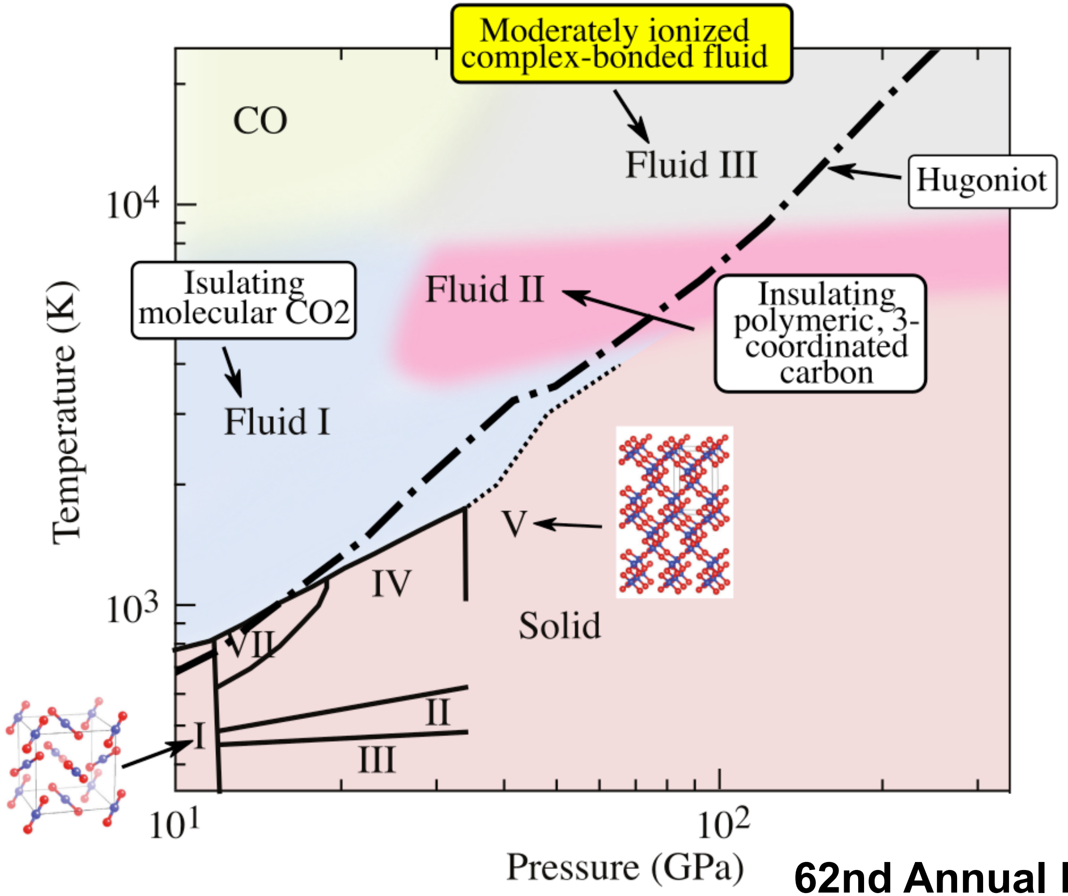
Equation of State and Transport of CO_2 Shock Compressed to 1 TPa



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University of Rochester
Laboratory for Laser Energetics

62nd Annual Meeting of the American Physical Society Division of Plasmas Physics
9–13 November 2020

Summary

First temperature and reflectivity measurements of shocked CO_2 reveal a complex bonded and moderately ionized state at 1 TPa and 100,000 K

- CO_2 was precompressed in diamond-sapphire anvil cells to liquid and solid phases (0.36 to 1.16 GPa), and then shock compressed up to 1 TPa
- This work provides the first temperature and reflectivity measurements of shocked CO_2
- No existing model[1,2] predicts the measured compressibility of CO_2 between 50 and 500 GPa
- Multiple initial densities allow us to extract derivative quantities including Grüneisen parameter and isentropic sound speed
- The trends of reflectivity and specific heat to 1 TPa are inconsistent with a simple atomic fluid; chemical bonding may be significant even at TPa conditions

1 TPa = 1,000 GPa
1 Mbar = 100 GPa

L. E. Crandall et al., Phys. Rev. Lett. 125, 165701 (2020)

[1] B. Boates *et al.*, J. Chem. Phys. 134, 064504 (2011).
[2] C. J. Wu *et al.*, J. Chem. Phys. 151, 224505 (2019).
[3] B. Boates, A. M. Teweldeberhan, and S. A. Bonev, Proc. Natl. Acad. Sci. 109, 14808 (2012).

Collaborators

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Outline

- Motivation
- Previous work
- Experimental technique
- Results
  - Pressure-density (P-ρ)
  - Derivative quantities: Grüneisen and sounds speed
  - Reflectivity and inferred conductivity
  - Temperature and specific heat capacity

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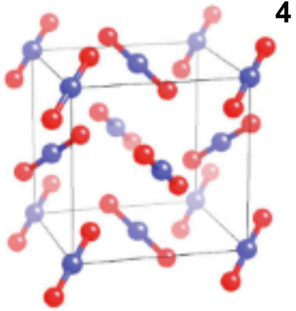
Motivation

The study of simple molecules at extreme conditions is of interest to multiple disciplines

- Carbon dioxide is a simple molecular species with stable chemical bonds at ambient conditions that exhibits complex phase transition behavior under increasing pressure and temperature[4]
- Behavior of simple molecules comprising H, C, O, and N at high pressure and temperature is vital to understanding the dynamo, convective flow, and evolution of giant planets[1]
- Carbon dioxide is an important byproduct of reacted chemical explosives; its conductivity at high pressure affects the reactive dynamics of these explosives[2,3]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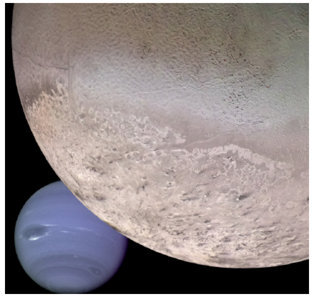
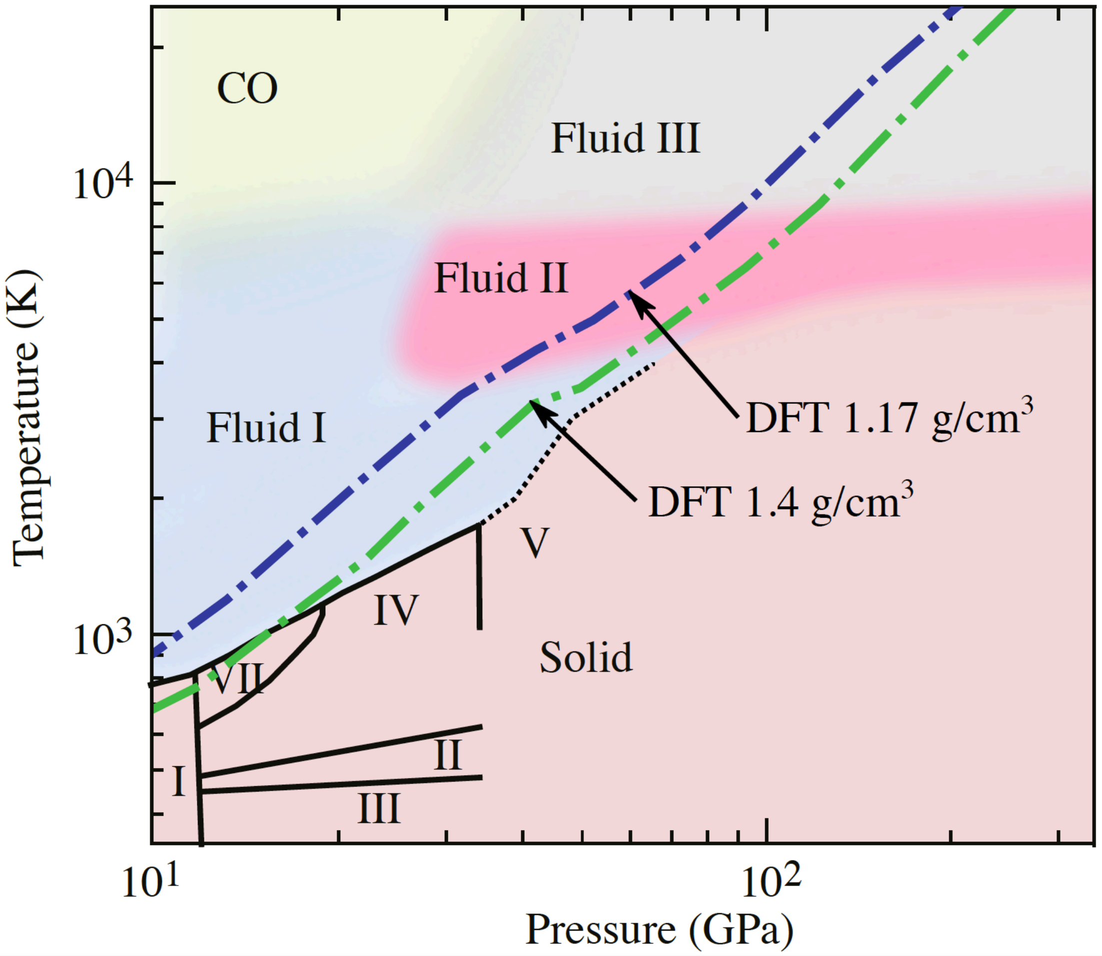


This work provides new insight into the multiform behavior of fluids in the warm-dense-matter regime.

[1] S. Stanley and J. Bloxham, Nature 428, 151 (2004).
[2] M. van Thiel and F. H. Ree, J. Appl. Phys. 62, 1761 (1987).
[3] V. V. Chaban, E. E. Fileti, and O. V. Prezhdo, J. Phys. Chem. Lett. 6, 913 (2015).
[4] C.-S. Yoo, Phys. Chem. Chem. Phys. 15, 7949 (2013).

The Hugoniot of CO_2 is predicted to cross at least three fluid phases. In this talk, we study Fluid III.



- **The solid phase diagram of CO2 has been extensively studied. The emerging fluid phases of CO2 may be equally complex.**
- **The Fluid I (CO_2-like) to Fluid II (3-coordinated carbon) transition is predicted to be of the first order.***
- **Fluid III was previously predicted to be a fully dissociated fluid.**
- **In this talk, we present evidence that Fluid III is not a simple atomic fluid, but a complex bonded and moderately ionized state.**

*B. Boates et al., PNAS 109, 14808

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Initially 1.17 g/cm^3 shocked CO_2 (blue) has been extensively studied. The work presented in this talk will probe higher initial densities.

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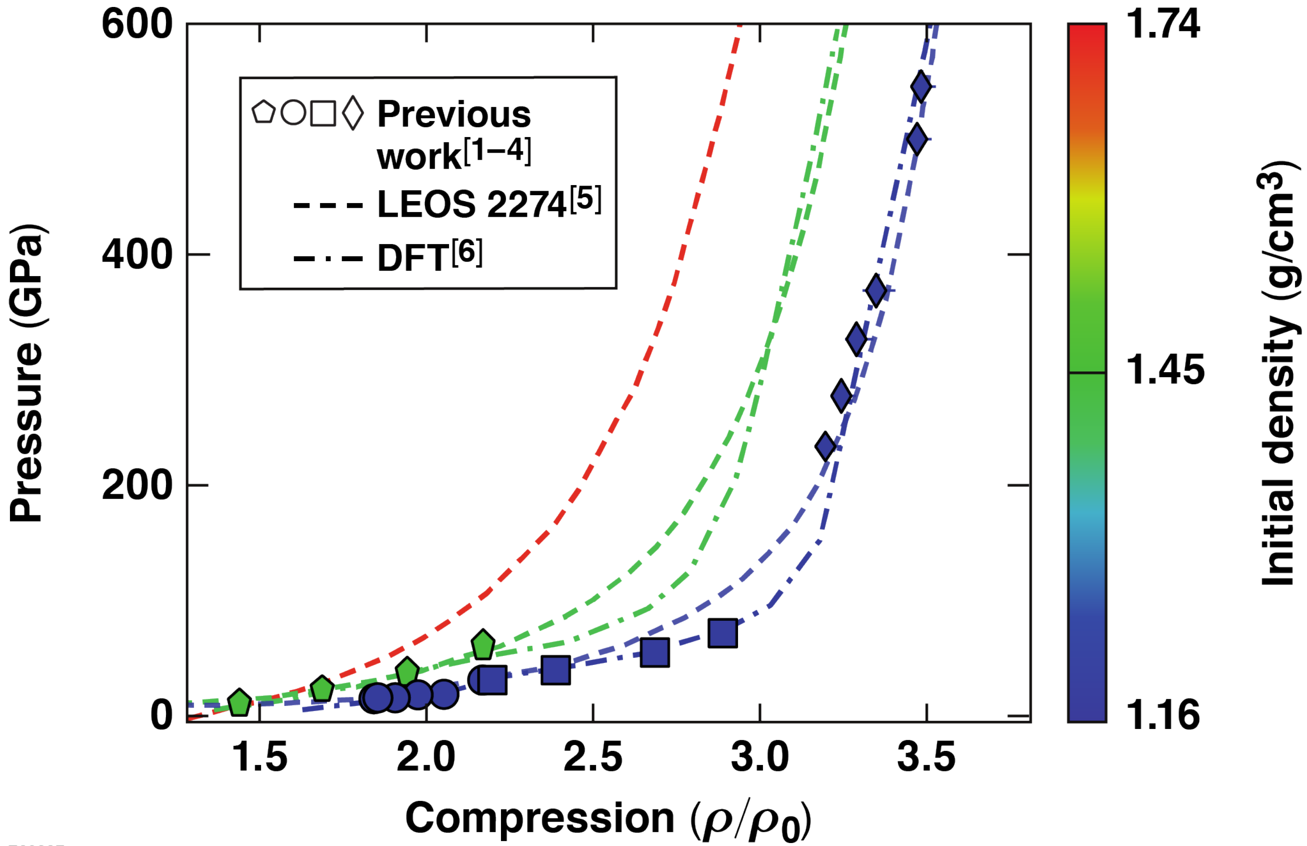

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- Variation in initial density (i.e. dry ice versus liquid) allows access to different Hugoniot curves
- DFT (2011) and LEOS (2019) disagree on the compressibility of CO_2 between 40 and 400 GPa
- Data on initially 1.17 g/cm^3 CO_2 supports DFT modeling

[1] V. N. Zubarev and G. S. Telegin, Sov. Phys.-Dokl. 7, 34 (1962).
[2] G. L. Schott, High Press. Res. 6, 187 (1991).
[3] W. J. Nellis *et al.*, J. Chem. Phys. 95, 5268 (1991).
[4] S. Root *et al.*, Phys. Rev. B 87, 224102 (2013).
[5] C. J. Wu *et al.*, J. Chem. Phys. 151, 224505 (2019).
[6] B. Boates *et al.*, J. Chem. Phys. 134, 064504 (2011);

DFT: density functional theory

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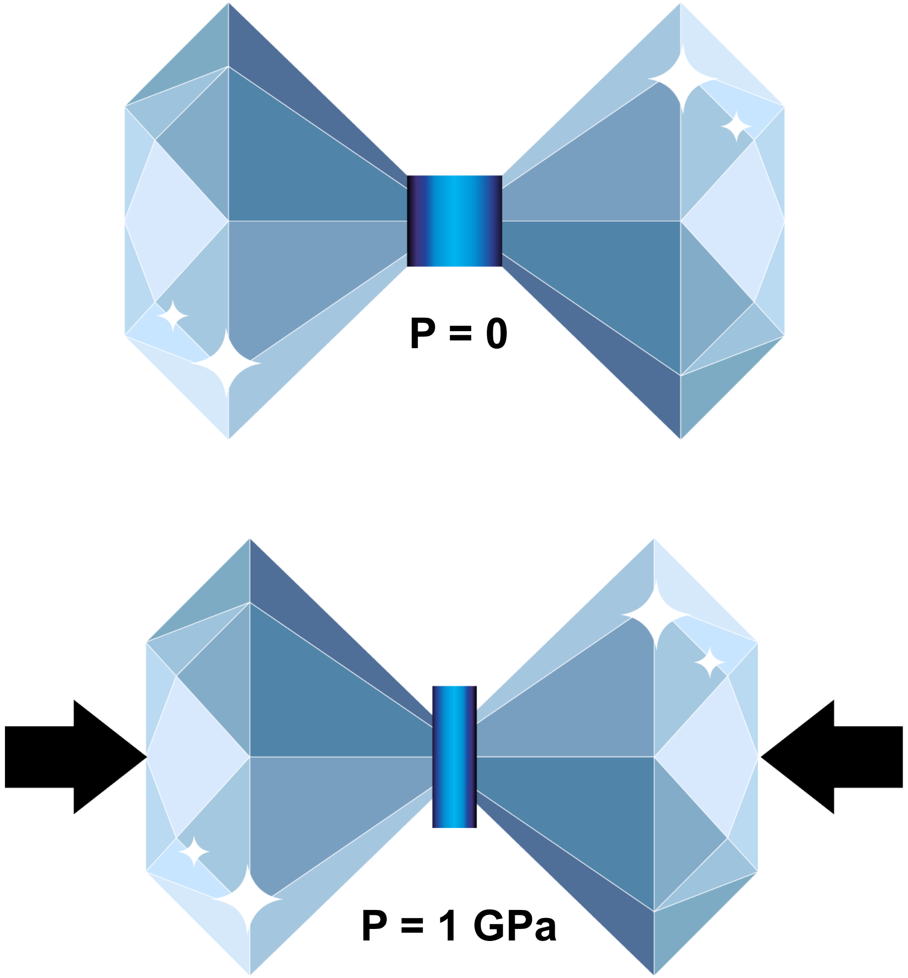
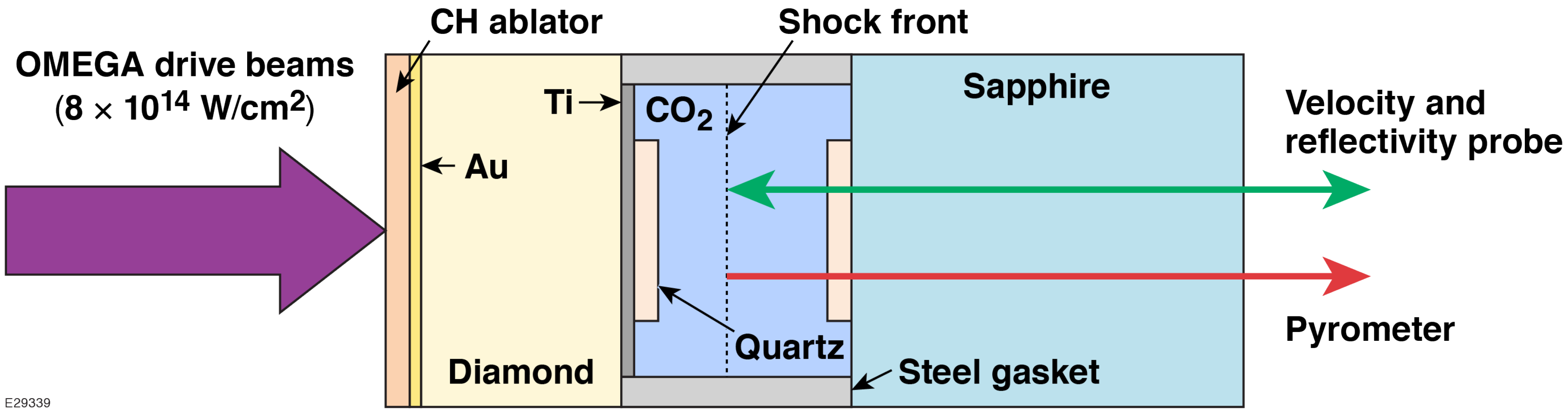
Diamond-anvil cells (DAC's) are used to precompress samples before they are laser shocked



- A sample is loaded into a stainless steel chamber between two diamonds; the diamonds are mechanically squeezed together, compressing the sample
- DAC's are used in static experiments to study the compression of materials to hundreds of GPa
- This study used DAC's to achieve variation in the initial density of the CO_2 samples

Precompressed CO_2 was shock compressed to TPa conditions with the OMEGA laser

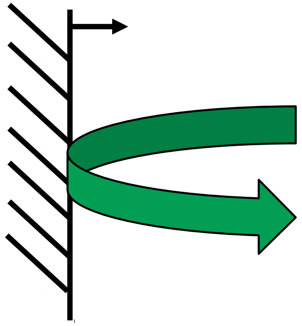
Diamond-anvil cell



- CO_2 precompression: ~1 GPa. Densities range from 1.35-1.74 g/cm^3
- Laser-drive shocks to 1 TPa (1,000 GPa)
- Shock velocity, emission, and reflectance were measured using VISAR* and SOP**
- Quartz standard for impedance matching, temperature, and reflectivity reference

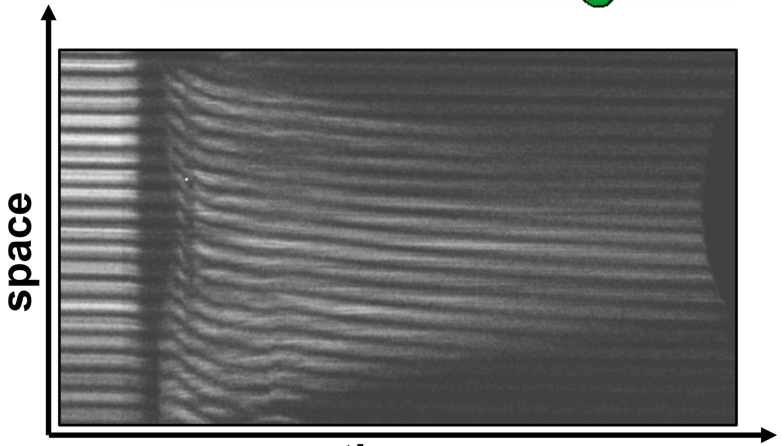
* VISAR: velocity interferometer system for any reflector
** SOP: streaked optical pyrometer

Laser velocimetry (VISAR) was the primary diagnostic used to measure the velocity of the shock front



Reflective surface moving at some velocity

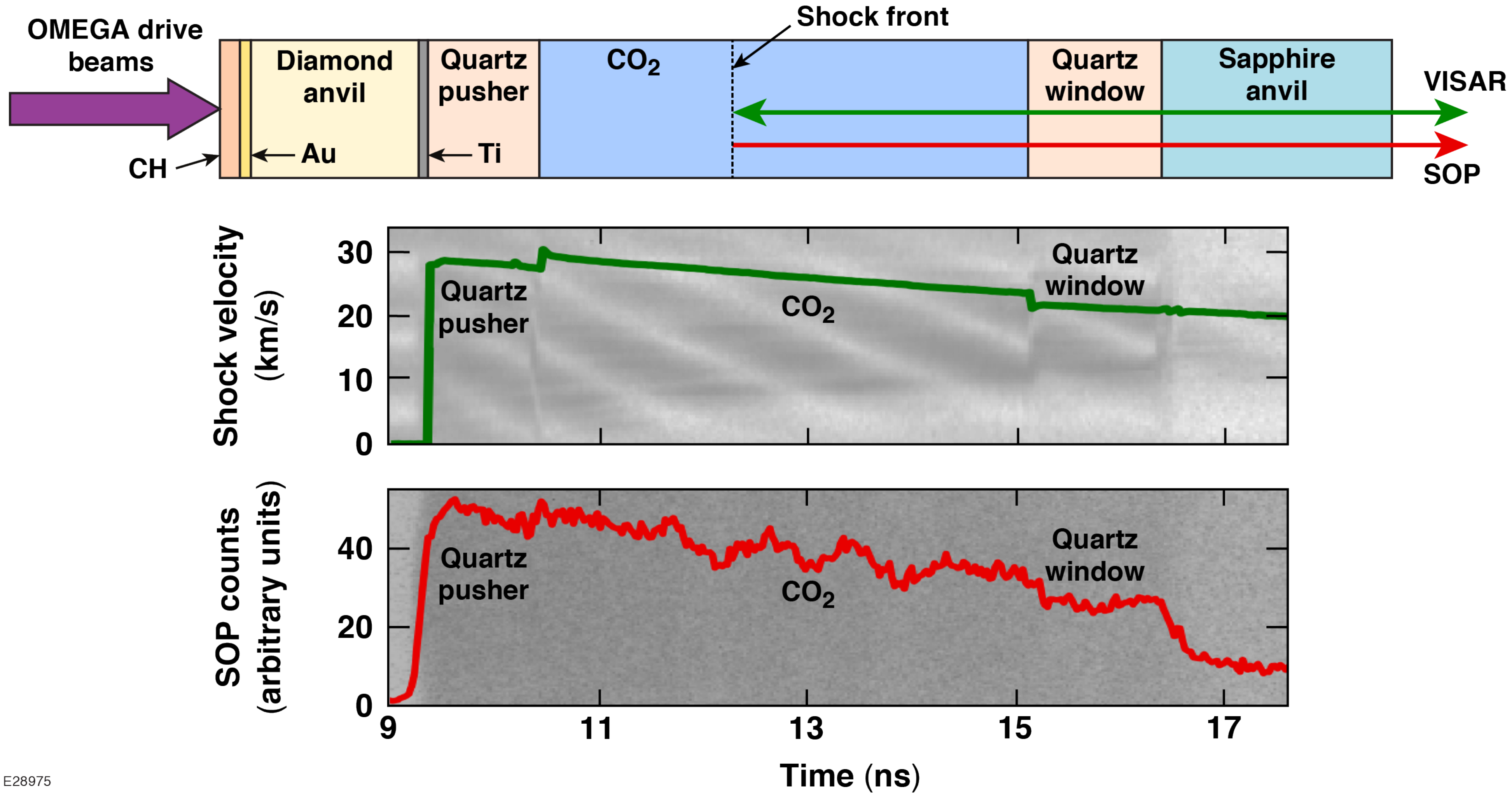
Raw VISAR image:



- Light from a probe laser reflects off of a moving surface (the shock front); that reflected light undergoes a doppler shift
- The light passes through a Mach–Zehnder interferometer with a known difference in path length
- The velocity of the reflecting surface is proportional to the motion of the interference fringes

Sample of Data

Simultaneous VISAR and pyrometer data provide a continuous temporal profile of shock velocity, reflectivity, and temperature



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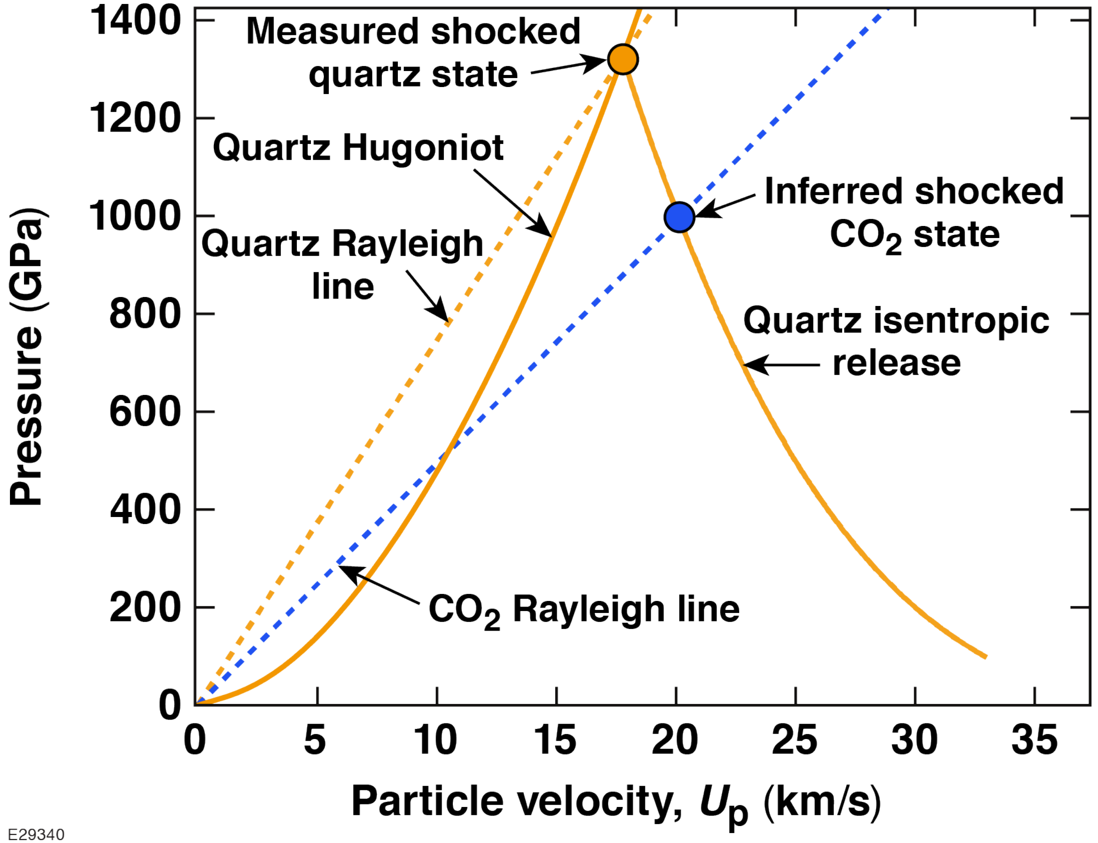
The pressure and density of the shocked CO_2 are determined from impedance matching to the quartz standard



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Rankine–Hugoniot conservation relations:

$$\frac{\rho}{\rho_0} = \frac{U_S}{U_S - U_P}$$

$$P - P_0 = \rho_0 U_S U_P$$

The Hugoniot and release behavior of quartz are known:[1–3]

$$U_S(U_P)$$

$$P_S - P_H = \frac{\gamma}{V}(E_S - E_H)$$

ρ : density
U_S : shock velocity
U_P : particle velocity
P : pressure
V : volume
γ : Grüneisen parameter
E: internal energy

1 M. D. Knudson and M. P. Desjarlais, Phys. Rev. B 88, 184107 (2013).
2 M. P. Desjarlais, M. D. Knudson, and K. R. Cochrane, J. Appl. Phys. 122, 035903 (2017).
3 S. Brygoo *et al.*, J. Appl. Phys. 118, 195901 (2015).

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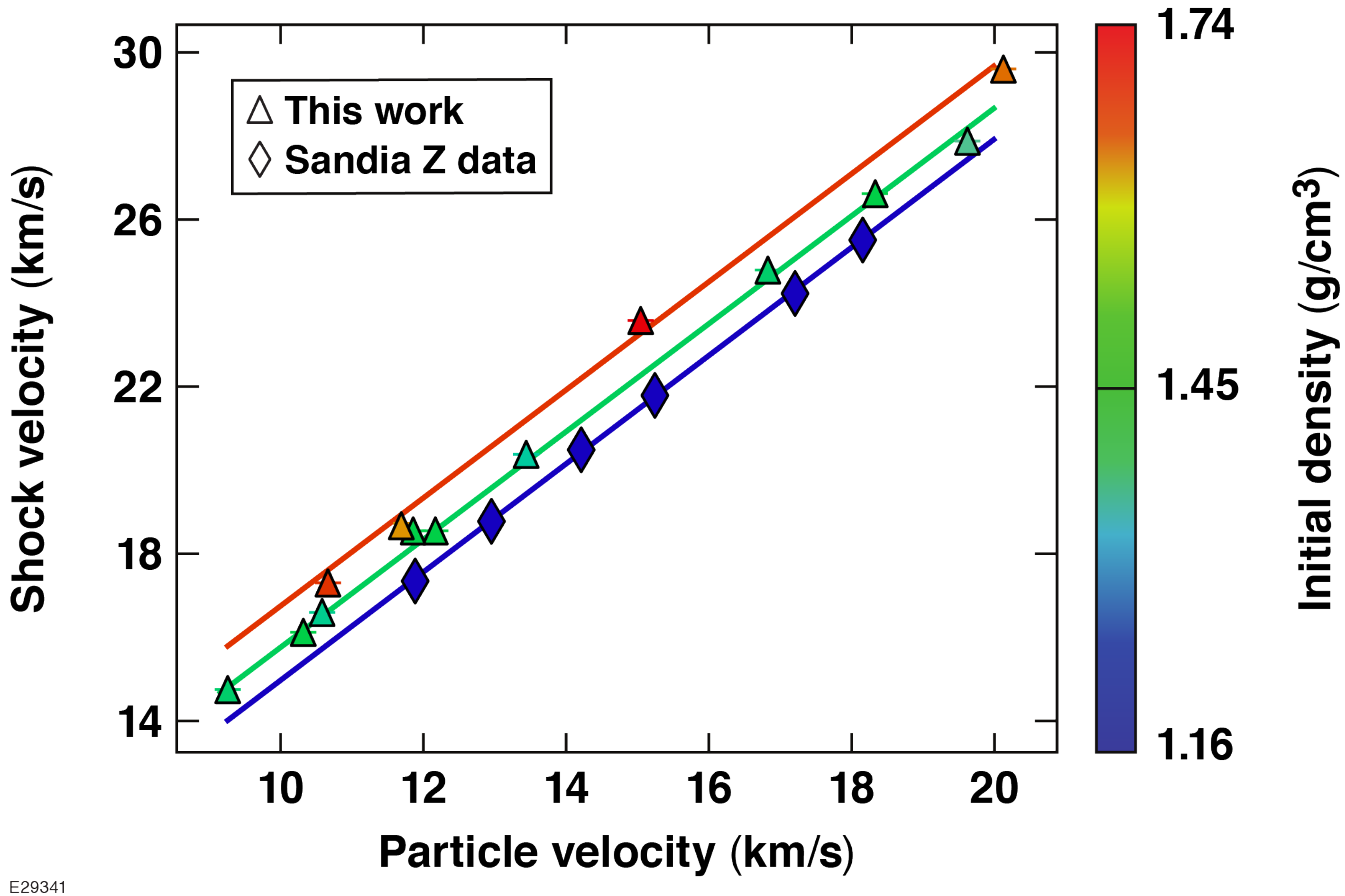
Results

The U_S–U_P relation for CO_2 between 189 and 995 GPa exhibits linear behavior when accounting for precompression



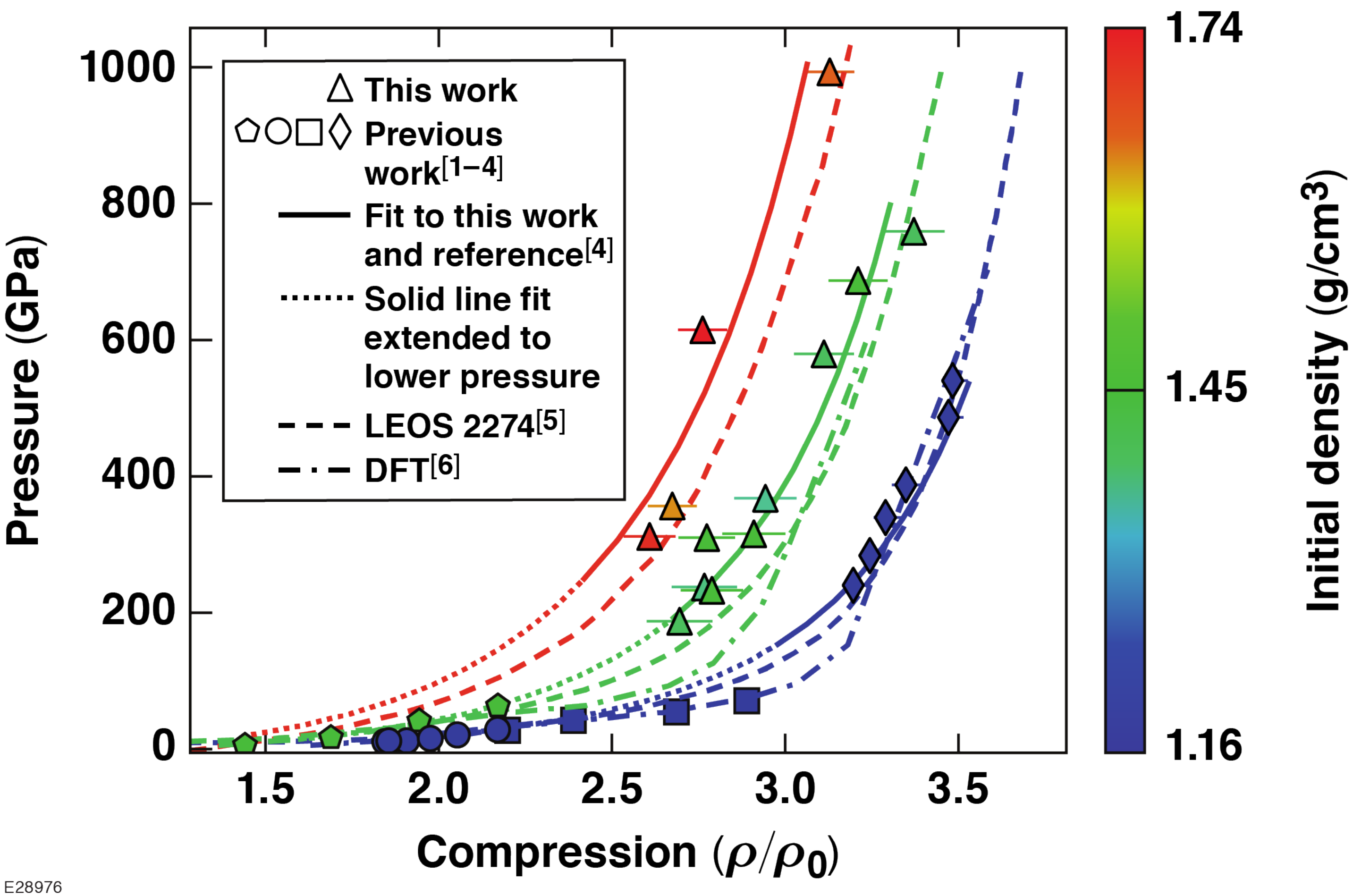
$$U_S = c_0 + s\,U_P + a\rho_0$$

$c_0\left(\frac{km}{s}\right)$	s	$a\left(\frac{km}{s}\frac{cm^3}{g}\right)$
-1.88	1.29	3.36

E29341

Sandia Z work: S. Root *et al.*, Phys. Rev. B 87, 224102 (2013).

Our initially 1.4 g/cm³ CO_2 (green) is less compressible than both LEOS and DFT below 600 GPa



E28976

Current models disagree on the compressibility behavior of CO_2, and none predict all existing data

1 TPa = 1,000 GPa
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[1] V. N. Zubarev and G. S. Telegin, Sov. Phys.-Dokl. 7, 34 (1962).
[2] G. L. Schott, High Press. Res. 6, 187 (1991).
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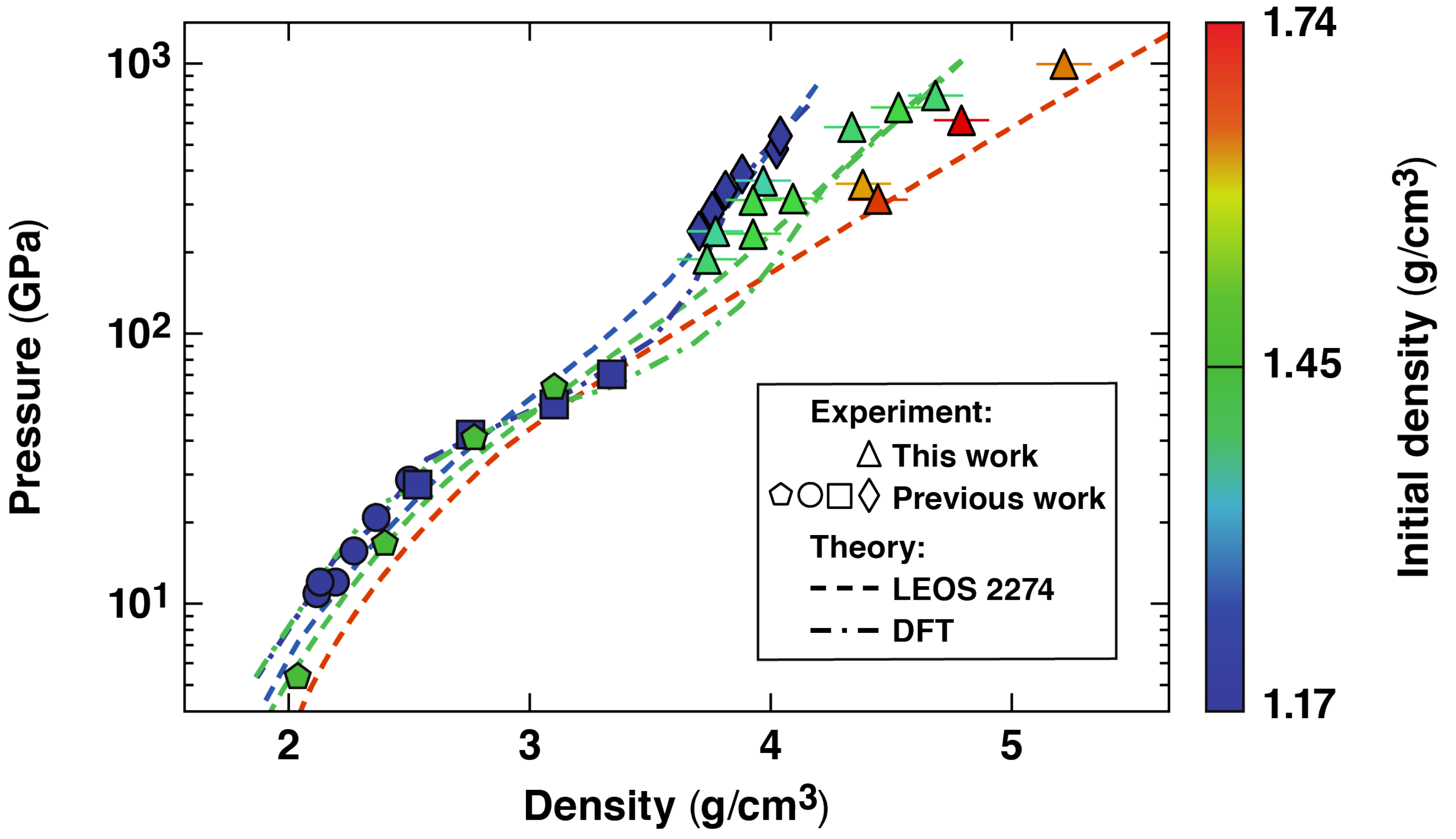

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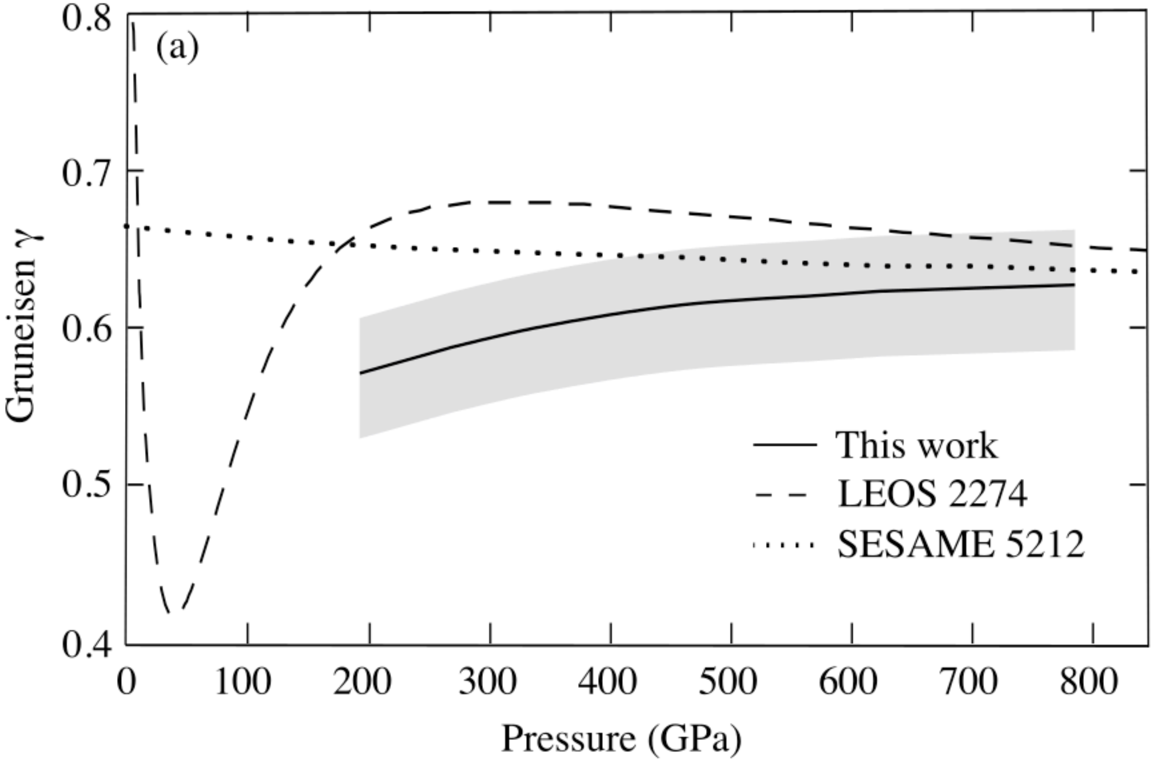
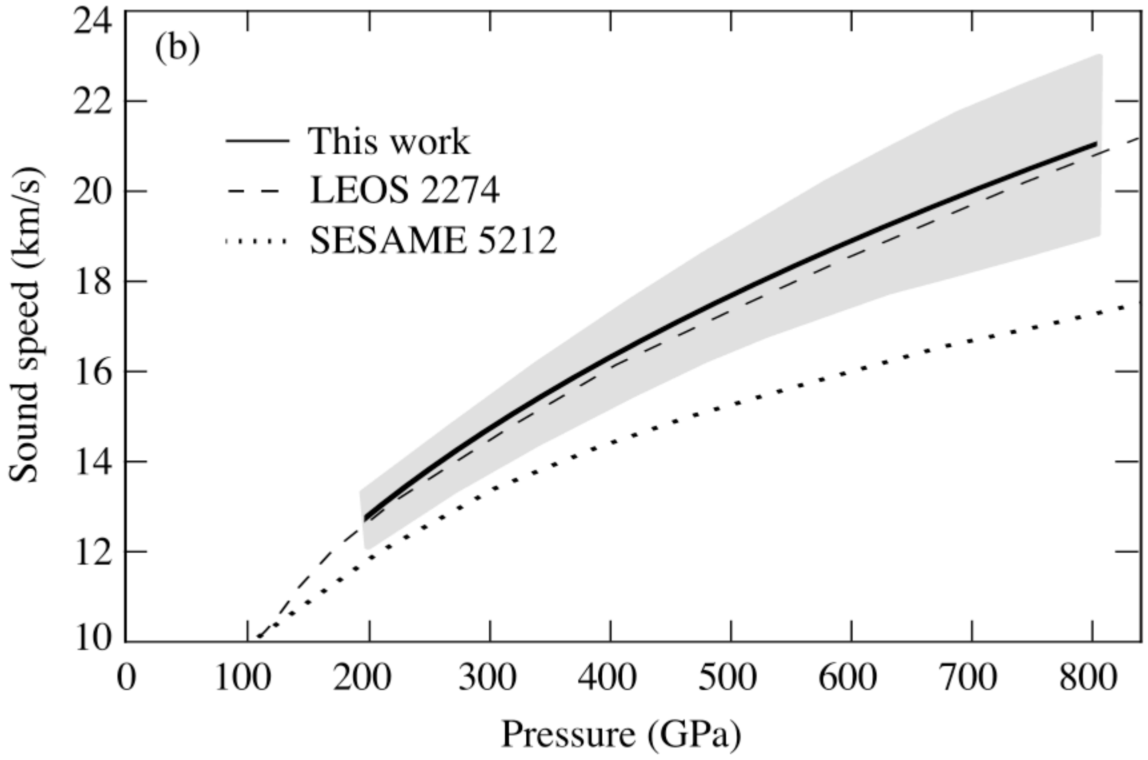
The variation in initial densities allowed us to measure multiple Hugoniots of CO_2, from which we can infer derivative quantities

$$\gamma = V \frac{\partial P}{\partial E}\bigg|_V \approx V \frac{\Delta P|_V}{\Delta E|_V}$$

$$C_s^2 = \frac{\partial P}{\partial \rho}\bigg|_S = V^2 \frac{\frac{\gamma}{2V} - P_H - \frac{dP}{dV}\big|_H (V_0 - V)}{\frac{dP}{dV}\big|_H}$$





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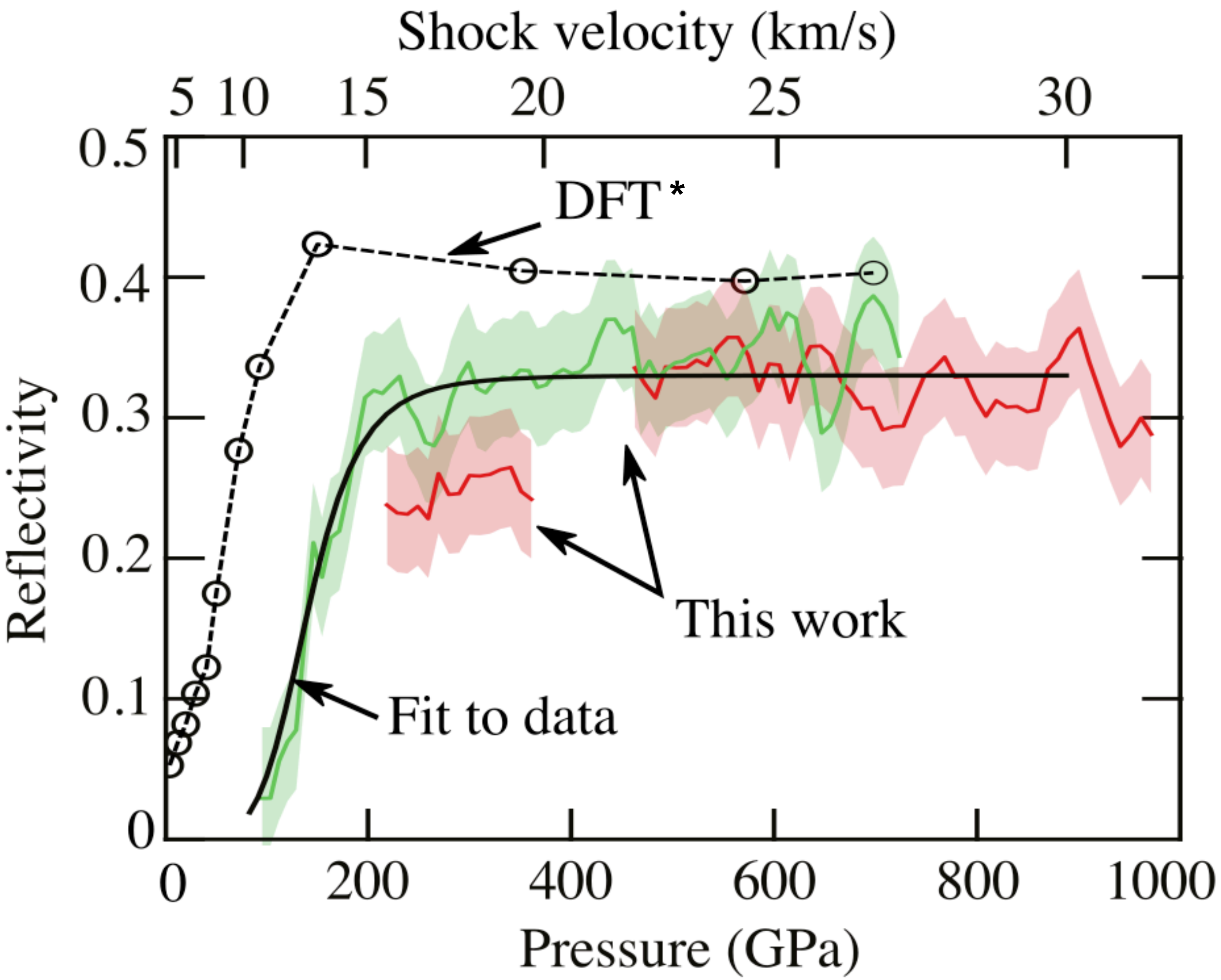
Reflectivity rises steeply from a few percent at 100 GPa to saturation at 32% above 200 GPa



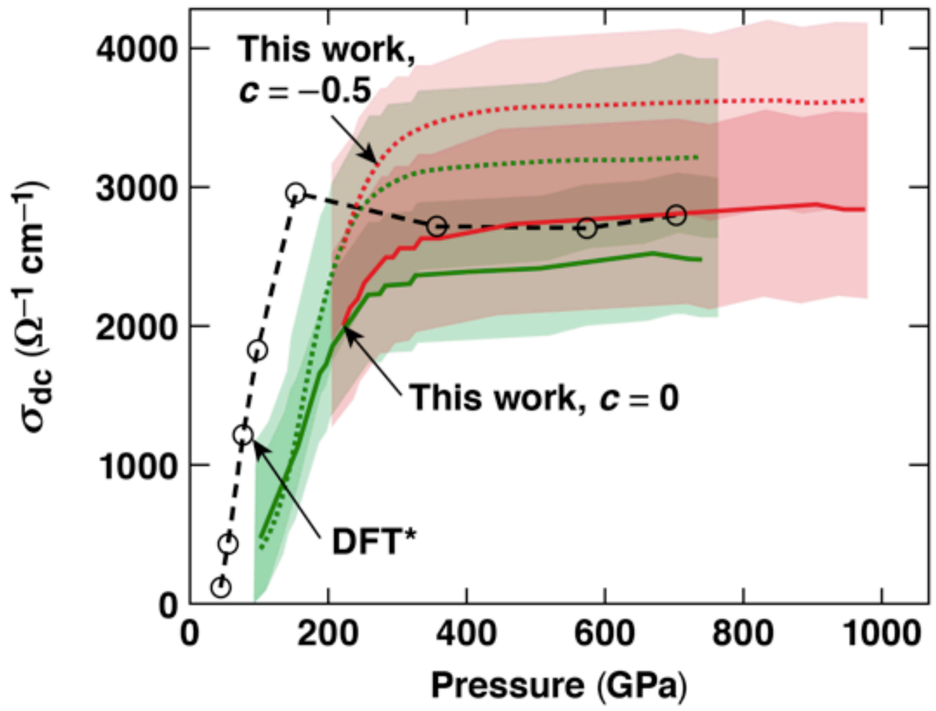
- The shock waves in these experiments were sufficiently strong to ionize the CO2 and produce a reflective shock front

- Reflectivity is inferred from the intensity of the VISAR signal and refenced to quartz**

*B. Boates *et al.*, J. Chem. Phys. 134, 064504 (2011).
**S. Brygoo *et al.*, J. Appl. Phys. 118, 195901 (2015).

Conductivity inferred from a Drude-Smith model implies a nearly constant carrier density above 200 GPa

- Conductivity: $\tilde{\sigma}(\omega) = \frac{\sigma_{DC}}{1-i\omega\tau}\left(1 + \frac{c}{1-i\omega\tau}\right)$
- Backscattering parameter $-1 < c < 0$ allows for non-Drude-like reductions in electron velocity
- Define $n_e = Z\, n_i$, vary ionization Z until the model yields the measured Fresnel reflectivity
- For zero backscattering, $Z \to 0.33$
- For moderate backscattering, $Z \to 1$



Saturated reflectivity implies a nearly constant carrier density above 200 GPa.

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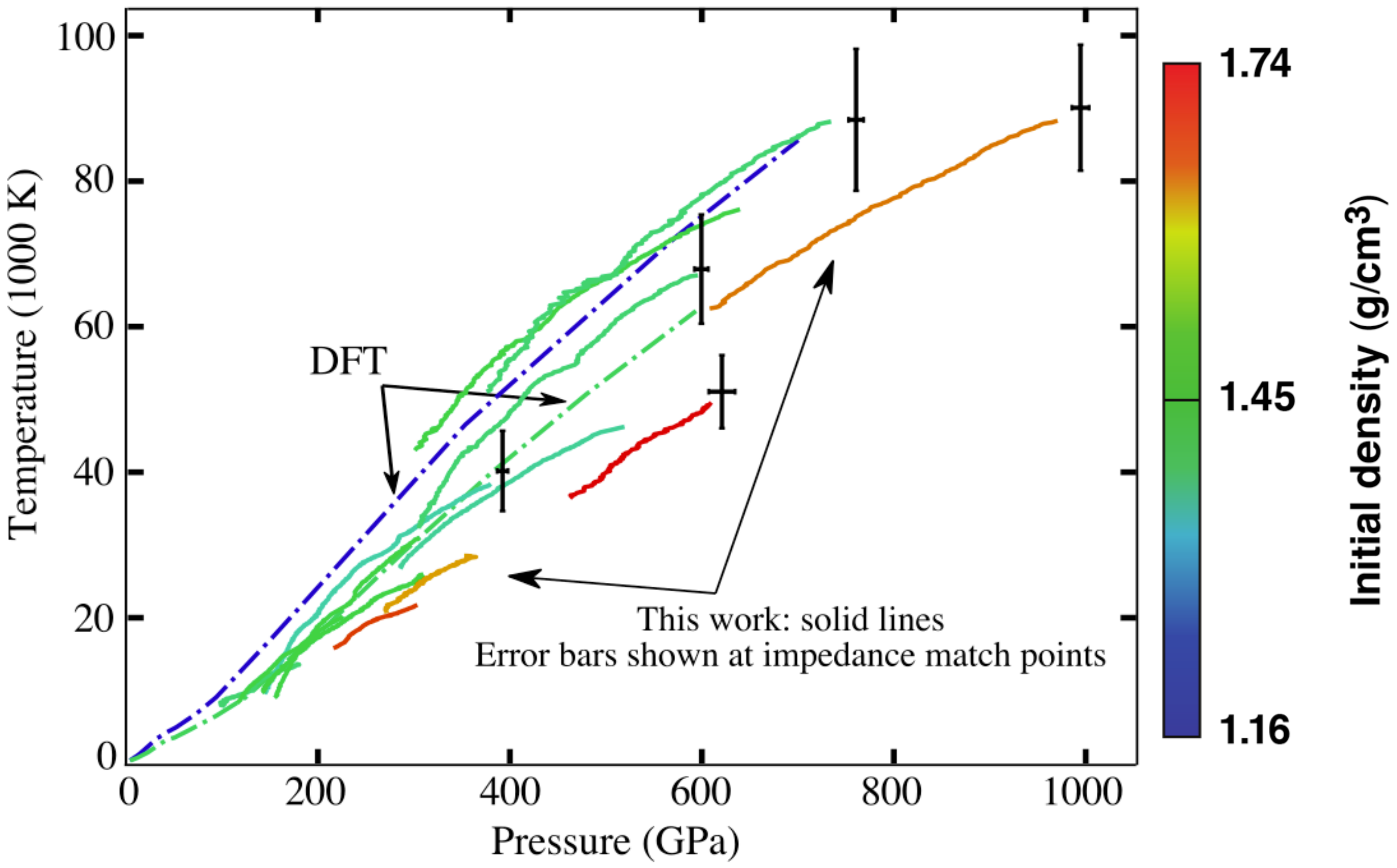
Decaying shocks in CO_2 provide a wide range of temperatures on a single shot



- Decaying shocks allow us to measure temperature in the entire range of 100 to 1000 GPa
- DFT* reasonably predicts our observed temperatures
- Higher precompression leads to lower shocked temperature

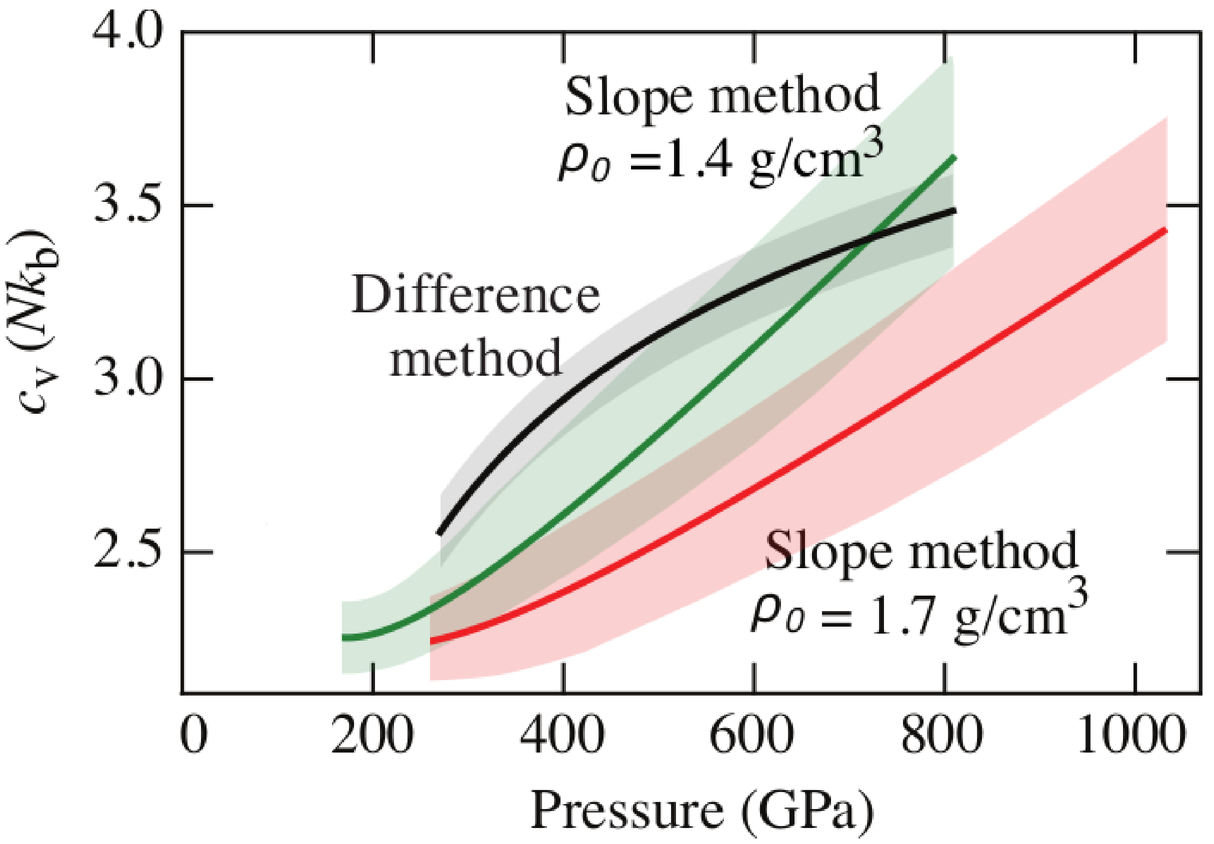
*B. Boates *et al.*, J. Chem. Phys. 134, 064504 (2011).

Specific heat increases with pressure, indicating an increase in degrees of freedom, possibly due to complex bonding

$$c_V = \frac{\partial E}{\partial T}|_V$$

Difference method*: $c_V \approx \frac{\Delta E}{\Delta T}|_V$

Slope method*: $c_V \approx \frac{\frac{\partial E}{\partial V}|_H + P}{\frac{\partial T}{\partial V}|_H + \gamma T/V}$



Chemical bonding may be significant even at TPa conditions.

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1 Mbar = 100 GPa

*D. G. Hicks et al.,, Phys. Rev. Lett. 97, 025502 (2006)

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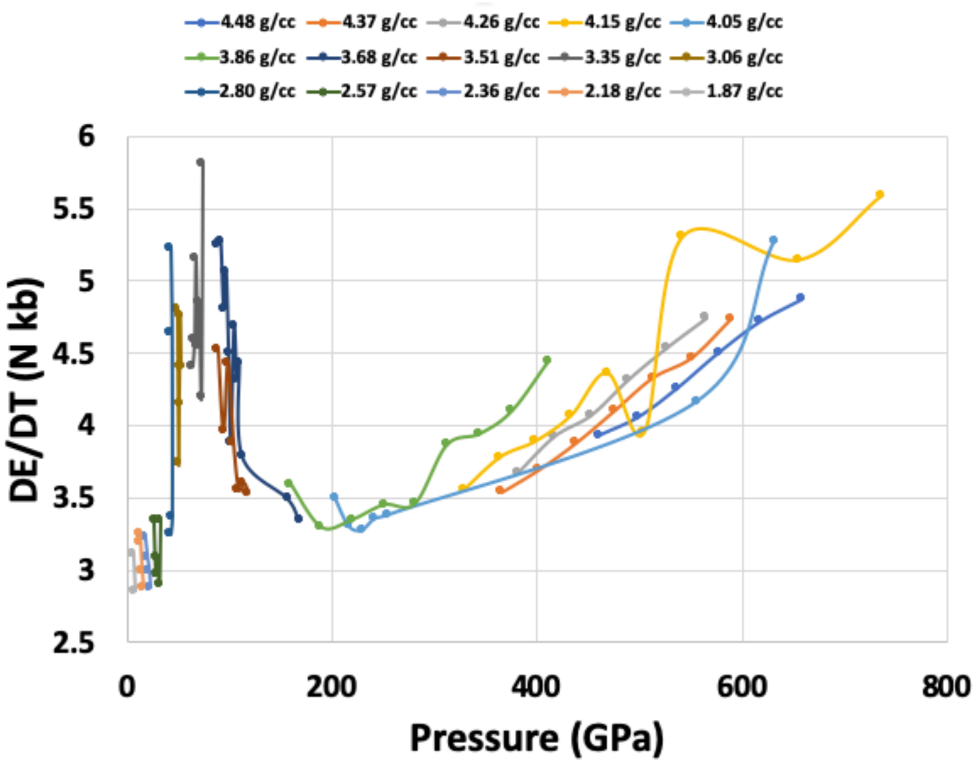
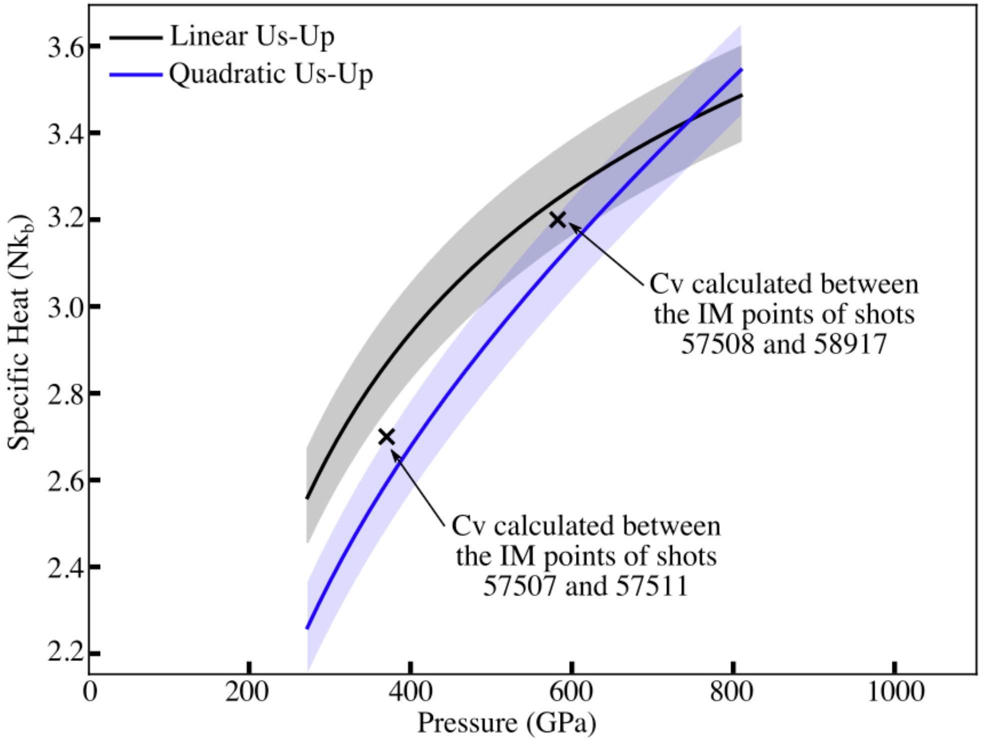


Specific heat extracted from the 15 DFT (PBE) isochores from B. Boates *et al.*, J. Chem. Phys. 134, 064504 (2011);



We had two pairs of data points with different initial volumes but the same final volume – so we can take a direct measurement of specific heat