Phase stability and structural properties of Fe_2S and its analog Co_2P at high pressures and temperatures

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1. Research Question and Goal

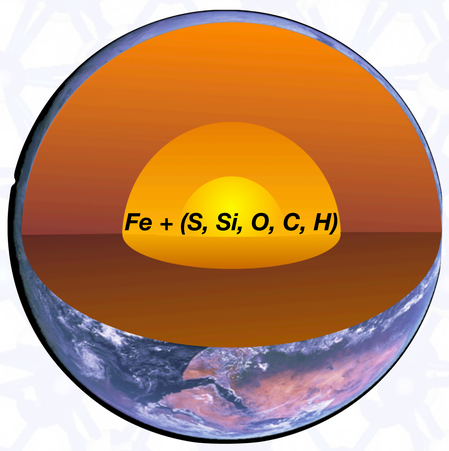


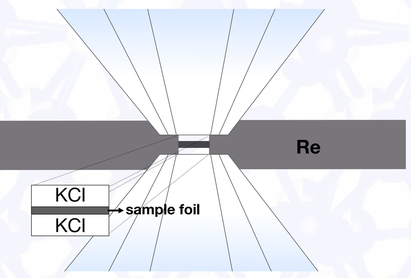
Figure 1. An artist's rendition of Earth's interior showing the layered mantle, outer core, and inner core structure. The cosmochemically abundant light elements that most likely alloy with iron in the core are labeled.

- Earth's core is an Fe-rich alloy with a light element component (likely Fe + S, O, Si, C, H).
- Fe_2S has recently been observed in Fe-rich compositions at 90 GPa and 306 GPa to high temperatures, making it an important sulfide to examine in relationship to Earth's core chemistry and dynamics.

(Zurkowski et al. submitted, Tateno et al. 2019)

- ***This study explores the stability of Fe_2S to Earth's core pressures and determines its structural evolution using Co_2P as a low pressure, single-crystal analog.***

2. Methodology

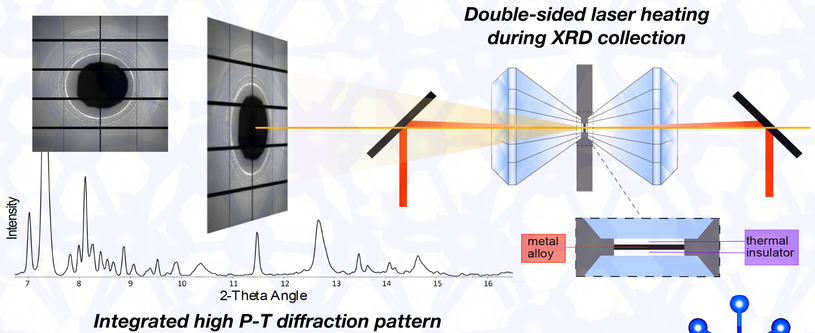


Sample Preparation

	Powder Diffraction Experiments	Multigrain Diffraction Experiments	Single Crystal Diffraction Experiments
Cell type	Symmetric	BX-90	BX-90
Diamonds and seats	standard cut, carbide seats	Boehler-Almax	Boehler-Almax
Loadings	Fe-S foils in KCl	Fe-S foils in KCl	Co_2P xtls with ruby in Ne

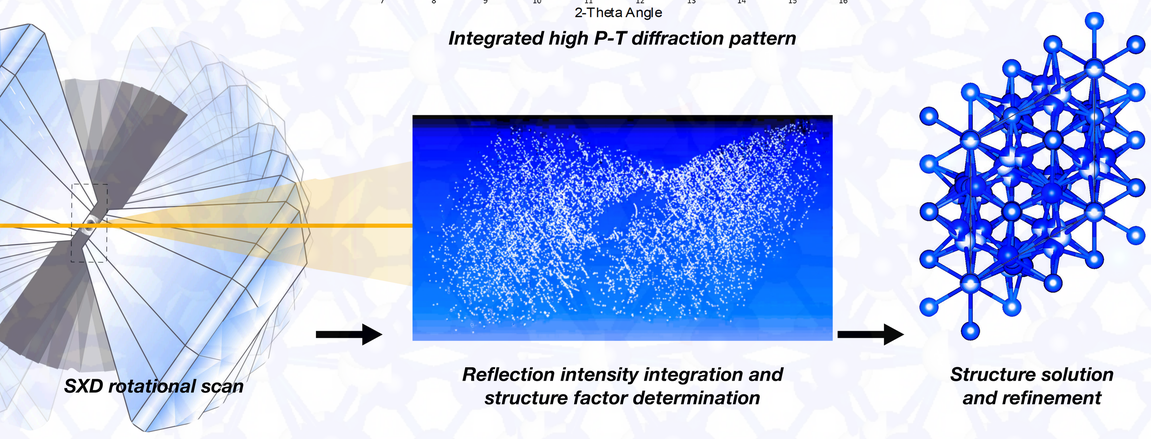
Powder X-ray diffraction + *in-situ* laser heating

- Monitor phase transitions and the phase and melting relations
- Assess suitable grain growth for SXD techniques



Double-sided laser heating during XRD collection

Integrated high P-T diffraction pattern



Single-crystal X-ray diffraction techniques after temperature quenching

- SXD techniques used for multigrain and single crystal loadings
- Upon temperature quenching at high pressures, rotational scans collected (+/- 60°)
- integrate reflections → solve structure → refine atomic positions and thermal parameters

3. Results - Fe_2S structure and stability

Stable structure of Fe_2S observed at high *P-T*

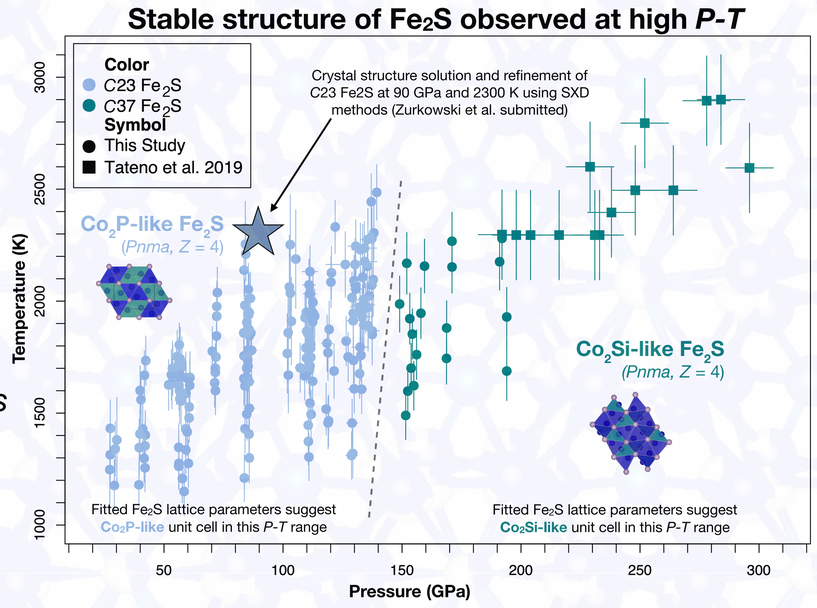


Figure 2. The structural stability of *Pnma* Fe_2S with pressure and temperature based on this study (up to 200 GPa) and the study by Tateno et al. 2019 (190-306 GPa). The unit-cell parameters measured by powder X-ray diffraction for Fe_2S suggest a Co_2P-like unit cell up to ~140 GPa and high temperature and a Co_2Si-llike unit cell above 150 GPa at high temperatures. Rotational scans were collected on a sample quenched at 90 GPa from 2300 K and grains of Fe_2S were identified in the reciprocal space. The crystal structure of Fe2S was determined to be the *C*23 (Co_2P-like) structure at these conditions (shown by the ★) (Zurkowski et al. submitted).

c/a ratio of Fe_2S at high *P-T*

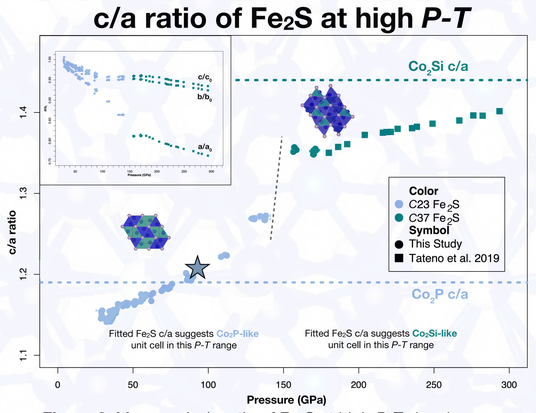


Figure 3. Measured c/a ratio of Fe_2S at high *P-T* showing an increase in c/a ratio with pressure and a discontinuity around 150 GPa, where the c/a ratio in Fe_2S changes from a more Co_2P-like geometry to a more Co_2Si-like geometry. The ★ indicates a SXD collection where grains of Fe_2S were determined to adopt a *C*23 structure. The inset plot shows the relative lattice parameters of Fe_2S with pressure and reveals that the *a* axis is highly compressible compared to the *b* and *c* axes.

A closer look at the *C*23 and *C*37 structures

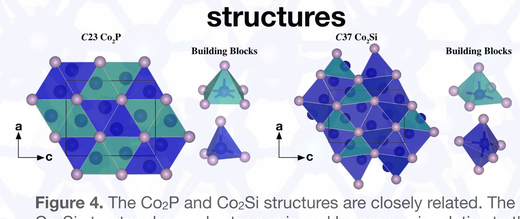
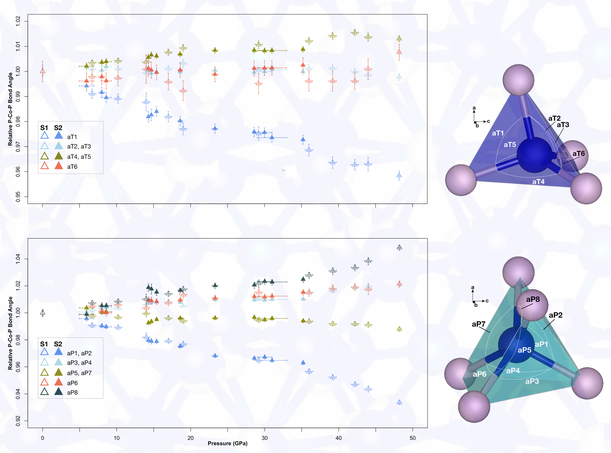


Figure 4. The Co_2P and Co_2Si structures are closely related. The Co_2Si structure has a shorter *a* axis and longer *c* axis relative to the Co_2P structure which results in a 4- to 5- fold coordination change on the CoP_4 tetrahedral site going from Co_2P to Co_2Si

4. Results - Co_2P as a low pressure analog of Fe_2S

P-Co-P bond angles measured in Co_2P



Is Co_2P compressing towards a coordination change?

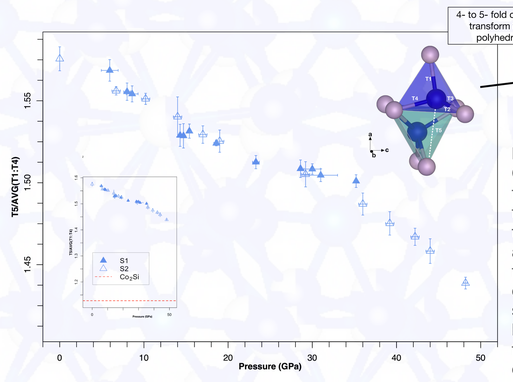


Figure 5. (above) Single crystals of Co_2P were examined under compression to 48 GPa. As Co_2P compresses, the P-Co-P bond angles in the tetrahedral and square pyramid building blocks compress anisotropically. Bond angles oriented parallel to the *a* direction narrow with pressure and bond angles oriented perpendicular to the *a* direction broaden with pressure. This behavior results in a highly compressible *a* axis, comparable to what is observed in Fe_2S (Figure 3 inset) and this behavior intensifies above 35 GPa.

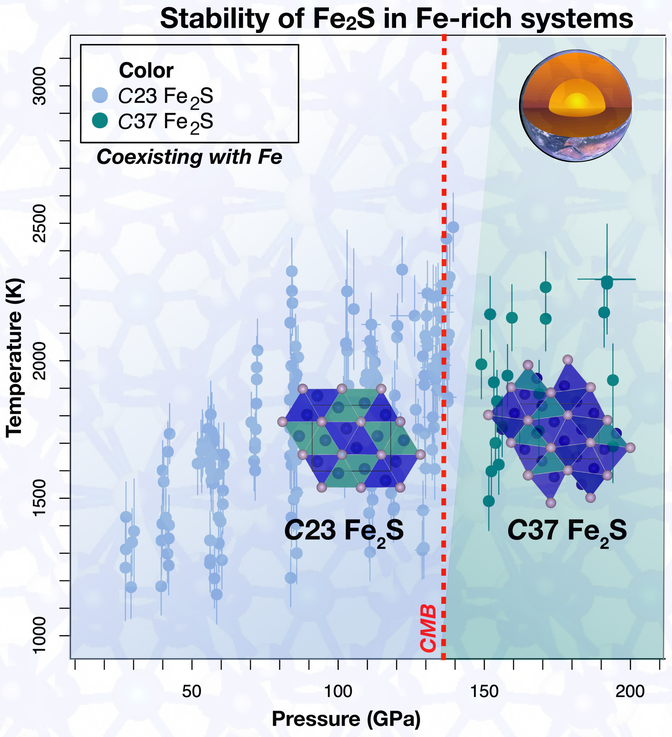
Figure 6. (left) As the *a* axis of Co_2P compresses more than the *b* and *c* axes, the Co1 tetrahedral site moves closer to the next nearest P neighbor along the *a* direction . This figure shows the ratio of the distance to the next nearest P site (T5) with the average bond length in the CoP_4 tetrahedron (AVG(T1:T4). Co_2P does not reach a value comparable to Co_2Si to 48 GPa (red dashed line in inset), but the discontinuity observed above 35 GPa, may indicate the onset of attractive forces between the Co1 site and this fifth nearest P neighbor.

5. Discussion

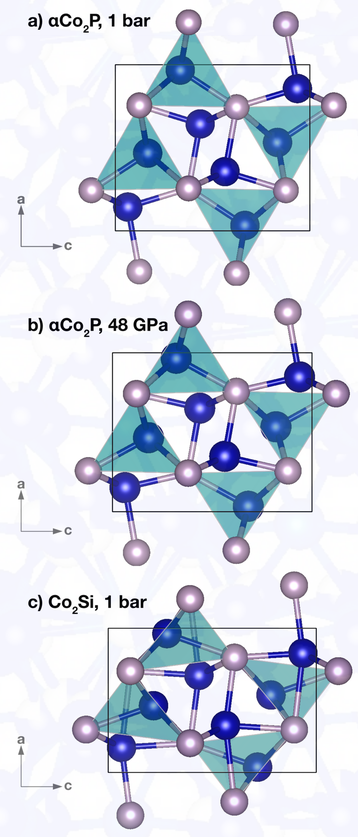
Figure 7. (right) As Co_2P-like structures, such as Fe_2S, compress, the bond angles distort significantly attributing to a highly compressible *a* axis (a, b). As atomic sites are forced closer together along the *a* direction, the Co1-tetrahedral site tends towards a 4- to 5- fold coordination change, which brings the Co_2P structure into coincidence with the Co_2Si structure (c). This compression behavior offers insight into the possible mechanism for the pressure-induced *C*23-*C*37 transition reported in Fe_2P (Nakajima et al. 2020) and inferred based on unit-cell geometry for Fe_2S (this study, Zurkowski et al. submitted, Tateno et al. 2019).

Figure 8. (right) In this study, we observed, through powder diffraction the stability of an orthorhombic Fe_2S phase coexisting with Fe between 25 and 200 GPa and up to ~2500 K. Grains of Fe_2S synthesized at 90 GPa and 2300 K were analyzed and the crystal structure of Fe_2S was determined to be *C*23 (Co_2P-type) at these conditions. The unit-cell parameters of Fe_2S, however show a highly compressible *a* axis and a discontinuity above 140 GPa, where the unit-cell better matches a Co_2Si-like cell. Our SXD analyses of Co2P with pressure support that the compressibility of the *a* axis in Co_2P, forms the *C*23 structure towards a *C*37 (Co_2Si-like) structure. This *C*23-*C*37 transition in Fe_2S may occur near CMB pressures and high temperatures and the material properties of both structures of Fe_2S may play a role in the thermodynamics of Earth's complex core.

Stability of Fe_2S in Fe-rich systems



How compression leads to a *C*23-*C*37 transition



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7. References

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Zurkowski C.C., Lavina B., Chariton S., Greenberg E., Prakapenka V.B. & Campbell A.J. The crystal structure of Fe2S at 90 GPa based on single-crystal X-ray diffraction techniques. Submitted to *American Mineralogist*.

8. Contact Info

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