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Infrared and infrared emission spectroscopic study of selected magnesium carbonate minerals containing ferric iron—Implications for the geosequestration of greenhouse gases

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ABSTRACT

The proposal to remove greenhouse gases by pumping liquid carbon dioxide several kilometres below ground level implies that many carbonate containing minerals will be formed. Among these minerals, the formation of two hydrotalcite-like minerals coalingite and brugnatellite is possible, thus necessitating a study of such minerals and their thermal stability. The two such carbonate-bearing minerals brugnatellite and coalingite have been characterised by a combination of infrared and infrared emission spectroscopy. Infrared emission spectroscopy is most useful to determine the stability of these minerals. The infrared spectra of the OH stretching region are characterised by OH and water stretching vibrations. Intense $(CO_3)^{2-}$ symmetric and antisymmetric stretching vibrations support the concept that the carbonate ion is distorted in these minerals. The position of the water bending vibration indicates that the water is strongly hydrogen bonded in the mineral structure. IES spectra show the temperature range of the thermal stability of these minerals.

1. Introduction

The ability to be able to easily and readily detect minerals is of importance [1,2], especially so where carbonate minerals are concerned. The technique of infrared spectroscopy does meet these requirements. What is not known is that many carbonate-containing minerals especially the secondary minerals are soluble and can translocate. The proposal to remove greenhouse gases by pumping CO_2 several kilometres below the ground implies that many carbonate containing minerals will be formed. Two such minerals are the ferric ion-bearing minerals coalingite $Mg_{10}Fe_2{}^{3+}(CO_3)(OH)_{24}{\cdot}2H_2O$ [3–10] and brugnatellite $Mg_6Fe^{3+}(CO_3)(OH)_{13}{\cdot}4H_2O$ [8,11–15]. The formulae of these minerals appear to be related to that of hydrotalcites. Pastor-Rodriguez and Taylor reported the crystal structure of coalingite and presented a model coalingite with a $d(0\,0\,3)$ spacing of 1.25 nm [10]. Brugnatellite is related to the mannesite and pyroaurite mineral group whereas coalingite is related to hydromagnesite and pyroaurite mineral group. Fundamental knowledge of these two minerals is lacking. Pumping greenhouse gases into magnesium-bearing mineral deposits is likely to result in the formation of these types of minerals.

There are many applications of near infrared spectroscopy [16–26]. Many of these studies have been applied to minerals and soils [1,2,24,27–29]. Many carbonate minerals contain both coordinated water and adsorbed water; several minerals contain hydroxyl groups [30,31]. Vibrational spectroscopy has proven very useful for the study of minerals [32–42]. Indeed, Raman spectroscopy has also proven to be very useful for the study of diagenetically related minerals as often occurs with many carbonate minerals. Some previous studies have been undertaken by the authors, using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions.

This paper reports the detection and structural analysis of two magnesium iron-carbonate minerals using infrared spectroscopy with an ATR accessory and infrared emission spectroscopy. The application of this work is important for the geosequestration of greenhouses gases and the consequential detection of carbonate bearing minerals.

2. Experimental

2.1. Minerals

The origin of the minerals is as follows: Brugnatellite—Monte, Ramazzo, Genoa, Liguria, Italy; Brugnatellite—Higasi-Kuroda-Guchi, Inasa-Cho, Inasa-Gun, Aichi Prefecture, Japan; Coalingite—

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Union Carbide Mine, Southern San Benito County, California. The minerals are associated with iron-containing brucite. The phase purity of the minerals was checked by X-ray diffraction and the chemical composition by EDX measurements.

2.2. *Infrared spectroscopy*

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The minerals were used as is. No sample preparation was involved.

Band component analysis was undertaken using the Jandel ‘Peakfit’ (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

2.3. *Infrared emission spectroscopy*

FTIR emission spectroscopy was carried out on a Nicolet Nexus 870 FTIR spectrometer, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere [29–31]. Approximately 0.2 mg of the carbonate mineral was spread as a thin layer on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic absorption graphite rod furnace, which is driven by a thyristor-controlled AC power supply capable of delivering up to 150 A at 12 V. A platinum disk acts as a hot plate to heat the carbonate mineral sample and is placed on the graphite rod. An insulated 125-μm type R thermocouple was embedded inside the platinum plate in such a way that the thermocouple junction was less than 0.2 mm below the surface of the platinum. Temperature control of ±2 °C at the operating temperature of the carbonate sample was achieved by using a Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple.

In the normal course of events, three sets of spectra are obtained over the temperature range selected and at the same temperatures; those of the black body radiation, the platinum plate radiation, and the platinum plate covered with the sample. Normally only one set of black body and platinum radiation is required. The emission spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum covered with the sample, and the result ratioed to the single beam spectrum of an approximate black body (graphite). This spectral manipulation is carried out after all the spectral data has been collected.

The emission spectra were collected at intervals of 50 °C over the range 200–750 °C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 s. It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. The spectra were acquired by co-addition of 64 scans for the whole temperature range, with an approximate scanning time of 45 s, and a nominal resolution of 4 cm^{-1}. Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret due to the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectracalc software package (Galactic Industries Corporation, NH, USA).

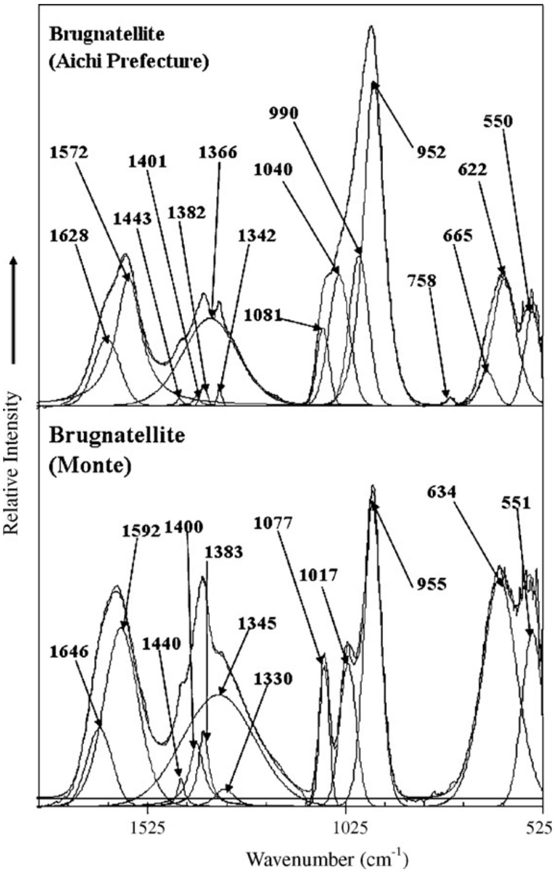

Fig. 1. Infrared spectra of brugnatellite in the 525–1625 cm^{-1} region.

3. Results and discussion

3.1. *Mid-infrared spectroscopy*

The infrared spectra of brugnatellite and coalingite in the 525–1625 cm^{-1} region are shown in Figs. 1 and 2, respectively. The sharp bands at 1081 (Aichi) and 1077 cm^{-1} (Monte) are attributed to the $(CO_3)^{2-}$ carbonate symmetric stretching mode. Such a band should not be observed in the infrared spectrum; however, the observation of this mode in the infrared spectra provides evidence for the distortion of the carbonate anion and consequential loss of symmetry. This band would be intense in the Raman spectrum (not shown). The band is observed at 1077 cm^{-1} for coalingite. The $(CO_3)^{2-}$ carbonate symmetric stretching mode is complimented with the antisymmetric stretching modes found in the 1300–1450 cm^{-1} region where a series of overlapping bands may be observed providing a complex spectral profile. The infrared spectrum of brugnatellite (Aichi) bands is observed at 1342, 1401 and 1443 cm^{-1} and for brugnatellite (Monte) at 1330, 1383 and 1400 cm^{-1}. In the infrared spectrum of coalingite the antisymmetric $(CO_3)^{2-}$ stretching modes are observed at 1372 and 1404 cm^{-1}.

Referring to Figs. 1 and 2, two infrared bands are observed at 1592 and 1646 cm^{-1} in the Monte brugnatellite spectrum. The