984). This estimates a value of 0.01 wt.% CO<sub>2</sub> in the thin-sections heated at 750°C for 1 h. If the incorporation of CO<sub>2</sub> into heated pyrophyllite is considered to be due to a diffusion process, the estimated concentration of CO<sub>2</sub> should be an averaged value across the whole sample. The CO<sub>2</sub> 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.

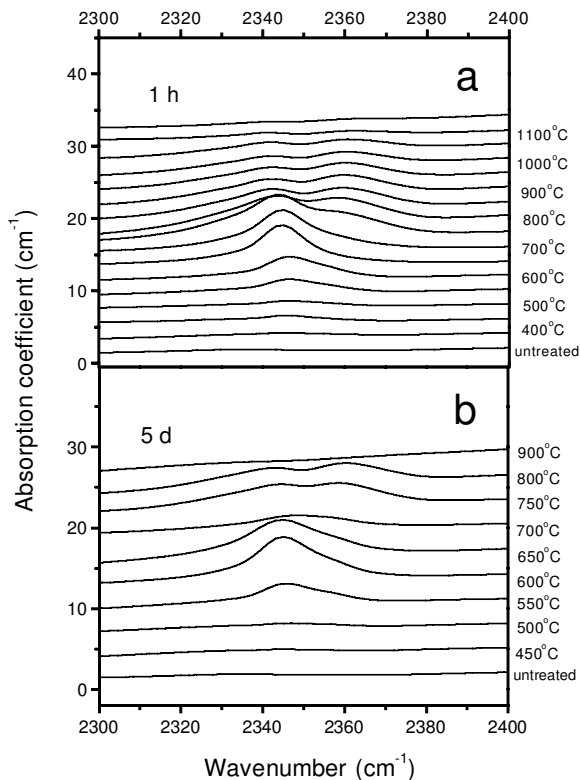


Figure 2. IR spectra of CO<sub>2</sub> in the region 2300–2400 cm<sup>-1</sup> in pyrophyllite SK06 (Shankou, Qingtian, China) samples (thin-sections) stepwise annealed at 400–1250°C for (a) 1 h, and (b) 5 days. Successive spectra have been offset vertically by 2 cm<sup>-1</sup> in Figure 2a and by 3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

We did not detect signals between 1300 and 1700 cm<sup>-1</sup> that would be expected from possible CO<sub>3</sub><sup>2-</sup> ions. A free undistorted carbonate group ( $D_{3h}$  symmetry) gives rise to a  $\nu_3$  band (antisymmetric stretching) near 1415 cm<sup>-1</sup>. According to White (1974) and Nakamoto

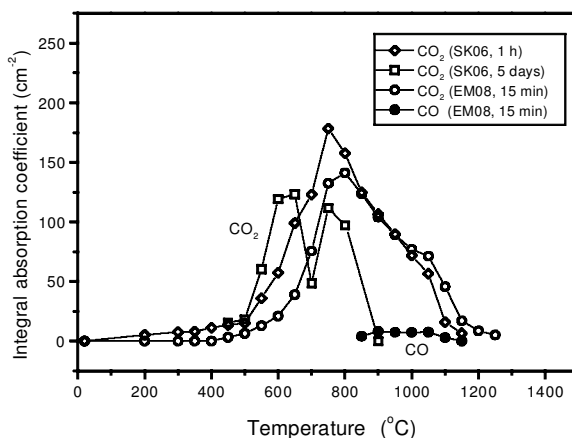


Figure 3. Temperature dependence of integral absorption coefficient (integral absorbance/sample thickness) of CO<sub>2</sub> (open symbols) and CO (filled circles) for different heating conditions (data from thin-sections).

(1978), distortion of the  $\text{CO}_3^{2-}$  group ( $C_{2v}$  symmetry) leads to a loss of the degeneracy and the occurrence of two bands near  $1610$  and  $1375\text{ cm}^{-1}$  with a splitting of  $235\text{ cm}^{-1}$ . These absorption lines were not observed in either the untreated or the thermally treated samples. Thus, the incorporation of  $\text{CO}_2$  in the heated pyrophyllite did not occur as a result of  $\text{CO}_3^{2-}$  within the structure, unless the concentration is too low to be detected. This observation supports the idea that the presence of  $\text{CO}_2$  was mainly related to diffusion rather than chemical reaction.

In order to understand whether the  $\text{CO}_2$  molecules are associated with local environments or local configurations, peak positions of the  $\text{CO}_2$  signals observed are plotted as a function of temperature in Figure 4. The absorption peak of the  $\text{CO}_2$  is centered near  $2347\text{ cm}^{-1}$  at  $450^\circ\text{C}$ . With increasing temperature between  $600$  and  $700^\circ\text{C}$ , the peak position starts to decrease weakly and a weak absorption line appears at  $2354\text{ cm}^{-1}$ . The  $2347\text{ cm}^{-1}$  signal drops further to  $2338\text{ cm}^{-1}$  at  $1200^\circ\text{C}$  upon annealing for 15 min or at  $900^\circ\text{C}$  after annealing for 1 h (Figure 4). The  $2354\text{ cm}^{-1}$  band shows a significant increase in wavenumber with increasing temperature, and it lies at  $2365\text{ cm}^{-1}$  at  $800^\circ\text{C}$ . With further heating, its wavenumber increase becomes weaker. Our observation of the systematic change of the  $\text{CO}_2$  peak positions in heated pyrophyllite indicates that the  $\text{CO}_2$  molecules are not in a free gaseous state, and they are somehow incorporated within the structure in specific local environments.

Apart from  $\text{CO}_2$ , CO was observed at temperatures between  $800$  and  $1100^\circ\text{C}$  in both samples (Figure 5). It is characterized by an additional signal near  $2156\text{ cm}^{-1}$ . It shows an absorption coefficient (band height) of  $0.6\text{ cm}^{-1}$  for sample EM08 annealed at  $850^\circ\text{C}$  for 1 h. The integral absorption coefficient of CO (in filled circles) is also plotted as a function of temperature in

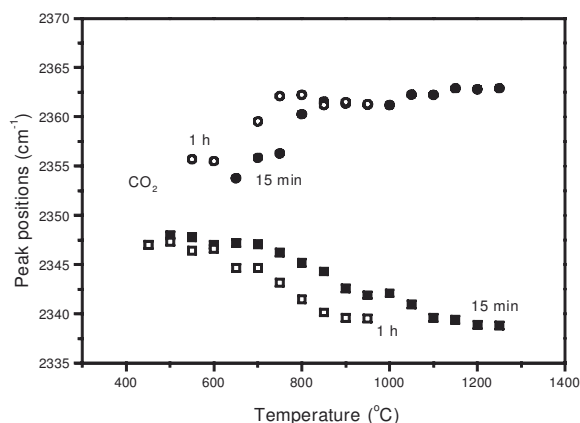


Figure 4. Temperature dependence of peak positions of  $\text{CO}_2$ . Open symbols represent data from sample SK06 (thick sections) annealed for 1 h and filled symbols from sample EM08 (thick sections) annealed for 15 min. The peak positions were obtained using curve-fitting or the second-derivative method.

Figure 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  $850^\circ\text{C}$ , whereas at  $700^\circ\text{C}$  it appeared (with a height of  $0.9\text{ cm}^{-1}$ ) in sample SK06 only after annealing for 5 days. Our data suggest that the formation of CO is at the expense of  $\text{CO}_2$ , as the signals related to  $\text{CO}_2$  show significant decreases starting near  $800^\circ\text{C}$  (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  $\text{CO}_2$  signals.

## DISCUSSION

It is advantageous to understand the physics behind the incorporation of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  rule out the possibility that they were caused by improper data acquisition. Secondly, the absence of  $\text{CO}_2$  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  $\text{CO}_2$  or CO) in the  $\text{CO}_2$  incorporation during high-temperature treatments. However, this is unlikely to be the dominant factor, because the treated powdered

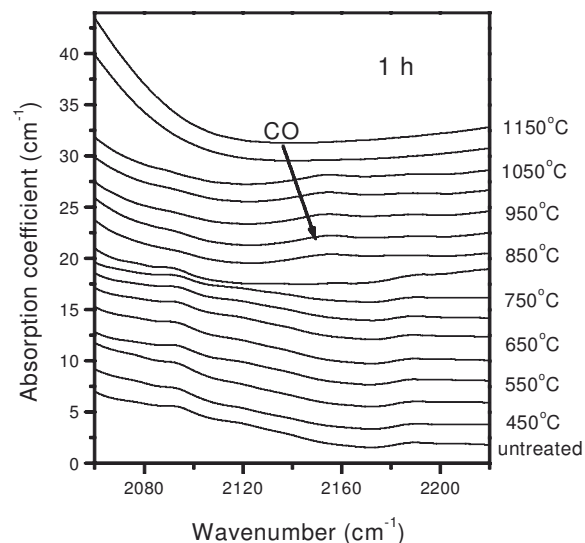


Figure 5. IR spectra of CO in the region  $2060$ – $2220\text{ cm}^{-1}$  in pyrophyllite EM08 samples (thin-sections) stepwise annealed for 1 h. Successive spectra have been offset vertically by  $2\text{ cm}^{-1}$  for clarity.

samples (with particle sizes of a few  $\mu\text{m}$ ) prepared in KBr pellets also showed the presence of CO<sub>2</sub>, although the averaged concentrations of CO<sub>2</sub> in heated powdered samples and thin-sections were different. In addition, CO<sub>2</sub> in cracks is not expected to give the systematic change of intensity observed in this study. Furthermore, CO<sub>2</sub> 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<sub>2</sub> in pyrophyllite is caused by diffusion of carbon-based substances which were present in the furnace (this is probably simply atmospheric CO<sub>2</sub> or CO). Unlike CO<sub>2</sub> in some silicate glasses and minerals, the presence of the CO<sub>2</sub> species in the heated pyrophyllite is not associated with the dissociation of CO<sub>3</sub><sup>2-</sup>, since no CO<sub>3</sub><sup>2-</sup> species were detected in the untreated samples. As the crystal structure of pyrophyllite consists of cages to accommodate OH<sup>-</sup> 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<sub>2</sub> signals and prolonged heating leads to the a shift of the temperature at which the maximum in CO<sub>2</sub> 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 450–800°C, we consider that the molecular CO<sub>2</sub> 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  $\mu\text{m}$ , the occurrence of CO<sub>2</sub> 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<sub>2</sub> molecule). However, the presence of the ‘double’ bands suggests the possible existence of both dissolved CO<sub>2</sub> and gaseous CO<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> is expected to be enhanced at temperatures above which dehydroxylation may occur.

## CONCLUSIONS

Our IR spectroscopic evidence shows that CO<sub>2</sub> and CO can be incorporated into the structure of pyrophyllite during dehydroxylation and structural transformations of pyrophyllite at high temperatures. The presence of CO<sub>2</sub> is characterized by the  $\nu_3$  band of CO<sub>2</sub> which begins to appear near 450°C. The CO<sub>2</sub> molecules are associated with the local structure rather than present as free gaseous CO<sub>2</sub>. Further heating results in the incorporation of CO, presumably at the expense of CO<sub>2</sub>. These observations suggest that carbon-bearing species can easily find their way into pyrophyllite during dehydroxylation.

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