

The stability and Raman spectra of ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, at high pressure and temperature

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ABSTRACT

Raman analyses of single crystals of ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, synthesized in a diamond-anvil cell at ambient temperature yield spectra from 0.14 to 4.08 GPa; the most intense peaks are at 228 and 1081 cm^{-1} corresponding to E_g (external) and A_{1g} (internal) modes of vibrations in CO_3^{2-} ions, respectively. These are in good agreement with Raman spectra previously published for ikaite in powder form at ambient temperature and pressure. Visual observations of a sample consisting initially of a mixture of calcite + water in a hydrothermal diamond-anvil cell yielded a P - T phase diagram up to 2 GPa and 120 °C; the boundary for the reaction ikaite \leftrightarrow aragonite + water has a positive slope and is curved convexly toward the aragonite + water field similar to typical melt curves. This curvature can be explained in terms of the Clapeyron equation for a boundary between a solid phase and a more compressible liquid phase or largely liquid phase assemblage.

INTRODUCTION

Calcium carbonate, CaCO_3 , an important constituent of the Earth's crust and oceans, occurs as several crystallographic structures. The anhydrous polymorphs of CaCO_3 include aragonite, calcite, and vaterite. Calcite can also undergo several metastable phase transitions at high pressures to form calcite I, II, and III (Merrill and Bassett 1975; Suito et al. 2001). There are two hydrous forms of calcium carbonate, ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$). They have been found to be stable at H_2O pressures greater than ambient or at temperatures below 25 °C, with the hexahydrate being more favored at higher pressure (Hull and Turnbull 1973). $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ was first synthesized in the laboratory by Pelouze (1831) but was not found in nature until 1963 when it was observed forming at the bottom of Ika Fjord in Greenland and was named ikaite (Pauly 1963). It was found in submarine columns with a temperature of 3 °C that extend up to 20 m above the fjord floor over springs located in the floor. To date there have been only about ten reports of natural ikaite in such places as the Zaire deep-sea fan (Jansen et al. 1987), Mono Lake, California (Council and Bennett 1993), and the Antarctic Shelf (Suess et al. 1982). In these cases as well as other studies, ikaite has been found in hydrous environments where the temperatures are close to 3 °C, but as shown in the laboratory, at warmer temperatures it rapidly decomposes into a cloudy, white suspension of calcite crystals (Marland 1975). It has been hypothesized by Shearman and Smith (1985) that ikaite is the precursor of the calcite pseudomorphs in thinolite tufa of

Pleistocene lakes that filled the Lahontan and Mono Basins.

Few studies have been conducted on ikaite to determine its stability at high pressures. Dickens and Brown (1970) first determined the crystal structure of ikaite. They found that ikaite is monoclinic with each CaCO_3 ion pair surrounded by an envelope of 18 H_2O molecules. Van Valkenburg et al. (1971) found that ikaite was more stable than calcite and aragonite at room temperature and high water pressure. Marland (1975) found that ikaite was stable at room temperature only at pressures above 0.5 to 0.6 MPa; however, the exact pressure range was not determined. The method used in the latter study required powdering the sample and, due to its instability, examining it within thirty minutes of preparation. Bischoff et al. (1993) examined the stability and solubility from 0 to 25 °C.

In a recent paper Scott et al. (2004) present evidence that co-existing H_2O and CaCO_3 in the presence of a reducing agent such as FeO at high P - T conditions will yield methane plus magnetite. It seems reasonable that co-existing ikaite and FeO might also yield methane plus magnetite at high P - T conditions. Our experiments as well as the natural occurrences of ikaite took place in the absence of any such reducing agent. There was no evidence in any of our experiments that diamond entered into the reaction. Likewise, the natural settings of ikaite appear to have been in relatively oxidizing conditions that favored ikaite as the stable phase.

Raman spectroscopy has been applied to ikaite only once before by Mikkelsen et al. (1999). That study did not use high pressure to synthesize ikaite, but rather precipitated it in the same way as Dickens and Brown (1970): by dissolving CaCl_2 in water and adding it to a solution containing Na_2CO_3 and $\text{Na}_5\text{P}_3\text{O}_{10}$. When this final solution was left for several months at 3 to 5 °C, crystals of ikaite grew. The crystals were then washed, dried with acetone, and ground to a fine powder.

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In this paper the objectives are threefold: (1) to obtain Raman spectra of a single crystal of ikaite over a range of pressures in a diamond-anvil cell, (2) to develop a technique for determining equilibrium relationships in a hydrothermal diamond-anvil cell, and (3) to investigate phase relations in the water-saturated calcium carbonate system to higher pressures and temperatures than in previous studies.

EXPERIMENTAL METHODS

For the first stage of this study ikaite crystals were synthesized, at ambient temperature, in a piston-cylinder type of diamond-anvil cell (DAC). The diamonds had 616 and 610 μm culet faces. A gasket was formed by drilling a 300 μm diameter hole into a 200 μm thick stainless steel gasket, and a sample consisting of aragonite, water, and ruby chips for pressure calibration was placed in the gasket hole. The aragonite was a high-purity natural sample from the Geophysical Laboratory research collection. Over several hours at 0.9 to 0.95 GPa the aragonite dissolved and ikaite crystallized. Raman spectra were then obtained from the crystals using 514 nm Ar^+ laser excitation, a 10 \times objective, and ~ 10 mW laser power at the sample surface. The spectra were typically collected for 300 s using an Andor CCD detector cooled to -90°C mounted on a TRIAX 550 spectrometer with a 1500 grooves/mm grating. The carbonate minerals were easily identifiable using Raman spectroscopy as the CO bands give rise to intense Raman bands.

In the second stage of the study ikaite crystals (Fig. 1) were synthesized in a hydrothermal diamond-anvil cell (HDAC) (Bassett et al. 1993). The diamonds used had 700 μm culet faces. Each experiment used a rhenium gasket with sample chamber size varying from 300 to 400 μm in diameter and from 125 to 250 μm in thickness. A pure sample of calcite from the Cornell study collection was loaded into the sample chamber with water. In both the Raman and phase relation studies, data collection began only after the starting material went into solution. Therefore, the structure of the starting CaCO_3 had no influence on the results. A small bubble was usually present as the cell was closed and helped us to estimate the bulk fluid density in the cell at the start of an experiment. The pressure in the cell was then increased until the bubble disappeared.

A video camera mounted on the microscope was used to continuously record the experiments as they progressed from start to finish. A separate camera was set up in front of the digital displays to record time and temperatures. These images were then combined using the picture in picture mode of a Videonics MX-1 digital video mixer. All images were recorded with a video cassette recorder. The rapidity with which some events took place required playing and replaying the images frame by frame or at slow speed before interpretations were made.

The calcite sample used is from Sweet Grass County, Montana and comes from the Cornell University collection. An analysis made with a JEOL model JXA-8900 electron microprobe gave 0.086% MnO and 0.014% SrO as the only impurities within the detection limits of the microprobe.

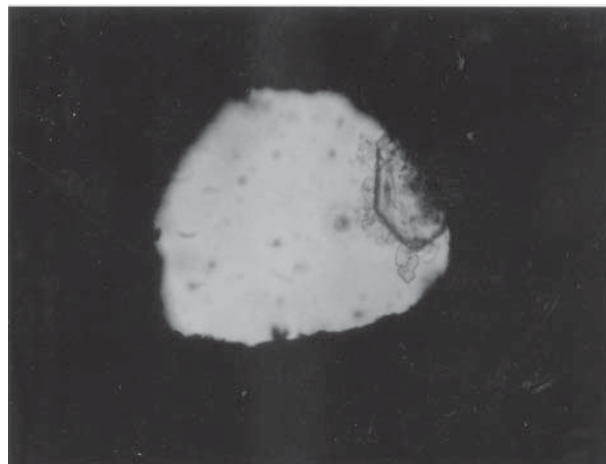


FIGURE 1. An ikaite crystal in a hydrothermal diamond-anvil cell with parallel overgrowths of other small ikaite crystals surrounded by water. Ikaite has lower refractive indices than the other calcium carbonate phases encountered in these runs.

Pressure calibration

In the first experiments a ruby chip was placed in the sample chamber for pressure determination (Barnett et al. 1973). For the experiments in the HDAC, a pressure determination technique suggested by Haselton et al. (1995) was used. As the experiment progressed, we would watch for any phase transitions based on the criteria discussed below. When we were confident that we were on the ikaite-aragonite phase boundary, for example, the temperature was noted (T_1). Cold nitrogen gas from a tank of liquid nitrogen was then used to lower the cell temperature until the water in the sample froze. The sample was then reheated and the exact ice melting temperature was noted. Using a water-ice phase diagram we were able to determine the pressure as well as the density of water at the melting point of ice. The pressure at T_1 was then calculated based on the assumption that the sample remained isochoric during heating. This technique was used for points on the phase boundary and in the stable regions of the minerals. The melting points were measured frequently throughout the experiments so as to establish density before and after the transitions were observed. For calculating pressures from melting points, we used equation of state data assuming pure water. We based this assumption on the very low CaCO_3 solubilities reported by Newton and Manning (2002). We believe that any error introduced by this assumption is negligible.

Techniques for determining equilibrium phase relations

The mineral phases observed in the HDAC were identified by their morphology and optical properties. Calcite takes the form of rhombohedral crystals while aragonite is acicular and ikaite is a transparent monoclinic crystal (Dickens and Brown 1970). Ikaite usually precipitated as a single crystal with low relief due to its low refractive indices, while aragonite was found in all sizes throughout the sample chamber, sometimes as individual crystals, sometimes as radiating clusters of needles.

Three types of observations were used in this study to determine when the sample was at a phase boundary: (1) when two solid phases coexisted at or near equilibrium, one started to dissolve in the water while the other began to precipitate in a different part of the sample chamber; (2) when a crystal of one phase transformed in place to another phase; and (3) when a sudden, "explosion-like" transition took place.

The first criterion was expected to yield pressure and temperature data closest to equilibrium. Using this method, we determined if we were on the phase boundary by watching as one of the existing solid phases slowly dissolved. This became apparent as the outline of the crystal began to lose facets and become more rounded, a phenomenon that was almost always more apparent than the growth of the other phase. We then noted the range of temperatures over which this occurred. This range was usually on the order of 10°C and was a result, to some degree, of the effect of the phase transition on the pressure within the constant volume sample chamber. Reversing the temperature change usually resulted in the rapid reestablishment of the faceted outline of the original crystal.

If a new phase does not immediately nucleate, as with the second criterion, the P - T conditions may exceed equilibrium, i.e., pass beyond the phase boundary. When this happens, the transition may take place in situ, and can be recognized by a darkening of the original crystal due to the scattering of light at interfaces between phases within the crystal. Reversing the temperature causes the crystal to become partially transparent again but with a larger hysteresis than observed in the first criterion.

The third criterion was used for another case in which nucleation was delayed. In this case, the transition was observed as a very rapid, explosion-like process in which the original crystal dissolved and small crystals of the new phase precipitated throughout the sample chamber in a matter of seconds. As with the previous criterion, this is expected to yield P - T conditions beyond equilibrium.

RESULTS AND DISCUSSION

Raman spectroscopy

Ikaite was synthesized several times at ambient temperature in the DAC, each time resulting in a crystal surrounded by water ice. The crystal was clear, colorless, and had a shape consistent with monoclinic symmetry. The crystal grew at the expense of the aragonite until the aragonite was completely consumed. The final ikaite crystal was approximately 100 μm long. After the crystal grew the Raman spectra were taken immediately and during the

following day. Two different experiments were conducted. In the first experiment, spectra were obtained at increasing pressure intervals, and the initial pressure at which the ikaite grew was found to be 0.9 GPa. The second experiment had an initial pressure of 0.95 GPa and the spectra were obtained at decreasing pressure intervals. In both cases the spectra were similar except for shifts in wavenumber due to the pressure. In the second experiment, the Raman spectra were obtained within a few minutes of reaching a stable pressure as there was a chance that the ikaite would decompose. Figures 2 and 3 show spectra at 7 different pressures and Table 1 lists the pressure shifts. The spectrum at 1.32 GPa shows eight peaks, four corresponding to E_g external vibrations of CO_3^{2-} ions at 228, 240, and 280/308 cm^{-1} , two corresponding to internal vibrations of CO_3^{2-} ions, namely, the E_g (internal) and A_{1g} (internal) vibrations at 729 and 1081 cm^{-1} , respectively (Fig. 2), and two peaks related to water at 3207 and 3403 cm^{-1}

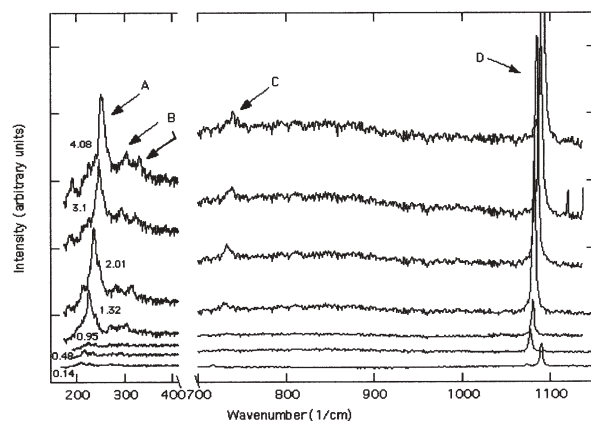


FIGURE 2. Series of Raman spectra of ikaite at pressures from 0.14 to 4.08 GPa in a diamond-anvil cell. The peaks between 200 and 400 cm^{-1} can be attributed to lattice vibrations. Peaks between 700 and 800 cm^{-1} correspond to E_g (internal) mode of vibrations in CO_3^{2-} ions. The arrows show the positions of the peaks referred to in Table 1. The intensity scale has arbitrary units.

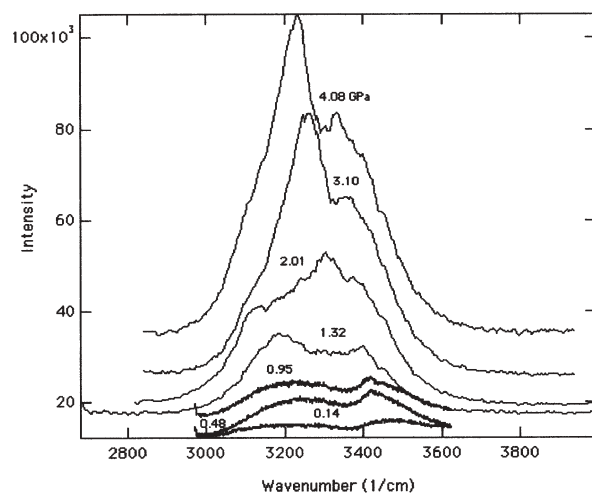


FIGURE 3. Series of Raman spectra from 0.14 to 4.08 GPa showing shifts of peaks in the range from 3000 to 3600 cm^{-1} that are related to water. The numbers are given in Table 1. The intensity scale has arbitrary units.

(Fig. 3) (Mikkelsen et al. 1999). Ikaite has a spectrum similar to the other calcium carbonate polymorphs (Rutt and Nicola 1974; Long 1977), but with water peaks visible between 3000 and 3600 cm^{-1} . The peaks become more intense as the pressure increases and the pressure-shifts become larger for the external (lattice) modes than the internal vibrations.

The columns in Table 1 are lettered in accordance with the peaks from left to right. Each of the peaks, A, B, and E consists of two closely spaced peaks. Some of the peaks were not visible at some pressures, but the major peaks were always visible and showed slight shifts with pressure. The shifts can be seen in a series of Raman spectra shown in Figures 2 and 3.

Phase diagram extension

We have modified and extended the water saturated calcium carbonate phase diagram (Fig. 4) beyond the earlier work done by Marland (1975). It was possible to obtain coexisting hydrous and anhydrous forms of calcium carbonate in the host solution. The water can be considered to serve a dual role in these experiments, as a reactant and as a pressure medium. It may be helpful to think of the water as consisting of a mixture of these two components when considering the relative volumes of the phases.

The characteristics of the crystals of the three phases were so distinctive that there was never any doubt as to which phases were present. Once the phase boundary between ikaite and aragonite was crossed, aragonite needles grew rapidly at the expense of the ikaite.

Marland (1975) observed transitions from ikaite to calcite at low P - T conditions (Fig. 4), whereas we observed transitions from ikaite to aragonite at higher P - T conditions. No reliable measurements of the calcite-aragonite phase boundary have been made at conditions below 0.4 GPa and 100 $^{\circ}\text{C}$ because this transition is extremely sluggish even with the solution and precipitation technique we used for determining the ikaite-aragonite boundary. Although it is possible that Marland's results taken together with ours may define the equilibrium calcite-aragonite boundary at low P - T conditions, more careful work needs to be carried out before such a conclusion can be made with confidence. The calcite-aragonite phase boundary shown in Figure 4 is based on the combined results of Goldschmidt and Newton (1969) and Crawford and Fyfe (1964). The dashed part of the line is a linear extrapolation of that boundary to lower P - T conditions.

Figure 4 shows isochores, data points, and ice melting curves used to calculate the pressures listed in Table 2. The melt curve of ice was determined using data based on Saul and Wagner (1989), and the densities of water at the melting points of ice

TABLE 1. Raman peak shifts due to pressure

Pressure (GPa)	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})	D (cm^{-1})	E (water peaks) (cm^{-1})
0.14	211/228	270/284	723	1074	3274/3490
0.48	216/234		732	1076	3257/3423
0.95	225/244	284	728	1080	3239/3417
1.32	228/240	280/308	729	1081	3181/3399
2.01	238/247	287/317	736	1086	3243/3304
3.1	247	296/322	741	1090	3258/3359
4.08	255	308/334	745	1092	3233/3334

Notes: Some of the peaks were not visible at all pressures. Columns, named A, B, C, D, and E refer to peaks from left to right.

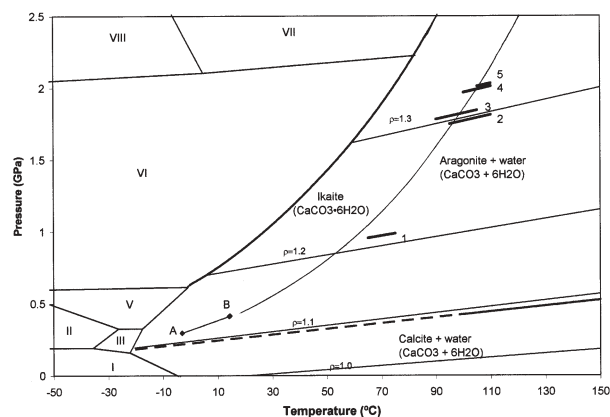


FIGURE 4. Phase diagram for the $\text{CaCO}_3\text{-H}_2\text{O}$ system extended to 2.5 GPa and 150 °C. The A-B portion of the ikaite \leftrightarrow aragonite + water boundary is taken from Marland (1975). The portion of the ikaite \leftrightarrow aragonite + water boundary beyond B is based on our results reported in Table 2. Our experimental points are represented by heavy lines, each extending over a range of observations along an isochore based on the melting point of ice measured at the end of each observation. The boundary is not a best fit to our data points as we have reason to believe that the nature of the observed transition determines whether the observation occurred at the boundary or at P - T conditions just above the boundary (see text). The short, heavy solid lines represent the isochoric P - T conditions over which both ikaite and aragonite + water coexist. The lighter straight lines are isochores for densities (ρ) = 1.0, 1.1, 1.2, and 1.3 g/cm^3 . The phases of H_2O ice (shown as areas with Roman numerals) and their melt curves are superimposed on the phase diagram for the $\text{CaCO}_3\text{-H}_2\text{O}$ system. The pure H_2O phases are included to help the reader better understand our method for determining the pressures of our observations.

were determined by using the computer program Loner23 (Bakker 2003). The pressures along the isochores were found using a computer program based on IAWPS-95 (Wagner and Pruss 2002). Data point no. 1 is based on the in situ transition criterion and is therefore expected to lie beyond the equilibrium phase boundary. Data points 2, 3, and 4 are based on the solution-precipitation criterion and are therefore expected to lie on the equilibrium phase boundary. Data point no. 5 is based on the sudden explosion-like criterion and is expected to plot just to the right of the equilibrium phase boundary. Line A-B was determined by Marland (1975) as the equilibrium boundary.

One of the most striking features of our phase diagram is the curvature of the ikaite \leftrightarrow aragonite + water phase boundary, a curvature similar to that found for typical melt curves. An explanation for the similarity is to be found in the fact that in one of the phase assemblages, aragonite + water, one molecule of CaCO_3 plus six molecules of the reactant part of the liquid water constitute the phases on one side of the boundary. Because a liquid is generally more compressible than the corresponding solid, ΔV rapidly decreases along the phase boundary with increasing pressure. Thus, according to the Clapeyron equation, $dP/dT = \Delta S/\Delta V$ (where P is pressure, T is temperature, S is entropy, and V is molar volume), the slope of the boundary becomes increasingly steep with increasing pressure.

TABLE 2. Data points for the ikaite \leftrightarrow aragonite + water equilibrium experiments

Point	Ice melting T (°C)	Density (g/cm^3)	Temperature range (°C)	Pressure range (GPa)
1	12.55	1.212	65–75	0.96–0.99
2	57.30	1.298	95–110	1.75–1.81
3	59.95	1.304	90–105	1.78–1.85
4	72.75	1.318	100–110	1.97–2.01
5	73.65	1.320	105–110	2.01–2.03
A			–3.0	0.296
B			14.5	0.415

Note: Points A and B are from Marland (1975).

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