High-Temperature High-Pressure Properties of Silica From Quantum Monte Carlo

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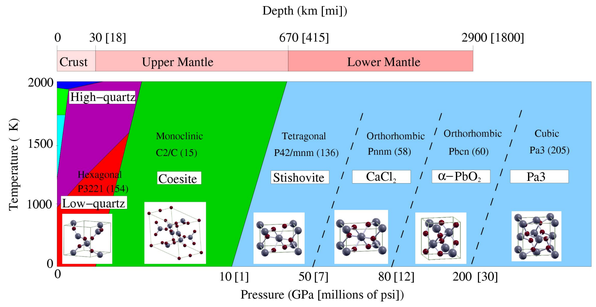
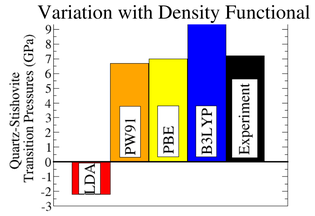
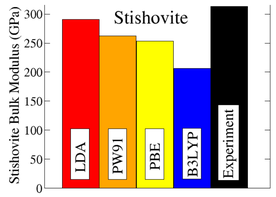
Introduction: computational mineral physics and the silica phase diagram







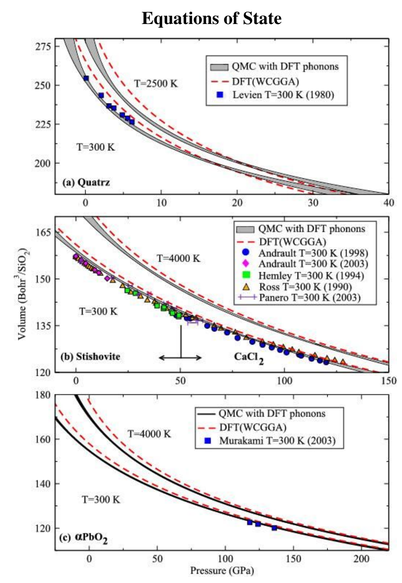
Motivation:

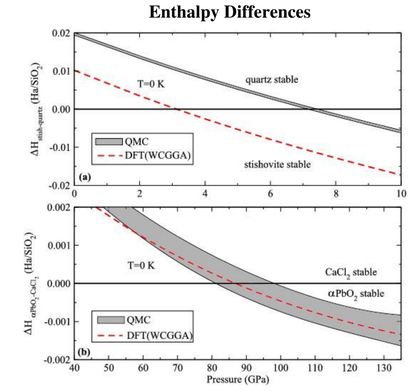
- Computational mineral physics is important in the guiding, understanding, and absence of experiments.
- Density functional methods (DFT, Nobel 1998) have made great contributions to Earth science.
- Here, we apply a new class of methods, Quantum Monte Carlo (QMC), which offer much higher accuracy, but at greatly increased computational cost (100-1000 times more CPU hours than a comparable DFT calculation).
- The aim is to use QMC for selected important problems in which a accuracy benchmark for DFT is paramount.

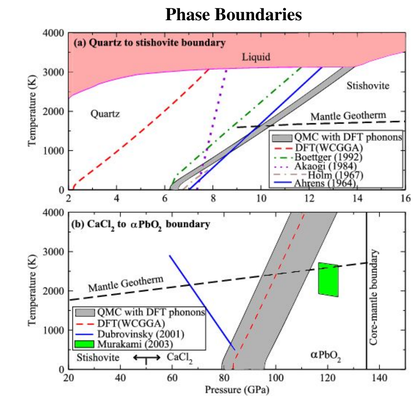
Why Silica?

- Silica is the simplest of Earth's silicates and a natural place to demonstrate the feasibility of QMC in obtaining equations of state and elastic and thermodynamic properties for geophysical applications.
- DFT generally works well for silica, but can unexpectedly fail and depend strongly on functional type.
- Silica undergoes a complex series of structural transitions with applied pressure, which exhibit first and second order behavior, elastic instabilities, and a four- to six-fold coordination change.
- Such a collection of physics is challenging for even the best computer simulations and experiments to untangle.

Computation of thermal equations of state and phase boundaries







Computational Method

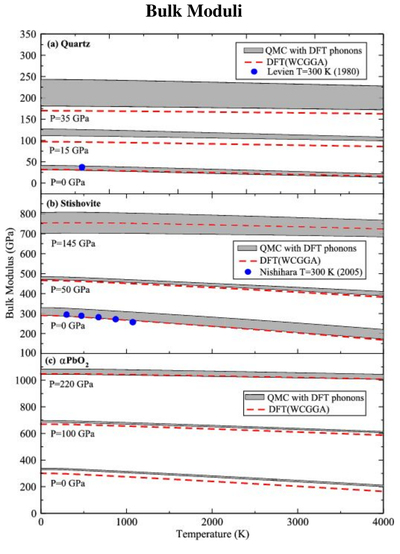
- Compute quasi-harmonic Helmholtz free energy: $F_{QHA} = E_{static}(V) + F_{vibration}(V,T)$

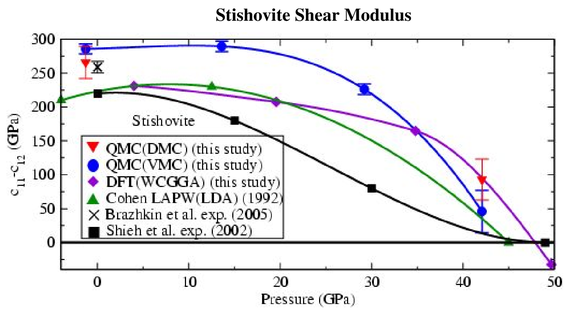
Compute static lattice energy with QMC
- Dominant energy contribution
- Most accurate method available for solids
- CASINO code

Compute vibrational free energy with DFT
- Currently too costly for QMC
- Vibrational energy is small and well described in DFT
- ABINIT, Linear Response, quasi-harmonic, WCGGA functional

- Plots show equations of state, enthalpy differences, and phase boundaries of silica phases.
- The thermal equations of state provide a route to all thermodynamic information, such as phase equilibria, elasticity, heat capacity, and thermal expansion.
- QMC improves equation of state agreement with experiment over DFT for each phase: quartz, stishovite, $CaCl_2$-structured, and αPbO_2-structured.
- Enthalpy differences and errors determine the equilibrium phase relations and their statistical accuracy.
- QMC provides accurate phase transformation boundaries for quartz-stishovite and $CaCl_2$-αPbO_2; DFT(WCGGA) gives quartz-stishovite 4 GPa too low.

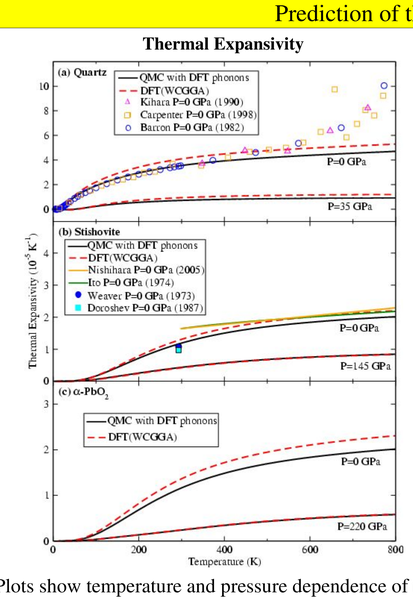
Prediction of elastic property behavior with pressure and temperature

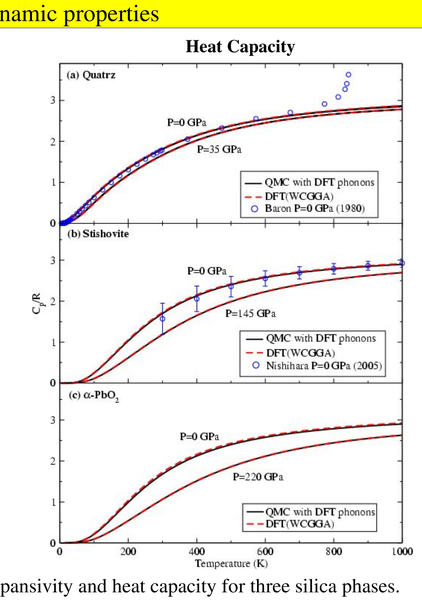




- Bulk moduli plots show temperature and pressure dependence of three silica phases.
- Stishovite shear modulus plot shows zero temperature pressure dependence.
- QMC and DFT bulk moduli agree well with available experimental data.
- Bulk moduli decrease linearly with temperature and increase linearly with pressure.
- Stishovite transforms to a $CaCl_2$ type structure at 50 GPa via instability in the elastic shear modulus, which softens under pressure.
- This work showcases the first QMC calculation of elastic constants, demonstrating it's feasibility and usefulness for geophysics applications.

Prediction of thermodynamic properties





- Plots show temperature and pressure dependence of thermal expansivity and heat capacity for three silica phases.
- QMC and DFT thermal expansivities and heat capacities agree well with available data for each silica phase.

Acknowledgments

- This work utilizes the CASINO[1] QMC code and ABINIT[2] DFT code.
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