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Characterization of Water and CO₂ Adsorption by Stores 3A Desiccant Samples Using Thermal Gravimetric Analysis and Fourier Transform Infrared Spectroscopy.

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Abstract

Two lots of manufactured Type 3a zeolite samples were compared by TGA/IR analysis. The first lot, obtained from Davidson Chemical, a commercial vendor, was characterized during the previous study cycle for its water and water- plus - CO₂ uptake in order to determine whether CO₂ uptake prevented water adsorption by the zeolite. It was determined that CO₂ did not hamper water adsorption using the Davidson zeolite. CO₂ was found on the zeolite surface at dewpoints below -40 °C, however it was found to be reversibly adsorbed. During the course of the previous studies, chemical analyses revealed that the Davidson 3a zeolite contained calcium in significant quantities, along with the traditional counterions potassium and sodium. Chemical analysis of a Type 3a zeolite sample retrieved from Kansas City (heretofore referred to as the 'Stores 3a' sample) indicated that the Stores sample was a more traditional Type 3a zeolite, containing no calcium. TGA/IR studies this year focused on obtaining CO₂ and water absorbance data from the Stores 3a zeolite. Within the Stores 3a sample, CO₂ was found to be reversibly absorbed within the sample, but only at and below -60 °C with 5% CO₂ loading. The amount of CO₂ observed eluting from the Stores zeolite at this condition was similar to what was observed from the Davidson zeolite sample but with a greater uncertainty in the measured value. The results of the Stores 3a studies are summarized within this report.

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1. Instrumentation and Methods

A thermogravimetric analyzer (TGA), manufactured by TA instruments was connected to a Bio-Rad FTS 40 Fourier transform infrared (FT-IR) spectrometer equipped with a 10 cm gas cell. A sample of powdered 3a zeolite was obtained from Allied Signal, Kansas City, Mo. Between 20 and 40 milligrams of the powdered zeolite sample was placed in the TGA balance pan. The sample was prepared for equilibration by heating the TGA oven to 700 °C and maintaining that temperature for 30 minutes while the sample was maintained under a dry nitrogen flow. Once cooled to 34 °C, under dry nitrogen flow, the dry mass of the sample was obtained. Samples were equilibrated at 34 °C to a constant mass as it was exposed to a gas flow of the desired composition. The 34 °C temperature was chosen for equilibration in order to match the equilibration temperatures used at the University of New Mexico Chemistry Department (Professor Thomas Niemczyk) for their infrared zeolite studies. Equilibrium was defined as the point at which no significant change in mass of the sample was observed. For the -20 °C dew point this condition was typically achieved in half a day where as for -60 °C dew point conditions, equilibrium required 10 days. The sample was then heated to 700 °C at 10 °C/minute followed by five minutes at 700 °C. Data from both the TGA and FT-IR were recorded; FT-IR data was saved as a Grams *.SPC multifile (Galactic Industries). Background FT-IR spectra were acquired at times long after data collection to correct for background changes.

Humidity for the appropriate dew point was generated using a Panametrics model 101 moisture generator and monitored with a chilled mirror (General Eastern, model 1311DR). The flow system prior to the TGA was slightly overpressurized (780 mmHg) compared to ambient (~620mmHg). Pressure in the system was monitored and recorded. The recorded system pressure values were used to convert dew points from the pressurized reading to those experienced by the sample at ambient pressure. In order to make adjustments for changes in atmospheric conditions both the ambient temperature and ambient barometric pressure were recorded (Precision Thermometer Instrument Company).

2. Analysis

Synthetic calibration sets over the concentration range of interest were generated for water and CO₂ using the MALT program (Professor David Griffiths, University of Wollongong, Australia) in conjunction with the HITRAN 96 database (Air Force Cambridge Research Laboratories). MALT uses theoretical optical calculations in conjunction with high precision infrared line measurements in order to simulate instrument conditions and settings. For the current analysis we used infrared lines from Hitran 96 to generate calibration spectra of water and CO₂ and combinations thereof. A calibration model of the calculated spectra of water and CO₂ was built using classical least squares (CLS). The CLS routine operates under the Grams AI environment within the PLS 2001 (Sandia National Laboratories) program. It is known that the IR spectrum of water cannot be linearly related to concentration when examined over a large concentration range. In order to account for this non-Beer's law behavior, an additional

component was added to the CLS model in addition to the concentration of water and CO₂. By adding the square of the water concentration as a extra component, a quadratic term was indirectly added to describe the spectral data. Calibrations were then applied to the experimental TGA FT-IR data to calculate water and CO₂ concentrations as function of elution temperature.

At all concentrations of water, a common deviation between the calculated calibration spectra and the experimental data were observed in the spectral residuals. This lack of fit arises from slight deviations between the true instrument and the ‘simulated’ instrument. Corrections for this lack of fit were made by augmenting the predicted data with the first eigen vector of the spectral residuals obtained from spectra collected at the highest water concentration.

Concentration data acquired from these calculations were then imported into Matlab 6.1 where routines written in house were employed to calculate the total mass of water and CO₂ desorbed during the experiment as observed by the FT-IR cell. Transfer from the TGA to the FT-IR was not 100% efficient so the mass calculated from the IR data is less than what is measured by TGA. To estimate the total amount of water and CO₂ desorbed a split function was calculated from the water desorption data where the weight calculated from the CLS calibration is plotted against the weight obtained from the TGA measurement for a range of water masses. The equation obtained for the resulting line was used as the split function to estimate the total mass desorbed in future water and CO₂ experiments.

3. Results

Results for the water only runs using the Stores 3a samples compared to the Davidson 3a samples are shown in Figure 1 and Figure 2, error bars represent 90% Student t confidence intervals. The TGA data (Figure 1) clearly shows that the uptake of water in the -50 to -40 °C region is twice as great for the Stores samples, $0.87 \pm .07$ compared to $.44 \pm .07$ (grams of water/100 grams of desiccant)/°C for the Davidson samples. Uptake of water from -60 to -50 °C is twice as great for the Davidson samples, $.28 \pm .07$ compared to $.13 \pm .07$ (grams of water/100 grams of desiccant)/°C for the Stores data. Both samples show relatively similar behavior at the higher dew points. The Stores IR data in Figure 2 shows agreement with the TGA data (in Figure 1), giving mass values of water that are indistinguishable from the TGA data within the uncertainties.

The IR data was used to calculate the amount of water and CO₂ at various dewpoints and CO₂ exposures. The results for various dewpoints and exposures of 3% and 5% CO₂ are shown in Figures 3, 4, and 5. The most striking feature of this data is that while the Davidson data show a clear trend of increasing CO₂ uptake with decreasing dew point, the stores shows no CO₂ uptake within the uncertainty. The exception to this is the exposure of the Stores sample to -60 C / 5% CO₂, where a value of 2.5 ± 1.5 grams of CO₂/100 grams of desiccant is observed.

Also notable is the elution temperature for CO₂ in both zeolites. For the Davidson sample, the bulk of the CO₂ is desorbed at 117 °C, with a minor desorption peak occurring at 257 °C. For the Stores sample, the only CO₂ desorption peak occurs at 278 °C for the 5% CO₂ loading at a -60 °C dew point. This peak is quite broad with a FWHM of 180 °C. Water desorption occurs at 178 °C for this same condition in the Stores

zeolite. The CO₂ release within the Davidson and Stores sample at higher temperatures may indicate CO₂ that is chemisorbed to the surface of the zeolite. A possible explanation for difference in CO₂ adsorption between the stores samples and the Davidson samples is the chemistry of the two samples. While the Stores sample is a traditional Type 3a zeolite containing sodium and potassium counterions, the Davidson sample incorporate calcium as well as sodium and potassium. This chemical difference could explain the difference in affinity for CO₂ between the two desiccants along with the differences in water uptake (see above).

Data of total mass loss for Stores samples as calculated from the IR data and mass loss determined by TGA is shown in Figure 6. With the errors of the methods no statistical difference between the two methods is observed for total mass loss during the desorption run. Table 1 lists all data given in Figures 1 through 6. Uncertainties listed in Table 1 (and the figures) are based on the 90% Student T confidence intervals.

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Figure 1

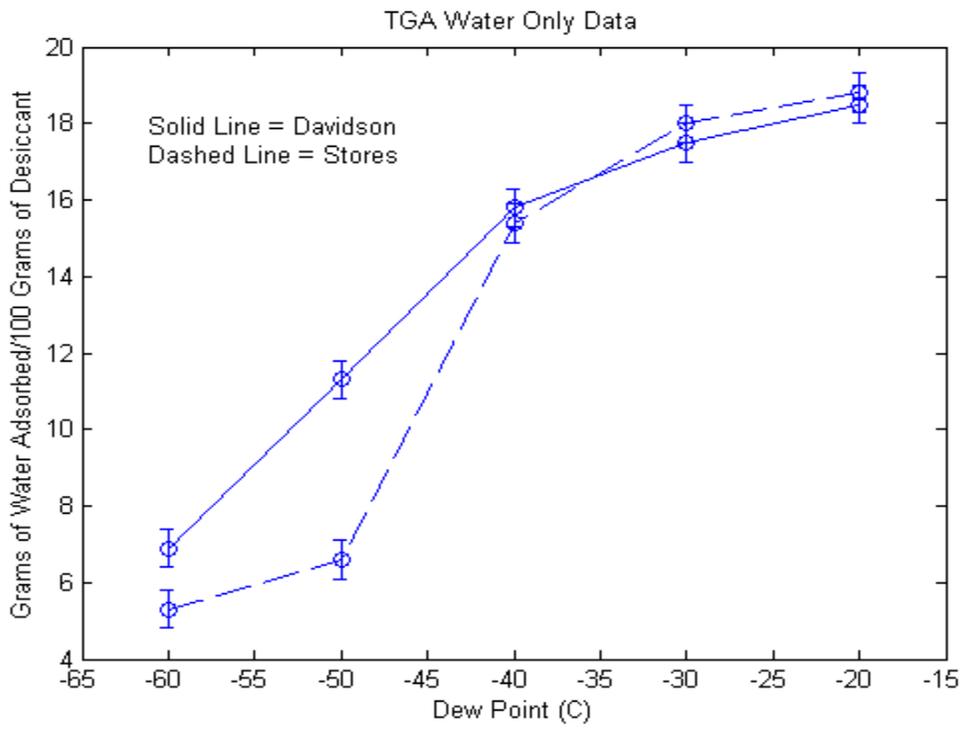


Figure 2

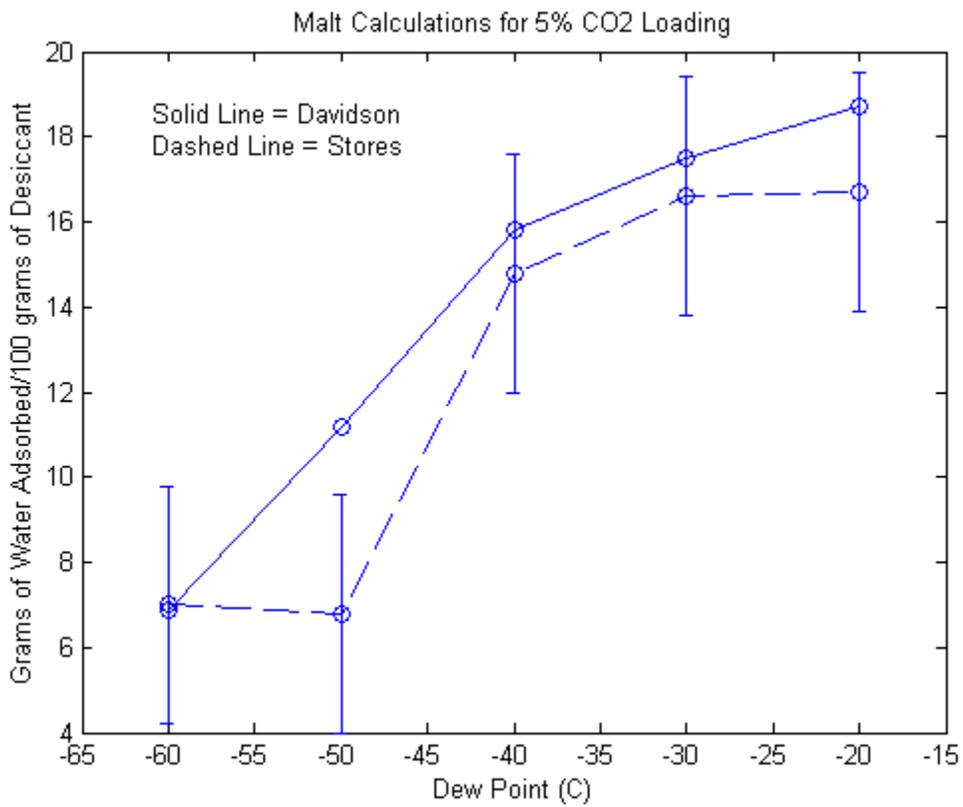


Figure 3

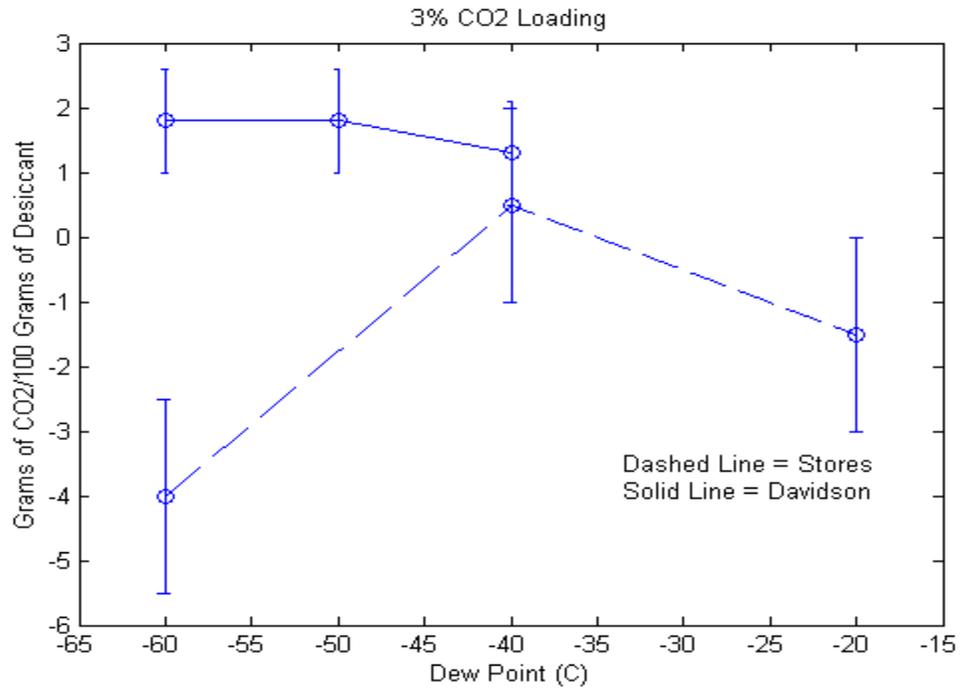


Figure 4

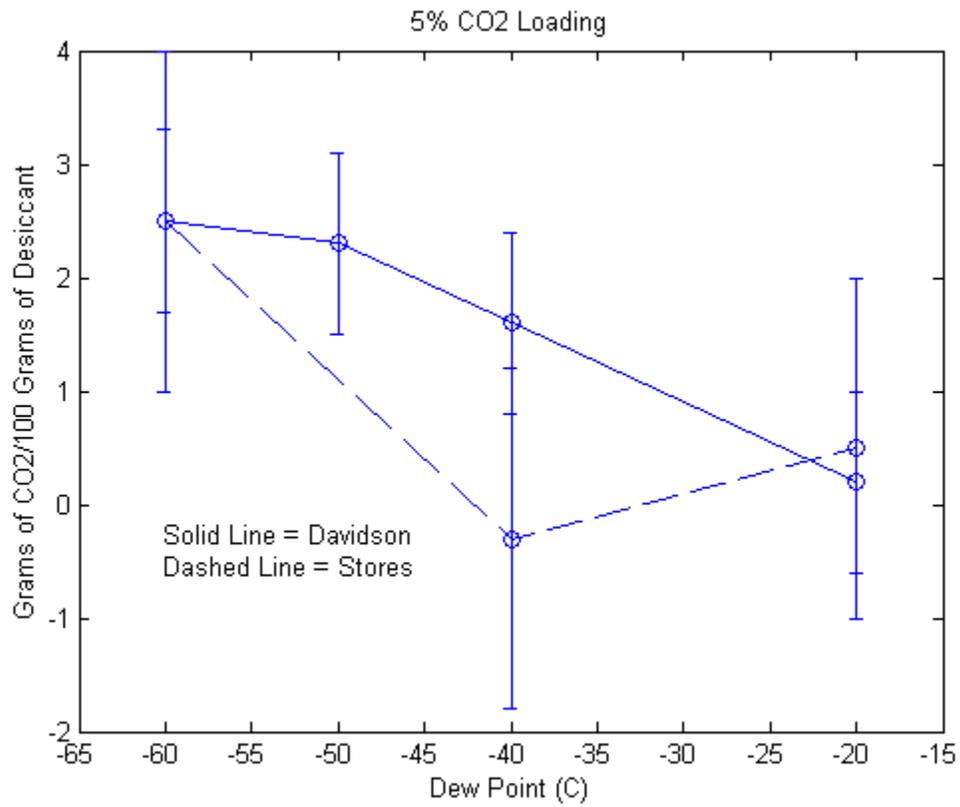


Figure 5

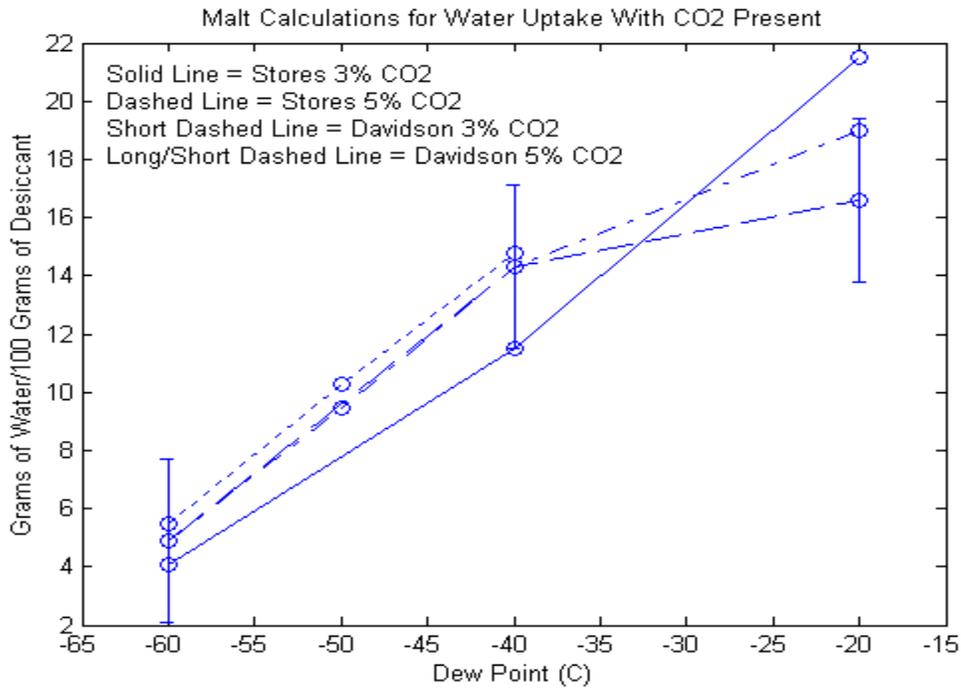


Figure 6

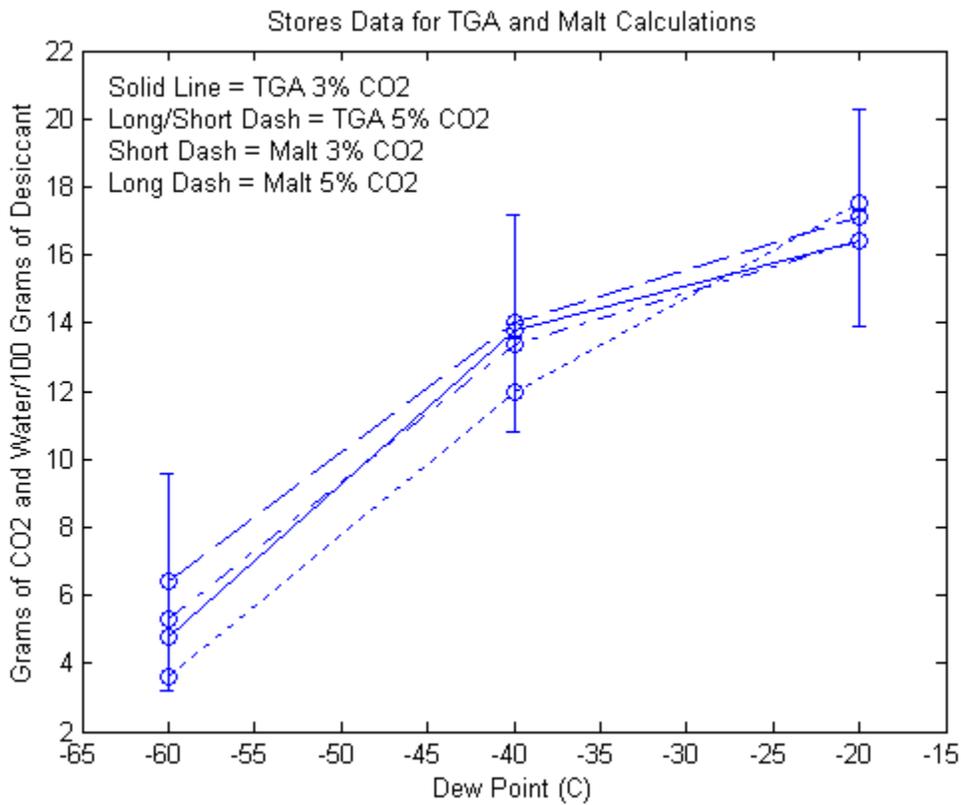


Table 1a: Stores TGA Data (Grams of CO₂ + H₂O/100g 3A Desiccant)

Dew Point	0% CO ₂	3% CO ₂	5% CO ₂
-20	18.8 ± .4	16.4 ± .4	16.4 ± .4
-30	18.0 ± .4		
-40	15.4 ± .4	13.8 ± .4	13.4 ± .4
-50	6.6 ± .4		
-60	5.3 ± .4	4.8 ± .4	5.3 ± .4

Table 1b: Stores Malt Data (Grams of CO₂ or H₂O/100g 3A Desiccant)

Dew Point	0% CO ₂	3% CO ₂	5% CO ₂
-20	16.7 ± 2.8	21.5 ± 2.8 (H ₂ O) -4.0 ± 1.5 (CO ₂)	16.6 ± 2.8 (H ₂ O) 0.5 ± 1.5 (CO ₂)
-30	16.6 ± 2.8		
-40	14.8 ± 2.8	11.5 ± 2.8 (H ₂ O) 0.5 ± 1.5 (CO ₂)	14.3 ± 2.8 (H ₂ O) -0.3 ± 1.5 (CO ₂)
-50	6.8 ± 2.8		
-60	7.0 ± 2.8	4.1 ± 2.8 (H ₂ O) -0.5 ± 1.5 (CO ₂)	4.9 ± 2.8 (H ₂ O) 2.5 ± 1.5 (CO ₂)

Table 1c: Davidson TGA Data (Grams of CO₂ + H₂O/100g 3A Desiccant)

Dew Point	0% CO ₂	3% CO ₂	5% CO ₂
-20	18.7 ± .4		19.0 ± .4
-30	17.5 ± .4		
-40	15.8 ± .4	15.8 ± .4	15.8 ± .4
-50	11.3 ± .4	12.1 ± .4	12.0 ± .4
-60	6.9 ± .4	7.4 ± .4	8.4 ± .4

Table 1d: Davidson Malt Data (Grams of CO₂ or H₂O/100g 3A Desiccant)

Dew Point	0% CO ₂	3% CO ₂	5% CO ₂
-20	18.7 ± .6		19.0 ± 0.6 (H ₂ O) 0.2 ± 0.8 (CO ₂)
-30	17.5 ± .6		
-40	15.8 ± .6	14.8 ± 0.6 (H ₂ O) 1.3 ± 0.8 (CO ₂)	14.3 ± 0.6 (H ₂ O) 1.6 ± 0.8 (CO ₂)
-50	11.2 ± .6	10.3 ± 0.6 1.8 ± 0.8 (CO ₂)	9.48 ± 0.6 2.3 ± 0.8
-60	6.9 ± .6	5.5 ± 0.6 (H ₂ O) 1.8 ± 0.8 (CO ₂)	4.9 ± 0.6 (H ₂ O) 2.5 ± 0.8 (CO ₂)

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