

INFRARED SPECTRAL EVIDENCE FOR A MINOR Fe(III) CARBONATE-BEARING COMPONENT IN NATURAL GOETHITE

Key Words—Carbonate, Goethite, Infrared spectroscopy, Iron, Solid solution.

Dehydration of natural goethite in vacuum at temperatures ranging from 160° to 270°C has been found to be accompanied by the release of small amounts of CO₂ (Yapp, 1983; Yapp and Poths, 1986; Yapp, 1987). Yapp and Poths (1986) found that this CO₂ was evolved only when the goethite structure broke down to hematite. Furthermore, the loss of CO₂ from goethite was correlated with the loss of structural hydrogen in the goethite. These results indicate that the CO₂ was contained (“trapped”) within the goethite structure. Yapp and Poths (1986) also found that admixed discrete carbonate phases, such as calcite, siderite, dolomite, etc., did not decarbonate at the temperature at which the CO₂ was evolved from goethite. Thus, such carbonate minerals do not appear to have been the sources of the CO₂ evolved during the goethite-to-hematite phase transformation. Yapp and Poths (1989) determined that the mineral-normalized concentration of “trapped” CO₂ evolved from natural goethite samples was the same both before and after removal of admixed organic matter by concentrated H₂O₂ solution at room temperature. This result implies that the H₂O₂-treatment had no measurable effect on the “trapped” CO₂ in goethite and that this CO₂ does not originate from the decomposition of admixed organic matter during the dehydration experiments.

Russell *et al.* (1975) presented infrared spectroscopic evidence for the formation of distorted carbonate molecules on the surface of moist goethite during CO₂-adsorption experiments. Their model for the formation of these surficial carbonate molecules involved the bonding of the carbon atom in a CO₂ molecule to a structural O²⁻ ion on the surface of the goethite. The surficial structural O²⁻ ions are located in channels parallel to the goethite crystallographic “c” axis, and the CO₂ was presumably accommodated in these channels. The chemisorption reaction: O²⁻ + CO₂ = CO₃²⁻ is readily reversed, as indicated by the fact that Russell *et al.* (1975) were able to remove the surface-adsorbed CO₂ by exposing the goethite to a dynamic vacuum at ~25°C. The structural O²⁻ ion to which the CO₂ was bound was in turn bound to a goethite Fe³⁺ ion. Thus, the results of Russell *et al.* (1975) show that a carbonate molecule bound to an Fe³⁺ ion is inherently unstable

and will easily decarbonate to CO₂. Dvorak *et al.* (1969) synthesized an Fe(III) carbonate that spontaneously decarbonated at room temperature under ambient atmospheric CO₂ partial pressure. Their results strengthen the argument that carbonate molecules bound to Fe³⁺ are relatively unstable.

Yapp (1987) noted that chemisorption of ambient CO₂ is also likely during growth of natural goethite crystals. As crystal growth proceeds some of the surficial CO₂ bound as carbonate to Fe³⁺ would probably be retained in the crystallographic channels and thus would essentially be “trapped” within the interior of the growing goethite structure. Yapp (1987) represented the overall stoichiometry of the reaction as: FeOOH + CO₂ = Fe(CO₃)OH. Because of its distribution in the goethite structure, the Fe(CO₃)OH component could be considered to be in solid solution in the goethite. The results of Dvorak *et al.* (1969) suggest that the hypothesized Fe(CO₃)OH component should break down to produce CO₂ at the relatively low temperatures employed in the goethite dehydration experiments of Yapp and Poths (1986, 1989). In addition, the model of Yapp (1987) predicts that this CO₂ will only be evolved from the Fe(CO₃)OH component in goethite when the local, confining goethite structure breaks down. All of these expectations are consistent with the experimental results of Yapp and Poths (1986, 1989) and Yapp (1987).

If the “trapped” CO₂ evolved during goethite dehydration originates in a carbonate-bearing component formed by the mechanism proposed above, infrared spectra of the goethite should contain peaks indicative of the type of distorted carbonate noted by Russell *et al.* (1975). This note presents evidence for such distorted carbonate in natural goethite.

METHODS

Three natural goethite samples for which the amounts of “trapped” CO₂ had been measured by the dehydration-decarbonation method (Yapp and Poths, 1986; Yapp, 1987) were selected for infrared spectroscopic analysis. The three samples represent the extremes of trapped CO₂ concentrations measured thus far in this laboratory. Sample NG-FCol-1 is at the low end of this

range and has a trapped CO_2 concentration of 0.03 wt. %. Goethite samples NG-NMx-2 and NG-PPColo-1 are at the high end of this range with trapped CO_2 concentrations of 0.52 and 0.62 wt. %, respectively (see Yapp and Poths, 1986; Yapp, 1987). These samples were treated at room temperature with concentrated H_2O_2 solution (30%).

Weighed amounts of powdered goethite were mixed with weighed amounts of KBr in a mortar and pestle under a heat lamp at an ambient sample temperature of about 40°C . These mixtures were pressed into pellets with a diameter of 7 mm and analyzed by infrared spectroscopy in a Nicolet Fourier-transform infrared spectrometer (FTIRS) in the laboratory of George Rossman at the California Institute of Technology, Pasadena, California. Three hundred scans were employed for each spectrum, and background was subtracted from each. A natural siderite sample was also analyzed. Because of the low concentrations of trapped CO_2 in the natural goethite samples, relatively large amounts of goethite were mixed with the KBr to facilitate detection of possible carbonate absorption peaks.

RESULTS AND DISCUSSION

Figure 1 contains the superposed infrared spectra of the samples of Table 1 over the range 1000 to 2000 cm^{-1} . The vertical scales of all the goethite spectra were expanded by the same factor using the data processing software of the Nicolet FTIRS to enhance the subtler absorption features. The peak at 1420 cm^{-1} in the siderite spectrum of Figure 1 represents the characteristic ν_3 absorption peak of carbonate (see Nakamoto, 1970). None of the three goethite spectra show evidence of the single ν_3 absorption peak corresponding to that of siderite or any other common carbonate. The spectra of samples NG-PPColo-1 and NG-NMx-2, however, contain shoulders at about 1345 and 1515 cm^{-1} . In contrast, the spectrum of sample NG-FCol-1 shows no absorption peaks in this region. If the weak absorption peaks at about 1345 and 1515 cm^{-1} in the spectra of samples NG-PPColo-1 and NG-NMx-2 are due to the small amounts of trapped CO_2 , it is not surprising that the much smaller concentration of trapped CO_2 in the sample NG-FCol-1 would be below the detection limits of this infrared method. The absorption shoulders at 1345 and 1515 cm^{-1} in the spectra of samples NG-PPColo-1 and NG-NMx-2 (Figure 1) are strongly suggestive of split ν_3 -carbonate peaks. The magnitude of the splitting is generally consistent with unidentate bonding of the CO_3 to the goethite Fe^{3+} cation (see Nakamoto, 1970). Such unidentate bonding is also consistent with the mechanism proposed above for the formation of carbonate ions in goethite.

In summary, the dehydration-decarbonation data of Yapp and Poths (1986, 1989) and Yapp (1987) indicate that the CO_2 evolved from natural goethites is trapped in the interior of the goethite crystal structure. The

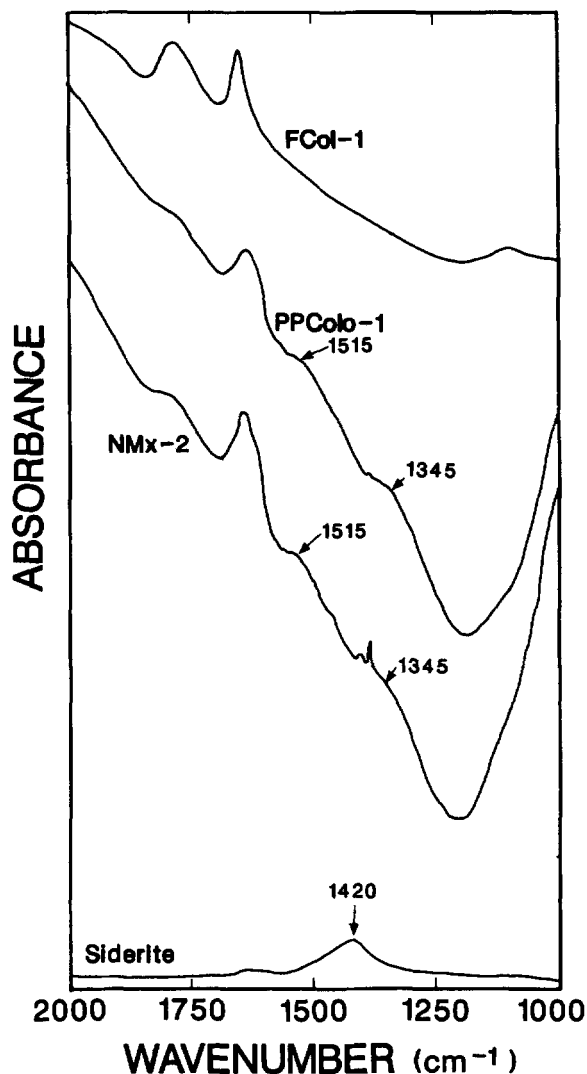


Figure 1. Infrared spectra of three natural goethite samples (FCol-1, PPColo-1, NMx-2) and a natural siderite sample in the region 1000 to 2000 cm^{-1} . Absorption shoulders labeled 1345 and 1515 cm^{-1} for samples PPColo-1 and NMx-2 (with 0.62 and 0.52 wt. % "trapped" CO_2 , respectively) represent split ν_3 -carbonate absorption peak. Thus, these absorption shoulders suggest that "trapped" CO_2 is present as distorted carbonate in these samples (see text). Absence of these absorption shoulders in the spectrum of sample FCol-1 indicates that the much smaller amount of "trapped" CO_2 in this sample (0.03 wt. %) is below the detection limit of this infrared method. The small peaks at about 1380 cm^{-1} in the spectra of samples PPColo-1 and NMx-2 are probably due to adventitious nitrate. Sample masses used in these infrared measurements were FCol-1 (0.7 mg), PPColo-1 (0.4 mg), NMx-2 (0.2 mg), and natural siderite (0.03 mg).

infrared spectra of Figure 1 suggest that this trapped CO_2 derives from a distorted carbonate molecule. These data are consistent with the model proposed by Yapp (1987) for the existence of the carbonate in $\text{Fe}(\text{CO}_3)\text{OH}$ as a minor component in solid solution in goethite.

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