Pressure-induced redox reversal of iron and the distribution of elements in deep Earth

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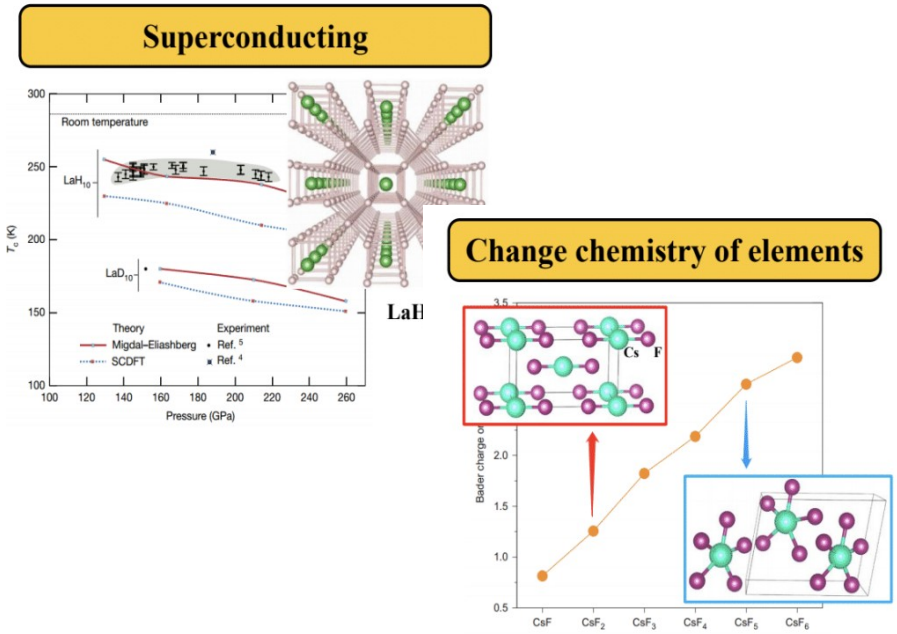
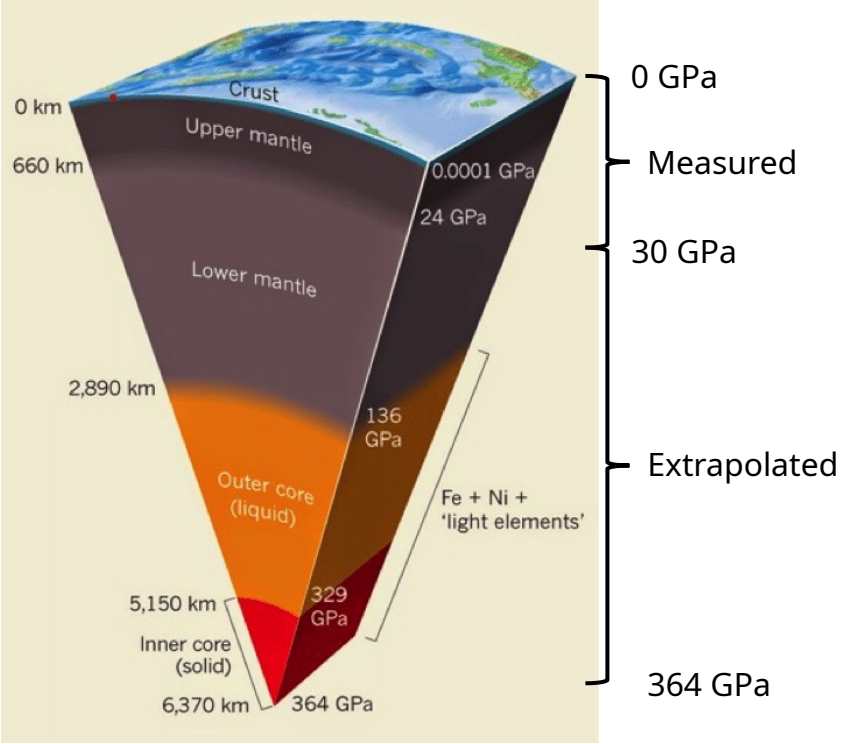
High pressure chemistry



- Normal rules break down
- Reordered orbital energies, new stoichiometries, unique bonding patterns …
- Induced changes in properties: stability, binding strength, hardness …
- Need to be considered in our model of deep Earth

Chemistry in the deep Earth

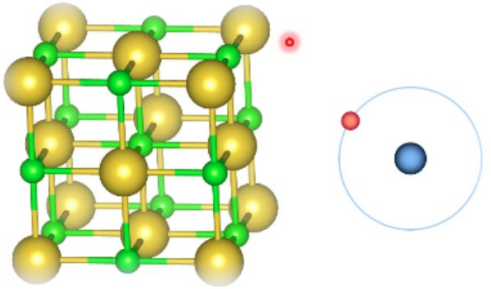


- Most metal-silicate experiments performed between 10-30GPa
- Extrapolate behavior of elements to pressures as high as 360 GPa
- Assumed elements keep same oxidation states, bonding behaviors, and preferences for binding with Fe

Methods

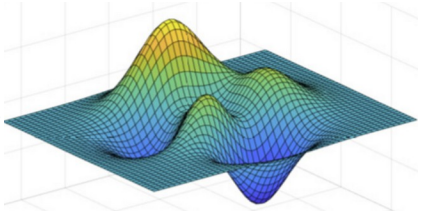
- First principles calculations based on density functional theory (DFT)
- Crystal structure search by particle swarm optimization (CALYPSO)
- Wide scale study of Fe reacting with p-block elements with varying compositions
- Varying pressures from ambient conditions to Earth's core (P, T)

First principles (QM)

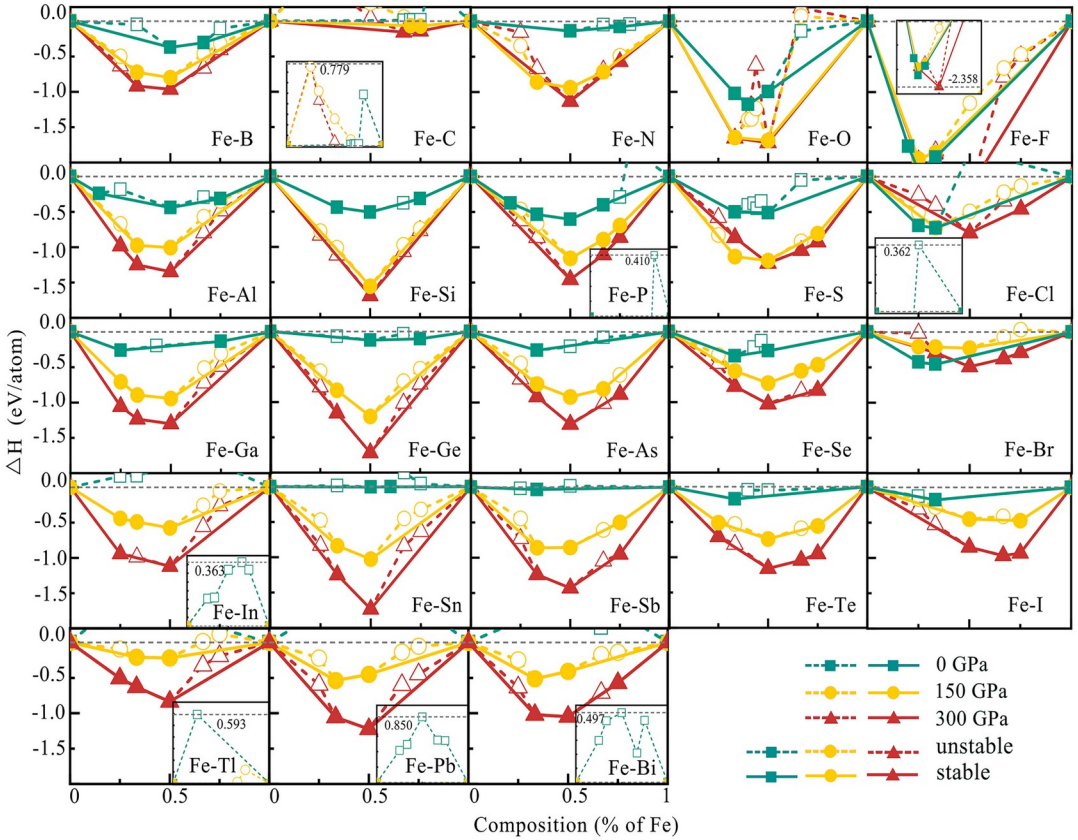


$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

CALYPSO



Stability of Fe-p-block compounds

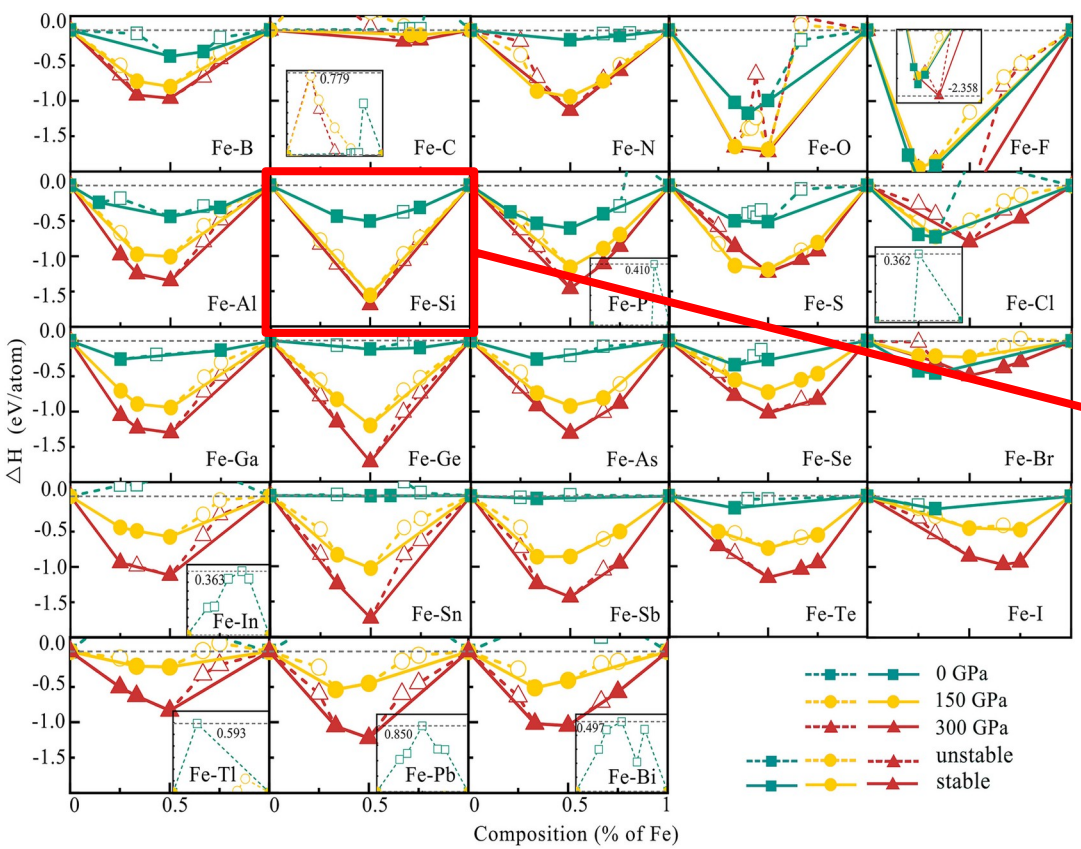


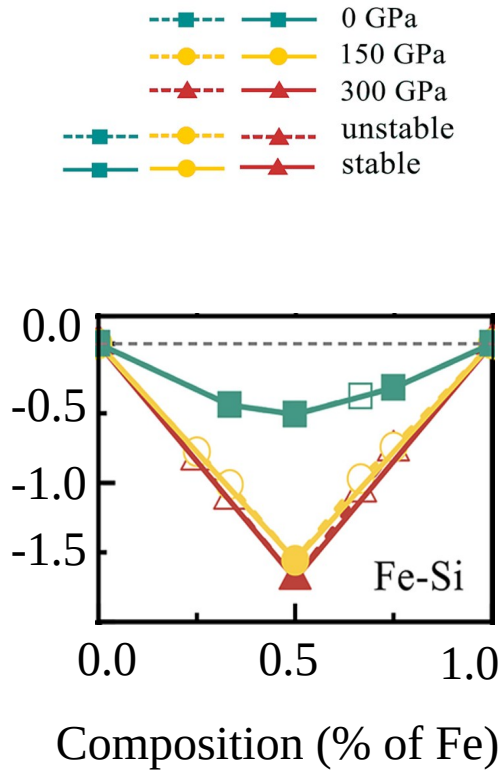
- Convex hull used to predict stability

  0 GPa – ambient
  150 GPa – core-mantle
  300 GPa – inner core

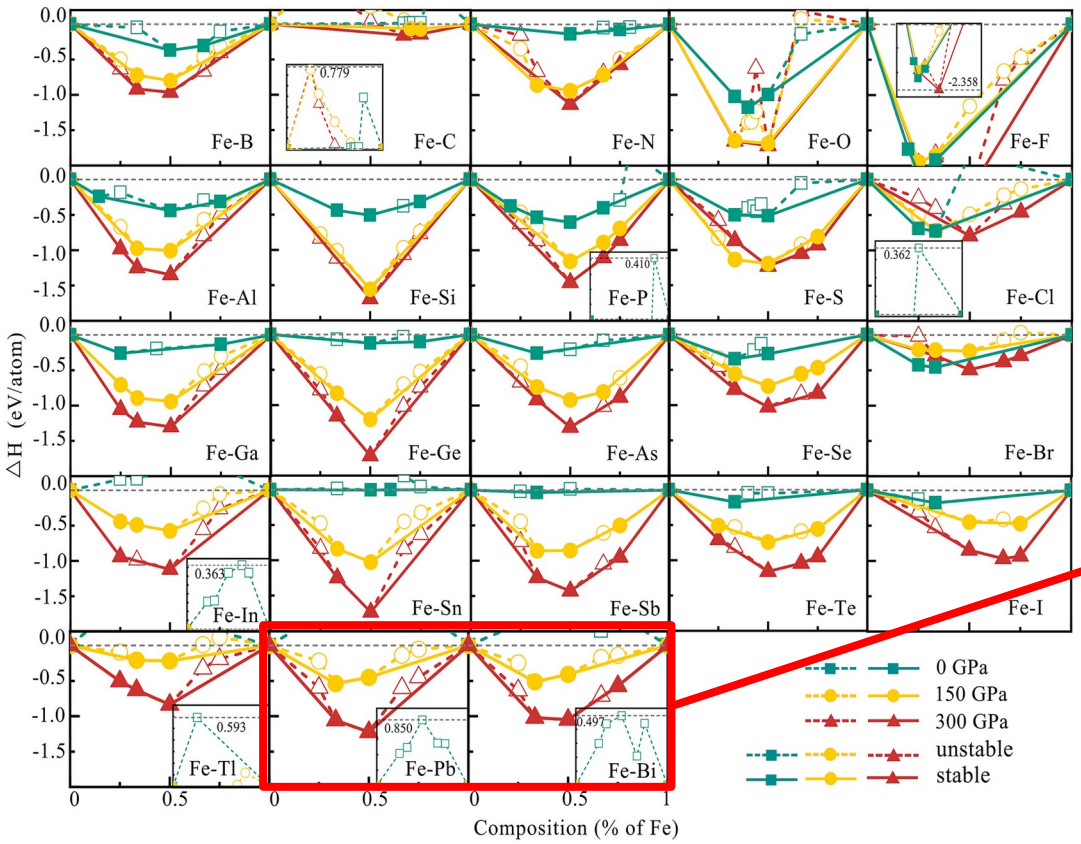
- Lowest energy points connected
- On the line = stable
- Above the line = decompose

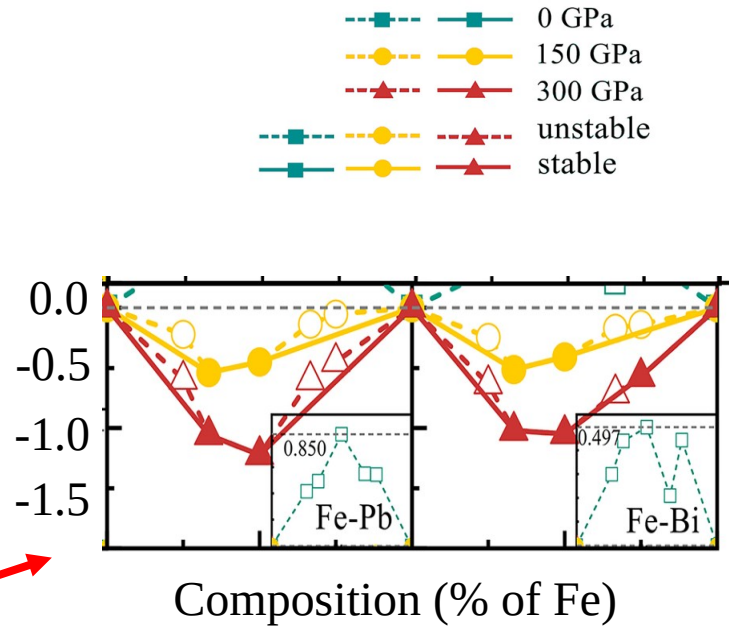
Stability of Fe-p-block compounds



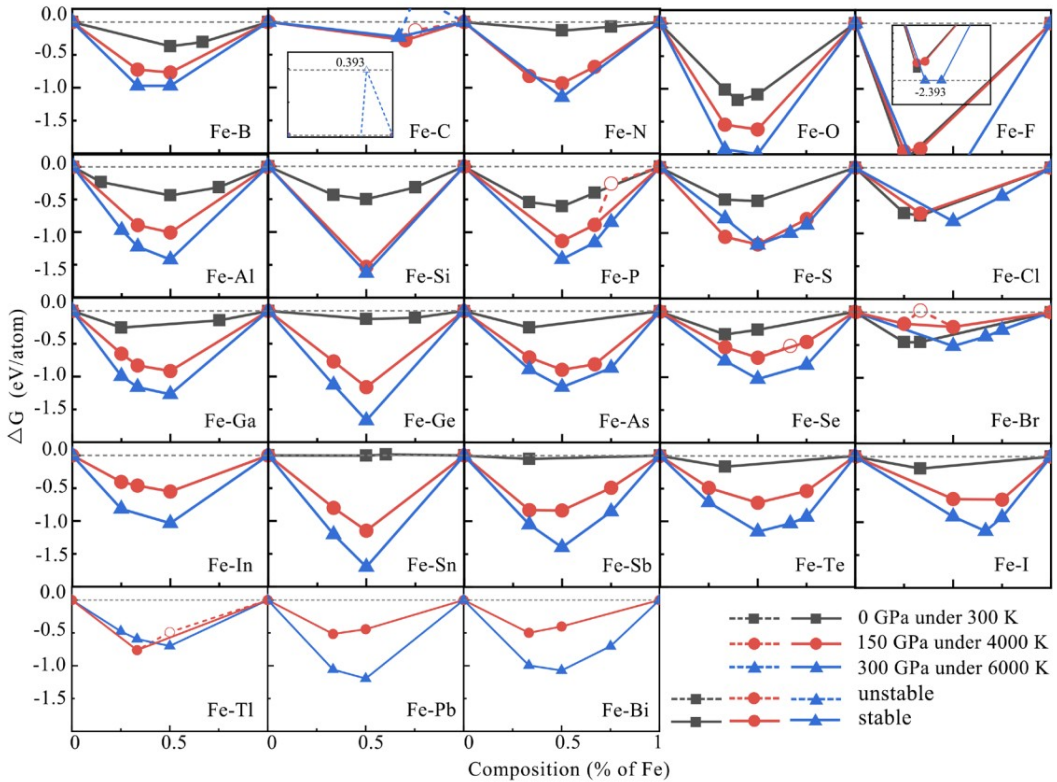


Stability of Fe-p-block compounds





Effects of temperature correlation and magnetism

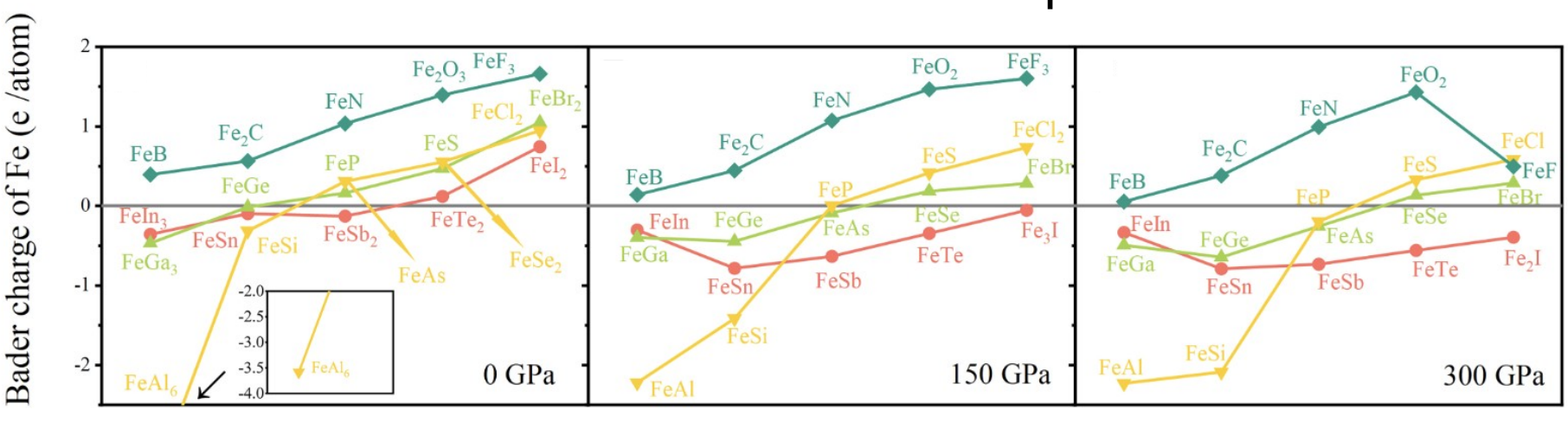


- Temperature effects included via phonon free energies (QHA)

  0 GPa – 300 K
  150 GPa – 4000 K
  300 GPa – 6000 K

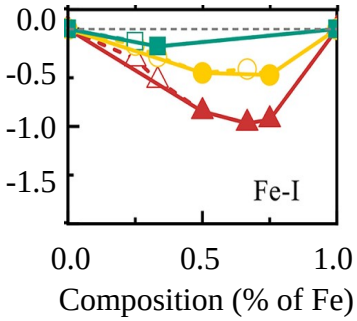
- Temperature, magnetism, and HSE corrections shift formation energies, but do not alter convexity

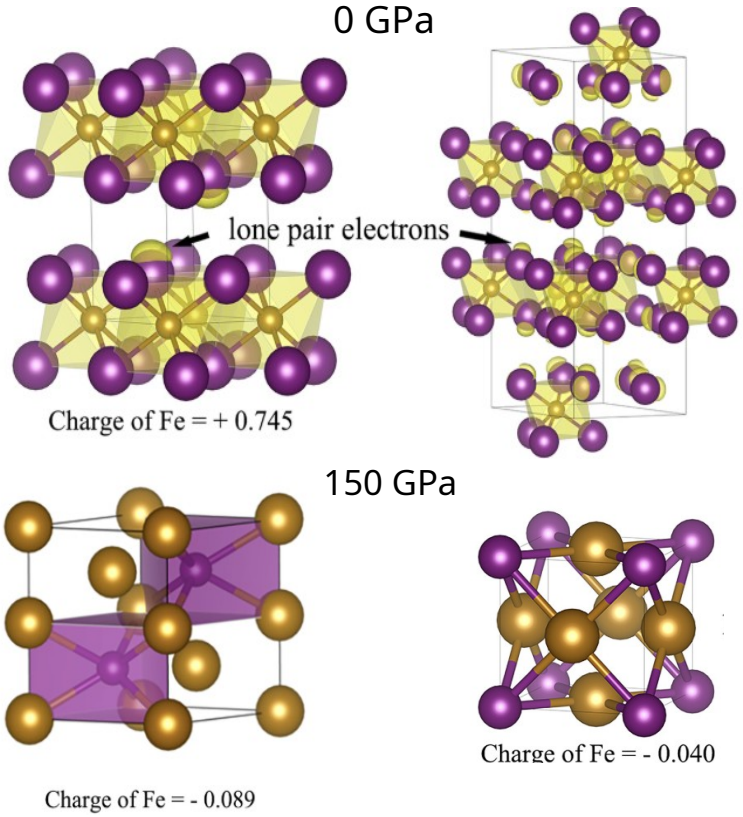
Iron redox reversal under pressure



- At 0GPa, Fe is mainly a reductant as expected
- At 150-300GPa, the curve shifts downward
- Fe experiences a **redox reversal** in compounds with Ge, P, As, Te, & I
- Fe becomes a strong oxidant with Si

Structural evolution of iron compounds

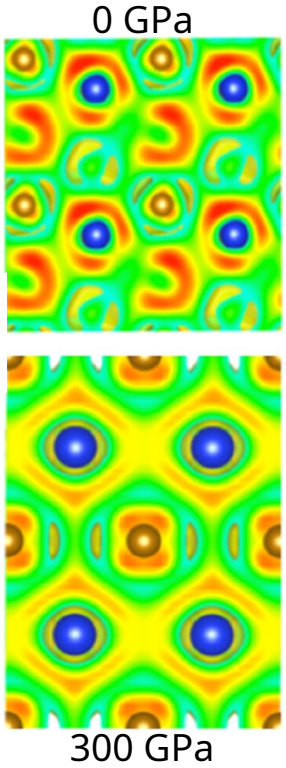


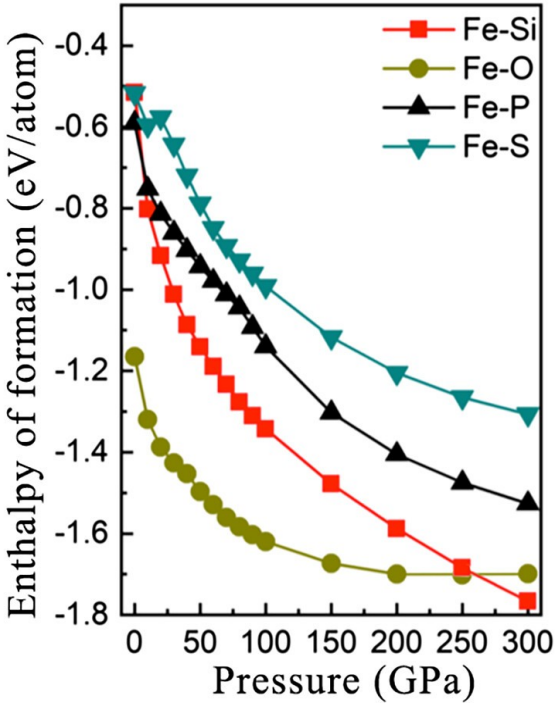


- Atoms arrange in an open, layered manner
- Lone pairs on p-block element
- Structure is compact with a higher coordination number
- Disappearance of lone pair

The silicon anomaly

- The Fe-Si binding strength increases, even surpasses Fe-O at 250 GPa
- The electron localization function (ELF) is highly localized between Fe and Si (0 GPa)
- Localized region between Fe and Si decreases (300 GPa)
- Bonding becomes more ionic (-2e, Fe)





Conclusion

- High pressure strongly stabilizes many Fe + p-block compounds
- Pressure can reverse the usual redox role of iron (leading to dense, high coordination, more ionic Fe compounds at deep Earth conditions)
- Fe-Si bonds become especially strong and favorable at core pressures
- **Taking into account high pressure chemistry at these extreme conditions is crucial to our understanding of the deep Earth**

Read our paper!

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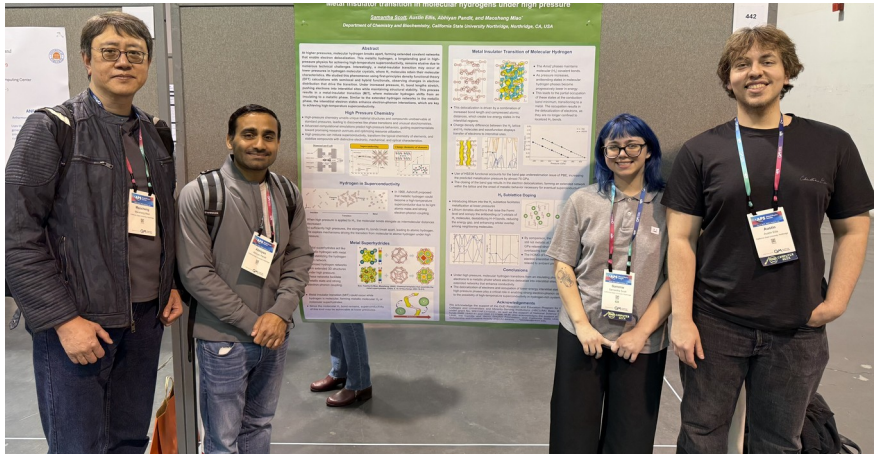
Acknowledgements



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