Introduction: At ambient pressure CO2 solidifies assuming an fcc lattice with isolated CO2 molecules on the lattice sites. Along with increasing pressure CO2 undergoes transitions to lower symmetry molecular phases based on the distorted fcc lattice. Decomposition of CO2 at elevated pressures and temperatures has been suggested based on the molar volumes of solid molecular CO2 in comparison to oxygen and diamond. Recent experimental studies, however, reported the transformation of molecular, solid CO2 (CO2-III) to a denser covalently bonded network structure at pressures higher than 35 GPa after laser heating above 1800 K by laser heating. This new structure was identified as an analogue of tridymite-O, one of the ambient pressure- high temperature phases of SiO2. Along with this experimental study, density functional calculations (DFT) indicated that at temperatures of 1000 to 2000 K, covalent crystalline phases of CO2 are more stable than any molecular CO2 phase as well as a mixture of diamond and oxygen. Other calculational work based on DFT supported the suggestion that covalent bounded CO2 phases assuming structures analogous to SiO2 at ambient pressure are stable. These findings give a striking example of a pure molecular solid at ambient pressure forming to three dimensional covalent structures at elevated pressure.

Here we present experimental evidence that solid CO2 decomposes to carbon and oxygen at pressures higher than 30 GPa and temperatures higher than 2000 K instead of assuming additional covalent structures. We confirm the formation of CO2-V and find evidence for another high pressure CO2 phase at lower temperatures, which we designate CO2-VI. Thermodynamic analysis of the transformations shows that the breakdown occurs as a result of the combined effects of density and entropy.

Methods and Materials: CO2 was condensed in a cooling trap. Transparent pieces of solid CO2 of about 50 x 50 x 30 µm3 volume were retained from the cooling trap and loaded in diamond cells. The load was increased to pressures between 50 - 70 GPa and the CO2 was heated with a CO2-laser with 60 W power by focusing the beam to a spot of less than 30 µm diameter. At those pressures the absorbance of CO2 at 10 µm wavelength is too low to exceed a temperature of about 1800 K under the given conditions. Therefore in order to reach temperatures between 2500 and 3000 K we used ruby or quartz that was ground to ~1 µm grain diameter and then pressed into pellets of 30x30x3 µm3 as absorbers. The main contribution to the incandescent light from the sample chamber was from the ruby and silica grains respectively. This indirect heating implied temperature gradients and further limited the accuracy of the temperature measurement. At pressures below 40 GPa CO2 could be heated directly to these temperatures. We heated the samples for 100 to 200 s. Above 30 GPa no phenomena related to melting were observed. After temperature quench the samples appeared to be darkened in the area of the hot spot. In addition, we performed an experiment on CO2 using a pellet pressed from quartz powder as absorber. This pellet was isolated from the lower diamond anvil by a ~µ3 m thick layer of NaCl. This assemble allowed us for the heating of an area of ~60 µm diameter to even higher temperatures than in the other experiments at a pressure of 63 GPa. The sample was kept for 150 s at 3000 K. Afterwards the surrounding and the outer range of the heated area were substantially darkened. X-ray diffraction patterns were collected at beamline X17C at the NSLS using polychromatic radiation and a Ge detector. Details of the set up are described elsewhere.

Results: we show that solid CO2 decomposes to oxygen and diamond at pressures higher than 30 GPa and high temperatures. Furthermore, it is indicated that CO is not stable under these conditions, otherwise it would be an end product of the decomposition of CO2 and a diamond polytype would not form. The C-O system at high pressure appears to be similar to that of C-S rather than Si-O at high pressure though expanded to a much larger scale of pressure and temperature. This indicates that the evolution of chemical properties of carbon-oxygen compounds with pressure is dominated by changes in the electronic structure of O rather than C. At pressures higher than 40 GPa the Raman spectrum of CO2-laser heated CO2 differs from CO2-V indicating another high P-T phase of CO2. X-ray diffraction data on this phase CO2-VI covering a pressure range from 62 to 100 GPa point to a complex, low symmetric structure of this new phase.

Acknowledgments: We thank J.Hu from NSLS for experimental help at the beamline X17C, C.S. Yoo, V. Iota, and J.J. Dong for communicating results prior to publication and for useful discussion. This work was supported by the NSF and DOE.

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Abstract No. tsch142
New Transformations of CO2 at High Pressures and Temperatures
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Beamline(s): X17C