

Mars: A New Core-Crystallization Regime

Andrew J. Stewart,¹ Max W. Schmidt,¹ * Wim van Westrenen,² Christian Liebske

¹ Institute for Mineralogy and Petrology, Switzerland.

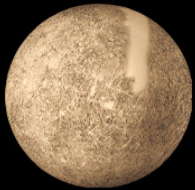
² Faculty of Earth and Life Sciences, Amsterdam, Netherlands.

Abstract

- Data from experiments performed on iron-sulfur and iron-nickel-sulfur systems indicate that
 - martian core is presently completely liquid //before upto 25 GPa Y. Fei, C. Bertka, Science 308, 1120 (2005).
- Planetary cooling will lead to core crystallization:
 - iron-rich solids nucleate in the outer portions of the core and sink toward the center,
 - or an iron-sulfide phase crystallizes to form a solid inner core

The terrestrial planets

■ Mercury



Venus



Earth



Mars



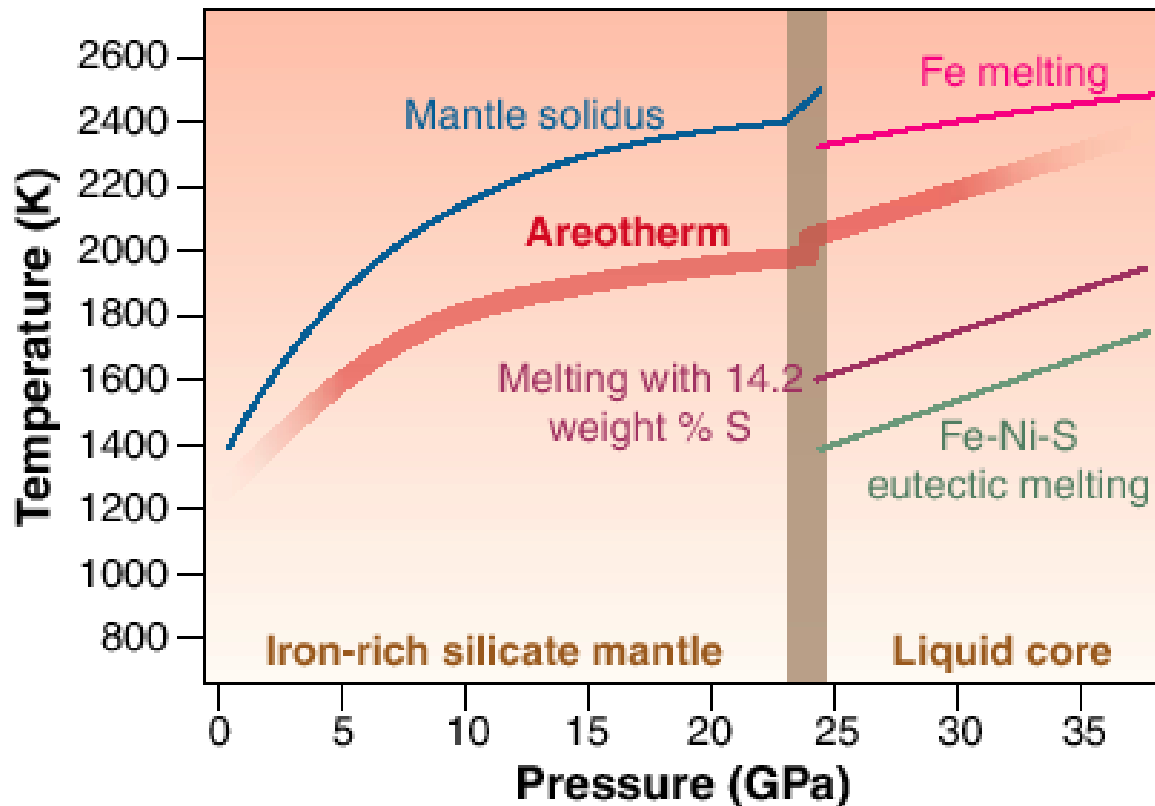
Background

- Mars has a **metallic core** and a **silicate mantle**
 - from density and the bulk chemistry of terrestrial planets
- **Core composition: Fe + Ni (8wt%) + S(10.6-16.2wt%)**
 - from martian meteorite geochemistry.
- **Core radius: 1,520-1,840 km** (Earth's: 3,488km)
 - from moment inertia and solar tidal deformation
- **Planetary radius: 3,390 km** (Earth's: 6,378 km)
- **Crust thickness: 30-80 km** (Earth's: 5-70 km)
 - from Topography and gravity data collected by Mars Global Surveyor

Martian core has been liquid throughout its history

1. Evidence for a subsequent **short-lived** (<0.4 billion years) **martian core dynamo around 3.75 billion** years ago would further strengthen the case for a liquid core, because it is difficult to produce a short-lived dynamo with multiple episodes if the core starts to solidify.
 - Dynamo theory describes the process through which motion of a conductive body in the presence of a magnetic field acts to regenerate that magnetic field. This theory is used to explain the presence of anomalously long-lived magnetic fields in astrophysical bodies. In such bodies, dynamo action depends on the presence of highly conducting fluids such as the Earth's liquid iron, outer core or the ionized gas of the sun
2. Measurements of the **solar tidal deformation of Mars**, obtained by analyzing Mars Global Surveyor radio tracking data.
3. Comparison of **melting curves of martian core** (Fei, Bertka, Science, 2005)// with the estimated **temperature profile (areotherm)** (Williams, Nimmo, Geology, 2004).

Y. Fei, C. Bertka, Science 308, 1120 (2005).



Core/mantle:
~23 GPa
1800 K

Center:
40 GPa
2200 K

- The martian mantle is solid,
 - because its temperature is lower than the mantle solidus. The minimum
- The core is liquid
 - because its temperature is higher than melting temperature in the Fe-Ni-S system.

Experimental procedure

quench experiments

- Walker-type, WC, 10/3.5 assembly, 23 GPa
- Split sphere oil bath, SD, 7/2, 40 GPa (500 bar oil pressure).
 - Cr_2O_3 -doped MgO pressure medium;
 - LaCrO_3 heater;
 - WRe thermocouple through heater;
 - RT pressure calibration ZnS, GaP, Zr

Calibration

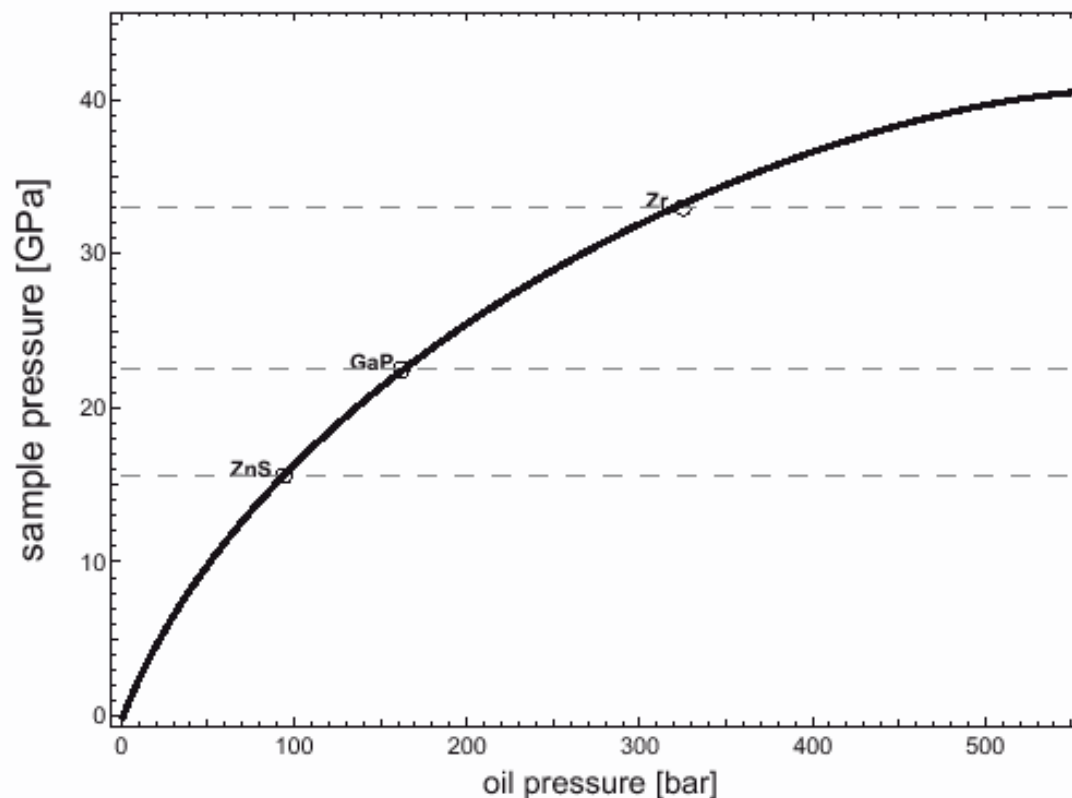


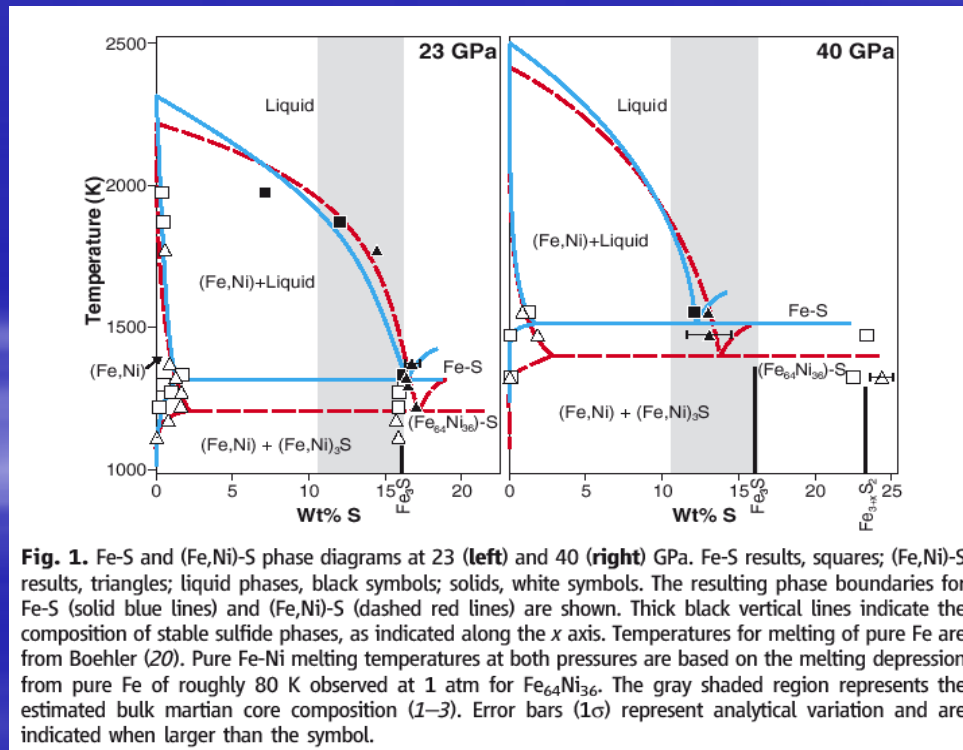
Fig. S1 Sample pressure as a function of hydraulic oil pressure derived from phase transitions in ZnS (S7), GaP (S8) and Zr (S9). The pressure calibration is not expected to change significantly at high temperature (S4).

Starting materials

- Fe + 6 wt% S
- Fe₆₄Ni₃₆ (invar) + 6 wt% S
- MgO capsule

Results /Eutectic Fe-S

- **Eutectic** behavior up to **40 GPa**.
- At 40 GPa eutectic at **1520 K**,
 - which is **800 K** lower than **Fe**
 - **200 K** higher than at **23 GPa**.
- The eutectic shifted from **16wt %S** at **23 GPa** to **12 wt %** at **40 GPa**.



Ni effect on eutectic

- Ni lowered the eutectic temperatures at both 23 and 40 GPa by **~125 K**,
 - Which widens the liquidus loop slightly by increasing the S content of the eutectic melt by 1 wt %.

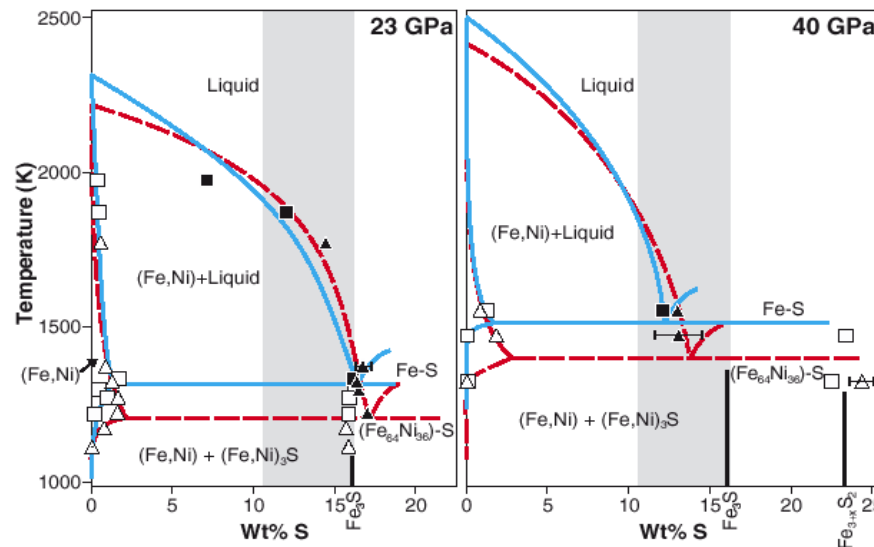
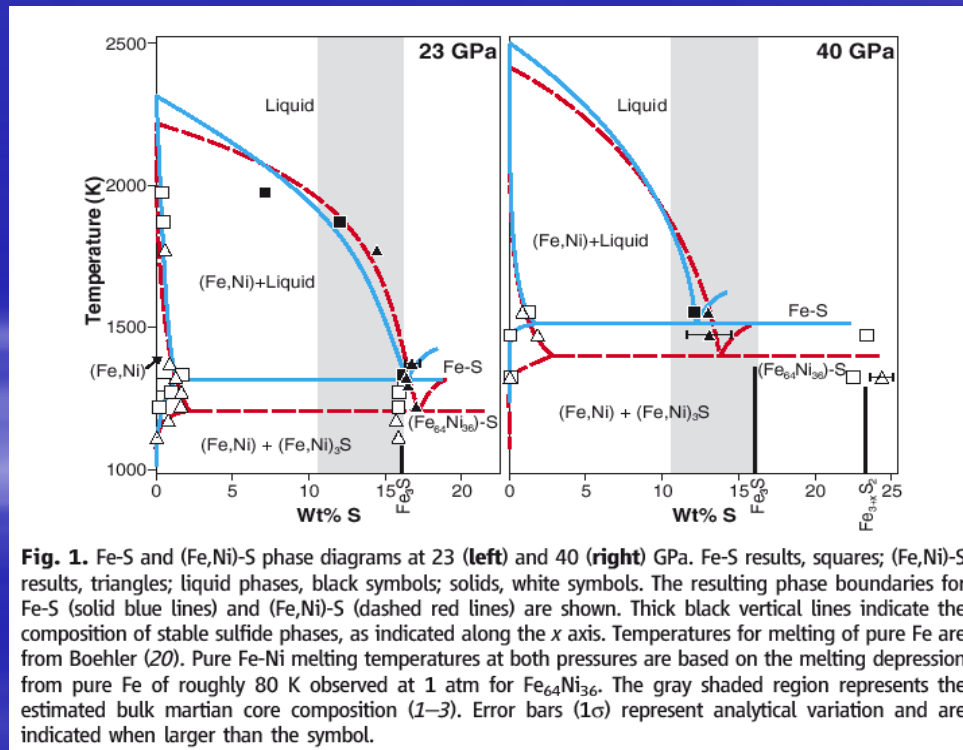


Fig. 1. Fe-S and (Fe,Ni)-S phase diagrams at 23 (left) and 40 (right) GPa. Fe-S results, squares; (Fe,Ni)-S results, triangles; liquid phases, black symbols; solids, white symbols. The resulting phase boundaries for Fe-S (solid blue lines) and (Fe,Ni)-S (dashed red lines) are shown. Thick black vertical lines indicate the composition of stable sulfide phases, as indicated along the x axis. Temperatures for melting of pure Fe are from Boehler (20). Pure Fe-Ni melting temperatures at both pressures are based on the melting depression from pure Fe of roughly 80 K observed at 1 atm for $\text{Fe}_{64}\text{Ni}_{36}$. The gray shaded region represents the estimated bulk martian core composition (1–3). Error bars (1σ) represent analytical variation and are indicated when larger than the symbol.

Ni effect on phase diagram

- Ni has no effect on the phases observed or the eutectic nature of the system
- Ni appears to substitute for Fe in all phases.



Sulfur

- Assuming that eutectic temperatures vary linearly with Ni content, a cosmochemical abundance of Ni (~8 wt %) will lower the eutectic temperature by ~30 K, which thus has only a minor effect on the S content of the eutectic composition.
- The solubility of S in the solid Fe metal phase increases with pressure to 25 GPa (Fei et al., EPSL, 2001). However, solubilities at 23 and 40 GPa in our Ni-bearing samples were similar (1.6 and 1.8 wt % S, respectively).

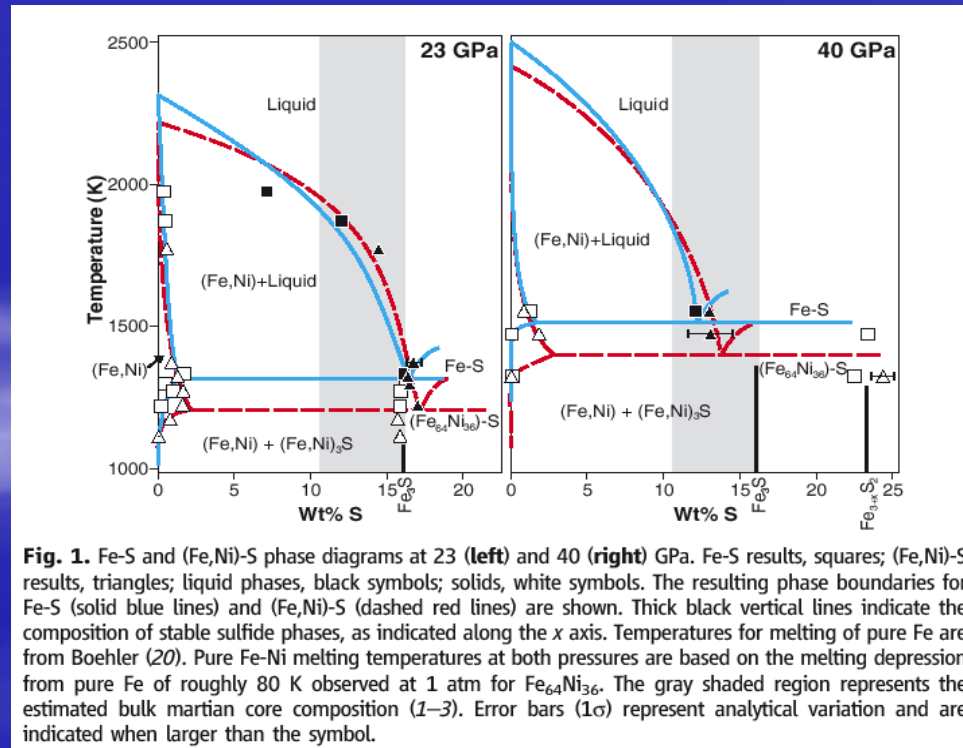
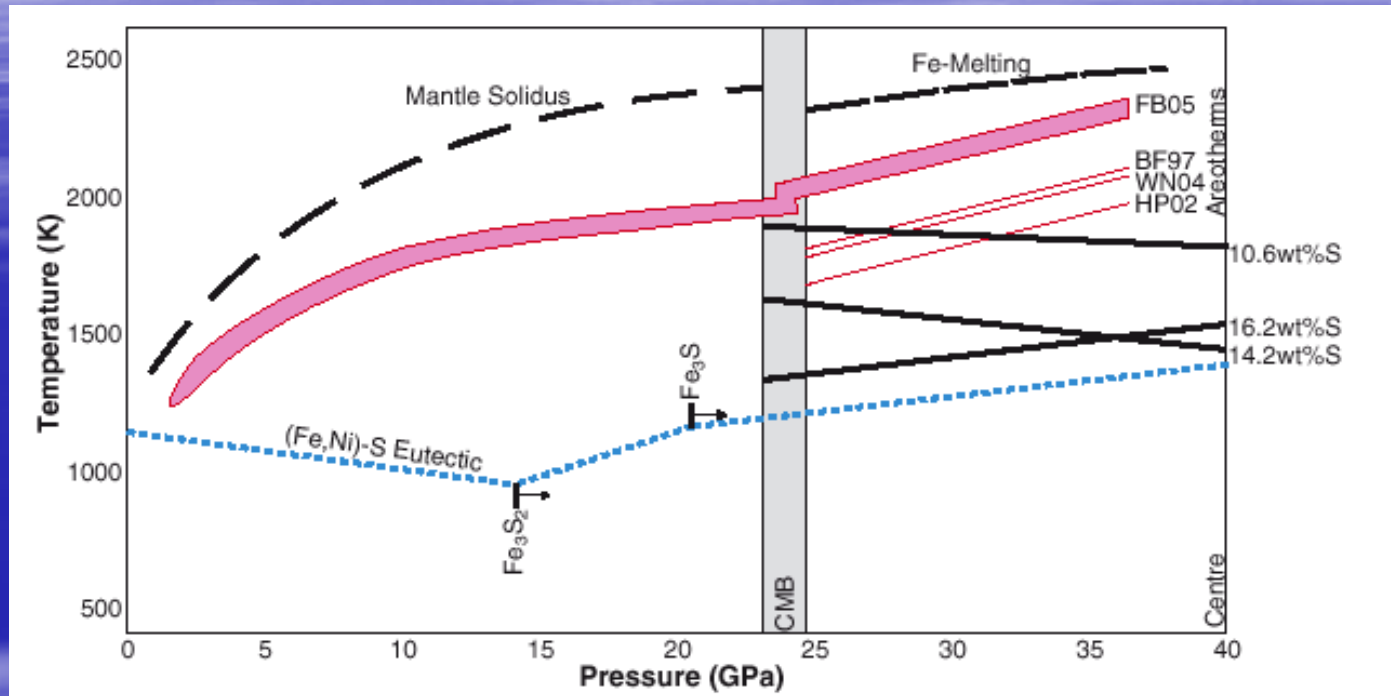


Fig. 1. Fe-S and (Fe,Ni)-S phase diagrams at 23 (left) and 40 (right) GPa. Fe-S results, squares; (Fe,Ni)-S results, triangles; liquid phases, black symbols; solids, white symbols. The resulting phase boundaries for Fe-S (solid blue lines) and (Fe,Ni)-S (dashed red lines) are shown. Thick black vertical lines indicate the composition of stable sulfide phases, as indicated along the x axis. Temperatures for melting of pure Fe are from Boehler (20). Pure Fe-Ni melting temperatures at both pressures are based on the melting depression from pure Fe of roughly 80 K observed at 1 atm for $\text{Fe}_{64}\text{Ni}_{36}$. The gray shaded region represents the estimated bulk martian core composition (1–3). Error bars (1 σ) represent analytical variation and are indicated when larger than the symbol.

Discussion /state of core



- Data indicate a complete absence of crystallization in most, if not all, of the present-day martian core.

Subsequent evolution of core

- Mars continues to cool, and the core will undoubtedly solidify in the geological future.
- The mechanisms of core crystallization will depend on
 - the **effect of pressure on crystallization temperatures** in the (Fe,Ni)-S system, the corresponding phase compositions,
 - and particularly on the bulk **S concentration** of the martian core.
- **Estimates of S contents**, obtained by comparing the chemical compositions of martian **meteorites** with those of other primitive meteorites, range from **10.6 to 16.2 wt %**.

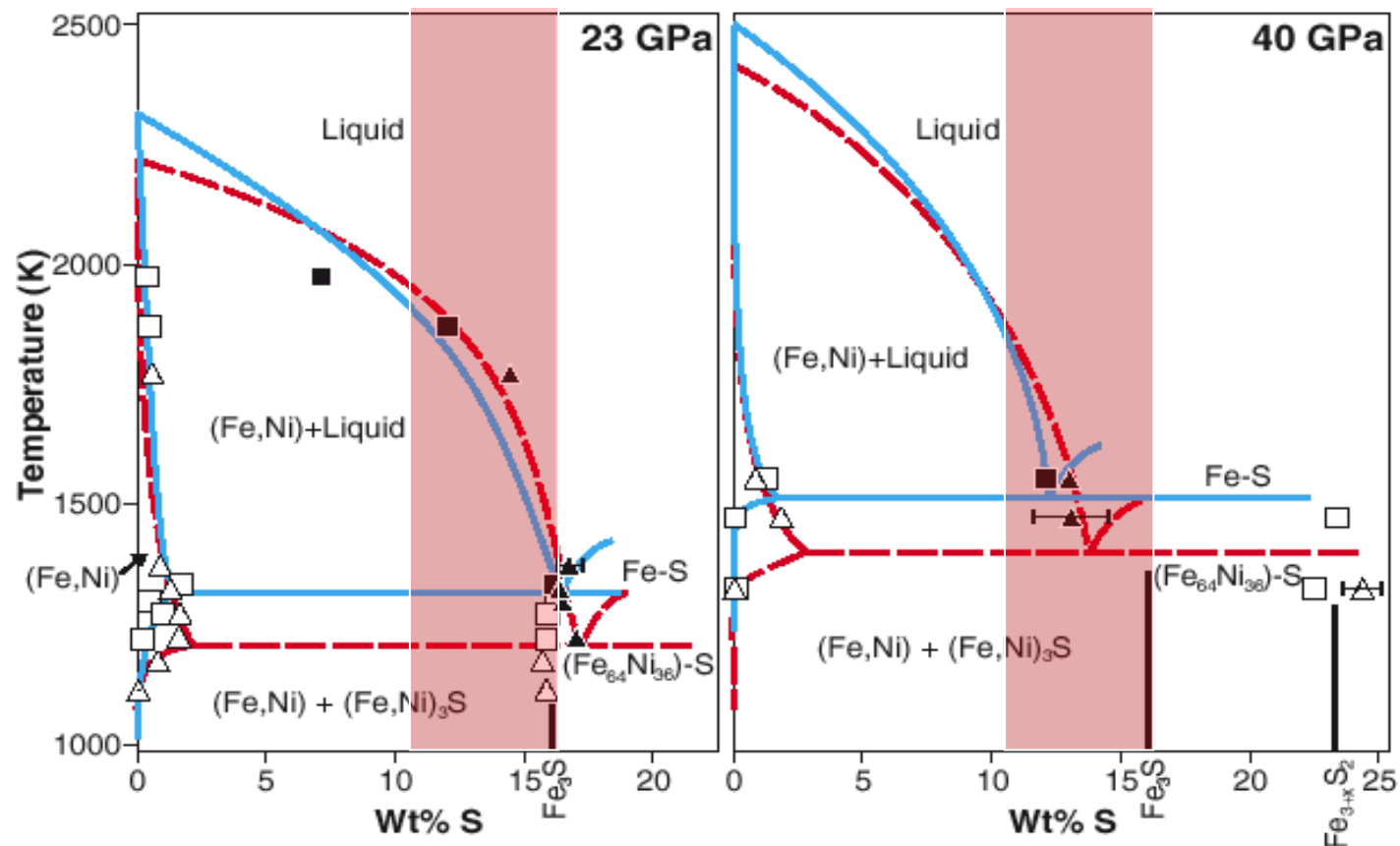
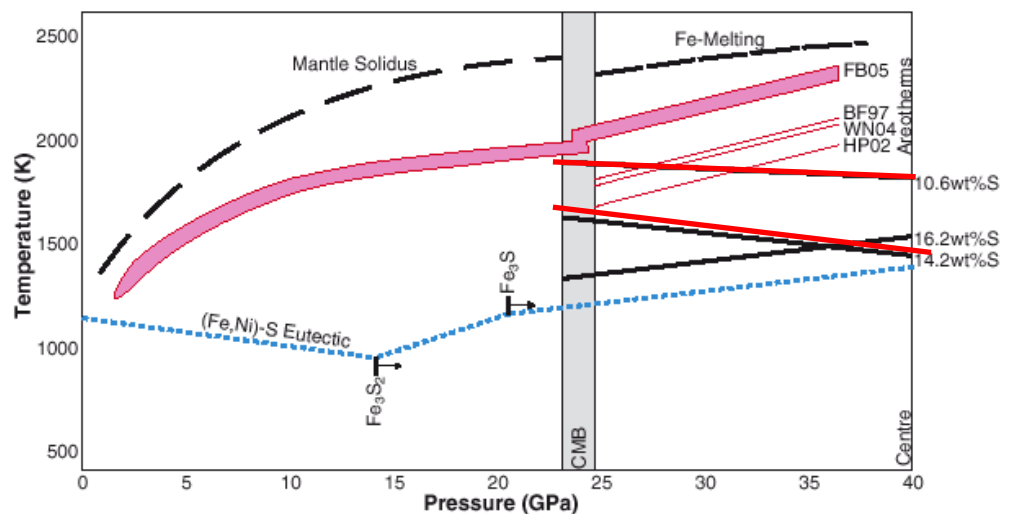
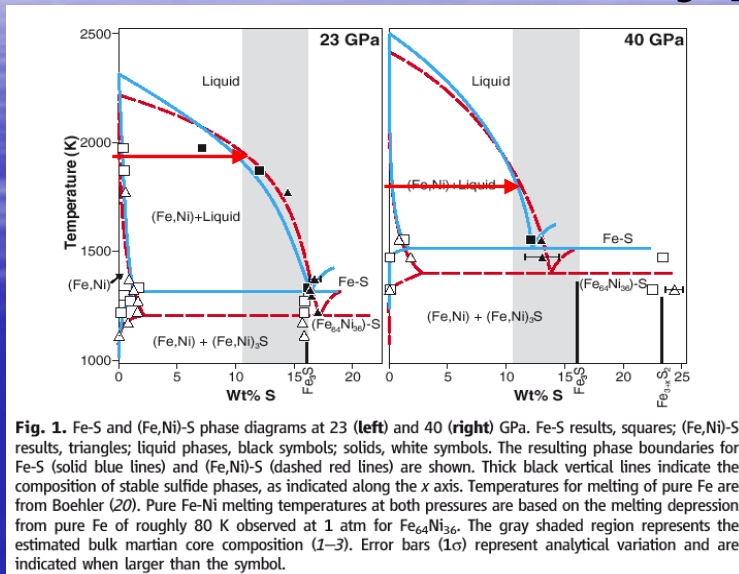


Fig. 1. Fe-S and (Fe,Ni)-S phase diagrams at 23 (**left**) and 40 (**right**) GPa. Fe-S results, squares; (Fe,Ni)-S results, triangles; liquid phases, black symbols; solids, white symbols. The resulting phase boundaries for Fe-S (solid blue lines) and (Fe,Ni)-S (dashed red lines) are shown. Thick black vertical lines indicate the composition of stable sulfide phases, as indicated along the *x* axis. Temperatures for melting of pure Fe are from Boehler (20). Pure Fe-Ni melting temperatures at both pressures are based on the melting depression from pure Fe of roughly 80 K observed at 1 atm for Fe₆₄Ni₃₆. The gray shaded region represents the estimated bulk martian core composition (1–3). Error bars (1σ) represent analytical variation and are indicated when larger than the symbol.

If $S < 14\text{wt}\%$ (snowing-core hypothesis)



- The slope of the liquidus temperature as a function of pressure is negative.
- Adiabatic areotherm must have a positive temperature-pressure (dT/dP) slope
- Crystallization of core melts at the core/mantle boundary.
- γ -Fe is denser than the coexisting liquid
 - 9.4 to 10.5 g/cm³ across core P at $T = 2050$ K,
 - Fe-S liquid 6.9 to 7.7 g/cm³ across core P and $T = 1773$ to 2123 K.
- Thus, any solid Fe-rich phase crystallizing from the S-bearing liquid should sink within that liquid, leading to the snowing-core hypothesis (Fig. 3A).

If $S < 14\text{wt}\%$ (snowing-core hypothesis)

- As core temperatures decrease with time, it is possible that an inner Fe-Ni core will form as a metastable sedimentary agglomerate of sinking Fe-rich solids.
- The liquid portion of the core will then become progressively enriched in S, until finally the core will complete its crystallization from a eutectic liquid crystallizing both (Fe,Ni) and $(\text{Fe,Ni})_3\text{S}$.

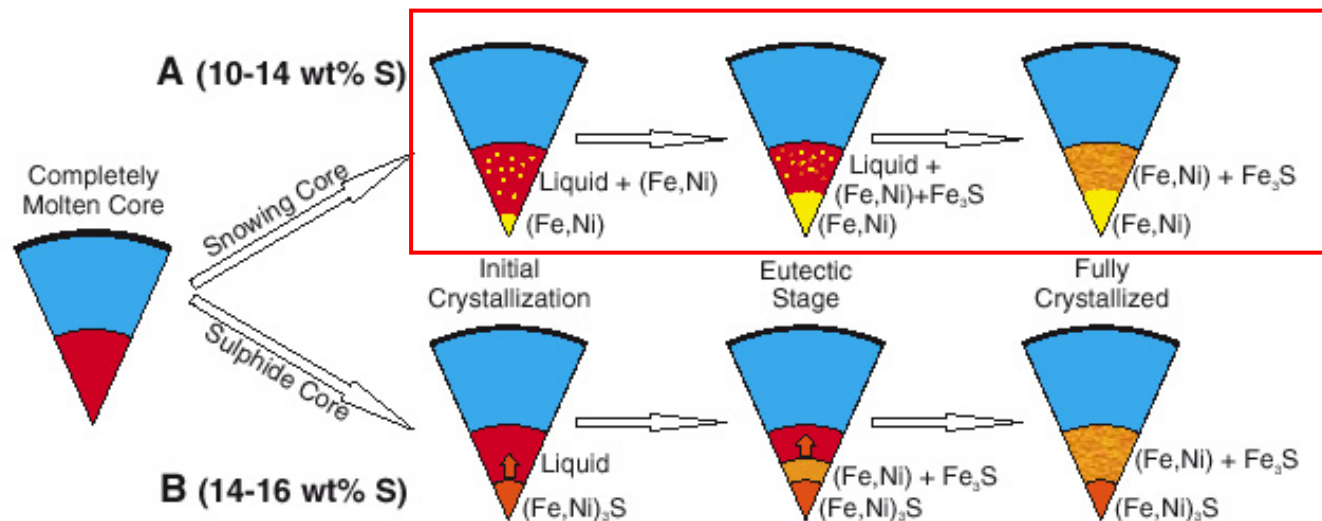
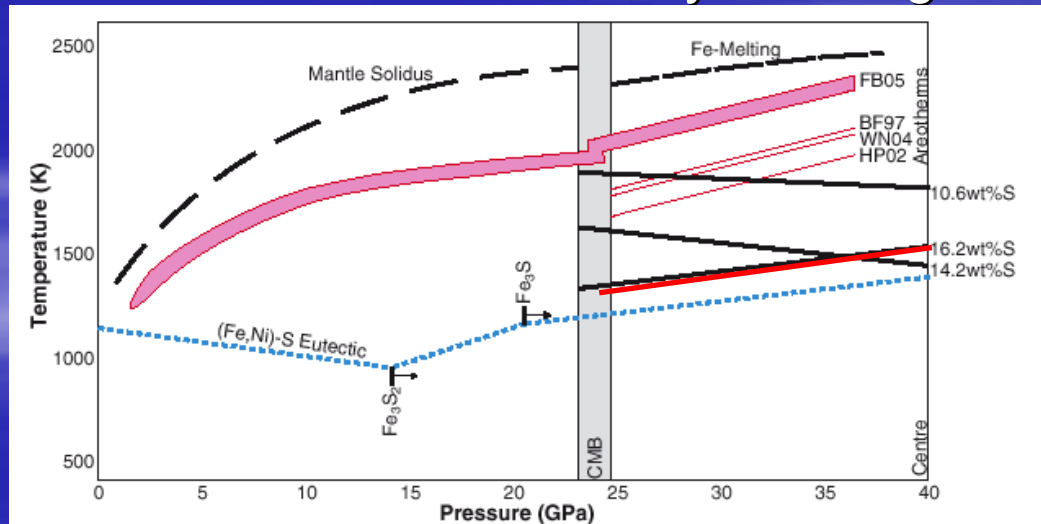


Fig. 3. Cross section through Mars, illustrating two possible crystallization regimes for the martian core. Solid (Fe,Ni), yellow; solid Fe_3S , orange; liquid sulfide, red; mantle, blue; crust, black (not drawn to scale). (A) Snowing-core hypothesis. (B) Sulfide inner-core hypothesis.

If $S > 14\text{wt}\%$

- Crystallization will first occur at high pressures. martian core melts would have compositions on the S-rich side of the eutectic and thus first crystallize an inner core of $(\text{Fe,Ni})_3\text{S}$.
- $(\text{Fe,Ni})_3\text{S}$ would remain at the center of the core because
 - Fe_3S density is $7.7\text{-}8.2\text{ g/cm}^3$ over the martian core pressure range, between 1600 and 2100 K
 - Fe-S liquid with 10 wt % S has density $6.5\text{-}7.7\text{ g/cm}^3$.



If $S > 14\text{wt}\%$

- Removing $(\text{Fe,Ni})_3\text{S}$ from the liquid core will cause the residual liquid compositions to evolve toward the high-pressure eutectic, finally forming a crystallizing outer martian core composed of (Fe,Ni) and $(\text{Fe,Ni})_3\text{S}$, with an inner core composed of $(\text{Fe,Ni})_3\text{S}$.

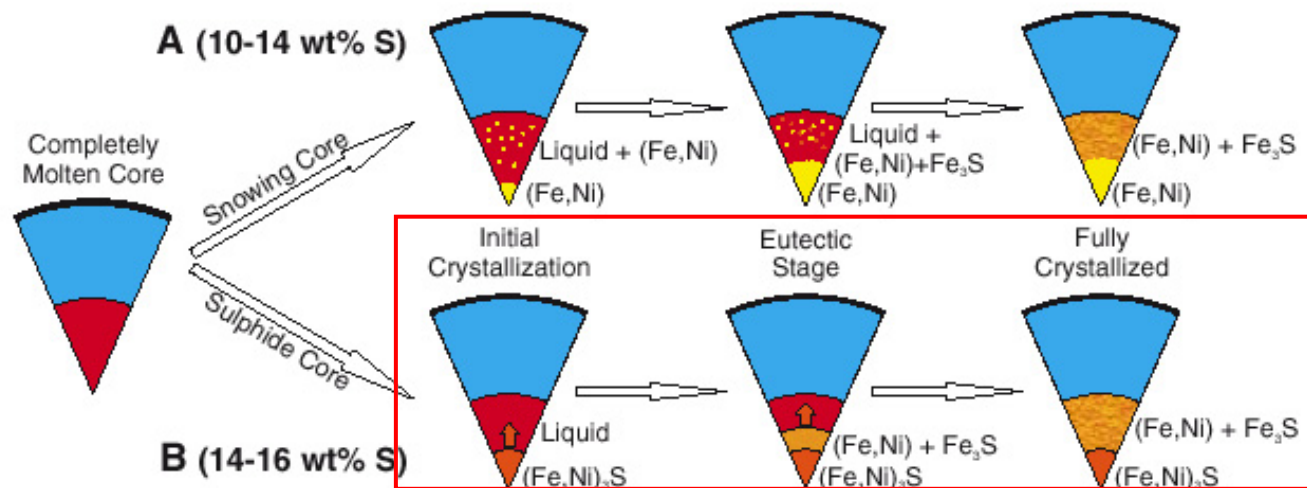


Fig. 3. Cross section through Mars, illustrating two possible crystallization regimes for the martian core. Solid (Fe,Ni) , yellow; solid Fe_3S , orange; liquid sulfide, red; mantle, blue; crust, black (not drawn to scale). (A) Snowing-core hypothesis. (B) Sulfide inner-core hypothesis.

