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Institute for Shock Physics, WSU, 10/03/2013

Multi-Mbar Equation of State Data for Planetary Science: CO_2 and MgO

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NNSA National Nuclear Security Administration

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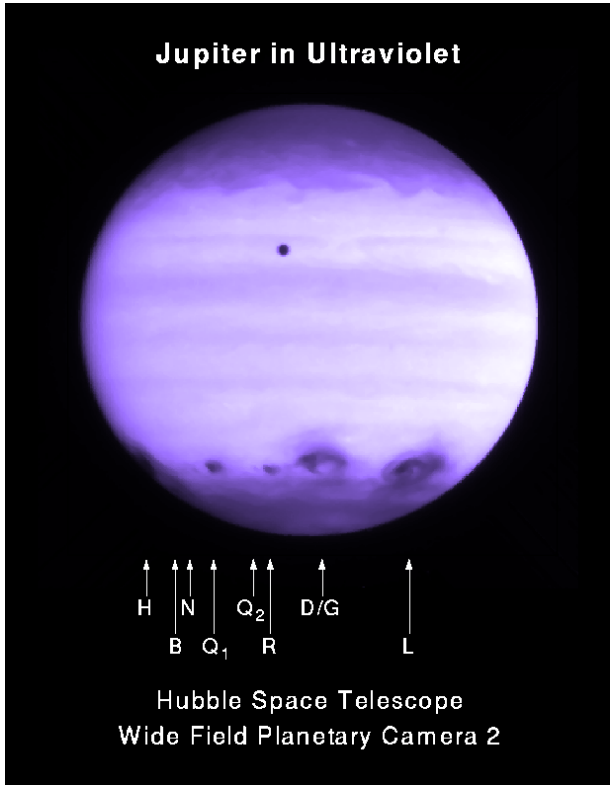
Collisions in Space…

- Giant impact event that form planets and satellites
- Impact craters from comets and meteorites
- Comet impacts may contribute to planetary atmospheres



Hubble Space Telescope Comet Team

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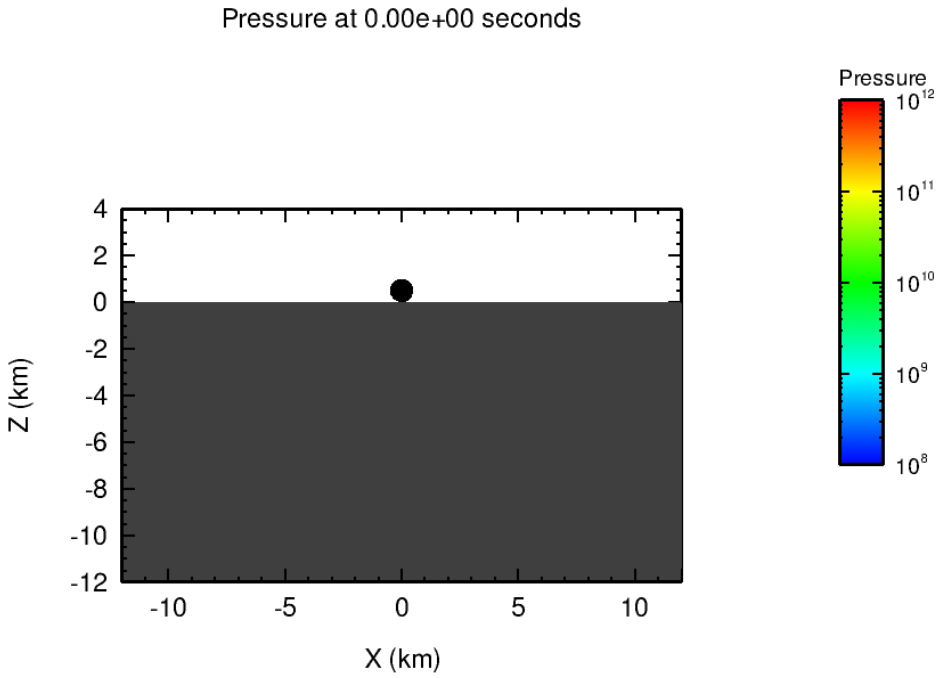
Example: Comet impact simulation on large body



- H_2O ice comet impacting a larger H_2O body
- Comet velocity = 25 km/s
- Impact angle = 45°
- 80 cores, 2 days of computation
- Pressures of 100s of Gpa
- Temperatures of 1000s of K

Modeling impact events require an equation of state for a wide range of pressures and temperatures!

Credit: R. G. Kraus, L. E. Senft, and S. T. Stewart, Icarus 214, 724, 2011

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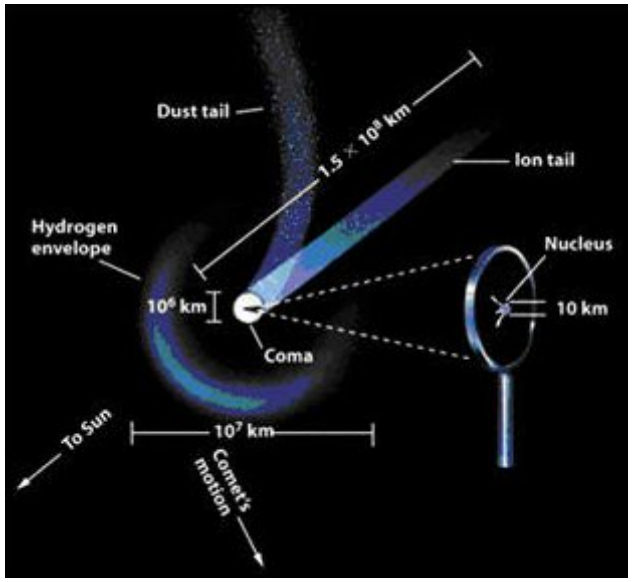
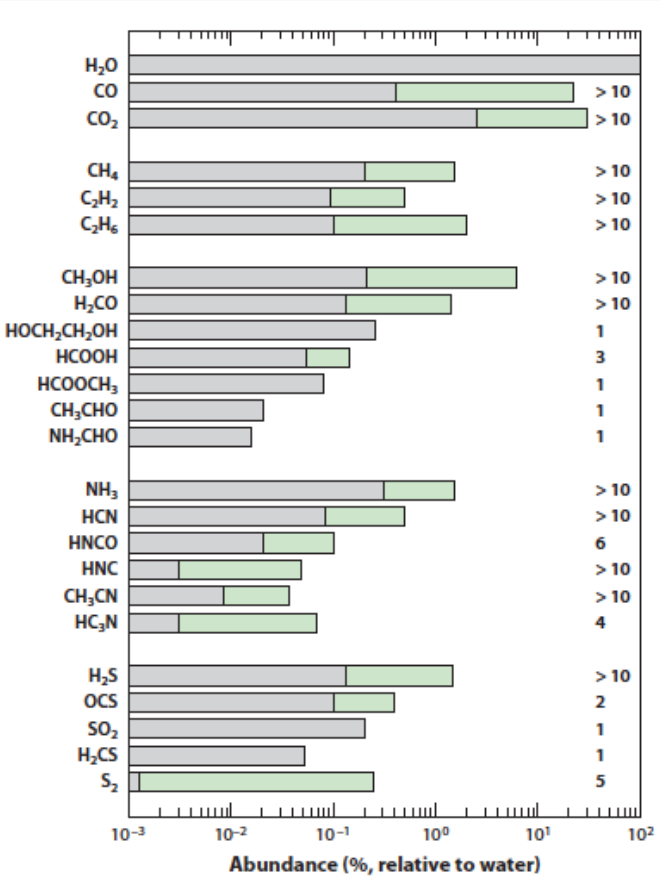
Comets Composition

- Comet nucleus contains rocky material and H2O ices
- CO and CO2 ices make up the next largest concentration of volatiles.
- Comet velocities vary depending on orbit and distance from sun, but are approximately 10s of km/s.





M. J. Mumma and S. B. Charnley,
Annu. Rev. Astron. Astrophys. **49**, 471, (2011).

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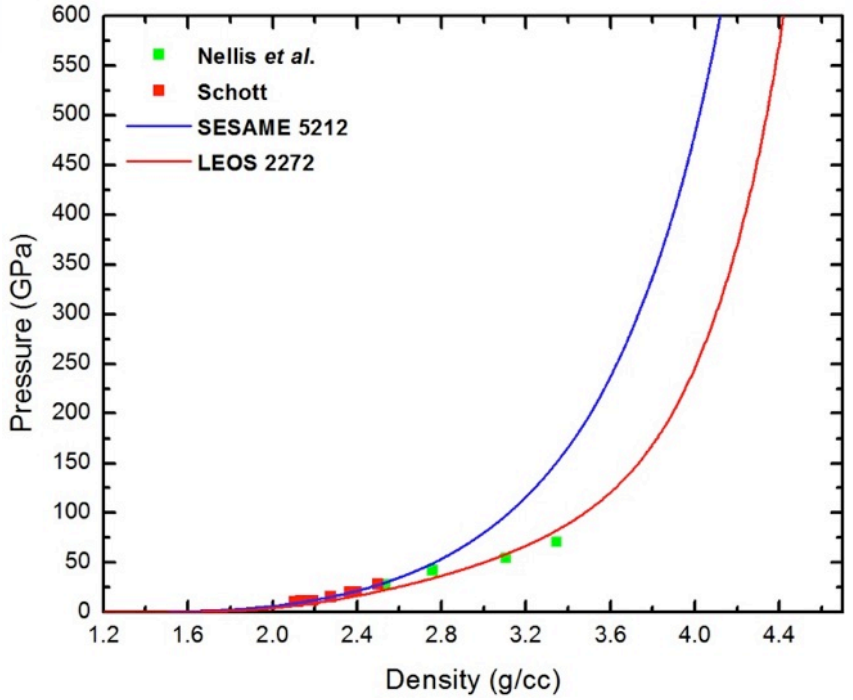
CO2 Equation of State

- **Large amount of thermodynamic data to 0.8 GPa and 1100 K**
- **Extensive static high pressure work on solid CO2 up to 80 GPa and temperatures from 40 K to 3000 K**
- **Hugoniot measurements to 80 Gpa**
- **Inflection in the Hugoniot data around 40 Gpa – attributed to dissociation**



- Two existing EOS models:
  - SESAME 5212 – no dissociation
  - LEOS 2272 – includes dissociation

Experiments and Simulations required to determine the high pressure – high temperature behavior of CO2

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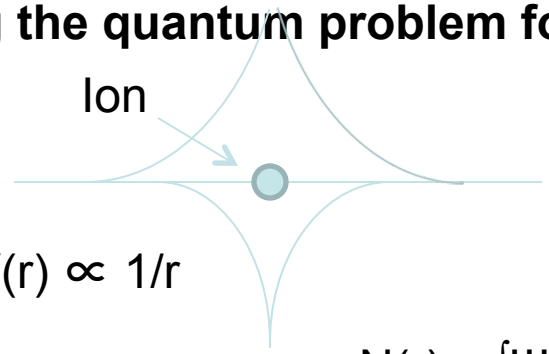
Density Functional Theory

- **For most materials ions are easy (classical)**
- **Electrons pose problem**
  - **Schrödinger Equation**

$$\hat{H}\Psi(r_1 \ldots r_N) = E\Psi(r_1 \ldots r_N)$$

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|}$$

- **Three insights make solving the quantum problem for the electrons tractable**
  - **Physical insight:**



$$N(r) = \int \Psi(r, r_2 .. r_N) dr_2 \cdots dr_N$$

  - *Wavefunction is not an observable but the density is*
  - *Replace the 3N dimensional wavefunction with density*
  - **Replace interacting electrons with noninteracting in an effective potential**

$$H[\Psi] = T[\Psi_s] + V_H[n] + V_{EI}[\Psi_S] + V_{XC}[n]$$

  - **Choose effective potential to be a local property of the density**

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Density Functional Theory

- DFT-MD simulations performed using VASP 5.1.40*
- Electronic states occupied according to Mermin's finite-temperature formulation
- Calculate energy and pressure for a given density and finite temperature
- Solve the Hugoniot Condition: $2\left(E - E_{ref}\right) - \left(P + P_{ref}\right)\left(v_{ref} - v\right) = 0$

- Initial conditions: ρ_0 = 1.173 g/cc, T_0 = 216 K, 32 or 64 atoms
- AM05 exchange correlation functionals
- Complex k-point sampling and 900 eV energy cut-off
- Standard Potentials: PAW C8Apr2002 and PAW O8Apr2002
- Convergence tested: number of atoms, energy cut off
- Methods demonstrated successfully on Xe, H_2O, C, quartz

* G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993) and Phys. Rev. B 49, 14251 (1994).

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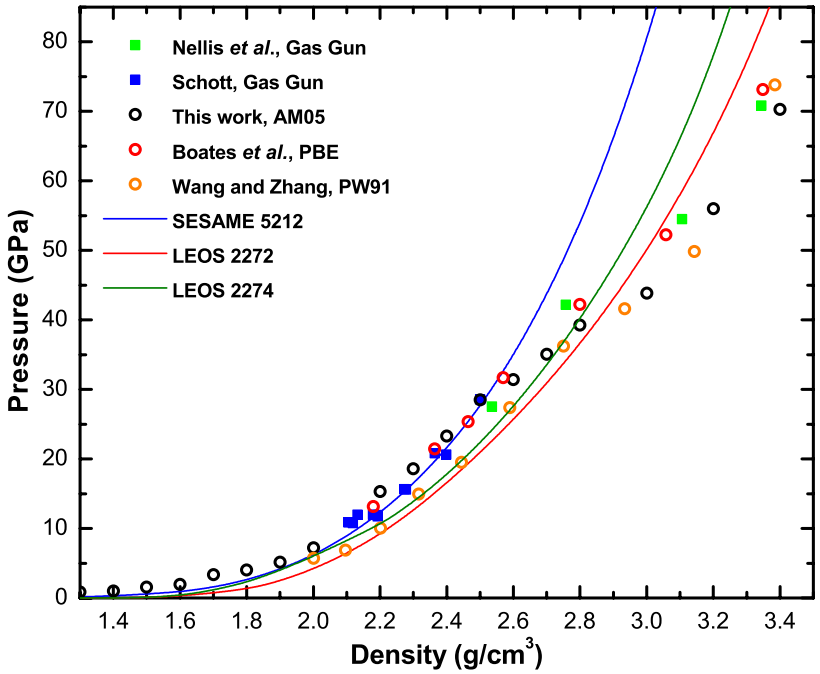
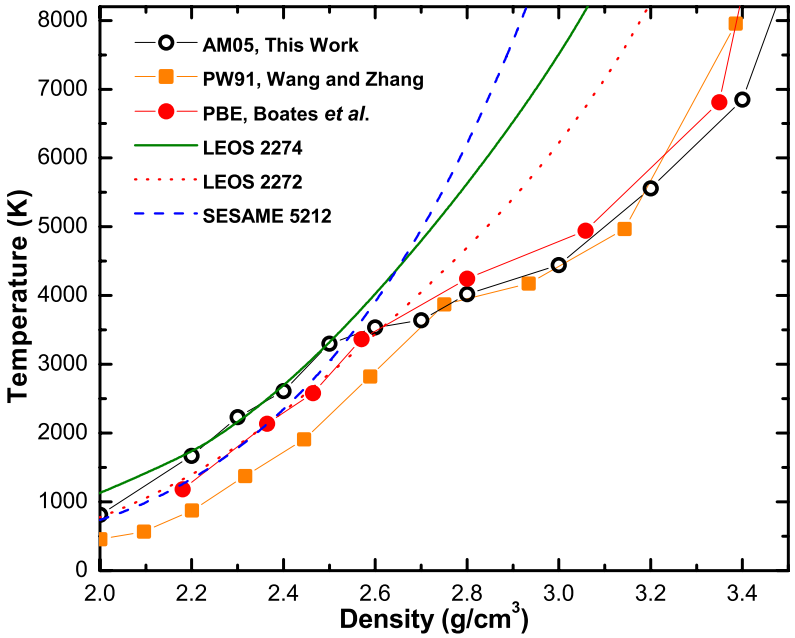
CO2 Hugoniot: Low Pressures

- **Three different exchange-correlation functionals used: AM05, PBE, PW91**
- **The PBE functional matches the data the best**
- **All DFT simulations show the Hugoniot inflection – better observed in ρ – T**
- **Below inflection, SESAME 5212 describes the Hugoniot the best**
- **LEOS 2272 and 2274 include dissociation, but need improvement in this region**





C. Wang and P. Zhang, J. Chem. Phys. **133**, 134503 (2010)
B. Boates *et al.,* J. Chem. Phys. **134**, 064504 (2011)

LEOS 2274 – recently developed, Sterne and Wu, LLNL

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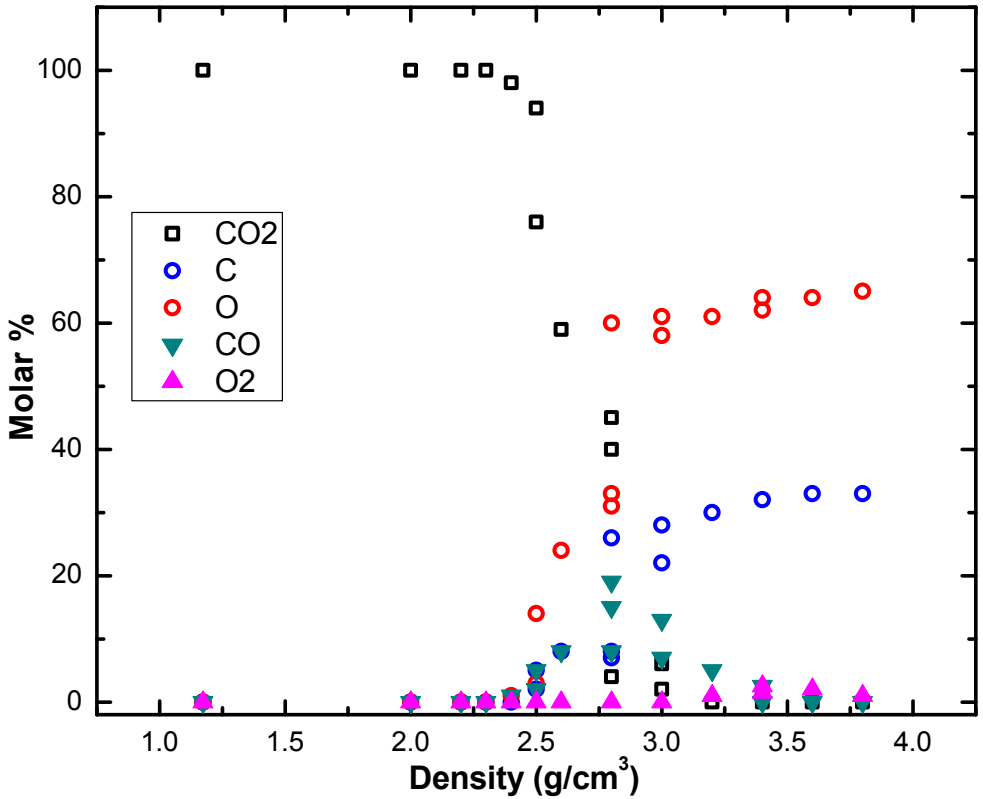
CO2 Dissociation on the Hugoniot

- Utilize a bond tracking scheme to examine dissociation in the DFT simulations
- Dissociation begins approximately 30 GPa
- Complete dissociation by 55 GPa
- CO2 dissociates into atomic C and O
- Small amounts of CO exist between 40 GPa and 55 GPa



Above 80 Gpa, liquid CO2 is now only atomic C and O, which influences the equation of state

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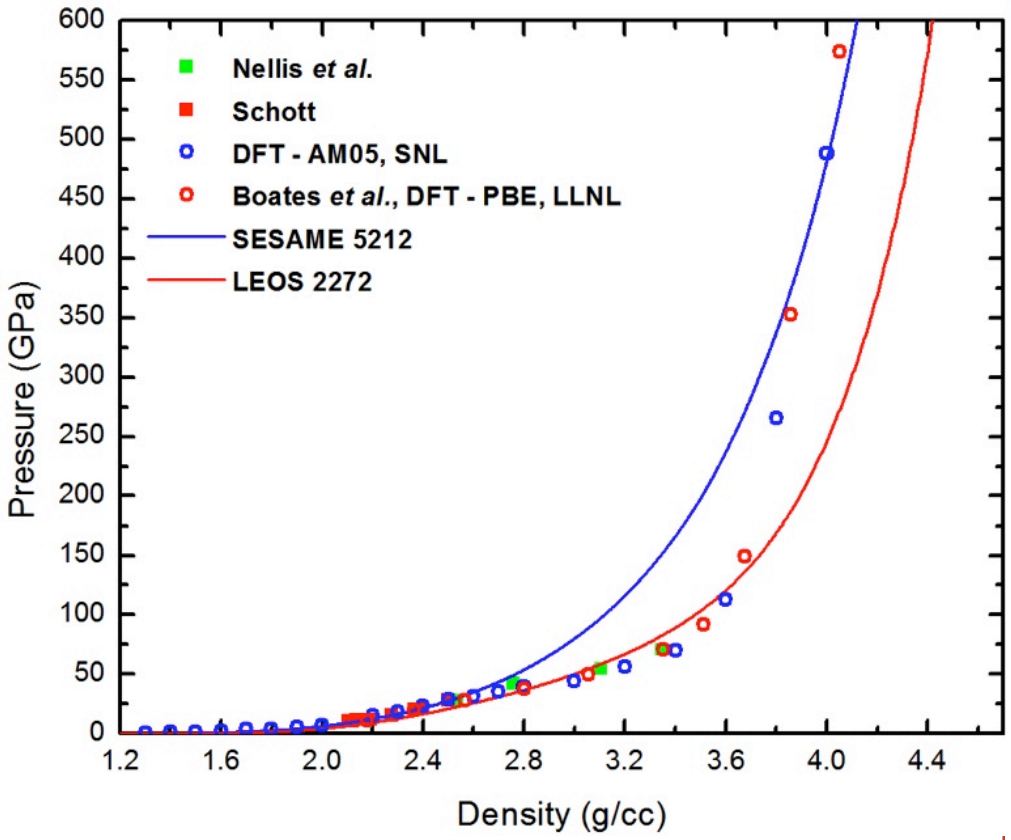
DFT CO2 Hugoniot: Multi-Mbar regime

- DFT simulations using AM05 and PBE show consistent results
- 7 Mbar using PBE, 5 Mbar using AM05
- Limitations: higher temperatures requires more energy bands to describe the system, which requires more computational time
- The LEOS 2272 table matches the DFT to 150 Gpa, but too compressible at higher pressures
- SESAME 5212 matches DFT between 3.5 and 5 Mbar, but slope is incorrect



1. Experimental data is needed in the Mbar regime to validate DFT simulations and EOS models
2. Neither 5212 or 2272 is adequate for Mbar regimes

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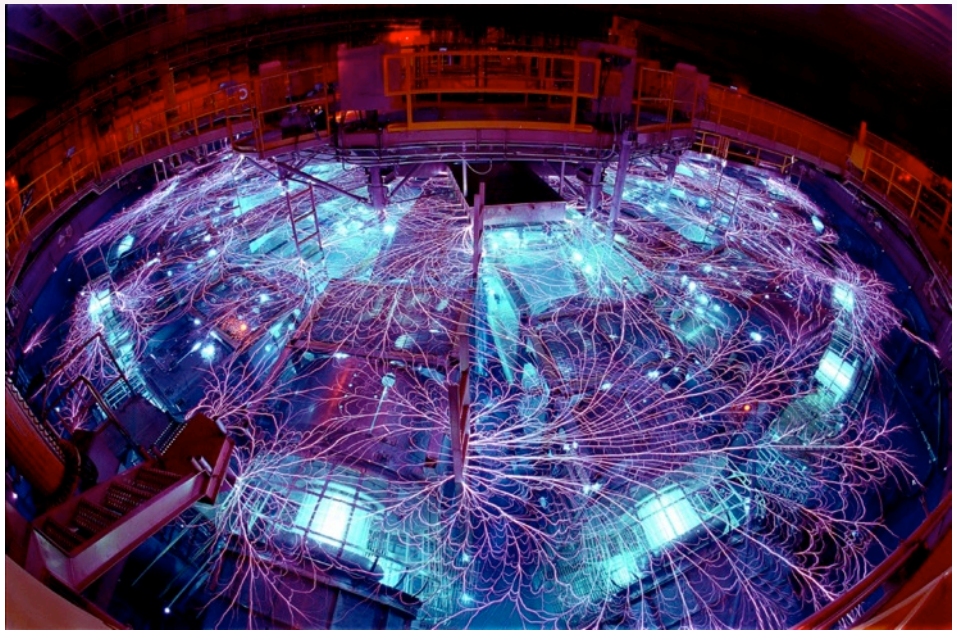
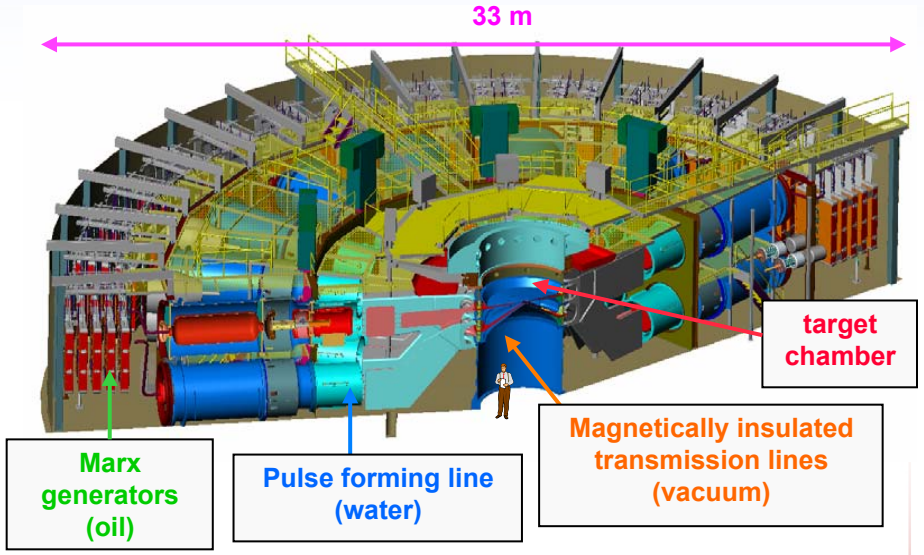
Sandia Z - Machine

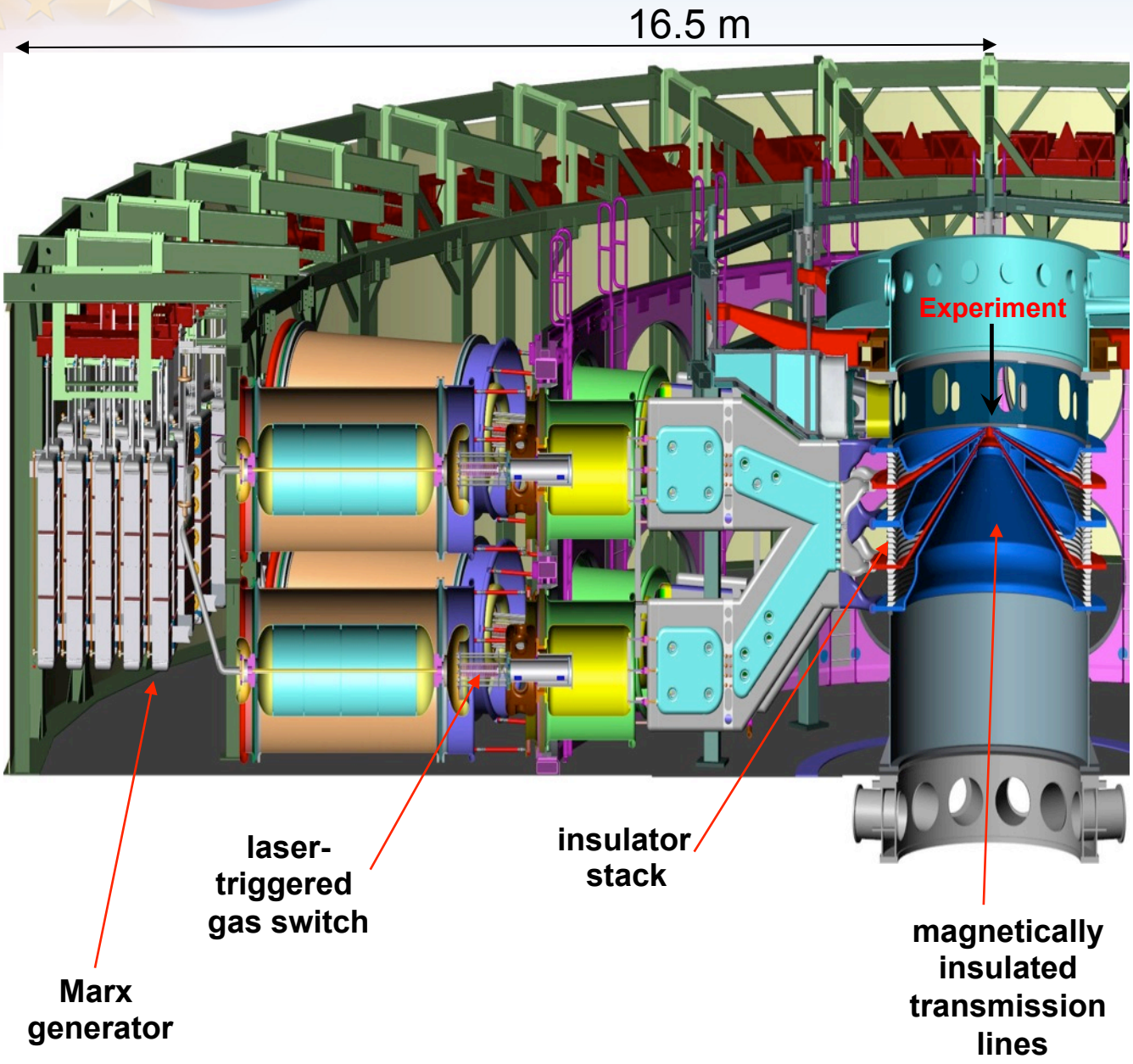




- 26 MA, 100-700 ns

- 2.65 x 10^6 L of oil
- 1.14 x 10^6 L of water
- 33 m in diameter
- 5 m in height

The Sandia Z Machine



22 MJ stored energy
~26 MA peak current
~100-1000ns rise time

Typical Target

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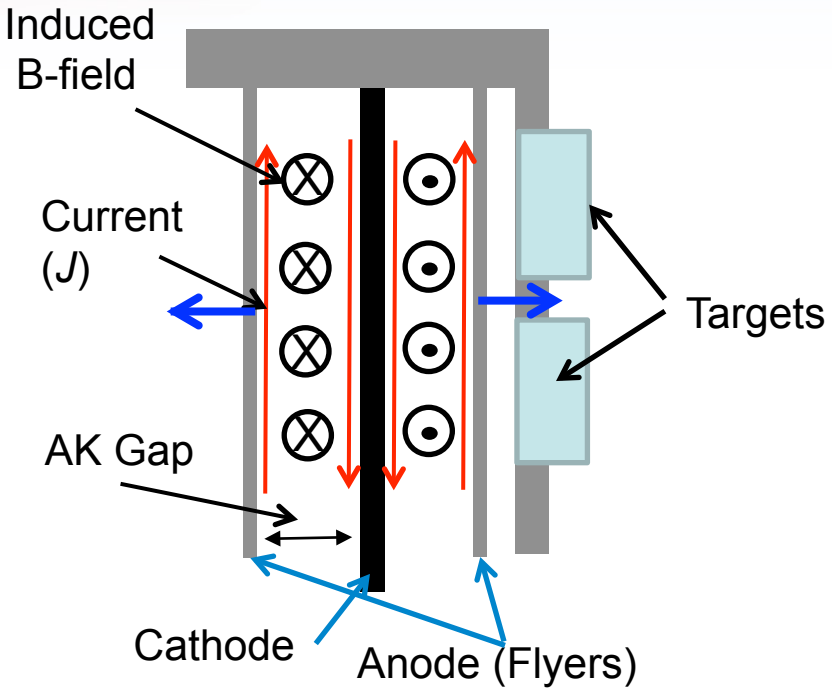
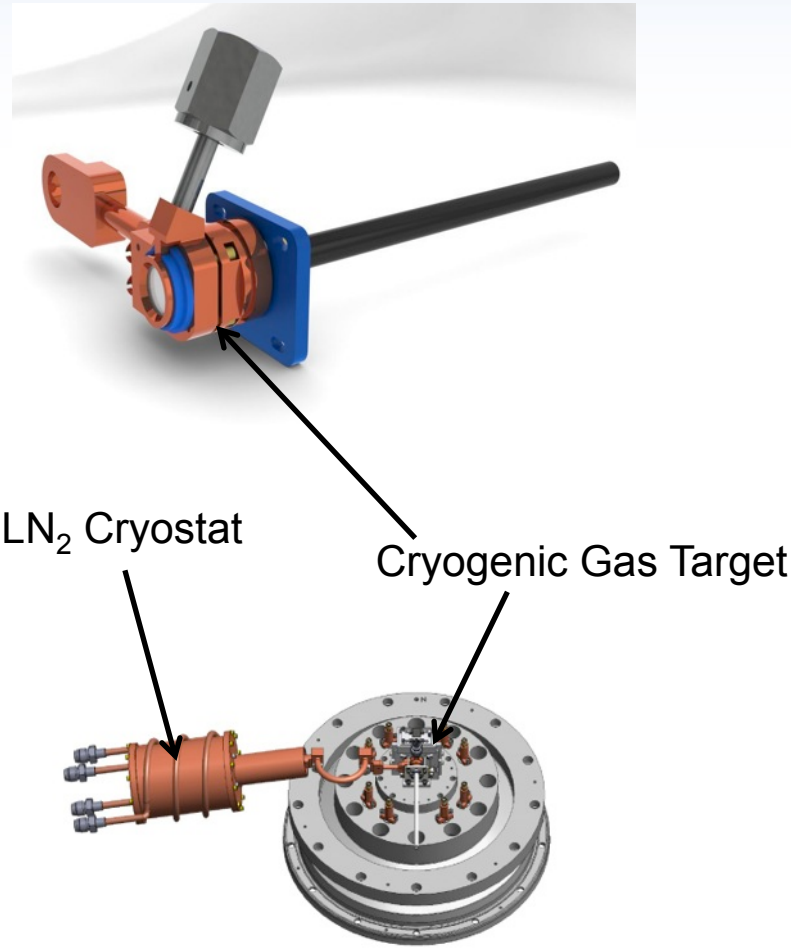
Z-Experiment Setup





- Current pulse loops through shorting cap inducing a *B* – field.
- Resulting *J x B* force accelerates anodes (flyers) outward up to 40 km/s
- Asymmetric AK Gaps result in two different flyer velocities (two Hugoniot points per experiment

- Liquid CO2 initial conditions
  - 220 K and 15.2 bar
  - ρ_0 = 1.167 g/cm³

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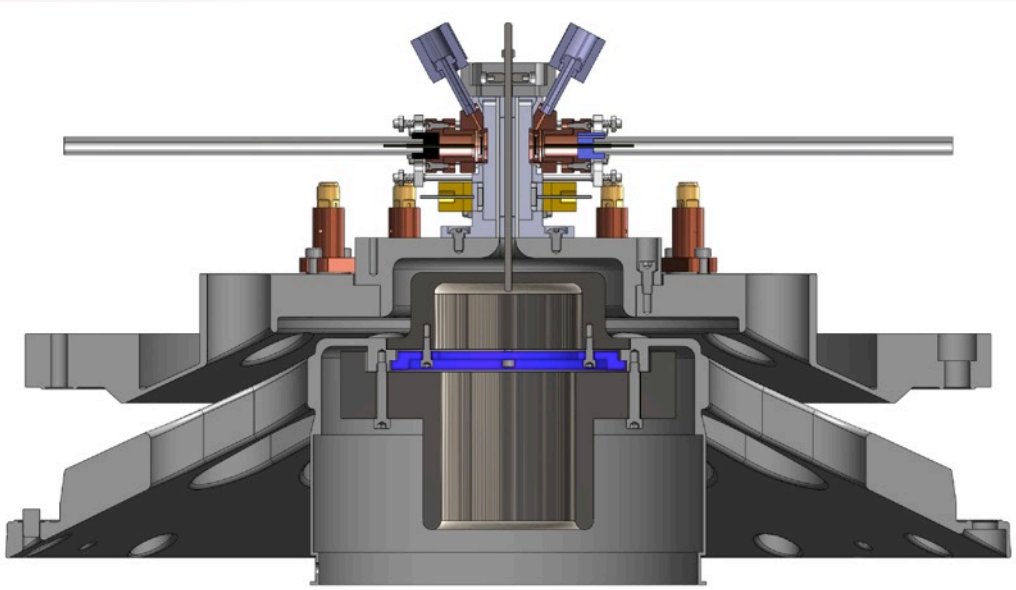
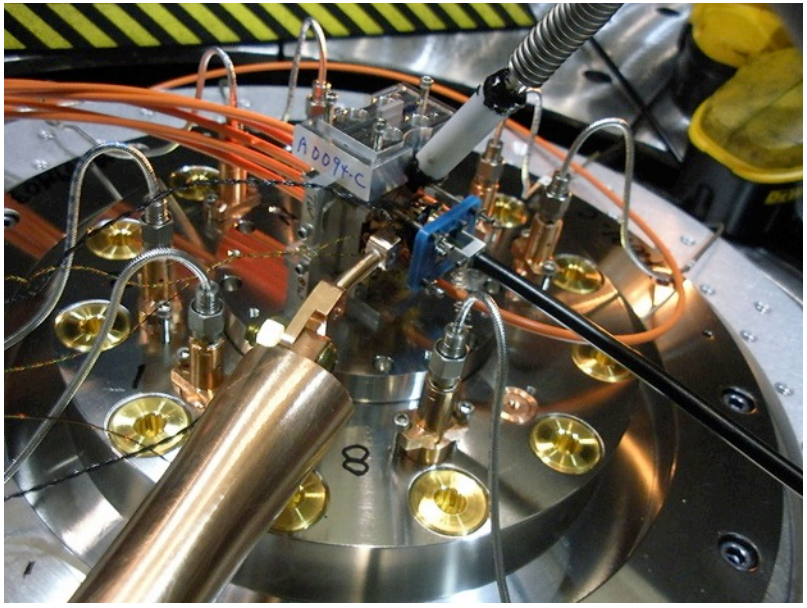
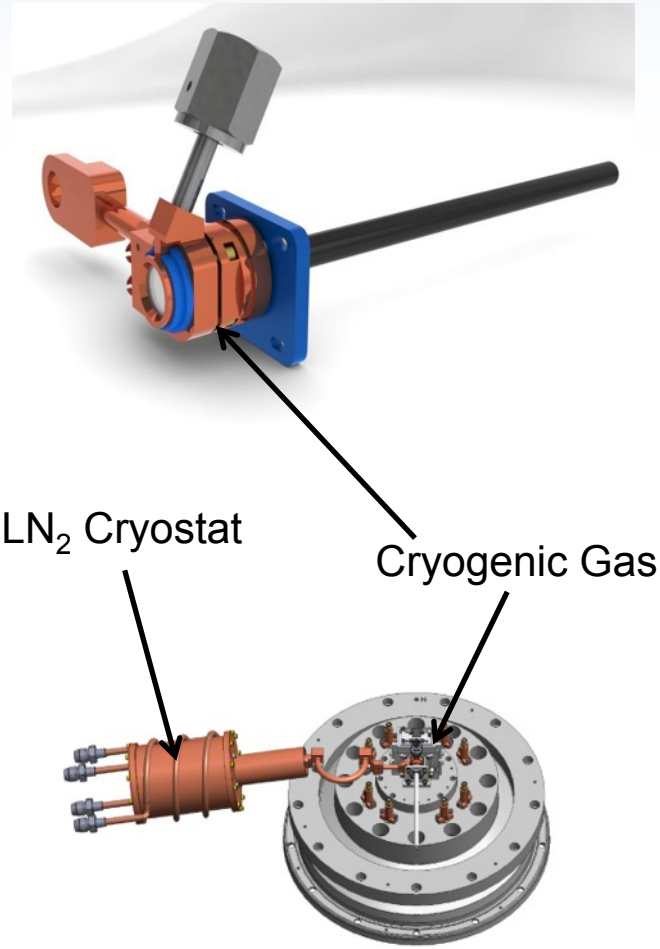
Z-Experiment Setup







- Liquid CO2 initial conditions
  - 220 K and 15.2 bar
  - ρ_0 = 1.167 g/cm³

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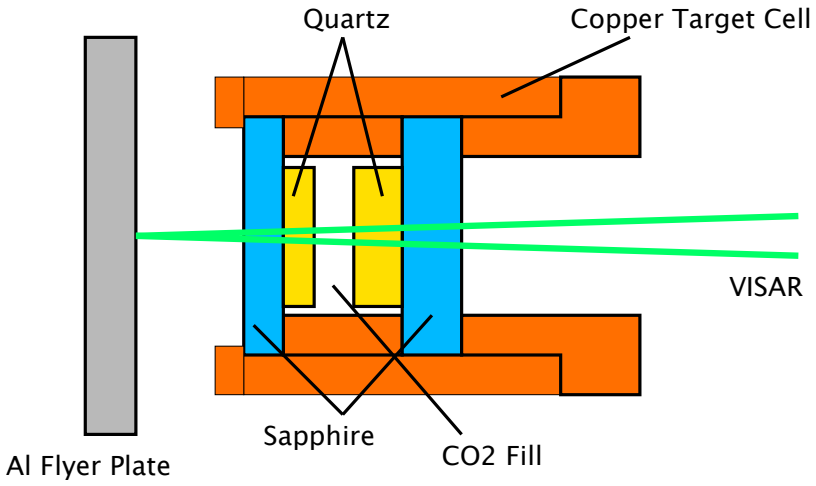
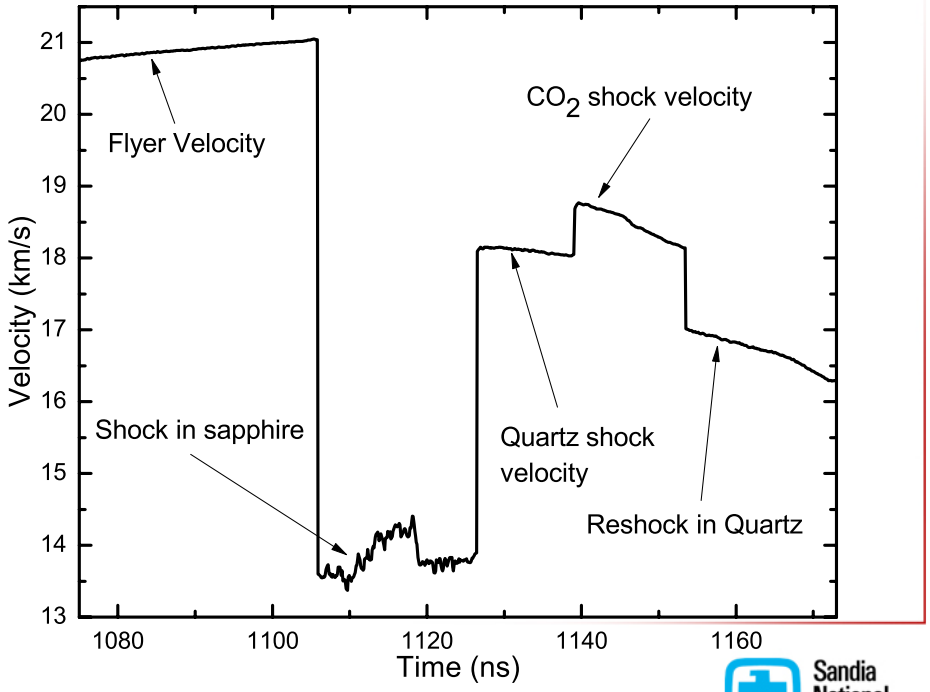
Experimental Measurement

- Starting from liquid provides a well-characterized, uniform initial state
- Target cell requires sapphire windows to handle initial pressures
- Quartz windows used for impedance matching
- VISAR measures flyer velocity, and shock velocities in quartz and CO2
- Target setup allows for measurement of reshock state





T = 220 K, P = 15.2 bar, and ρ_0 = 1.167 g/cc

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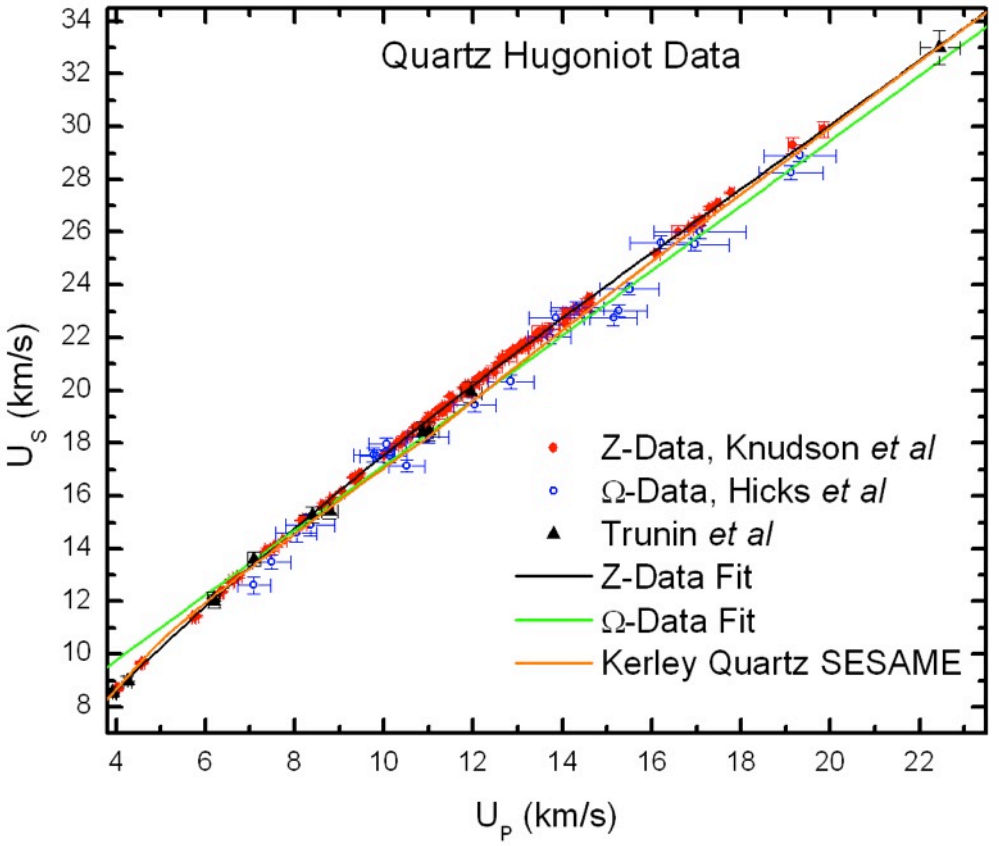
Quartz Us-Up Data and Fits

- **Nearly 300 quartz Hugoniot data points obtained using Z**
- **Data includes uncertainty from Al and Cu Hugoniot standards**
- **Correlation Matrix propagates all uncertainties**



Sandia Z Cubic Fit:

$U_S = 6.98x10^{-3}U_P^3 - 0.0384U_P^2 + 1.915U_P + 1.559$

Correlation Matrix:

U_P^3	U_P^2	U_P^1	U_P^0
1	-0.9976	0.9900	-0.9730
-0.9976	1	-0.9971	0.9848
0.9900	-0.9971	1	-0.9946
-0.9730	0.9848	-0.9946	1

Direct measurement of flyer and shock velocity leads to high precision data

- **M. D. Knudson and M. P. Desjarlais, Phys. Rev. Lett. 103, 225501 (2009).**
- **D. G. Hicks *et al.*, Phys. Plasmas 12, 082702 (2005).**
- **R. F. Trunin, *Experimental Data on Shock Compression and Adiabatic Expansion of Condensed Matter* (2001).**

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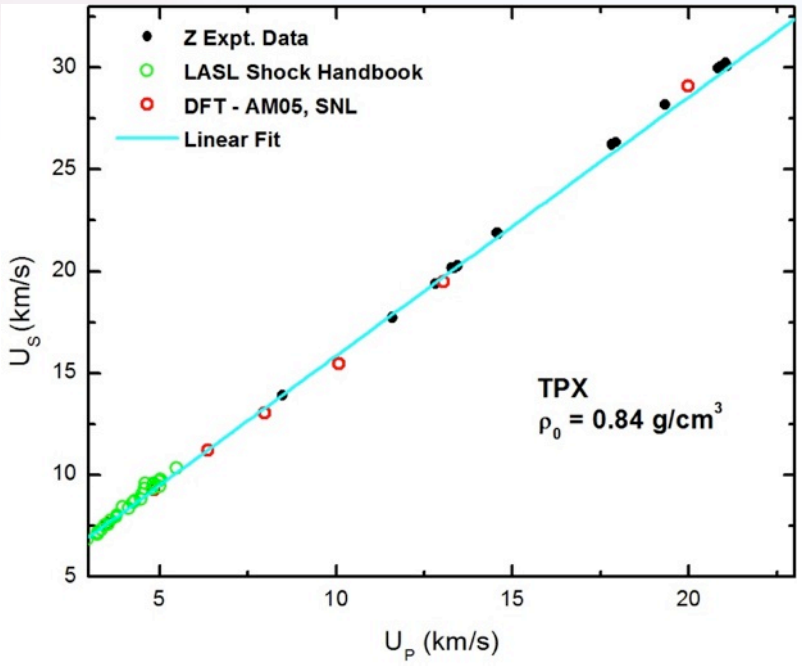
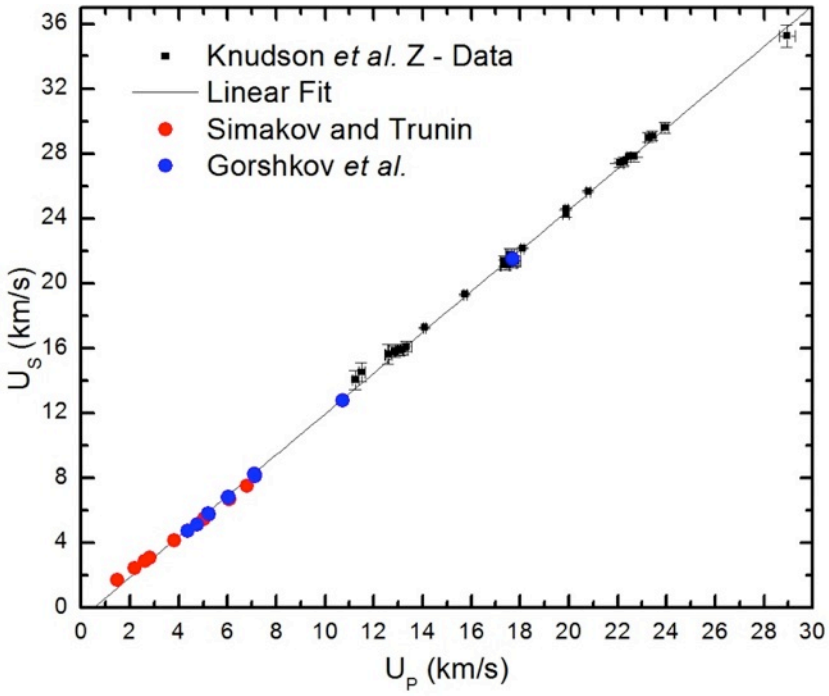
Hugoniot Standards for Release Measurements

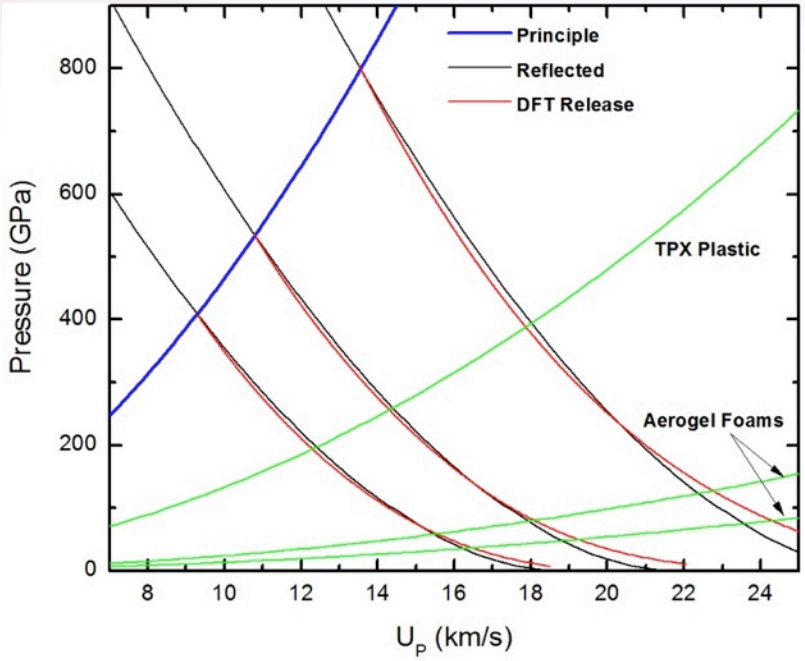


- Develop Hugoniot standards for low density materials: TPX and Aerogels
- Plastic and Aerogels have reflective shock fronts increasing the accuracy of the Hugoniot measurement

- TPX plastic 0.84 g/cm^3
- TPX Hugoniot to 540 GPa
- 200 mg/cc and 100 mg/cc silica aerogels
- Aerogel Hugoniot measurements to 200 GPa

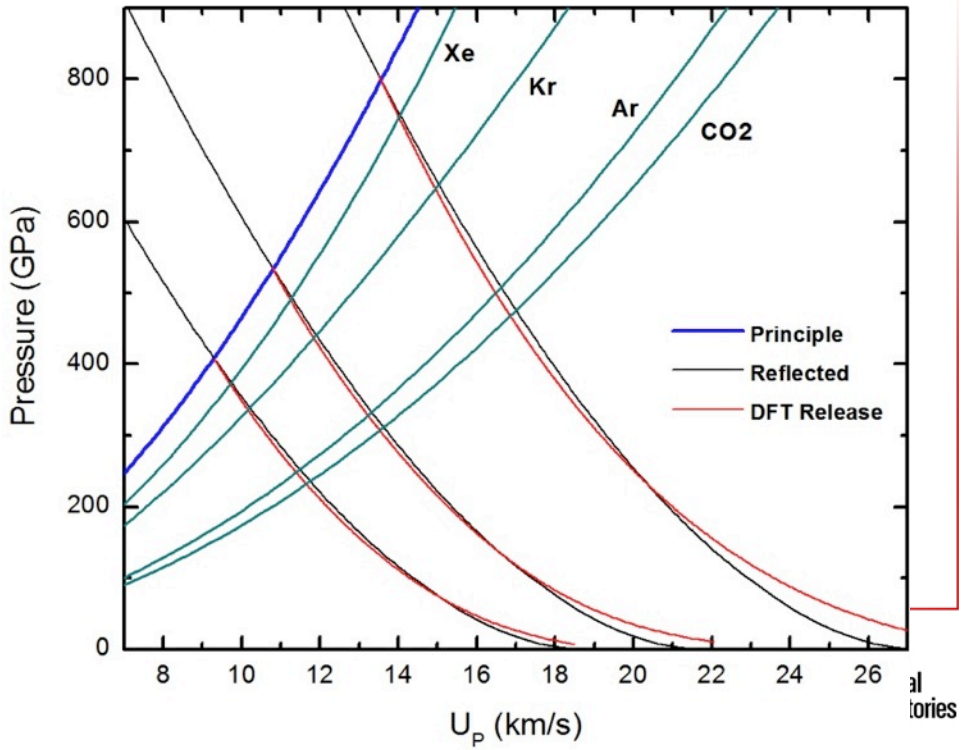


Quartz Release



- Quartz release measured using TPX and aerogel foam standards
- Determine an effective Gruneisen Γ as a function of quartz Hugoniot state
- Calculate the quartz release path

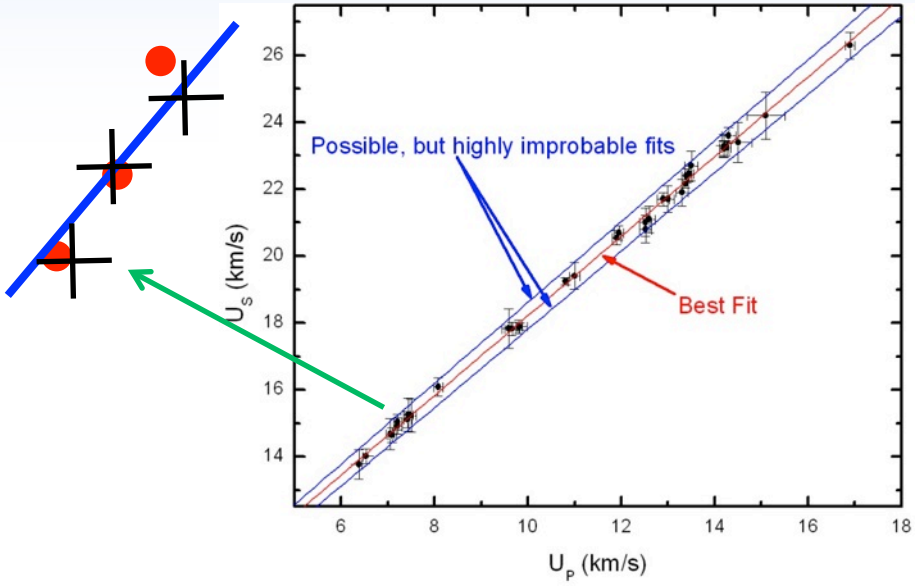
- Difference between reflected Hugoniot and release path is small for xenon
- For lower density gases: Ar, Ne, CO2, etc, the reflected versus release difference is significant



Monte Carlo (MC) Impedance Matching

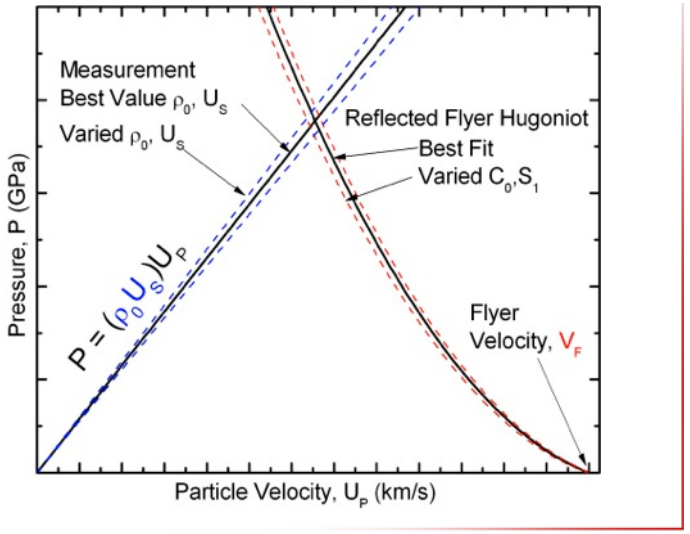
Aluminum

- Uncertainty in experimental data (Knudson *et al.*, JAP 2003)
- Vary each U_S-U_P point by an uncorrelated random number with σ = expt. Uncertainty
- Solve for linear fit parameters
- Determine mean, σ, and correlation of fit parameters



Quartz

- Vary measured parameters (V_F, U_S, ρ_0) with uncorrelated random numbers, σ = experimental uncertainty
- Vary Al fit parameters using correlated random numbers
- Calculate U_P, P, and ρ
- Determine mean and σ



Monte Carlo **technique accounts for all experimental uncertainty and propagates the Al and Cu standards' error into the quartz data.**

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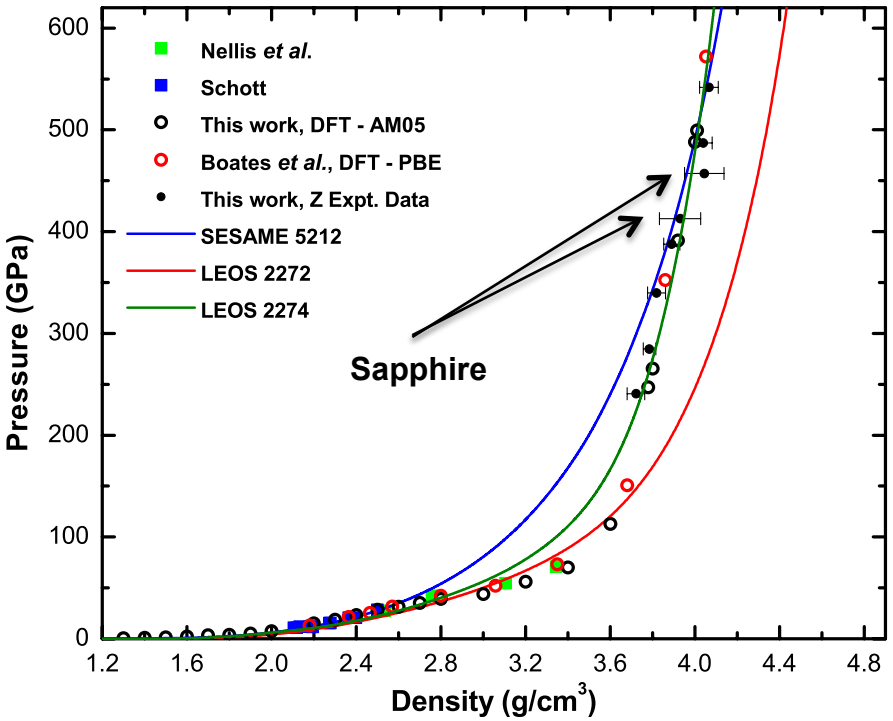
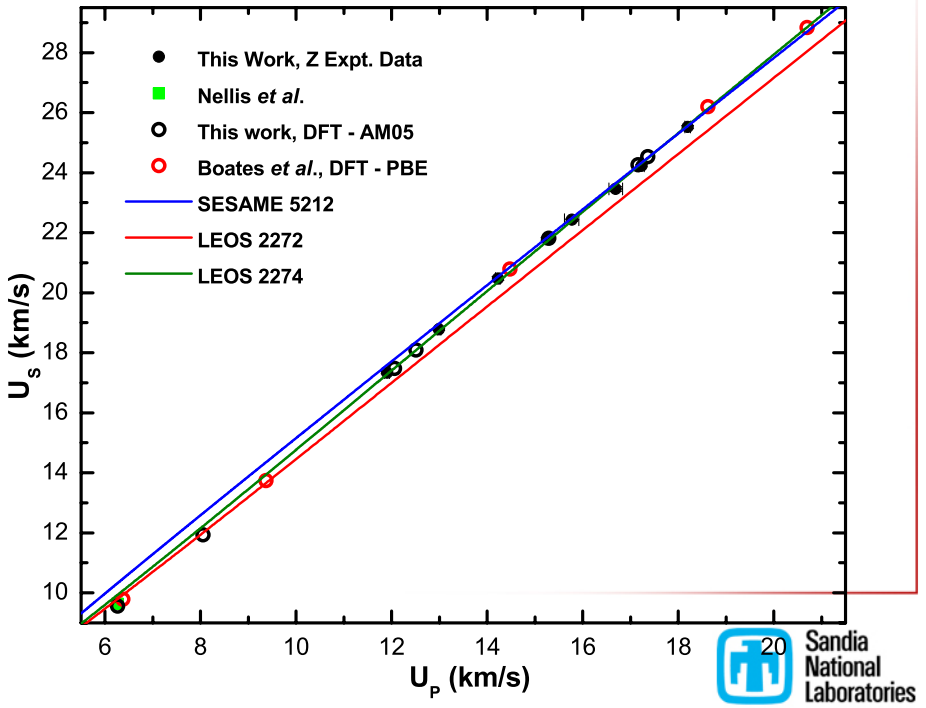
Experimental CO2 Hugoniot Results

- Hugoniot measured to 5.5 Mbar – validate the DFT results
- Data determined using quartz and sapphire impedance matching – consistent results regardless of impedance standard
- Experiments show a less compressible Hugoniot after dissociation
- LEOS 2272 is too compressible and SESAME 5212 has different trajectory
- LEOS 2274 utilized the DFT and Z experimental results for high pressure Hugoniot





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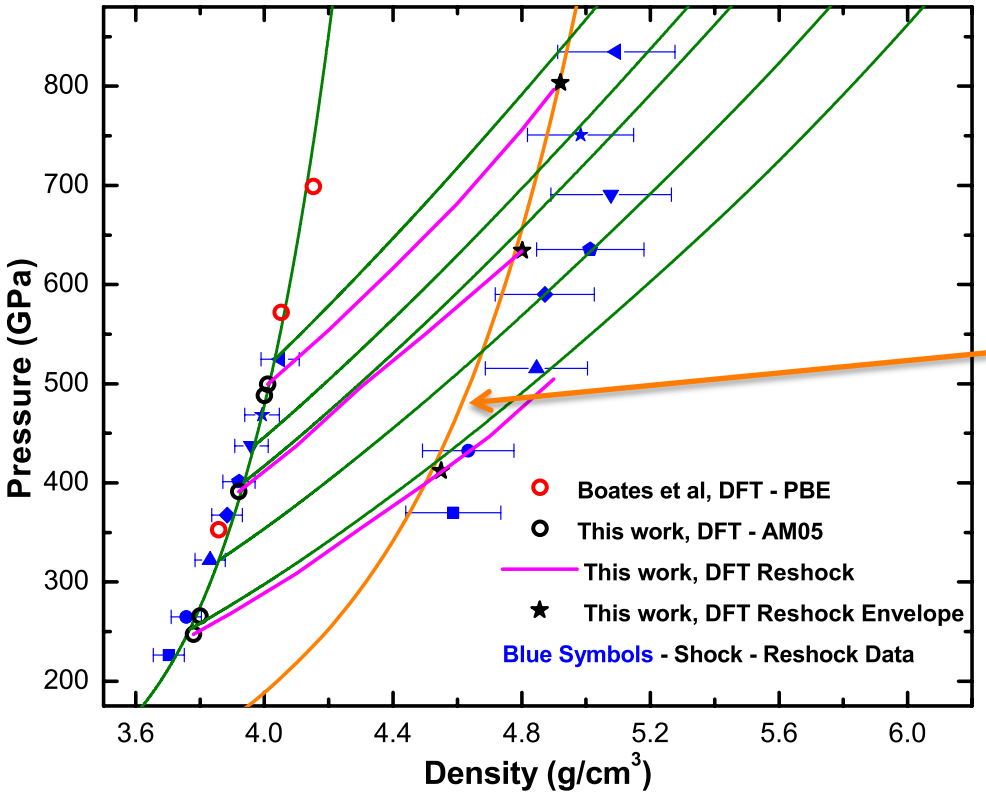
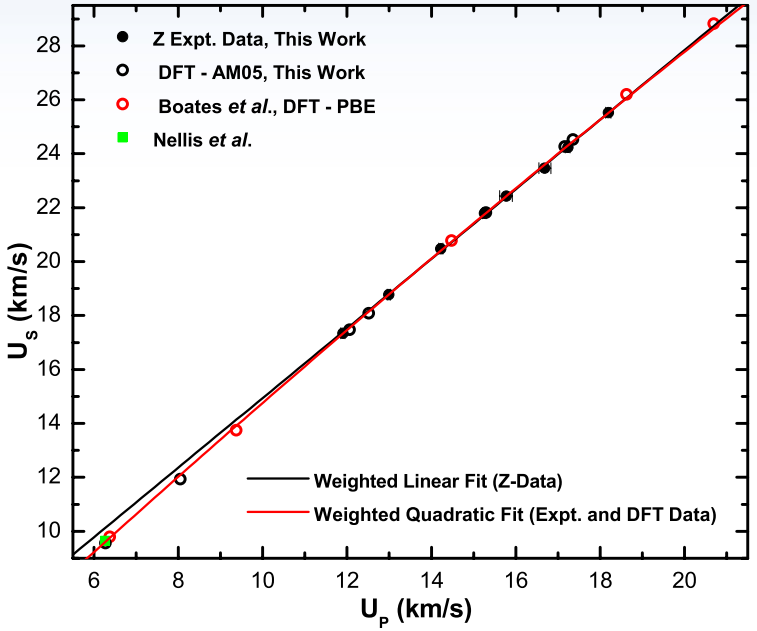
CO2 Reshock

- A weighted linear fit and weighted quadratic fit determined for the data
- Because of some attenuation of the shock we use fit and CO2 shock velocity to calculate state prior to reshock at rear quartz window
- Reshock state determined from quartz shock velocity





- CO2 reshock state measured to 8.4 Mbar
- Reshock end states determined from LEOS 2274 and quartz Hugoniot
- Experimental data shows more compressibility on reshock than predicted by DFT

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Summary

- **Experimental measured the liquid CO2 Hugoniot to 5.5 Mbar and reshock states to 8.4 Mbar**
- **Experimental data validated the DFT simulations using PBE and AM05**
- **DFT simulations indicate that above 65 Gpa, CO2 dissociates into atomic C and O**
- **Experimental and DFT results showed that SESAME 5212 and LEOS 2272 are inadequate to model CO2 in the Mbar regime**
- **LEOS 2274 is a significant improvement, but still needs refinement**
- **The experimental and DFT results provide accurate data sets for EOS development**
- ***Integration of DFT, high-precision Hugoniot standards, and Z experiments constitutes a solid basis for understanding the high pressure response of materials.***

Linear (U_S > 17 km/s): $U_S = (2.110 \pm 0.234) + (1.285 \pm 0.015)U_P$

Quadratic (10 < U_S < 25 km/s): $U_S = (0.543 \pm 0.253) + (1.487 \pm 0.045)U_P - (6.378 \pm 1.831) \times 10^{-3}U_P^2$

S. Root *et al.*, Physical Review B 87, 224102, (2013).

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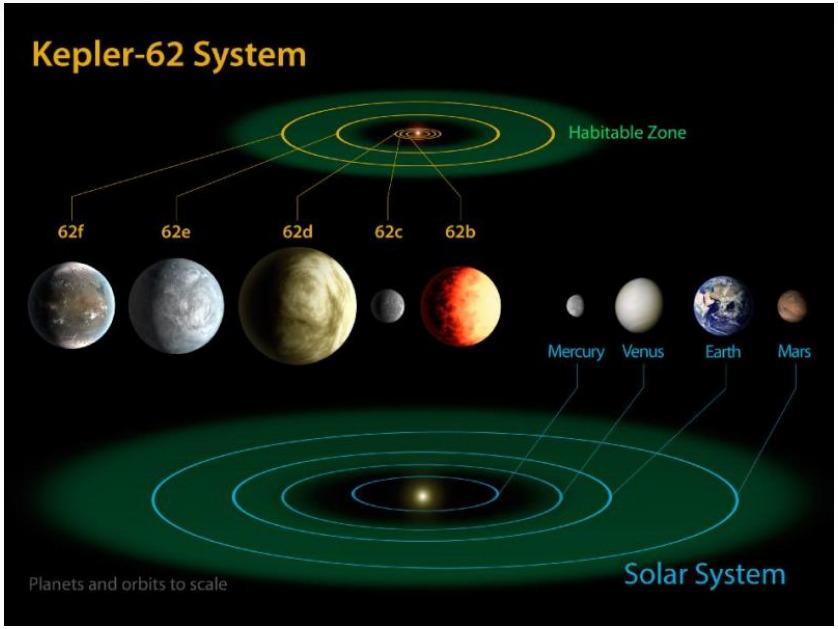
Planetary and Satellite Formation from Collisions



- How are planets formed during impacts?
- Earth – Moon system formed during an impact with the proto-Earth
- Earth – Moon have similar compositions
- Isotopics (O, Cr, Ti) are very similar
- Various hypotheses on the Earth – moon formation:
  - Giant Impact ($M_l \sim O(M_{earth})$)
  - Small Impact with similar composition
  - Nuclear Fission Event

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Example: Small Impactor with similar composition

- Fe Cores
- MgSiO3 mantles
- 10 km/s impact
- Planetoid is 1/10th Earth mass
- ***Simulation results strongly depend on the equation of state!***

David Crawford, Sandia National Laboratories
512 cores ~ 3 weeks of run time

Shocks with ~~Rocks~~... Minerals!

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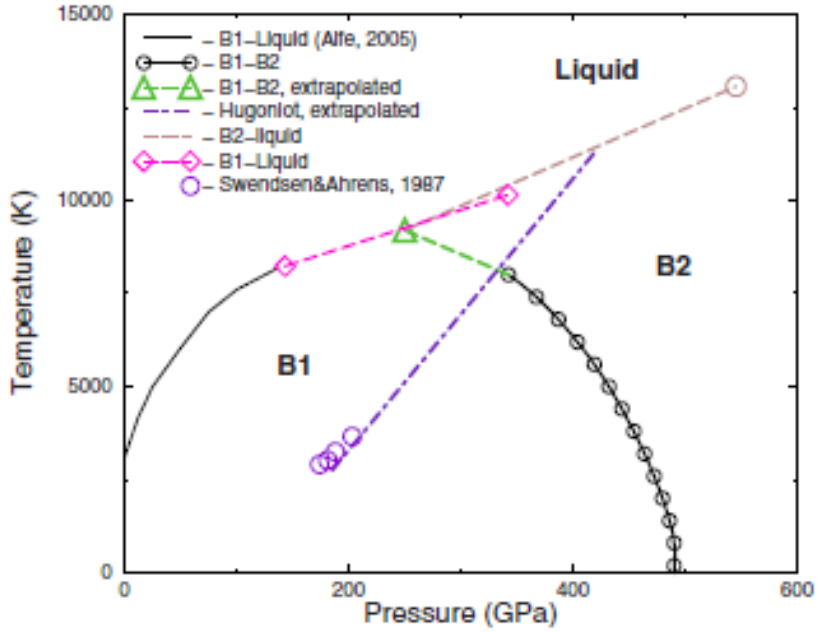
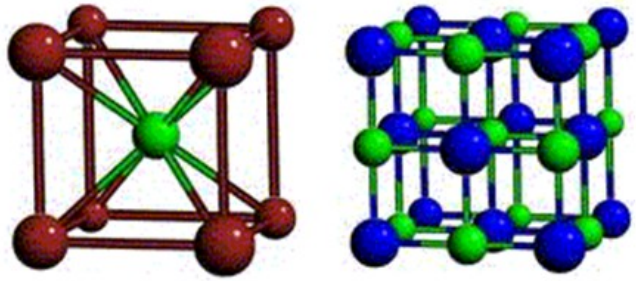
MgO Background

- MgO is abundantly found the Earth's mantle and likely other terrestrial exo-planets
  - Magnesiowüstite (Mg,Fe)O
- Understanding the high P-T behavior of MgO is important for modeling Earth's interior and planetary formation
- Static pressure data show no phase transition up to 227 Gpa at ambient temperature
- Hugoniot data (starting at ambient temperature) to ~ 200 GPa – no phase transition
- Belonoshko et al predict a B1-B2 phase transition near 350 GPa and melt near 5 Mbar and 12000 K.
- McWilliams *et al* predict B1-B2 transition at 440 GPa and melt at 650 GPa



Belonoshko *et al.*, Phys. Rev. B **81**, 054110 (2010)



CsCl NaCl

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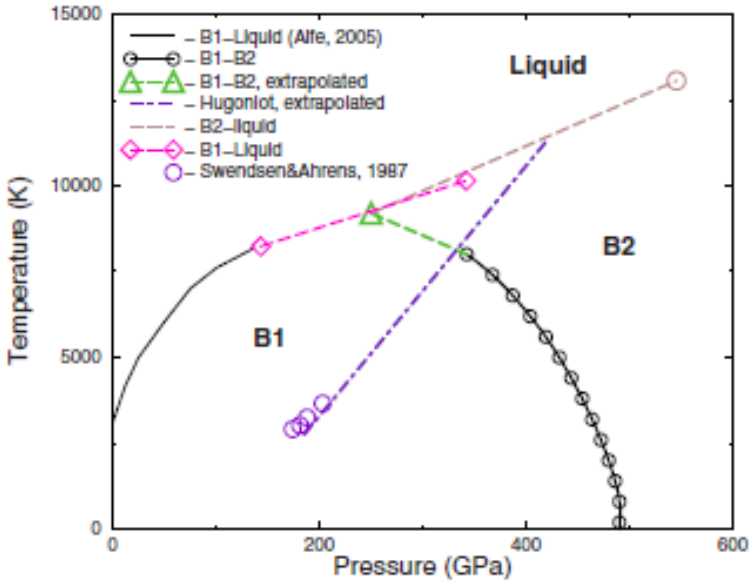
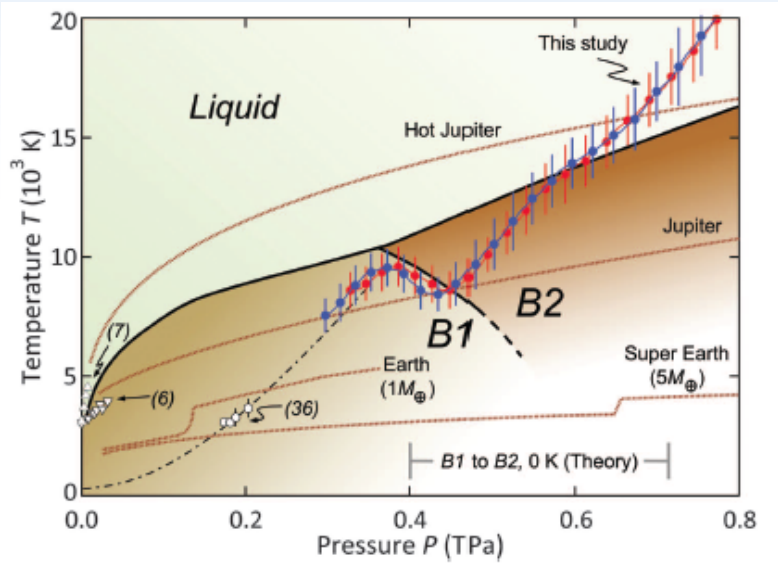
MgO Phase Diagrams

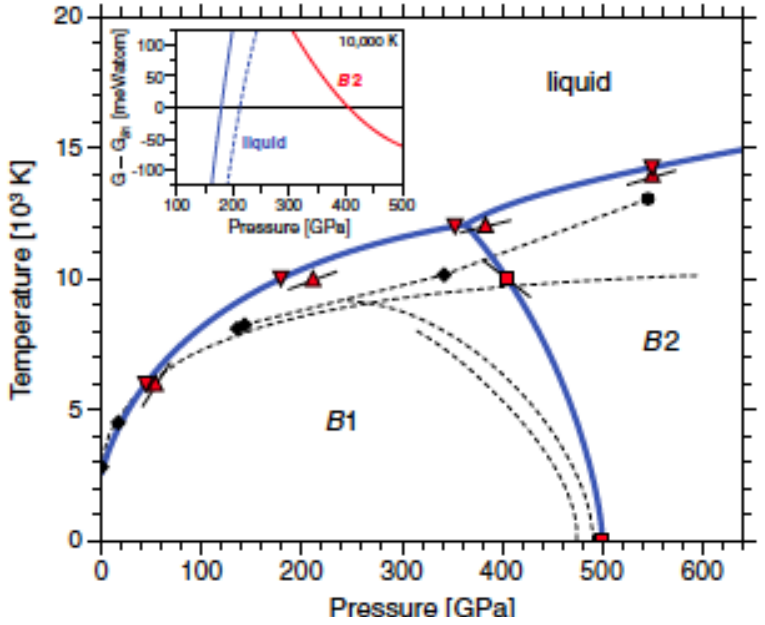


Belonoshko *et al.*, PRB **81**, 054110 (2010)



McWilliams *et al.*, Science **338**, 1330 (2012)

- **Multiple phase diagrams published**
- **B1-B2 phase boundary in disagreement in all phase diagrams**
- **Melt boundary in disagreement**
- **No consensus on phase boundaries**



B. Boates and S. Bonev, PRL **110**, 135504 (2013).

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Objectives

- Measure the MgO Hugoniot to 12 Mbar using the Sandia Z - Machine

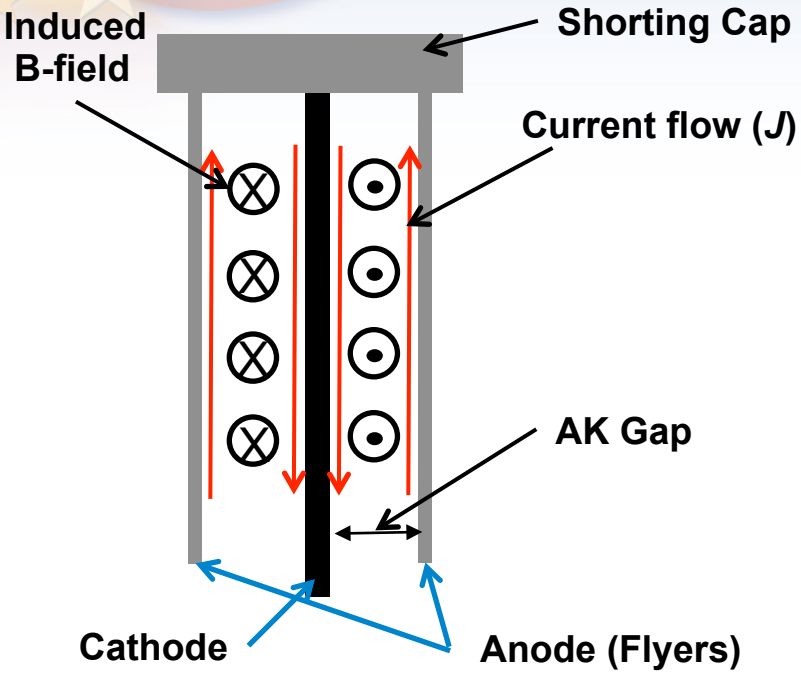
- Experimentally determine the proposed solid-solid phase transition

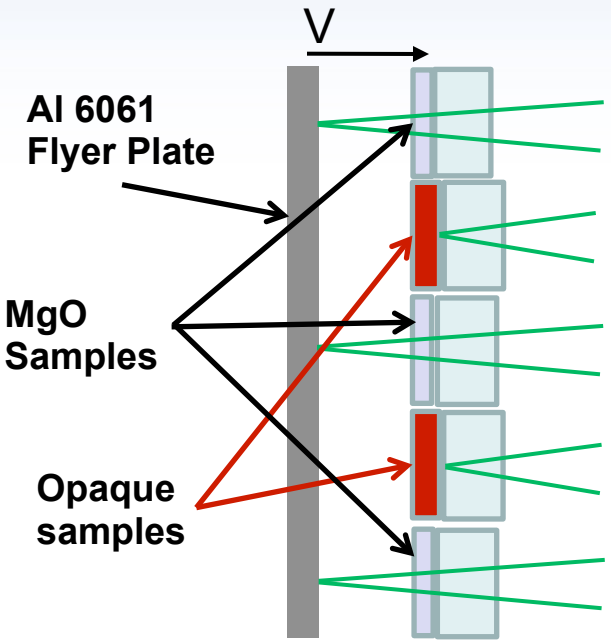
- Determine melt on the Hugoniot

- Apply Density Functional Theory methods to corroborate experimental findings

- Update the MgO phase diagram

Z Experimental Approach





- Current pulse loops through shorting cap inducing a *B* – field.
- Resulting *J x B* force accelerates anodes (flyers) outward up to 40 km/s
- Asymmetric AK Gaps result in two different flyer velocities (two Hugoniot points per experiment

- Multiple samples per experiment
- MgO windows are initially transparent and are backed by quartz, TPX plastic, or aerogel windows
- VISAR used to measure flyer velocity
- Multiple VPFs per sample – reduces uncertainty

Method produces steady shock state in the MgO

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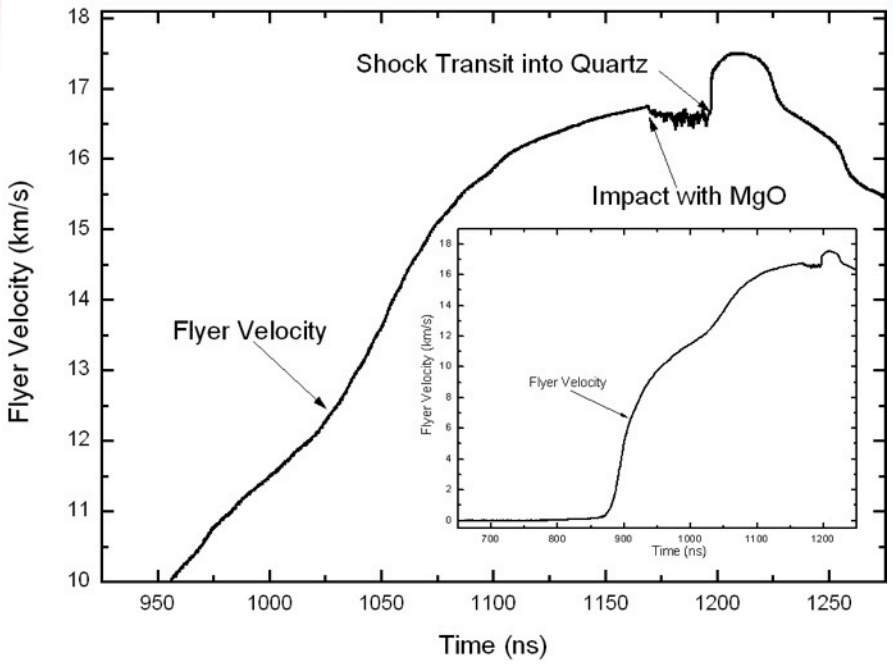
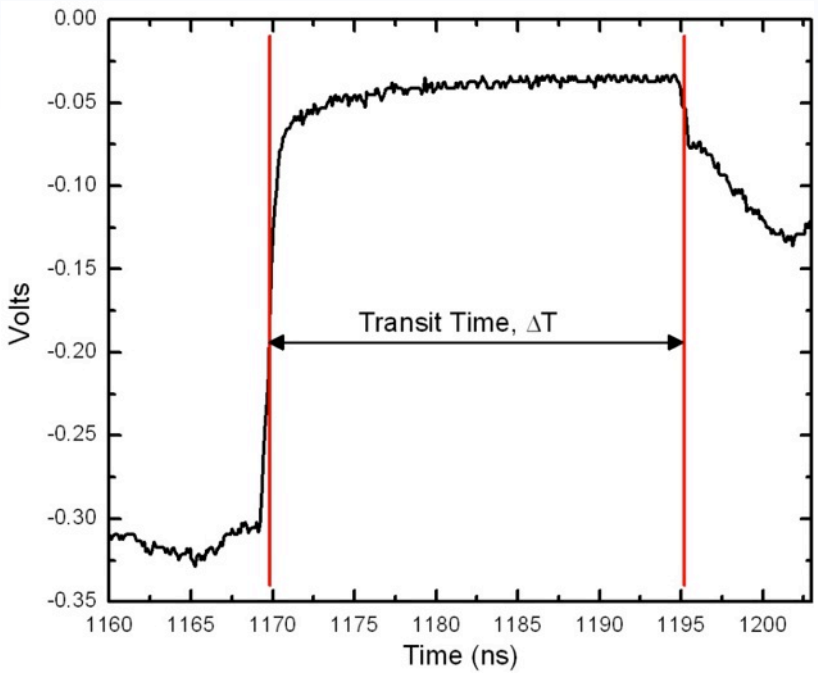
VISAR Measurements and Analysis





- **VISAR tracks flyer plate velocity up to impact**
- **Shock front in MgO not reflective – Loss of contrast in VISAR signal**
- **Clear impact and shock transit fiducials – transit time analysis**
- **At higher pressures, MgO shock front reflective and shock velocity measured directly**
- **Shock front in back window is reflective – release state for MgO is determined (not discussed here)**

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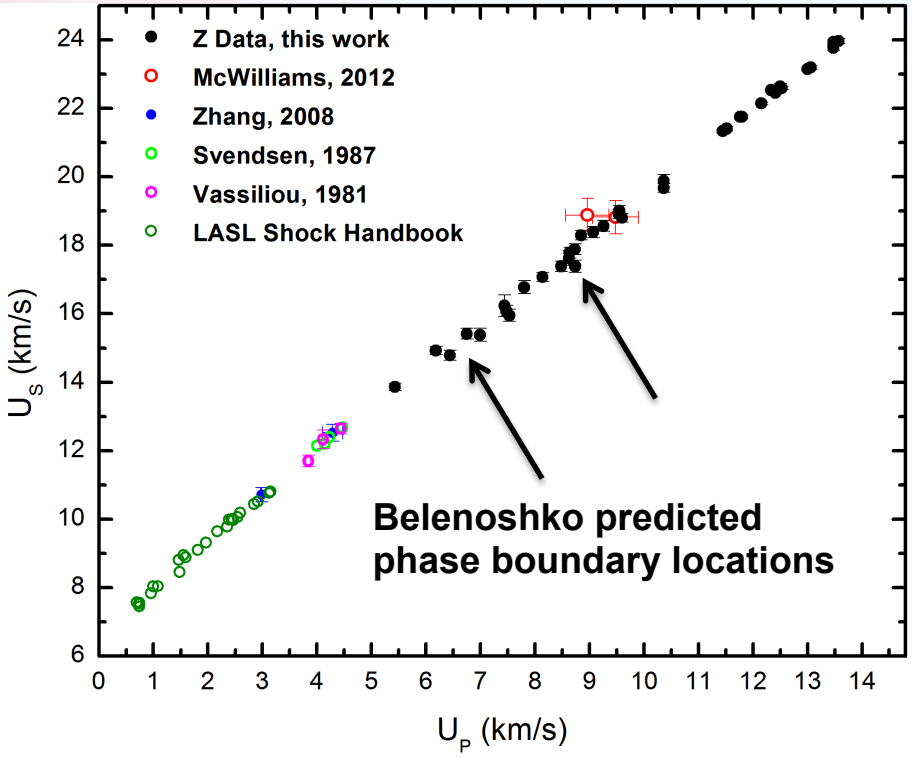
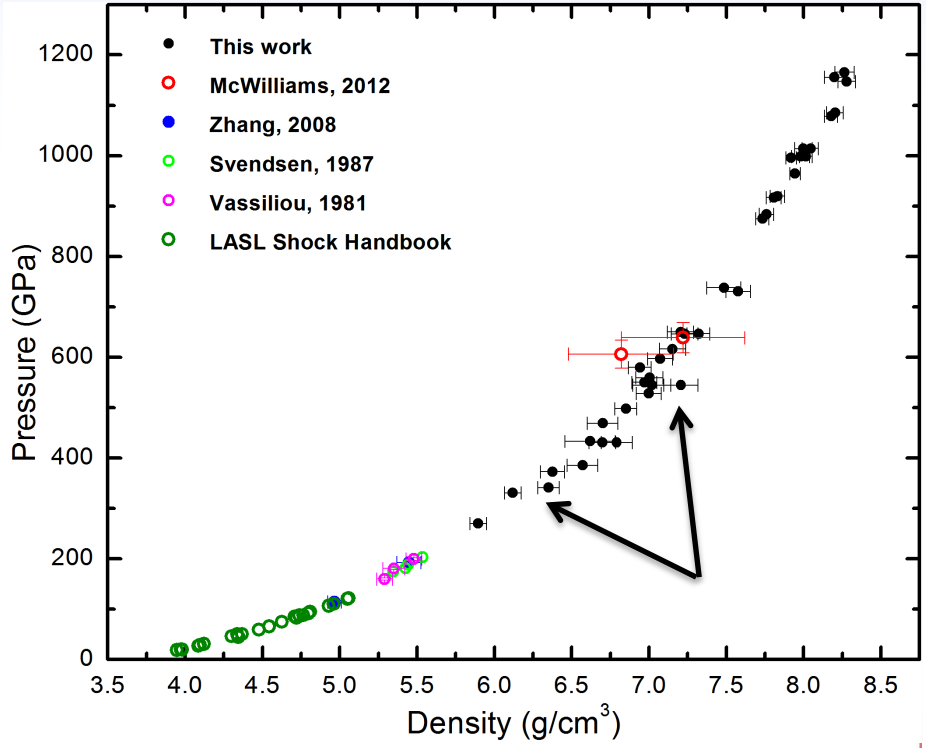
Experimental Hugoniot Results





- Total of 38 Hugoniot measurements
- Highest pressure Hugoniot measurement - 1160 Mbar
- Lowest pressure Hugoniot measurement – 270 Gpa
- No reflective shock front below 7 Mbar
- Data spans the B1-B2 transition and the B2 - melt transition

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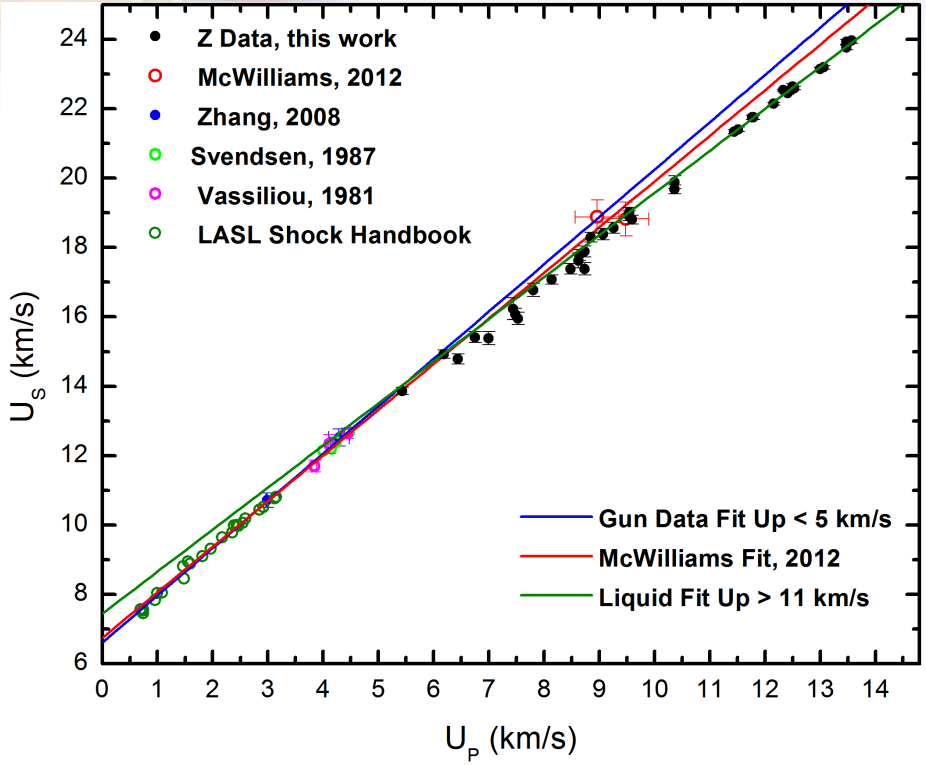
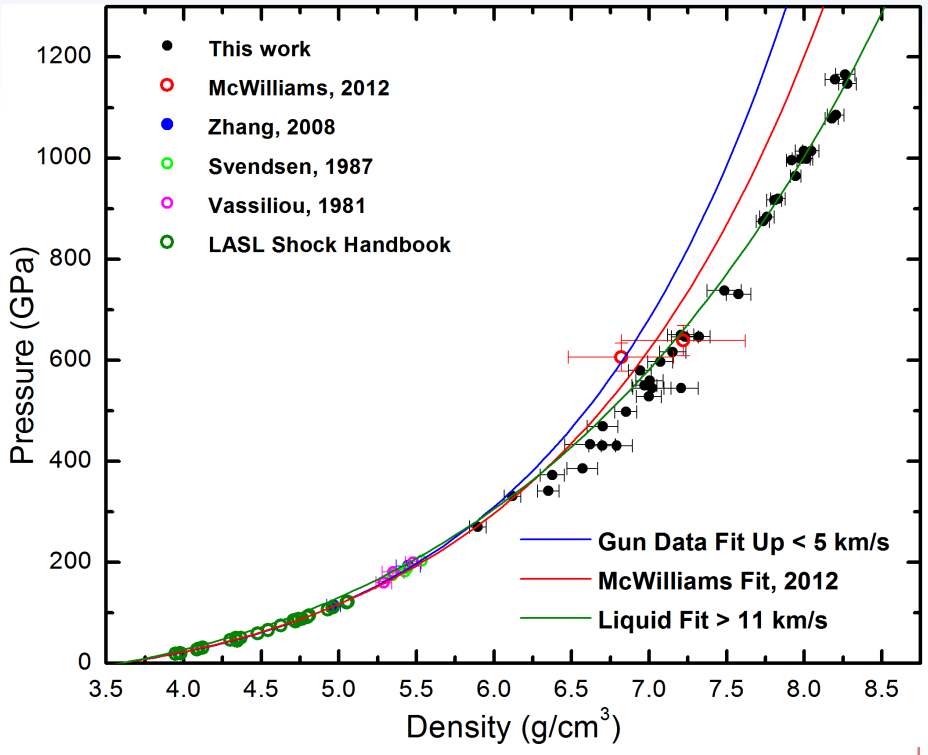
Comparison To B1 Solid Fit and Liquid Fit





- **Z data deviate from the extrapolated gun data fit at 330 Gpa**
- **Z data also deviate from the McWilliams *et al* fit near 330 Gpa**
- **Suggests the B1-B2 solid phase transition starts around 330 Gpa**
- **2-piece linear fit suggests that MgO has at least 3 phases – as predicted.**

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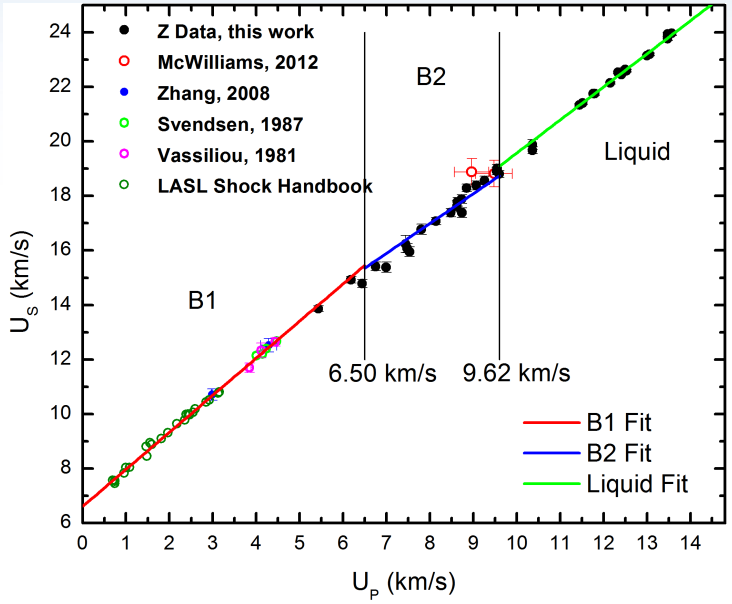
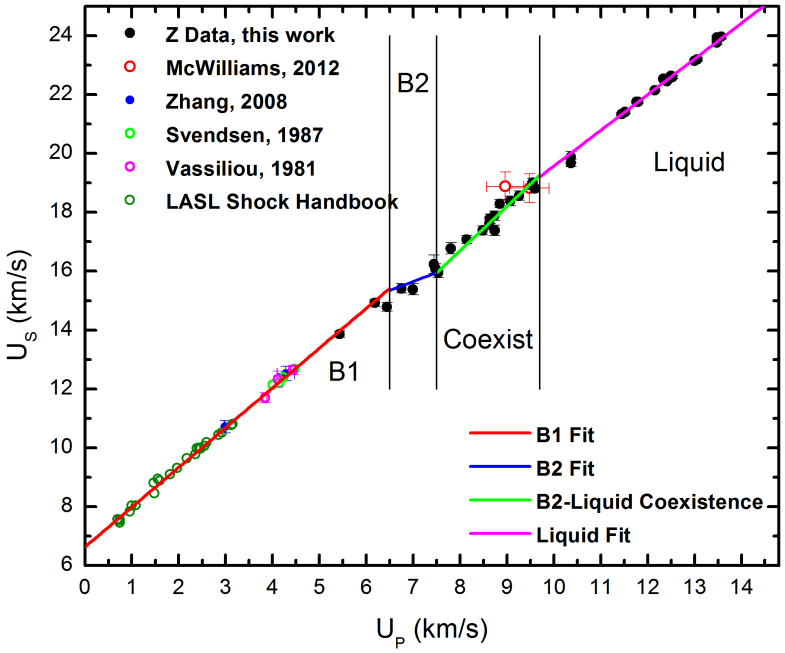
Optimization for Phase Boundaries

- GA method optimizes ‘break points’ for a multi-piece linear fit using linear regression
- 3 – Piece uses B1, B2, Liquid regions
- 4 – Piece uses B1, B2, Coexistence region, and liquid region
- Similar method applied to diamond (Knudson et al, Science 322, 1822 (2008).
- Several optimization runs performed to estimate uncertainty in break points
- 3-piece linear fit suggests a large B2 region inconsistent with previous phase diagrams and large discontinuous behavior at B2-Melt
- 4-Piece fit shows better behavior over entire range





Optimization Results for 4-Piece Fit

B1 – B2 Boundary

Up = 6.50 ± 0.04 km/s

P = 360 ± 5 Gpa

B2 – Liquid Coexistence Boundary

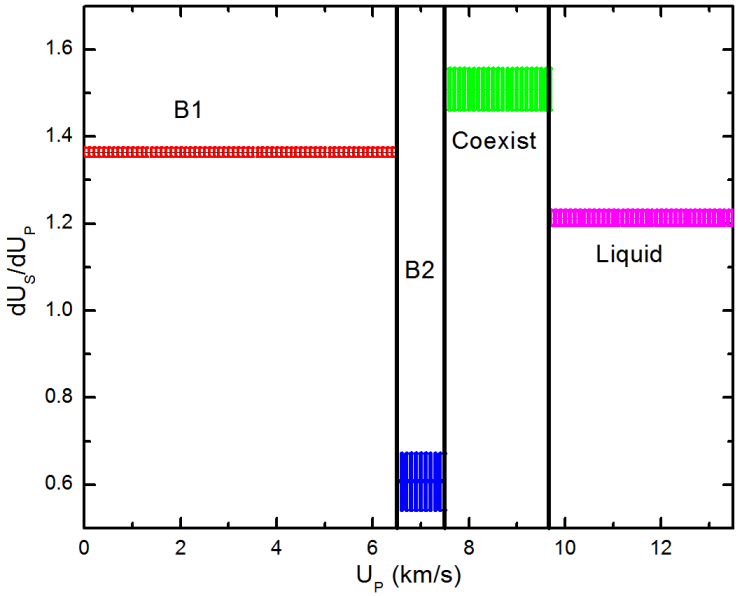
Up = 7.51 ± 0.06 km/s

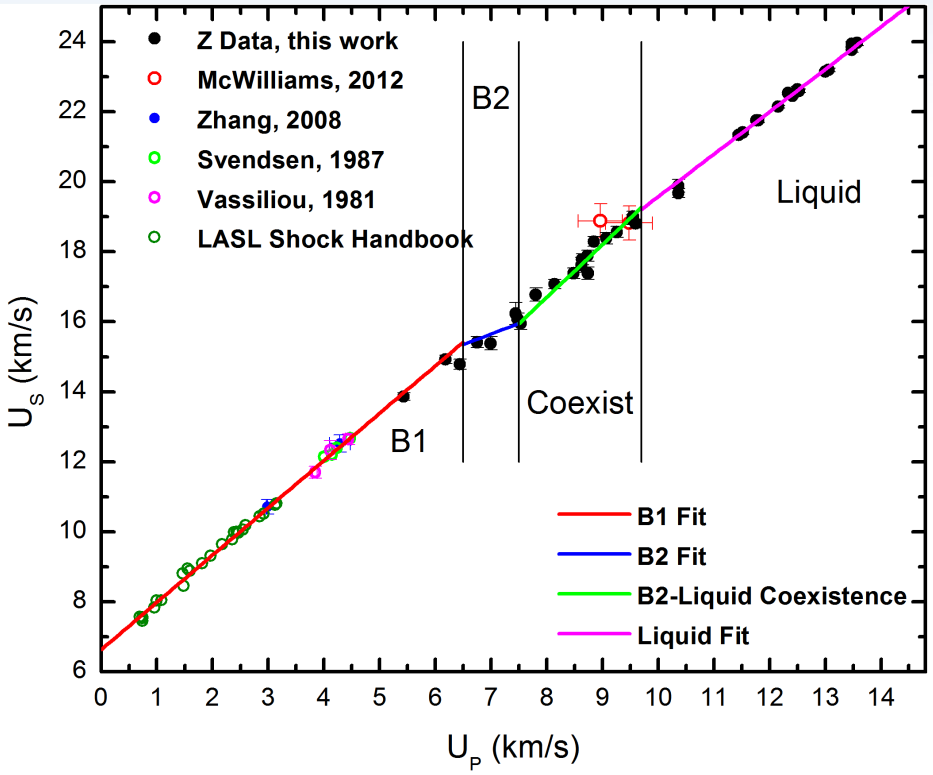
P = 430 ± 5 Gpa

Coexistence – Liquid Boundary

Up = 9.67 ± 0.06 km/s

P = 664 ± 7 GPa





- **Optimized slopes are significantly different through each region**
- **Suggests a large B2-coexistence region**
- **Can we corroborate with DFT methods?**

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Density Functional Theory Methods

- **Use DFT-MD to assess the state of MgO at high pressures on the Hugoniot and examine the phase boundaries**

- **DFT-MD simulations performed using VASP 5.2.12***
- **Electronic states occupied according to Mermin's finite-temperature formulation**
- **Calculate energy and pressure for a given density and finite temperature**
- **Satisfy the Hugoniot Condition:** $2\left(E - E_{ref}\right) - \left(P + P_{ref}\right)\left(v_{ref} - v\right) = 0$

  - **Simulations start from the B1 and the B2 phase**
  - **216 atoms per simulation (B1 phase); 250 atoms (B2 phase)**
  - **AM05 (Armiento-Mattsson) exchange correlation functional**
  - **Checked for convergence: number of atoms, energy cutoff, etc**
  - **VASP PAW potentials: Mg($3s^2$) and O($2s^2p^4$) for low temp (< 1eV)**
    Mg($2s^22p^63s^2$) and O($2s^2p^4$) for (> 1eV)

* G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993) and Phys. Rev. B **49**, 14251 (1994).

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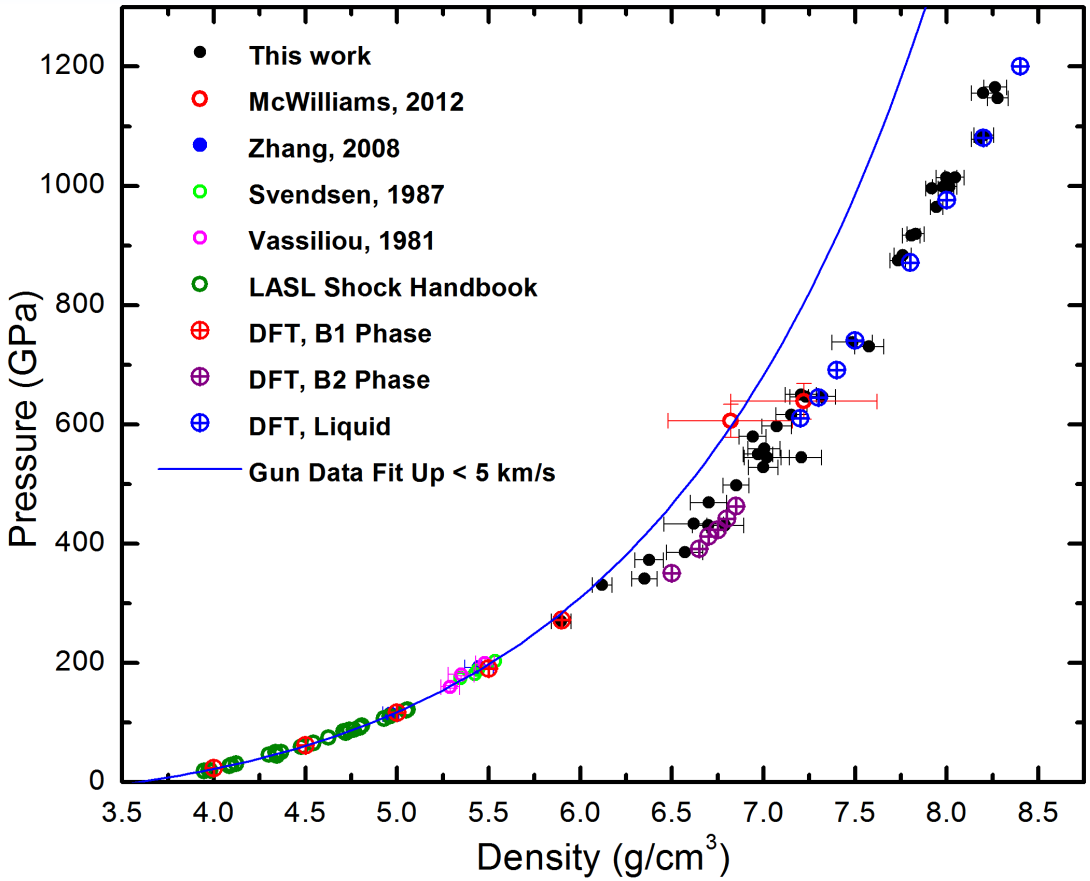
DFT Hugoniot Results

- DFT simulations to 12 Mbar
- Simulations start from B1, B2, or liquid phase
- Excellent agreement with the experimental data over the entire range
- DFT data suggest a large region for B2 – Melt coexistence on the Hugoniot
- The coexistence region is consistent with the experimental data



- Examine the phase boundaries

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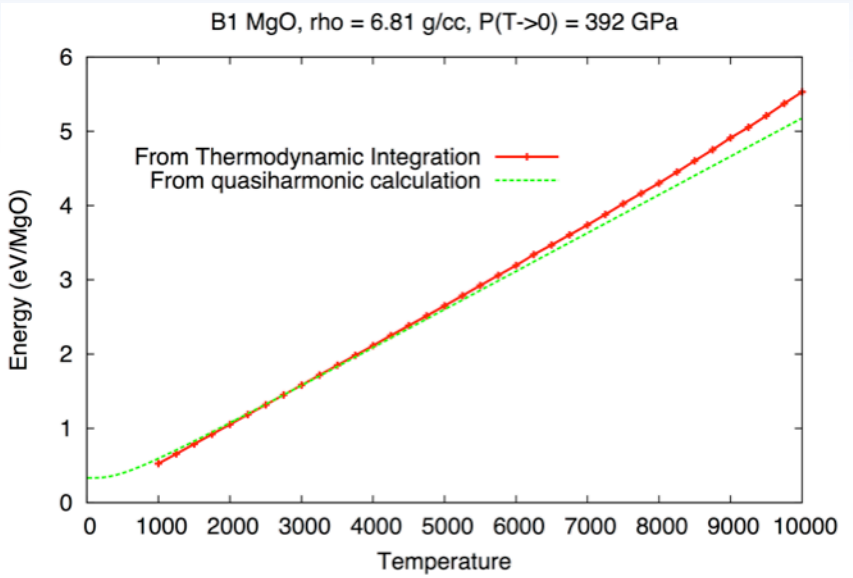
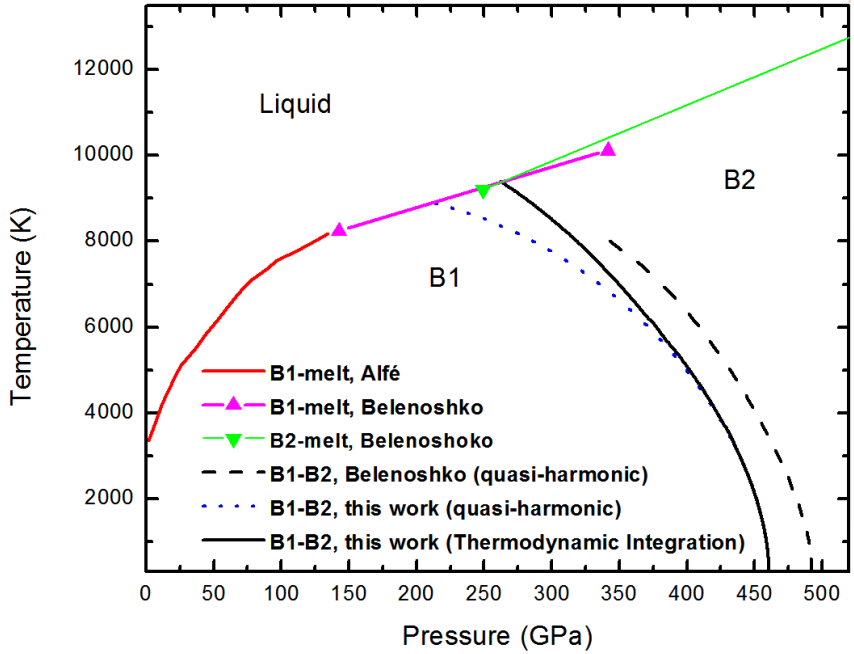
Calculation of Solid-Solid Phase Boundary

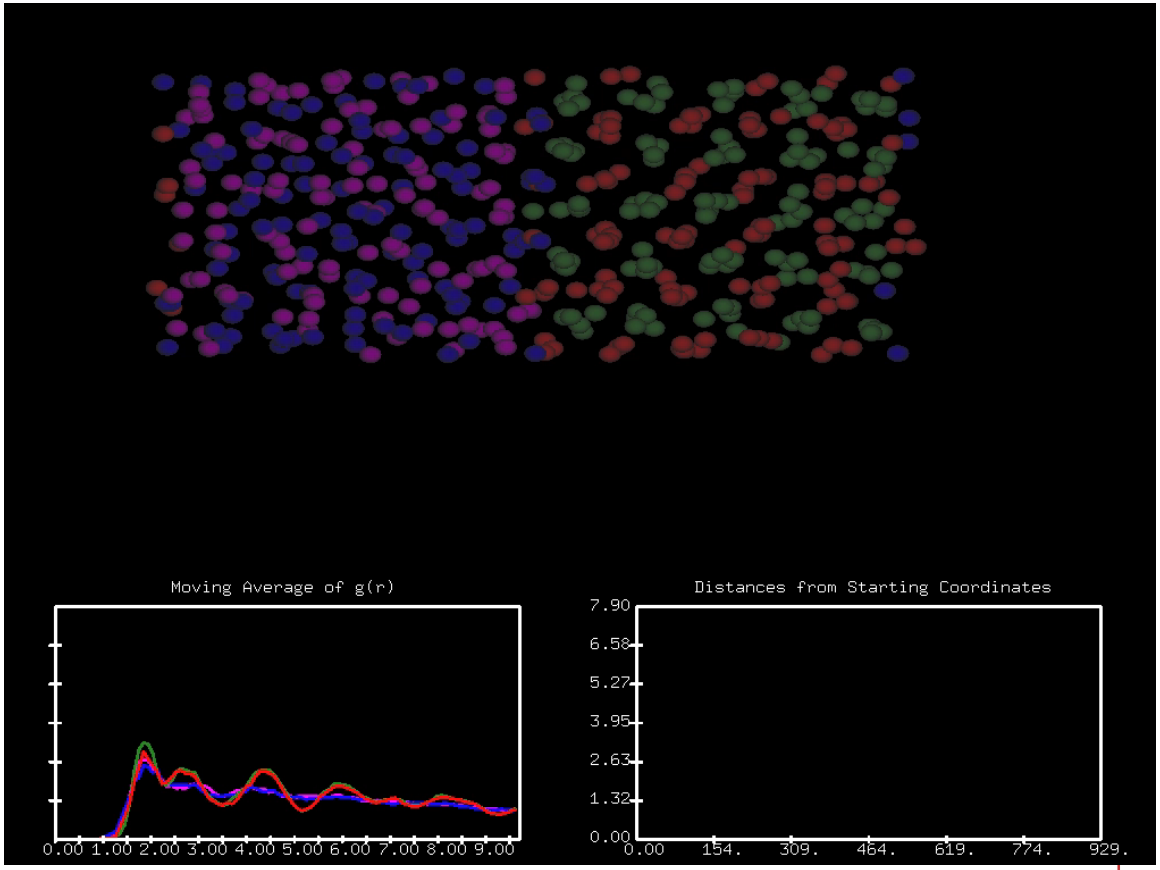
- Pressure and Energy are directly calculated in DFT-MD
- For finite temperature phase transitions entropy is necessary
- At low temperatures, harmonic phonon approximation provides solution
- Entropy can be calculated directly using analogy to finite temperature quantum harmonic oscillator
- Approximation breaks down for moderate temperatures
  - Effect is strongest in B1 phase
- Switch to thermodynamic integration using multiple DFT-MD calculations along each isochore





Solid – Melt Boundaries

- For melting boundary use two phase coexistence simulations
- Place solid and liquid in contact with each other
- Run at different temperatures and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of phase coexistence
- Follow work of Belonoshko, but include quantum calculations of B2 phase melting



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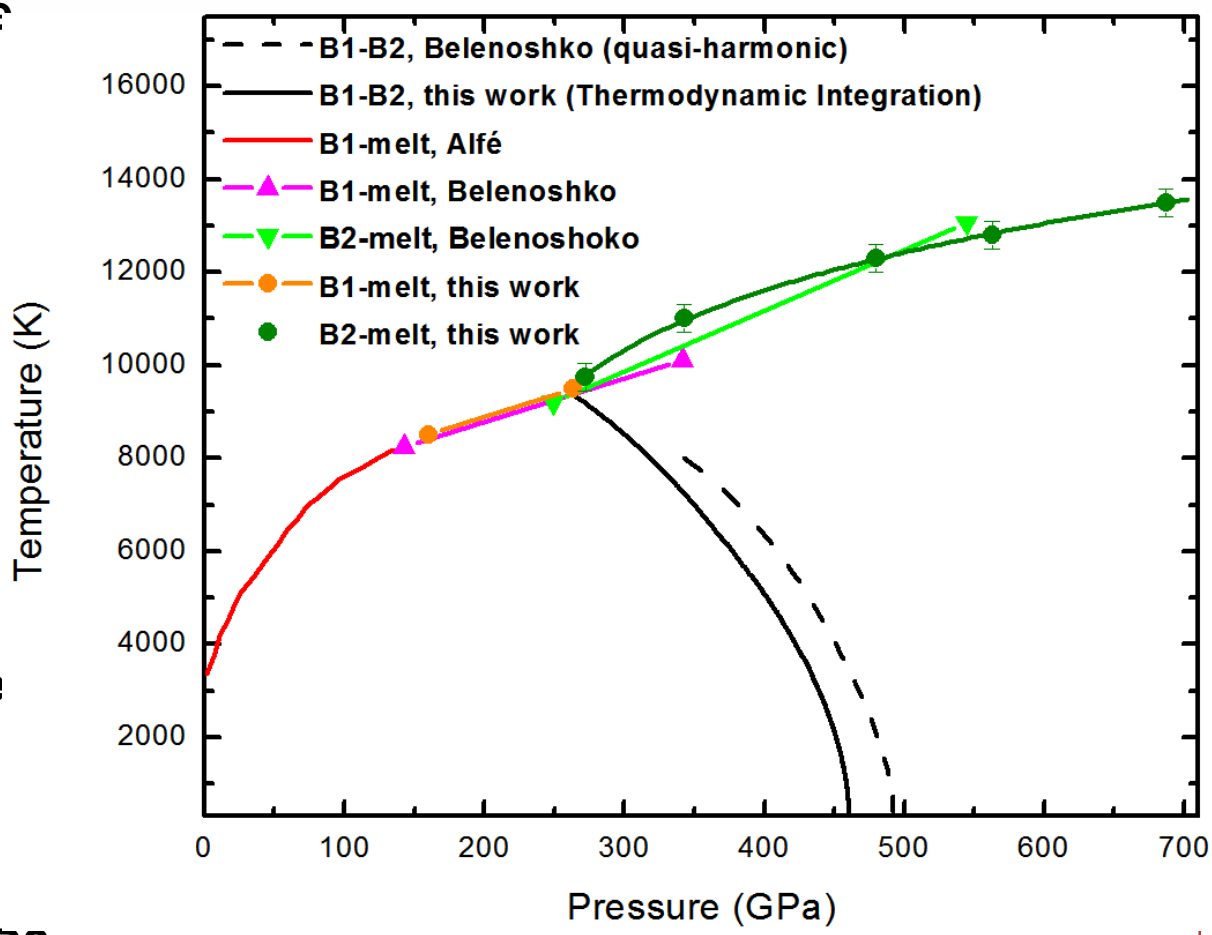

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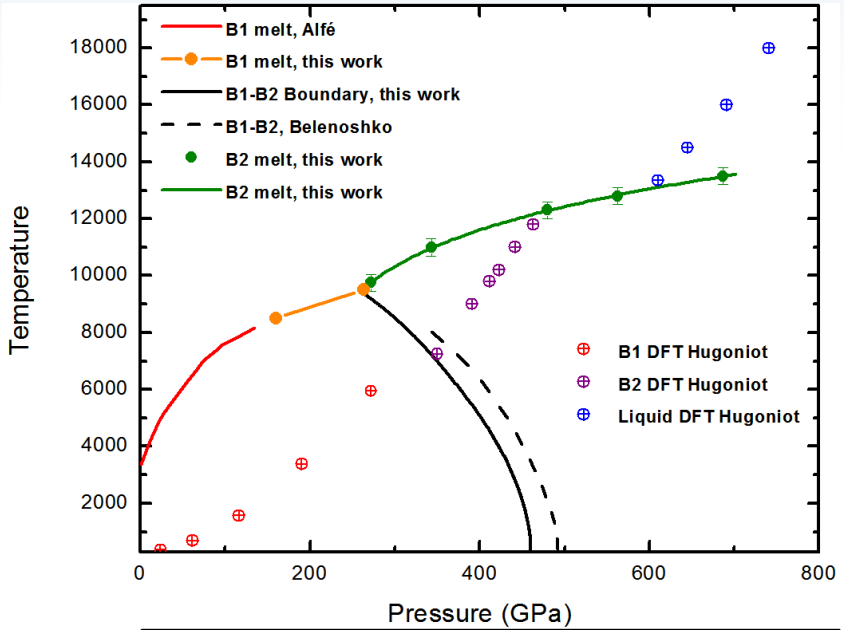
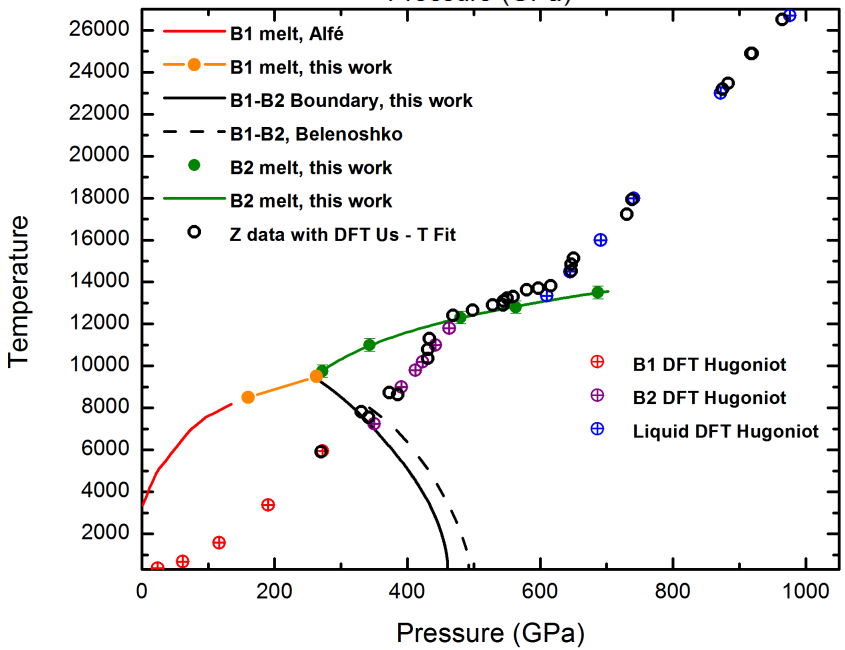
MgO Phase Diagram and the Hugoniot

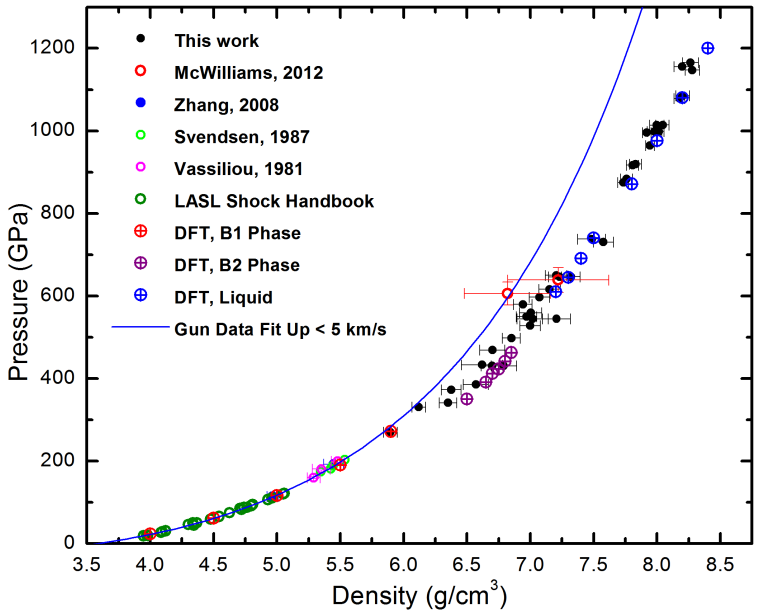
- B1 – B2 phase boundary occurs lower than predicted by Belenoshko
- B1 – B2 shift at 0K is caused by difference b/w PBE and AM05
- B1 – melt boundary consistent with Alfé
- DFT Hugoniot shows a large region of coexistence on the B2 – melt boundary
- US – Temperature Fit applied to experimental data
- Region of B1 – B2 coexistence from DFT ranges from 330 – 350 GPa
- Region of B2 – melt coexistence ranges from 430 – 660 GPa

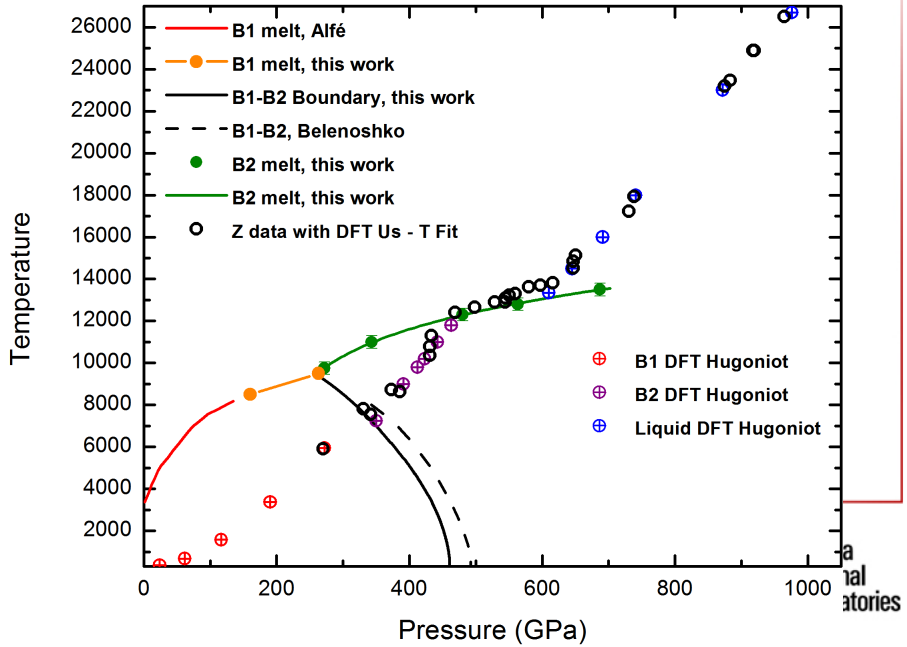




Summary

- Accurately measured the MgO Hugoniot from 270 GPa to 1160 Gpa
- Determine the phase boundary regions for the B1, B2, and Liquid phases of MgO along the Hugoniot
- Show MgO has a large coexistence region along the Hugoniot between B2 and liquid
  - Significant importance to planetary and moon formation
  - Shock pressures of ~7 Mbar or greater needed to completely melt MgO
- Developed an updated phase diagram for MgO





Acknowledgements

- Luke Shulenberger, Kyle Cochrane, and Thomas Mattsson (DFT)
- Ray Lemke – Z pulse shape designs
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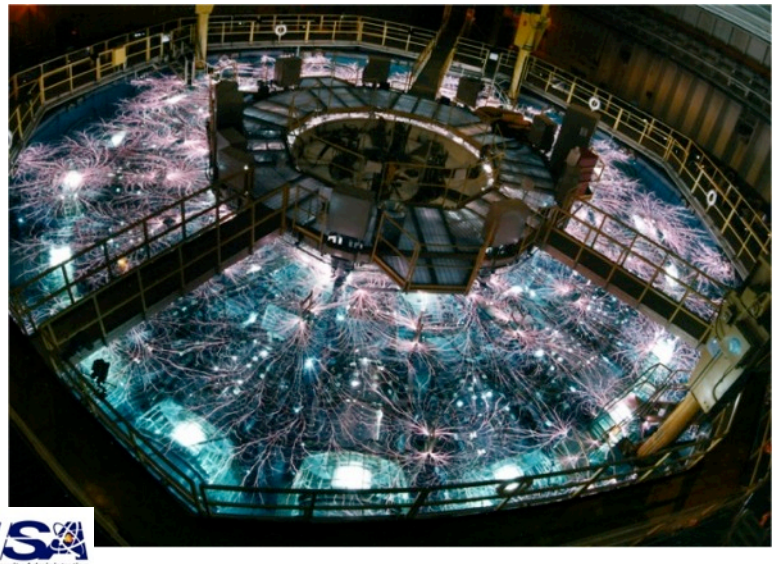
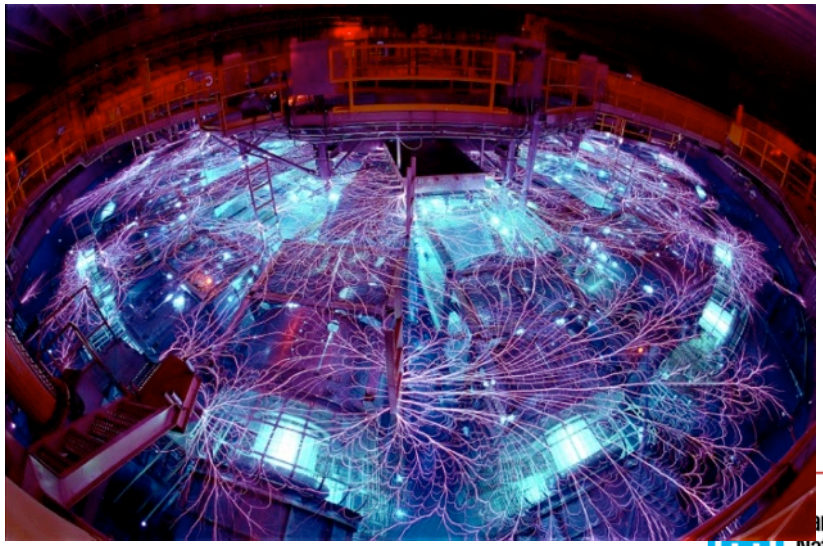
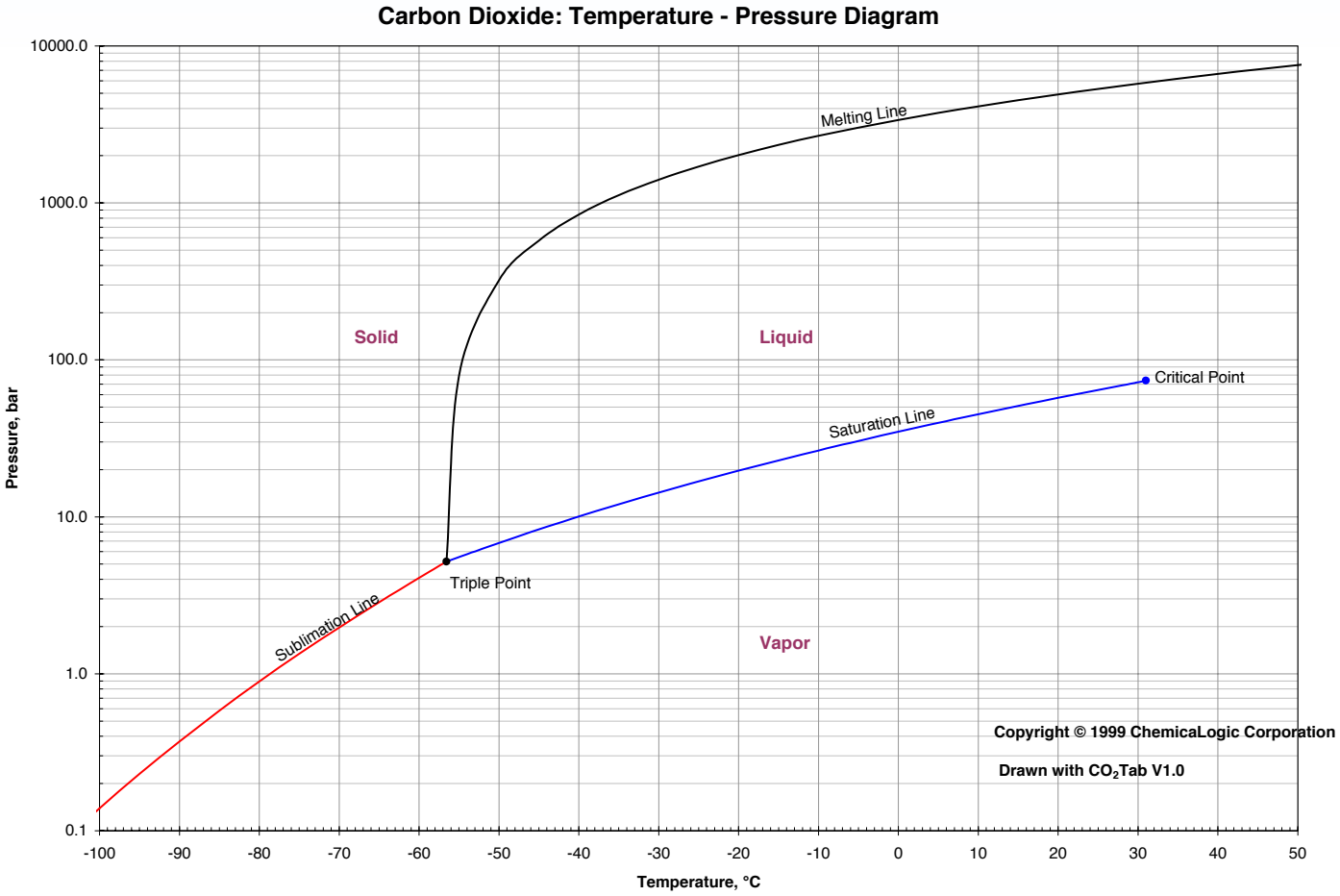
- Phil Sterne and Christine Wu (LLNL) CO_2 EOS
- Mike Desjarlais, Marcus Knudson, and Rick Kraus (LLNL)

All members of the Sandia Z-Operations Team and Target Fab./ Metrology Team





Extra Slides



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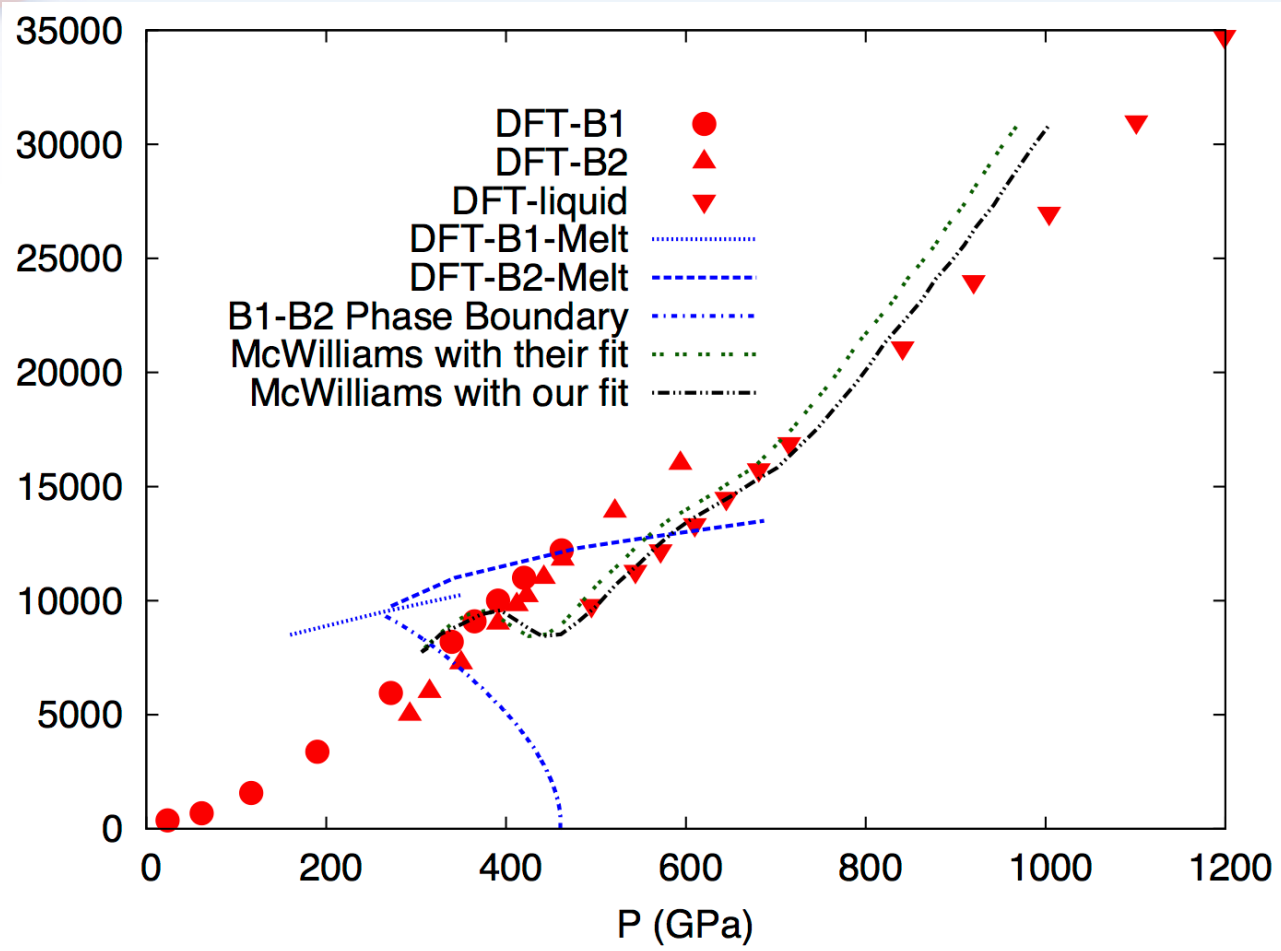
Comparison to McWilliams et al



- **The B1-B2 transition occurs at lower pressure**
- **Larger B2 – Liquid coexistence region**
- **DFT temperatures lower than measured temperatures in the liquid state**

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