ESRF	**Experiment title:** High-pressure formation of supercarbonic carbonates with polymerized tetrahedral network units	**Experiment number**: ES 488
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Report:

Carbon dioxide, CO_2, is one of the most important chemicals in nature. It is also, after water, the second most abundant volatile in the Earth's interior. Despite the simple stoichiometry, CO_2 has quite a complex phase diagram consisting of a number of crystalline molecular polymorphs below 40 GPa. On further compression it starts to polymerize forming at moderate temperatures (up to 680 K) amorphous glass containing carbon in threefold and fourfold coordination, while the laser heating above 1800 K / 40 GPa yields an extended covalent crystal phase (CO_2-V, space group $I4\bar{2}d$), described as a network of fourfold coordinated carbon atoms interconnected by oxygen bridges resembling structurally β-cristobalite SiO_2. Apparently the substantial kinetic barrier resulting from reconstruction of the bonding scheme may preclude further transformation at ambient temperature leading to quenching metastable states in the stability field of CO_2-V, which has stirred major controversies. In this experiment we have tackled the problem of chemical and phase stability of carbon dioxide at megabar pressures, the range unexplored in previous studies.

Liquefied CO_2 was loaded cryogenically at -25˚C and 23 bar into the diamond anvil cell, together with a tiny ruby sphere for controlling the initial pressure and several specks of $MgCO_3$, which facilitated heating on the sample due to its laser absorbance. No thermal insulation of the diamonds was applied. The sample was subsequently compressed to about 85 GPa while monitoring the XRD pattern. A progressive broadening and eventual full disappearance of the Bragg peaks evidenced the formation of amorphous glass, in agreement with previous reports. Subsequently, the sample was laser-heated for 5-10 min to ~2700 K in two cycles (Figure). Magnesium carbonate served as a sufficient absorber of laser energy, allowing to reach much higher temperature than in previous studies. The diffraction pattern

collected after temperature quenching proved the crystalline nature of the product obtained in course of laser heating, which was indexed as polymeric CO_2-V phase, while additional weak reflections were assigned to the Re gasket. It should be emphasized that the minor broad features present at the both sides of the most intense CO_2-V reflection disappeared after the second cycle of laser heating, while the peaks attributed to CO_2-V became sharper and less textured. Hence, our experimental data demonstrate that the other forms of carbon dioxide, either amorphous or crystalline, reported previously within this pressure-temperature window, are actually kinetically trapped metastable states. Moreover, in contrast to earlier reports we did not find any proof for splitting carbon dioxide into its two component elements carbon and oxygen or the transformation to ionic carbonates above one megabar. On the other hand, our results are perfectly consistent with the recent calculations indicating that the polymeric CO_2 does not decompose up to at least 200 GPa and 10000 K (Boates *et al.*, *PNAS*, 2012, *109*, 14808-14812).

Extension of the phase diagram of carbon dioxide is fundamental for pure chemistry and physics of matter, helping us to understand better the nature of the chemical bond. On top of that, this experiment expands our knowledge on the prototypical carbon-bearing system to yet more extreme high temperature and pressure conditions relevant to the geotherm, and therefore has profound implications to the deep carbon cycle.

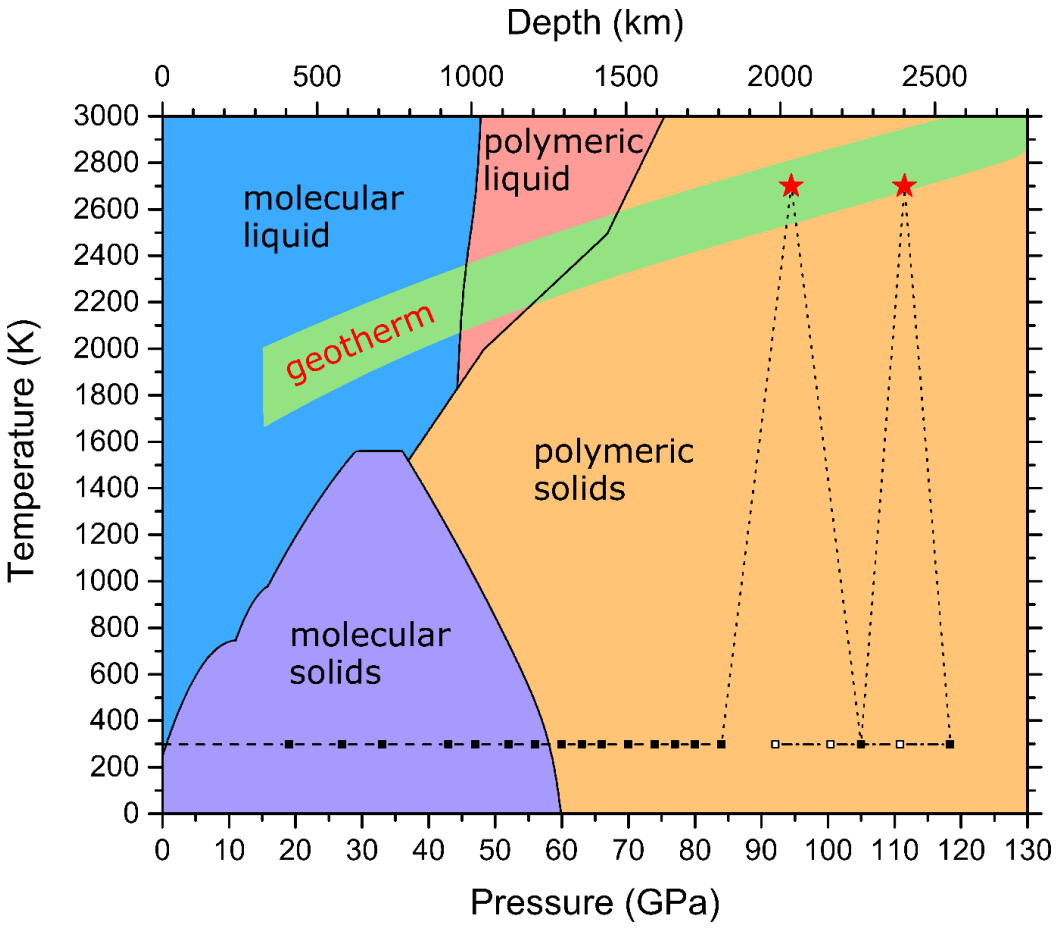

Figure. Experimental pressure-temperature route and the phase diagram of CO_2. Solid lines delineate regions of stability of molecular and polymeric phases, and the melting curve (after Boates *et al.*, *PNAS*, 2012, *109*, 14808-14812). The conditions relevant to the geotherm are shown in green. The dashed line corresponds to isothermal compression up to *ca.* 85 GPa, the dotted lines show the tentative heating and cooling cycle, the dash-dot line follows the decompression run. Red asterisks are placed at P-T conditions of laser heating cycles. Squares denote experimentally measured XRD patterns (filled on compression, empty on decompression).