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# ATP4040: CO<sub>2</sub> Trapping in Amorphous H<sub>2</sub>O Ice: relevance to Polar Mesospheric Cloud Particles

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## Abstract

Polar mesospheric clouds form in the summer high latitude mesopause region and are primarily comprised of H<sub>2</sub>O ice, forming at temperatures below 150 K. Average summertime temperatures in the polar mesosphere (78°N) are approximately 125 K and can be driven lower than 100 K by gravity waves. Under these extreme temperature conditions and given the relative mesospheric concentrations of CO<sub>2</sub> and H<sub>2</sub>O (~360 ppmv and ~10 ppmv, respectively) it has been hypothesised that CO<sub>2</sub> molecules could become trapped within amorphous mesospheric ice particles, possibly making a significant contribution to the total condensed volume. Studies of CO<sub>2</sub> trapping in co-deposited gas mixtures of increasing CO<sub>2</sub>:H<sub>2</sub>O ratio (deposited at 98 K) were analysed *via* temperature programmed desorption. CO<sub>2</sub> trapping was found to be negligible when the H<sub>2</sub>O flux to the surface was reduced to  $4.8 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. This corresponds to an average of 0.4 H<sub>2</sub>O molecules depositing on an adsorbed CO<sub>2</sub> molecule and thereby trapping it in amorphous ice. Extrapolating the experimental data to mesospheric conditions shows that a mesospheric temperature of < 100 K would be required (at a maximum mesospheric H<sub>2</sub>O concentration of 10 ppmv) in order to trap CO<sub>2</sub> in the ice particles. Given the rarity of this temperature being reached in the mesosphere, this process would be an unlikely occurrence.

*Keywords: amorphous ice, carbon dioxide trapping, temperature programmed desorption, polar mesospheric clouds*

## 1. Introduction

Polar mesospheric clouds (PMCs) (also known as noctilucent clouds) are optically thin clouds that form in the summer polar mesopause region. PMCs primarily consist of small H<sub>2</sub>O ice particles with median radii of ~51 nm (von Cossart et al., 1999, Hervig et al., 2001), which can form when the temperature falls below the water frost point (150 K). Larger ice particles which sediment to the bottom of the ice layer, at altitudes between 82 and 85 km, scatter sufficient light to become optically visible (Rapp and Thomas, 2006).

A major source of ice nuclei for heterogeneous nucleation in the mesosphere are meteoric smoke particles (MSPs) (Rapp and Thomas, 2006, Plane, 2011). MSPs are a product of ablation and subsequent recondensation of meteoric material (Saunders and Plane, 2006), of which somewhere between 10 and 110 tonnes enters the atmosphere daily (Plane, 2012). Average temperatures in the high latitude upper mesosphere (78°N) during summertime are approximately 125 K, while gravity waves can drive temperatures lower than 100 K (Lübken et al., 2009). Murray and Jensen (2010) showed that homogeneous nucleation may also be possible under extreme mesospheric temperature conditions below 110 K. These authors also suggested that amorphous ice may preferentially nucleate due to a lower energy barrier to nucleation compared to crystalline ice. Satellite measurements indicate PMCs are composed primarily of crystalline ice but could not rule out amorphous ice formation (Hervig and Gordley, 2010).

H<sub>2</sub>O is present in the high latitude mesopause during the summertime at concentrations of up to 10 ppmv (Rong et al., 2010). The source of H<sub>2</sub>O vapour in the mesosphere is due to a combination of atmospheric upwelling and methane oxidation via reaction with O(<sup>1</sup>D) and

OH radicals (Thomas, 1991). CO<sub>2</sub> is well mixed vertically with concentrations >360 ppmv up to altitudes of approximately 80 km, above which UV photolysis of CO<sub>2</sub> (to CO and O) and gravitational separation with respect to lighter gas species become dominant removal processes. Due to increasing anthropogenic sources of CO<sub>2</sub>, a global decadal increase of  $23.5 \pm 6.3$  ppmv is currently observed (Emmert et al., 2012). Given the concentrations of trace species present in the mesosphere during the PMC cloud season and the extreme low temperatures, it is possible that CO<sub>2</sub> trapping in amorphous solid water (ASW) ice could be a viable process. However, it should be noted CO<sub>2</sub> cannot become trapped when ASW has irreversibly crystallised to crystalline solid water (CSW) ice, or when ice is initially deposited as CSW ice.

CO<sub>2</sub> trapping in ASW ice has been experimentally observed under conditions relevant to the interstellar medium (ISM) (Galvez et al., 2007, Malyk et al., 2007, Mate et al., 2008). However, these studies looked at deposition temperatures below atmospheric relevance ( $\leq 90$  K) and low CO<sub>2</sub>:H<sub>2</sub>O ratios ( $\sim 0.02:1$  to  $0.7:1$ ) due to the composition of interstellar ice. Experimental studies have also investigated CO<sub>2</sub> trapping in the Martian regolith (Trainer et al., 2010), but these were at higher temperatures and pressures than those observed during the PMC cloud season. To our knowledge, studies of co-deposition of high CO<sub>2</sub>:H<sub>2</sub>O ratio gas mixtures at conditions relevant to the Earth's mesosphere have not been performed. In the present study, the co-deposition of high CO<sub>2</sub>:H<sub>2</sub>O ratio mixtures were studied using temperature programmed desorption (TPD) to determine the mesospheric conditions under which CO<sub>2</sub> trapping in ASW ice would be possible. The experimental procedure is described in section 2, and the results and discussion in section 3.

## 2. Experimental Procedure

The experiments were undertaken in an ultra-high vacuum (UHV) chamber with an internal volume of  $\sim 25$  L (see Figure 1). This system has been previously described by Vondrak et al. (2006). Briefly, the chamber is pumped *via* a  $550 \text{ L s}^{-1}$  turbo-molecular pump (Varian Turbo-V 551 Navigator) backed by a rotary pump (Varian, DS302), achieving a base pressure of typically  $< 7 \times 10^{-10}$  mbar. The chamber is equipped with a quadrupole mass spectrometer (QMS) (Hiden, HAL 3F 301 RC PIC), a needle valve (NUPRO, SS4BK) for gas dosing and an inert ion ( $\text{Ar}^+$ ) sputter source (PSP technology Ltd., ISIS 3000) which was modified to function as a leak valve for this study. Within the centre of the UHV chamber is a cylindrical Cu (111) crystal sample of 12 mm diameter and 2.5 mm thickness, polished to  $1 \mu\text{m}$  and oriented to  $\pm 0.5^\circ$  of the (111) plane. The crystal is mounted *via* tungsten (W) heating wires onto an oxygen free high conductivity (OFHC) cold finger (shown in Figure 1), which in turn is mounted onto an xyz $\theta$  manipulator. The sample is liquid nitrogen cooled to a base temperature of approximately 98 K and can be heated resistively by the W wires embedded in the perimeter of the Cu (111) crystal. The surface temperature is monitored using a K-type thermocouple positioned in a small hole on the side of the Cu (111) crystal. Prior to each experiment the Cu (111) crystal was annealed to 800 K for 30 minutes.

$\text{H}_2\text{O}$  (deionised) was subject to three freeze-pump-thaw cycles and  $\text{CO}_2$  (from dry ice) was first purified by pumping.  $\text{CO}_2:\text{H}_2\text{O}$  gas mixtures at ratios varying from 1:1 to 13:1 were prepared using manometric techniques on a glass gas-handling line, and then dosed onto the Cu (111) crystal *via* the needle valve in the form of a collimated effusive beam. This beam has a diameter only slightly larger than the Cu (111) crystal and therefore minimises adsorption (and therefore desorption) of either species onto other nearby surfaces such as

the OFHC cold finger (see figure 1). Any species adsorbed onto the W wires would desorb immediately upon heating. The dosing rates were calibrated for CO<sub>2</sub> and H<sub>2</sub>O separately through beam flux calibrations based on the procedure of Oakes (1994). Briefly, the beam flux ( $F_{beam}$ ) is calculated from the exponential decay of a gas species from the point where the input gas flow has been terminated. The exponential decay is described by:

$$P = P_0 \exp^{-C_m t} \quad (1)$$

where  $P$  is the pressure,  $P_0$  is the initial pressure at the termination of the dose,  $C_m$  is the pumping coefficient for the gas, and  $t$  is the time from the start of the decay. From this  $F_{beam}$  is given by:

$$F_{beam} = \frac{V_{system} C_m P_0}{k_B T A_{beam}} \quad (2)$$

where  $V_{system}$  is the volume of the chamber,  $k_B$  is the Boltzmann constant,  $T$  the temperature of the gaseous species and  $A_{beam}$  the cross sectional area of the molecular beam. The CO<sub>2</sub> and H<sub>2</sub>O fluxes varied from  $(3.4 - 6.3) \times 10^{14}$  molecules cm<sup>-2</sup> s<sup>-1</sup> and  $(0.5 - 3.4) \times 10^{14}$  molecules cm<sup>-2</sup> s<sup>-1</sup>, respectively.

In a typical experiment, the gas mixture was dosed for 7200 s onto the Cu (111) crystal at a base temperature of 98 K. This enabled the H<sub>2</sub>O film to form as ASW ice. The absorbed species were then analysed *via* TPD, where the Cu crystal was heated between 98 and 200 K at a heating ramp of 0.25 K s<sup>-1</sup>. This ensured that all dosed species had desorbed. The CO<sub>2</sub> TPD profiles described in the following section were corrected against a pure CO<sub>2</sub> TPD trace to remove the surface CO<sub>2</sub> desorption. This surface CO<sub>2</sub> is weakly physisorbed to the ASW ice surface and rapidly desorbs upon sample heating, peaking at temperatures of approximately 125 K, which is more than 20 K lower than the observed initial desorption of trapped CO<sub>2</sub>.

### 3. Results and Discussion

The background corrected CO<sub>2</sub> TPD traces are shown in Figure 2 and display only the desorption features of CO<sub>2</sub> trapped within the water ice matrix. The first desorption feature prominently occurring in the 1:1 and 3:1 CO<sub>2</sub>:H<sub>2</sub>O ratio experiments appears at approximately 157 K and is known as a molecular volcano peak (Smith et al., 1997). The other CO<sub>2</sub> desorption feature (co-desorption peak) appears between 165 - 175 K and is more prominent at higher ratios compared to the molecular volcano peak. As the CO<sub>2</sub>:H<sub>2</sub>O ratio in the dosing mixture is increased (and thus the H<sub>2</sub>O flux decreased), the molecular volcano peak becomes less prominent, followed by a reduction in the co-desorption peak until no CO<sub>2</sub> desorption features were observed. Therefore the 13:1 CO<sub>2</sub>:H<sub>2</sub>O ratio was determined as the point where no CO<sub>2</sub> desorption occurred from the ice matrix in this study. This observation of the CO<sub>2</sub> desorption features reducing with respect to increasing CO<sub>2</sub>:H<sub>2</sub>O ratio is consistent with the findings of Galvez et al. (2008).

The CO<sub>2</sub> trapping processes can be explained by comparing the CO<sub>2</sub> TPD traces with their corresponding H<sub>2</sub>O TPD trace (Figure 3). Each H<sub>2</sub>O TPD trace contains two peaks: an ASW desorption peak; followed by the desorption feature for CSW at a higher temperature. The H<sub>2</sub>O ice layers were of sufficient thickness (125 - 880 nm) for the CSW peak to be observed at all CO<sub>2</sub>:H<sub>2</sub>O ratios. The ASW desorption peak occurs at approximately the same temperature as the corresponding CO<sub>2</sub> molecular volcano peak. As the H<sub>2</sub>O film thickness increases the ASW peak (and therefore the CO<sub>2</sub> molecular volcano) shift to higher temperatures. The CSW desorption peak also coincides with the CO<sub>2</sub> co-desorption peak. These peaks also shift to higher temperatures with increasing H<sub>2</sub>O film thickness. Both of

these observations are consistent with previous studies of trapped species in ASW ice films (May et al., 2012, 2013).

The release of trapped CO<sub>2</sub> (molecular volcano feature) from the ASW ice matrix can be explained using one of two theories: the glass transition; and crystallisation-induced cracking. In the first theory, the ASW film undergoes a glass transition during annealing (Jenniskens and Blake, 1994) which transforms the film into a viscous liquid enabling the H<sub>2</sub>O molecules to re-organise and freeze into the crystalline phase (CSW ice). This molecular reorganisation causes cavities in the ice matrix to open, releasing the trapped CO<sub>2</sub> molecules (as a molecular volcano) in the upper-most part of the H<sub>2</sub>O film. The temperature of this H<sub>2</sub>O glass transition is dependent on several variables including the initial deposition temperature and the heating rate applied (Jenniskens and Blake, 1996). The end of the glass transition can be observed in H<sub>2</sub>O TPDs as a reduction in ASW desorption rate as crystallisation to CSW dominates, before CSW desorbs. In the second theory, the H<sub>2</sub>O ice remains in the solid phase throughout the ASW to CSW transition. During crystallisation, cracks propagate down through the H<sub>2</sub>O film enabling the CO<sub>2</sub> trapped in cavities to escape to vacuum (May et al., 2012, 2013). Both of these theories successfully describe the observation of the CO<sub>2</sub> molecular volcano. However, whether the ASW to CSW phase transition remains in the solid phase or temporarily transforms into a viscous liquid does not affect the conclusions of the present study regarding the mesospheric significance of CO<sub>2</sub> trapping.

The CO<sub>2</sub> co-desorption peak appears at the temperature where maximum desorption of CSW occurs. This corresponds to the release of the remaining CO<sub>2</sub> trapped in the lower



layers of the ice matrix that did not have access to the outer surface of the H<sub>2</sub>O film during crystallisation (Kumi et al., 2006, Malyk et al., 2007).

As the CO<sub>2</sub> flux increases with increasing CO<sub>2</sub>:H<sub>2</sub>O ratio, CO<sub>2</sub> trapping is limited by the reduction in the H<sub>2</sub>O flux until no CO<sub>2</sub> desorption features from the water ice matrix were observed (13:1 CO<sub>2</sub>:H<sub>2</sub>O ratio). Experimentally, this corresponds to a lower limit H<sub>2</sub>O flux of  $4.8 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. H<sub>2</sub>O fluxes below this value are therefore not high enough to close micro-pores at the ASW surface before CO<sub>2</sub> molecules desorb during dosing (Galvez et al., 2008).

Using the experimental value for the H<sub>2</sub>O flux lower limit (required for CO<sub>2</sub> trapping in ASW) a comparison to a realistic value of H<sub>2</sub>O flux in the polar mesosphere can be undertaken. The mesospheric H<sub>2</sub>O flux (in units of molecules cm<sup>-2</sup> s<sup>-1</sup>) is given by:

$$\text{H}_2\text{O flux} = \frac{\bar{c}}{4} [\text{H}_2\text{O}] \quad (3)$$

where  $\bar{c}$  is the mean thermal velocity of the H<sub>2</sub>O molecules (in units of cm s<sup>-1</sup>) and is given by:

$$\bar{c} = 1.46 \times 10^4 \sqrt{T/M} \quad (4)$$

where  $T$  is the absolute temperature and  $M$  is the molar mass (in g). The concentration of H<sub>2</sub>O molecules, [H<sub>2</sub>O], in the polar mesosphere was calculated assuming optimal PMC cloud season conditions (10 ppmv of H<sub>2</sub>O at a total pressure of 1 Pa at 83 km). At a temperature of 98 K, the maximum H<sub>2</sub>O flux would be  $6.3 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>, which is higher than the experimental threshold determined in this study ( $4.8 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>). A mesospheric CO<sub>2</sub> flux of  $1.2 \times 10^{15}$  molecules cm<sup>-2</sup> s<sup>-1</sup> (360 ppmv of CO<sub>2</sub> at a total pressure of 1 Pa at 83 km) can be estimated in the same way. This is higher than the experimental CO<sub>2</sub>

flux range used in this study ( $(3.4 - 6.3) \times 10^{14}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ) indicating that sufficient  $\text{CO}_2$  would be available in the mesosphere. However, this is at a temperature of 98 K, which is very rarely encountered (Lübken et al., 2009). Furthermore,  $\text{H}_2\text{O}$  would have likely condensed, either via heterogeneous (Rapp and Thomas, 2006, Plane, 2011) or homogeneous (Murray and Jensen, 2010) nucleation, to form pure ice particles well before such a low temperature was reached.

In order to determine the complete range of conditions that would be required in the mesosphere to trap  $\text{CO}_2$ , it is necessary to estimate the average number of  $\text{H}_2\text{O}$  molecules depositing onto an already adsorbed  $\text{CO}_2$  molecule, in order to prevent it desorbing. First, the residence time of an adsorbed  $\text{CO}_2$  on the ASW surface,  $\tau$ , is the reciprocal of the desorption rate coefficient,  $k_{des}$ , which is given by Attard (1998) as:

$$\tau = \frac{1}{k_{des}} = \frac{1}{A \exp\left(\frac{-E_{des}}{RT}\right)} \quad (5)$$

where the pre-exponential factor  $A$  is the frequency of oscillation corresponding to the average of the librational modes of  $\text{CO}_2$  ( $2.9 \times 10^{12} \text{ s}^{-1}$ ) and  $E_{des}$  is the binding energy of  $\text{CO}_2$  on ASW ( $23.7 \text{ kJ mol}^{-1}$ ), which have been measured by Sandford and Allamandola (1990). The  $\text{CO}_2$  surface residence time at 98 K is  $\tau = 1.48 \text{ s}$ . Taking the collision cross section of a  $\text{CO}_2$  molecule as  $0.52 \text{ nm}^2$  (Atkins and De Paula, 2002) and the measured lower limit of the  $\text{H}_2\text{O}$  flux ( $4.8 \times 10^{13}$  molecules  $\text{cm}^{-2} \text{ s}^{-1}$ ), a minimum of 0.4  $\text{H}_2\text{O}$  molecules must deposit on an adsorbed  $\text{CO}_2$  molecule in order to trap it in the amorphous ice.

This result can now be used to determine the minimum  $\text{H}_2\text{O}$  mixing ratio (in units of ppmv) required for  $\text{CO}_2$  trapping in ASW across a range of temperatures in the upper mesosphere, as shown in Figure 4. The region above the red line indicates plausible conditions for  $\text{CO}_2$  trapping in ASW. The current maximum mesospheric  $\text{H}_2\text{O}$  concentration typical of the PMC

cloud season is 10 ppmv (Rong et al., 2010), which implies that a temperature below 100 K would be required for CO<sub>2</sub> trapping within PMC ice particles. At higher temperatures (~110 K) the H<sub>2</sub>O concentration would need to be over an order of magnitude higher for CO<sub>2</sub> trapping to become a significant process.

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## Figure Captions

**Figure 1:** Schematic diagram of the UHV chamber upper level (top) and Cu (111) crystal mount (bottom).

**Figure 2:** CO<sub>2</sub> background corrected TPD traces showing the desorption rate (arbitrary units) against temperature for trapped CO<sub>2</sub>/ice films (offset for clarity; the zero in each plot is the value at 145 K.). The CO<sub>2</sub>:H<sub>2</sub>O ratio in the dosing mixture is indicated on the right-hand side of each plot.

**Figure 3:** H<sub>2</sub>O TPD traces showing the desorption rate (arbitrary units) against temperature for the same CO<sub>2</sub>:H<sub>2</sub>O ratios as in Figure 2 (note that the traces are offset for clarity).

**Figure 4:** A plot of the minimum H<sub>2</sub>O concentration (ppmv) required to trap CO<sub>2</sub> in ASW, as a function of temperature (K).

Figures:

Figure 1.

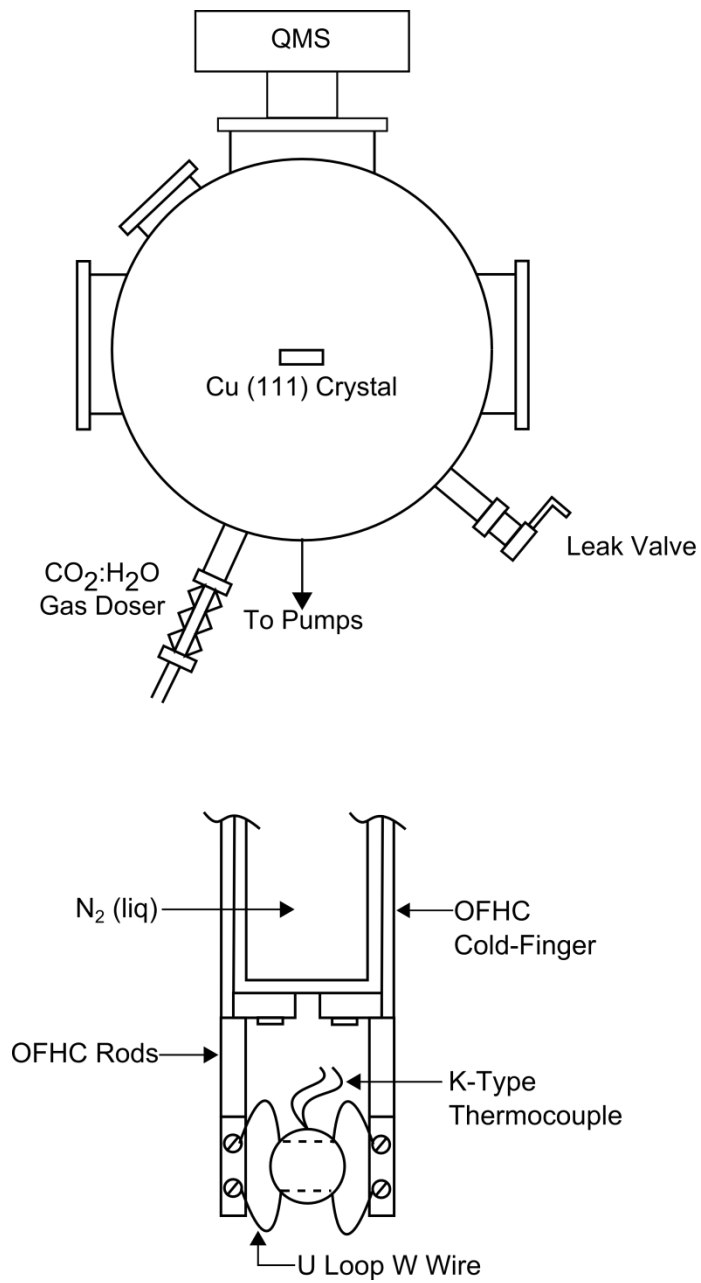




Figure 2.

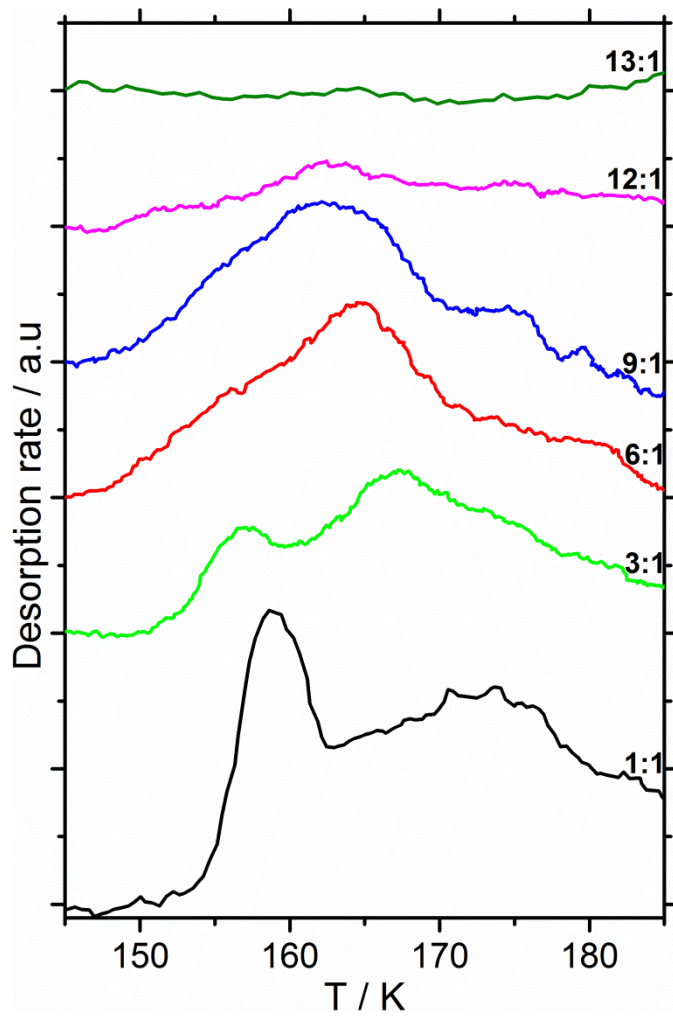


Figure 3.

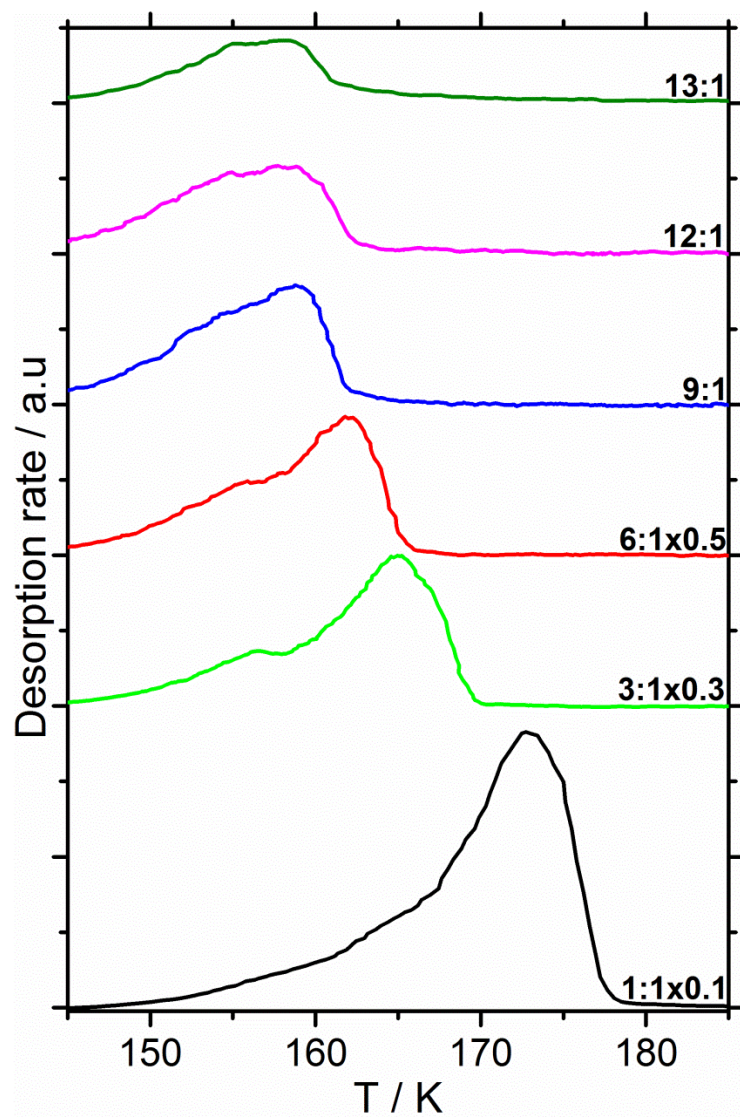


Figure 4.

