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PAPER

Clathrate hydrate formation after CO₂–H₂O vapour deposition

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We study vapour condensation of carbon dioxide and water at 77 K in a high-vacuum apparatus, transfer the sample to a piston-cylinder apparatus kept at 77 K and subsequently heat it at 20 MPa to 200 K. Samples are monitored by *in situ* volumetric experiments and after quench-recovery to 77 K and 1 bar by powder X-ray diffraction. At 77 K a heterogeneous mixture of amorphous solid water (ASW) and crystalline carbon dioxide is produced, both by co-deposition and sequential deposition of CO₂ and H₂O. This heterogeneous mixture transforms to a mixture of cubic structure I carbon dioxide clathrate and crystalline carbon dioxide in the temperature range 160–200 K at 20 MPa. However, no crystalline ice is detected. This is, to the best of our knowledge, the first report of CO₂ clathrate hydrate formation from co-deposits of ASW and CO₂. The presence of external CO₂ vapour pressure in the annealing stage is not necessary for clathrate formation. The solid–solid transformation is accompanied by a density increase. Desorption of crystalline CO₂ atop the ASW sample is inhibited by applying 20 MPa in a piston-cylinder apparatus, and ultimately the clathrate is stabilized inside layers of crystalline CO₂ rather than in cubic or hexagonal ice. The vapour pressure of carbon dioxide needed for clathrate hydrate formation is lower by a few orders of magnitude compared to other known routes of CO₂ clathrate formation. The route described here is, thus, of relevance for understanding formation of CO₂ clathrate hydrates in astrophysical environments.

Introduction

Amorphous solid water (ASW) is produced by water vapour condensation at low temperature (<130 K) and low pressure (<1 mbar).^{1–5} ASW is thought to be the most abundant form of water in the universe and believed to be present as frost on interstellar dust grains, on the particles of planetary rings, on the icy satellites of the giant planets and on comets, at least in the course of their evolution.^{6–10} When deposited at 77 K or below ASW is a highly microporous solid^{7,8,11–13} and shows surface areas up to a few thousand m² g^{−1}.¹⁴ Depending on deposition conditions, *e.g.*, angle of incidence and temperature, the porosity maybe up to 80%.^{15–18} This microporous solid is highly capable of trapping atoms or small molecules like Ar, N₂, O₂, CO, CO₂ or CH₄.^{19–28} At >100 K annealing causes a dramatic reduction of porosity, number of surface sites, surface area, and a bulk water density of 0.94 g cm^{−3} results.^{29–31} Comparison of dense and microporous thin films of ASW has revealed that the total amount of gas adsorbed may be up to 50 times larger in the latter case.¹⁴ Studies by Hallbrucker and Mayer in Innsbruck have shown that some of the molecules adsorbed in micropores become practically irreversibly trapped in the course of annealing. These molecules

can no longer desorb or be pumped off because all possible pathways leading to the exterior are blocked in the pore network. Even at much higher temperature, *e.g.*, 200 K, these molecules remain trapped in the interior of the solid water sample. Bar-Nun *et al.* inferred that the formation of clathrate hydrate cages around these trapped molecules may be possible at >150 K after crystallization of ASW to cubic ice.^{19,20,22} Hallbrucker and Mayer have succeeded in preparing cubic structure II hydrate after trapping of NO,³² N₂,³³ O₂^{33–36} and Ar³⁷ by loading of the micropores in ASW at 77 K with guest gas. The cubic structure I hydrate was produced from ASW in the pioneering study by Bertie and Devlin after trapping of oxirane³⁸ and by Hallbrucker and Mayer after trapping of CO.³⁷ The clathrate hydrates typically form at 170–200 K in these experiments, and typically 1 bar of external guest gas pressure was used for filling the micropores of ASW. In case of polar guest molecules such as formaldehyde,³⁹ oxirane³⁸ or methanol,⁴⁰ which may form weak hydrogen bonds with the cages, formation of the clathrate may even take place at <150 K.⁴¹ In case of non-polar guest molecules (such as carbon dioxide) clathrate hydrates may be vapour deposited only with the help of a low percentage of helper molecules capable of accepting protons or with the aid of epitaxial growth on a suitable substrate.⁴¹

Carbon dioxide clathrate has been suggested to be present in the Mars ice caps as early as 1970,⁴² and this hypothesis is still discussed vividly and controversially.^{28,43–50} Also its presence

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on icy satellites such as Europa is discussed.^{51,52} Furthermore, the possibility of carbon dioxide clathrate on the Moon was postulated.⁵³ Besides this astrophysical relevance carbon dioxide clathrates are discussed for the fixation/sequestration or sedimentation/storage of carbon dioxide in the context of greenhouse warming,^{54–61} and its formation and stability in the (deep) ocean is investigated.^{62–65} CO₂ clathrates are also discussed in more industrially oriented applications such as fire suppression systems⁶⁶ and frozen desserts.⁶⁷

Carbon dioxide clathrate hydrate was first noted in 1882,⁶⁸ the ratio CO₂:H₂O $\approx$ 1:6 was established in 1897,⁶⁹ and it was found to show the cubic structure I type in 1954.⁷⁰ Typically, it is produced at high temperature (>250 K) in the presence of external gaseous or liquid carbon dioxide, often at rather high pressure.^{56,71} FT-IR studies have allowed to analyze the distribution of CO₂ molecules in the cages, and shown that the large (5¹²6²) cages are fully occupied, and in addition some of the small (5¹²) cages.^{48,72–74} In the presence of helper gas Fleyfel and Devlin succeeded to obtain carbon dioxide trapped in a cubic structure II clathrate.⁷⁵ Also in natural quartz veins carbon dioxide was shown to be trapped in the metastable structure II clathrate phase from infrared spectroscopic studies.⁷⁶ Besides infrared spectroscopy also X-ray/neutron diffraction,^{77–86} Raman spectroscopy^{61,87,88} and ¹³C NMR^{73,86,89–91} have helped in improving our understanding of the carbon dioxide clathrate hydrate.

Malyk *et al.* have studied the trapping and release of CO₂ in ASW films and recorded infrared spectra and temperature-programmed desorption traces in an ultrahigh vacuum chamber.^{25,92} While they clearly distinguish crystalline carbon dioxide atop the ASW film and carbon dioxide molecules diffused into the ASW pores, they conclude it is unlikely that clathrate hydrate cages are formed at 185 K, their film sublimation temperature.²⁵ Also Galvez *et al.* claim to be able to discriminate between external and internal carbon dioxide in amorphous ice spectroscopically.^{26,93} Also these authors do not report on clathrate hydrate formation from ASW, maybe because they did not investigate IR spectra at sample temperatures above 140 K. Furthermore, time-resolved molecular beam analysis of carbon dioxide on amorphous ice surfaces in the range 100–160 K corroborates an efficient trapping on amorphous ice at <120 K, but does not hint at conversion to clathrate at higher temperature.²³ That is, formation of clathrate hydrates from carbon dioxide trapped in ASW has not been observed so far. However, Trainer *et al.* interpret their IR spectra in favour of clathrate hydrate formation²⁸ from vapour-deposits of crystalline ice at 140–165 K in the presence of up to 300 mbar of CO₂. The formation of cubic structure I carbon dioxide clathrate hydrate from amorphous solid water prepared at 77 K is evidenced herein from powder X-ray diffractograms. Isobaric piston-cylinder experiments at 20 MPa allow for *in situ* volumetric observations, which reveal clathrate hydrate formation to take place in the temperature range 140–200 K. The vapour pressure of carbon dioxide needed for clathrate hydrate formation using our approach is lower by a few orders of magnitude compared to other known routes of CO₂ clathrate formation. The route described here is, thus, of relevance for understanding formation of CO₂ clathrate hydrates in astrophysical environments, where

liquid carbon dioxide or high CO₂ vapour pressures are unlikely present.

Experimental

The procedure for preparing bulk samples of ASW was described previously, and a sketch of the apparatus was shown in Fig. 1 of ref. 37. Briefly, water vapour from a reservoir of ambient temperature liquid water was admitted through a fine metering valve and a copper tube with 13 mm inner diameter into a high-vacuum system. The base pressure of the system is better than 10^{−6} mbar. Deposition was done at a water vapour pressure of $\sim$ 0.5 mbar on a cryoplate made from copper, which was kept at 77 K by direct cooling with liquid nitrogen. The cryoplate is mounted at a distance of $\sim$ 5 cm in the line of sight of the copper tube, which acts as a nozzle and ensures supersonic flow of water vapour. Bulk samples of $\sim$ 2–3 mm thickness are prepared after vapour deposition of about 4 hours. In sequential deposition experiments CO₂ was admitted from a cylinder (Linde, CO₂, purity $\geq$ 99.995%) through the fine metering valve and the copper tube. The CO₂ vapour pressure was set to $\sim$ 0.05 mbar, and deposition times of $\sim$ 4 hours were used. Alternatively, also experiments with a CO₂ partial pressure of $\sim$ 0.5 mbar were done, albeit at shorter deposition times of $\sim$ 30 minutes. In co-deposition experiments a total vapour pressure of $\sim$ 0.55 mbar, and a ratio of CO₂:H₂O partial pressures of 1:10, was employed for deposition experiments of $\sim$ 4 hours. After deposition the apparatus was pressurized with N₂ from a cylinder (Messer; N₂, >99.5%) and the sample kept at 77 K quickly immersed in liquid nitrogen.

The samples were then either transferred to the sample holder (copper plated nickel) of the X-ray diffractometer, which was precooled to $\sim$ 83 K or filled into the bore (8 mm inner diameter) of a steel-cylinder kept at 77 K, which was lined with a thin indium foil as originally proposed by Mishima *et al.*⁹⁴ The diffractograms (Cu K α_1) were recorded at $\sim$ 83 K on a diffractometer in θ – θ geometry (Siemens, model D 5000), equipped with a low-temperature camera of Anton Paar and a Goebel-mirror. Phase identification was done by employing the known crystal structures with the aid of the program PowderCell.⁹⁵ X-Ray diffraction of pure water vapour deposits samples shows the broad halo peaks expected for an entirely amorphous sample. Thus these samples are identical to the microporous ASW samples prepared earlier in Innsbruck.^{5,7,8} Powder X-ray diffractograms of samples prepared by sequential deposition and co-deposition of CO₂ and H₂O are shown in Fig. 1.

By contrast to earlier studies done in the Innsbruck laboratory in the context of clathrate hydrate formation from ASW samples^{33–37} we did not anneal the samples in the high-vacuum chamber at 120 K or higher. Rather, the temperature of the sample holder was kept at 77 K at all times. Also, we did not pressurize the apparatus to $\sim$ 1 bar with the guest gas in the clathrate hydrate, which is CO₂ in the present case. That is, the CO₂ partial pressure was kept at <1 mbar in the whole study. We infer astrophysical relevance because of these low CO₂ vapour pressure conditions throughout the whole experiment. Using this type of approach the sintering of micropores and

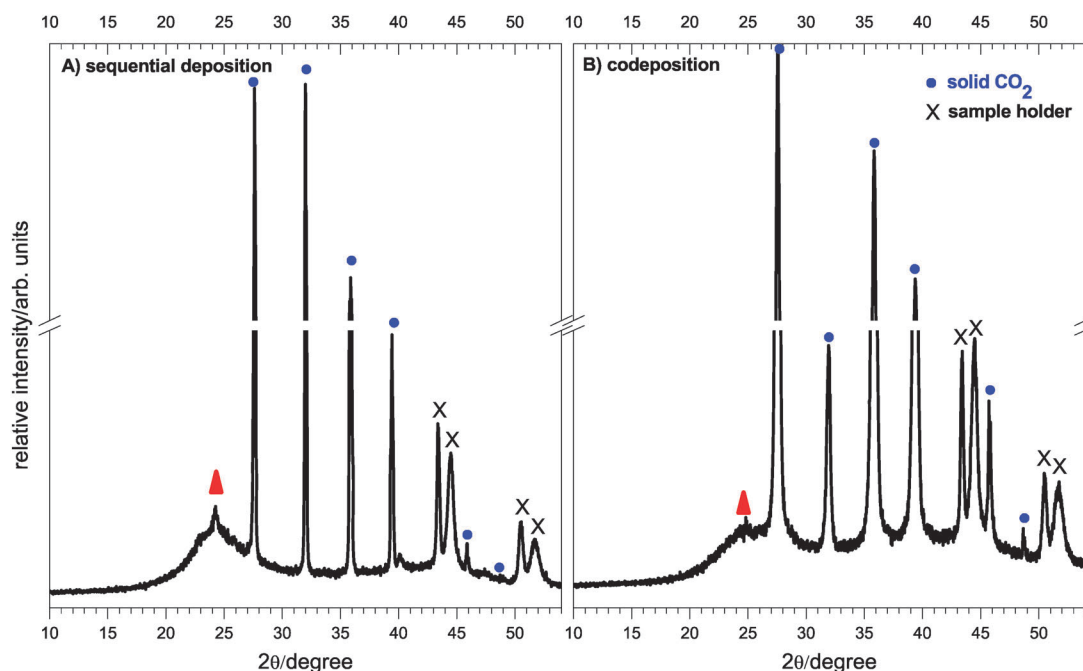


Fig. 1 Powder X-ray diffractograms ($\text{Cu-K}\alpha_1$) (A) obtained after 2 hours of water vapour deposition followed by 30 minutes of carbon dioxide vapour deposition (both at 0.5 mbar partial pressure), and (B) after 4 hours of $\text{CO}_2/\text{H}_2\text{O}$ co-deposition (0.50 mbar water and 0.05 mbar carbon dioxide vapour pressure). The samples were kept at 77 K at all times. The filled red triangle marks the amorphous halo peak maximum, filled blue circles indicate crystalline CO_2^{103} and X indicates sample holder (nickel-plated copper) reflections.

desorption of the crystalline guest gas adsorbate are avoided, which are known to take place at > 100 K.

Volumetric measurements were done in a hardened, stainless steel piston-cylinder setup as described in our earlier publications.^{96–100} Temperature and temperature change rates are controlled by a thermostat (Lakeshore CI330), where cooling is achieved by sucking liquid or gaseous nitrogen through copper loops in direct contact with the steel cylinder and heating is achieved by two resistive heaters sitting in two additional bores in the steel cylinder. Uniaxial force and pressure are controlled by a computerized material testing machine (Zwick, model BZ100/TL3S). Its positional reproducibility is ± 5 μm , and the spatial resolution of the drive is 0.01 μm . Isothermal pressure-displacement (Fig. 2A and Fig. 4A) and isobaric temperature-displacement curves (Fig. 2B) were recorded with the TestXpert V 7.1 Software of Zwick. Indium linings were used to avoid pressure drops and shock-wave generation during compression.^{94,101} We do not know the exact sample mass transferred into the cylinder, because the solid is transferred grain by grain with a spoon into the bore. Typically, a cylindrical sample of ~ 10 mm in height and 8 mm in diameter was recovered after the isobaric experiments at 20 MPa, which would correspond to ~ 500 mg of sample when assuming a sample density of ~ 1 g cm^{-3} . After volumetric experiments the sample can be quench-recovered to 77 K and 1 bar by first immersing the whole setup in liquid nitrogen and then slowly releasing the pressure. Monitoring of the piston displacement in the course of quenching and pressure release indicates that no phase transitions (see Fig. 2 and Fig. 4) take place in the process of quench-recovery, just like in the case of our earlier studies on amorphous ice, crystalline ice and clathrate hydrates.^{96–100}

Results

Fig. 1 shows the powder X-ray diffractograms obtained after sequential deposition (Fig. 1A, left) and co-deposition (Fig. 1B, right) of water and carbon dioxide. In both cases a broad halo peak centered at $2\theta \approx 24.0^\circ$ (marked by full red triangles) and a number of sharp Bragg reflections are evident. The broad halo peak is typical of amorphous solid water as obtained from water vapour deposition experiments^{5,7,8} without deposition of carbon dioxide. Partial radial distribution functions for this amorphous state have been reported by Bowron *et al.*¹⁰² The second halo maximum expected at $2\theta \approx 43.0^\circ$ is obscured by the sharp Bragg reflections. These sharp peaks are caused by the presence of the sample holder (marked by an X in Fig. 1) and crystalline carbon dioxide (marked by full blue circles). Six reflections centered at $2\theta \approx 27.6^\circ$, 32.0° , 35.9° , 39.4° , 45.8° and 48.7° are in excellent agreement with the known reflections from the CO_2 crystal structure (space group $Pa3$, $a = 5.624$ Å).¹⁰³ These Bragg peaks arise from crystalline carbon dioxide domains co-existing with ASW, which was labelled “external” carbon dioxide by Galvez *et al.*^{26,93} There is no evidence for a second type of carbon dioxide phase in these diffractograms. As expected “internal” carbon dioxide molecules trapped in ASW micropores are not evident in the diffractograms, which implies that the molecules trapped in the micropores do not show long-range ordering. Detection of carbon dioxide molecules trapped in the micropores and further refinement of their binding situation would require other methods such as infrared spectroscopy. This is not attempted here in view of the excellent literature studies available on the topic.^{13,25,26,41,72,75,92,93,104} We emphasize, however, that the guest

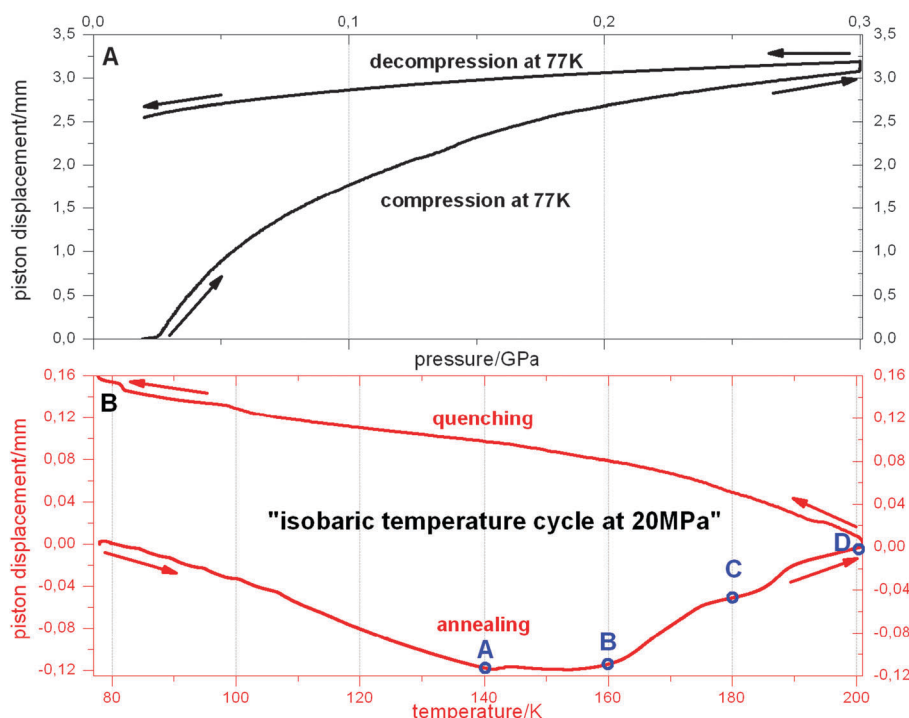


Fig. 2 Piston displacement curves, where the upward direction corresponds to densification of the sample. (A) Isothermal pre-compression and decompression of the loose CO_2/ASW powder at 77 K, and (B) Isobaric heating and cooling of the compacted sample cylinder at 20 MPa. In addition to the sample quenched here at point D, three other samples were quenched from the points A, B and C. Powder X-ray diffractograms of the corresponding quench-recovered samples are shown in Fig. 3.

gas is co-existing as a crystalline phase with ASW at 77 K after recovery from the apparatus, by contrast to earlier studies of clathrate formation from ASW, in which the guest gas phase has been pumped off prior to recovery from the apparatus.^{32,36}

In the next step this heterogeneous mixture of ASW and crystalline carbon dioxide was transferred to the piston-cylinder setup without raising the sample temperature significantly above 77 K. Fig. 2A shows the evolution of the piston position in the initial isothermal pre-compression step to 0.3 GPa. The loose powder is compacted to a dense cylinder in this step. The compaction is practically complete at ~ 0.2 GPa using the compression rate of $0.14 \text{ GPa min}^{-1}$. Upon decompression the cylindrical sample expands elastically, and a total, permanent compaction of ~ 2.5 mm has been achieved in the pre-compression step. The sample is decompressed to 20 MPa at 77 K, where it is kept isobarically for the following step. In this step the sample is heated at a rate of $\sim 3 \text{ K min}^{-1}$ to 200 K and then quenched back to 77 K by immersion in liquid nitrogen (which results in an average cooling rate of $\sim 24 \text{ K min}^{-1}$). We emphasize that crystalline carbon dioxide does not melt or sublime even at the highest temperature experienced in this experiment (200 K) under these conditions. Temperatures exceeding 220 K would be required at 20 MPa to melt crystalline carbon dioxide according to the CO_2 phase diagram. Monitoring the sample length changes as a function of temperature, we observe rather linear thermal expansion of the sample in the temperature range 80–140 K, which is followed by deviation from linearity and even an increase in sample density in the temperature range 160–200 K. The quenching process shows a rather linear shrinking of the sample in spite

of the uncontrolled, changing rate of cooling. This shrinking on cooling from 200–80 K is practically parallel to the expansion on heating at 80–140 K. The density increase observed at ~ 160 –200 K is not reversed by cooling. In the experiment shown in Fig. 2B the permanent densification amounts to ~ 0.16 mm.

In order to assess the structural changes underlying the volumetric observations we have quench-recovered in total four samples from 140 K, 160 K, 180 K and 200 K (marked by A, B, C and D in Fig. 2B) and analyzed these samples again by powder X-ray diffraction. The four diffractograms are shown in Fig. 3. The diffractogram depicted in Fig. 3A is highly similar to the two diffractograms depicted in Fig. 1. The only exception are tiny Bragg peaks observed at the position of cubic ice, plus the hexagonal (100) reflection indicating hexagonal stacking faults in cubic ice (marked by green hash-marks), which indicate the presence of a trace amount of cubic ice.^{105,106} That is, after transfer to the piston cylinder setup at 77 K, pre-compaction at 77 K to 0.3 GPa, heating to 140 K at 20 MPa and quench-recovery the sample has remained practically unaffected. After heating to 160 K at 20 MPa some changes are evident in the diffractogram. Mainly, the area under the ASW halo peak has decreased significantly (by about 30%) relative to the area of the most intense CO_2 reflection at $2\theta \approx 27.6^\circ$. While this difference between Fig. 3A and Fig. 3B can in principle be also be due to different $\text{CO}_2/\text{H}_2\text{O}$ ratios deposited at 77 K, the variation from experiment to experiment is expected to be much less than 30%. We estimate the reproducibility of band ratios to be on the order of 5%. No significant crystallization of ASW to cubic ice is observed as

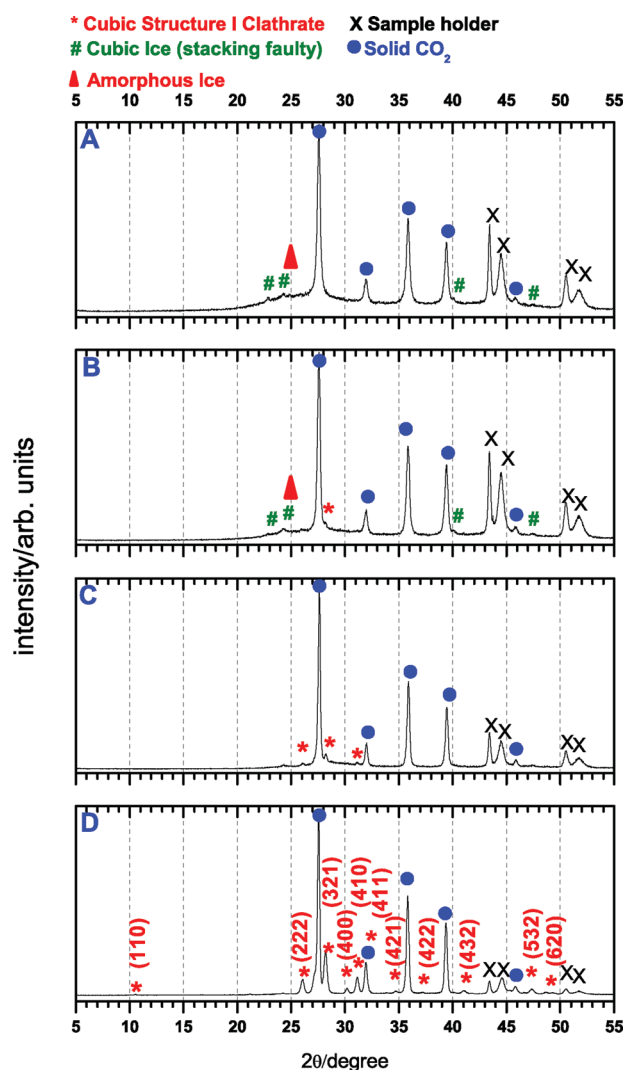


Fig. 3 Powder X-ray diffractograms (Cu-K α_1) recorded at <1 mbar and ~ 80 K for the four samples quench-recovered from points A, B, C and D in Fig. 2. The filled red triangle marks the amorphous halo peak maximum, filled blue circles indicate crystalline CO₂,¹⁰³ green hashmarks indicate traces of cubic ice with some hexagonal stacking faults¹⁰⁶ and X indicates sample holder (nickel-plated copper) reflections. In D the Miller indices of the cubic structure I CO₂ clathrate are indexed.

judged from the comparable trace amounts of cubic ice in Fig. 3A and Fig. 3B. However, a shoulder on the high-angle side at the position of the most intense cubic structure I clathrate hydrate reflection at $2\theta \approx 28.2^\circ$ hints at clathrate formation. The X-ray diffractogram in Fig. 3C recorded after quench-recovery from 180 K (position C in Fig. 2B) shows the trends observable in Fig. 3B in a more pronounced way. The broad ASW halo peak has practically disappeared, and also the tiny Bragg peaks of cubic ice have practically disappeared. On the other hand the shoulder at $2\theta \approx 28.2^\circ$ has grown, and also additional cubic structure I clathrate (CS-I) hydrate reflections at $2\theta \approx 26.1^\circ$ and $2\theta \approx 31.1^\circ$ appear. Powder cell estimates a CS-I fraction of $15 \pm 5\%$ in the matrix of crystalline CO₂. Even more CS-I Bragg peaks appear after heating to 200 K, and a total of eleven CS-I reflections are indexed in Fig. 3D.

The most intense (321) peak has developed into a clearly distinct peak at this stage. The CS-I fraction is estimated to be $40 \pm 5\%$ and is stabilized in solid carbon dioxide. We emphasize that earlier clathrate hydrates produced from ASW were stabilized in cubic or hexagonal ice rather than in crystalline guest matrices.^{32,33,35–37} The yields of O₂, Ar, N₂, NO and CO clathrate hydrates of cubic structure I or II were estimated to be 15%, 7%, 5%, 10% and 4%, respectively.^{32,33,35–37} That is, the yield for the CO₂ CS-I clathrate is much higher than the yield obtained in past work. The lower yield in the earlier studies might be due to the removal of external (crystalline) guest gas prior to clathrate production, whereas we here have refrained from pumping off crystalline carbon dioxide. Alternatively, the use of the piston cylinder technique and a pressure of 20 MPa rather than 0.1 MPa, or the different chemical nature of the guest might contribute to the high yield obtained here. We emphasize that the yield might be improved in future studies by heating to even higher temperature or keeping the sample for prolonged periods at, e.g., 200 K and 20 MPa. We emphasize that the transformation to the clathrate hydrate represents a solid state reaction between ASW and crystalline CO₂. In the temperature range 140–200 K water molecules in ASW become sufficiently mobile, so that symmetric cage structures can form. Without the presence of solid CO₂ ASW crystallizes in this temperature region.¹⁰⁷ No liquid or high pressures of gaseous CO₂ are necessary for the formation of the clathrate structure, and so this mechanism is also relevant in co-condensates of CO₂ and H₂O in astrophysical environment. The structure I clathrate hydrate is produced in its stability field in the CO₂–H₂O phase diagram.

We finally show in Fig. 4 that clathrate hydrate production does not take place at 130 K even at much higher pressure of 1600 MPa. Also under these conditions no liquid or gaseous CO₂ are expected according to the phase diagram. Fig. 4A shows piston displacement (*i.e.*, change of sample volume) upon compression and decompression, in a similar manner to Fig. 2A. Please note that the pre-compression step shown in Fig. 2A was also done in this experiment prior to the experiment shown in Fig. 4A. In Fig. 4A, compression is done at 130 K rather than at 77 K to an end pressure of 1.6 GPa rather than to 0.3 GPa. The decompression was again done at 77 K in order to avoid decompression-induced phase transitions. A step in piston displacement is noticed at 0.26–0.39 GPa on compression, and otherwise no phase changes are evident in the piston-displacement trace in Fig. 4A. This step in piston displacement results in a substantial permanent densification of ~ 2 mm, much higher than the densification of ~ 0.16 mm observed in Fig. 2B. Quench-recovery and analysis of the powder X-ray diffractogram (Fig. 4B) shows that clathrate hydrate formation has not taken place even at 130 K and 1.6 GPa. Crystalline CO₂ remains unaffected by the procedure, whereas the ASW halo peak has shifted from $2\theta \approx 24^\circ$ to $2\theta \approx 28^\circ$ (see vertical dotted lines in Fig. 4B). This structural transition is well known and was observed in pure amorphous ice samples by Mishima *et al.*^{108,109} and ourselves.¹¹⁰ At 130 K the upstroke transition is observed in pure, bulk amorphous water at ~ 0.3 GPa,¹⁰⁹ in excellent agreement with the observation in Fig. 4A. The amorphous ice network experiences a jumplike density increase from 0.94 to 1.15 g cm⁻³ in these experiments,^{31,111} and the

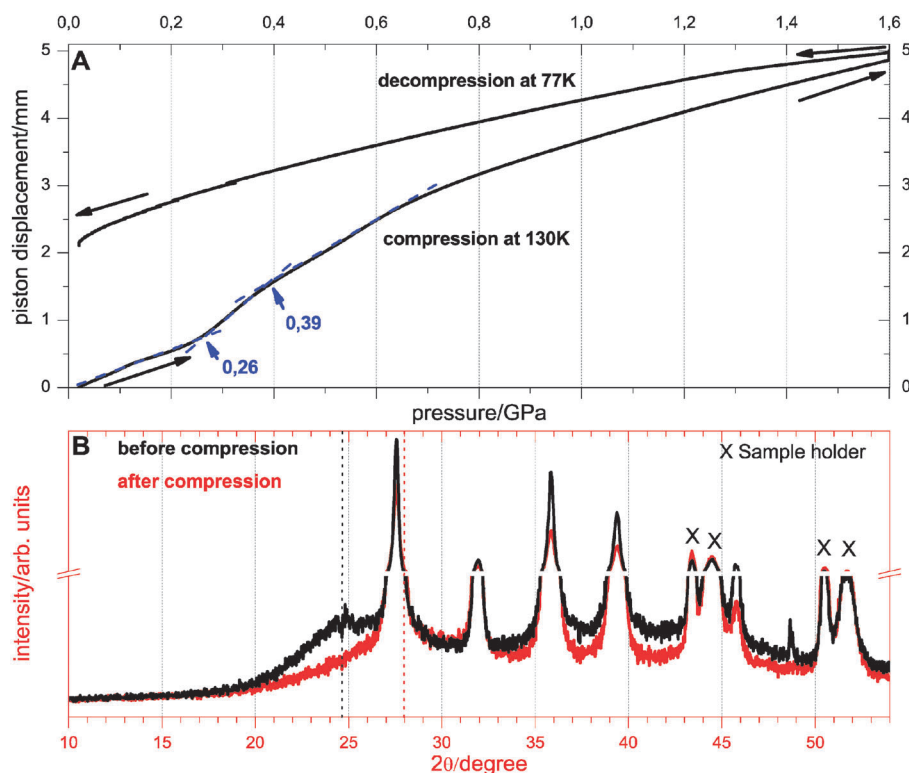


Fig. 4 (A) Piston displacement curve obtained by compression of a co-deposited CO_2/ASW sample at 130 K, quenching to 77 K at 1.6 GPa and decompression. The pre-compression step shown in Fig. 2A was done prior to the recording of this curve. (B) Powder X-ray diffractograms ($\text{Cu-K}\alpha_1$) recorded at <1 mbar and ~ 80 K before (black trace) and after (red trace) the compression step at 130 K. The shift of the amorphous halo peak is marked by two vertical dotted lines. Sample holder reflections are marked by X.

amorphous halo-maximum shifts from $2\theta \approx 24.0^\circ$ to $2\theta \approx 29.5^\circ$.¹¹⁰ The mobility of water molecules necessary to accomplish the amorphous–amorphous transition in the water network is not sufficient for the formation of symmetric cages, by contrast to the increased mobility at 200 K reported above.

We finally rationalize the observed piston displacements and the yield of clathrate hydrates estimated from X-ray diffractograms by some simple density estimates. The permanent density increase incurred in Fig. 2B due to clathrate hydrate formation can be approximated as 0.02 g cm^{-3} . The density of solid carbon dioxide at 1 bar is 1.56 g cm^{-3} and of dense ASW 0.94 g cm^{-3} . The empty CS-I CO_2 clathrate shows a density of 0.74 g cm^{-3} (using $11.82 \text{ \AA}$ as lattice constant),¹¹² and when filled at the maximum occupancy ratio of 8:46 (equals 1:5.75) with CO_2 the density is 1.00 g cm^{-3} (assuming no volume change upon filling). The density increase observed upon formation of CS-I clathrate from CO_2 and ASW can be rationalized in terms of a density increase incurred when the water molecules forming the sintered micropore in ASW rearrange to the clathrate cage. In the absence of crystalline CO_2 the expected increase in density would be 0.06 g cm^{-3} (1.00 minus 0.94 g cm^{-3}). The observed density increase of approximately 0.02 g cm^{-3} can be interpreted in the sense that roughly one third of the sample mass has converted from ASW to clathrate, under the assumption of crystalline CO_2 acting as an uninvolved spectator phase. This simplified back-of-the-envelope estimation of 33% clathrate is in good agreement with the estimate of $40 \pm 5\%$ deduced from the powder X-ray diffractogram depicted in Fig. 3D.

Discussion and conclusions

We have studied mixed vapour deposits of carbon dioxide and water by powder X-ray diffraction and volumetric experiments. Both sequential and co-deposition results in a heterogeneous mixture of amorphous solid water (ASW) and crystalline carbon dioxide. In addition to (external) crystalline carbon dioxide we also infer (internal) carbon dioxide molecules trapped irreversibly in the micropores of ASW. This type of sample has been transferred as a loose powder to a piston-cylinder setup. After a pre-compression step (at 77 K to 0.3 GPa), the compacted sample cylinder was studied isobarically at 20 MPa. We observe a densification of approximately 0.02 g cm^{-3} in the temperature range 160–200 K. X-Ray diffractograms reveal formation of the cubic structure I clathrate hydrate of carbon dioxide to be at the origin of the densification. By contrast, at 130 K even pressurization to 1600 MPa is not sufficient for producing the clathrate. We, therefore, conclude that the mobility of water molecules increases much more when increasing the temperature rather than increasing the pressure. In pure amorphous water both routes are known to induce water mobility. When raising the temperature, the ASW sample crystallizes above ~ 150 K, and when raising the pressure the ASW sample experiences enhanced water mobility resulting in an amorphous–amorphous transition at 130 K and ~ 0.3 GPa. In the presence of CO_2 the mobility of water molecules at 150 K is sufficient to adopt positions of symmetrical cages, whereas the mobility at 130 K is not sufficient, even at pressures >0.3 GPa. The only transformation

incurred at 130 K is the polyamorphic transition from the low-density amorphous form to the high-density amorphous form at ~ 0.3 GPa.¹¹¹ The yield of the clathrate is estimated to be about 40% at 200 K, where the clathrate is embedded in a matrix of crystalline carbon dioxide. By contrast, in earlier studies O₂, N₂, CO, NO and Ar clathrates produced from ASW samples were embedded in a matrix of cubic or hexagonal ice.^{32–35,37} Cubic ice has been found to be present only as a trace component here. Production of clathrates embedded in crystalline guest gas rather than in an ice matrix might be of interest when studying the self-preservation phenomenon of anomalously slow decomposition in *p*, *T*-regions outside the thermodynamic region of clathrate stability.^{84,113–119} This is especially so because ice covering the clathrate may⁸⁴ or may not¹¹⁴ be at the origin of self-preservation. The yield in the present study of 40% is much higher than the yields in the earlier studies, which were on the order of 10%. We assume that the higher yields can be explained on the basis that we did not pump-off (external) crystalline guest gas from the ASW sample prior to annealing the sample to ~ 200 K. Thus, both crystalline, external CO₂ molecules and single, trapped, internal CO₂ molecules participate in the formation of the clathrate hydrate. We furthermore did not employ partial pressures of the guest gas of 1 bar or higher. Instead the CO₂ partial pressure remained < 1 mbar in the deposition stage, and no external CO₂ was supplied in the annealing stage. These low vapour pressures of CO₂ are low enough so that the route to the clathrate hydrate described here might be of relevance in astrophysical environment, e.g., at the pole caps of Mars or for comets approaching the sun. Our study represents, to the best of our knowledge, the first observation of clathrate hydrate formation from CO₂ trapped in ASW micropores of bulk samples, without the use of any helper gas.

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