Constraints on the lunar core composition and thermal state from geophysical data and thermodynamic properties of liquid iron alloys

A. Rivoldini[1], M-H. Deproost[1], T. Van Hoolst[1], G. Morard[2], and H. Terasaki[3]
[1]Observatoire Royal de Belgique, Belgique; [2]Osaka University, Japan; [3]Sorbonne Université, France

Constraints on the core of the Moon

- has liquid part (libration from LLR)
  Williams 2001

- cooled fast enough to generate an early magnetic field

- radius 278-440 km and mean density **3900-6750 kg/m³** (seismic data, LLR, tides, induction)
  … Garcia 2011; Williams 2014; Khan 2014; Matsumoto 2015, Matsuyama 2016

  ⇒ iron ($\rho_{l\text{-}Fe=}$7400kg/m³) -rich alloy with a significant amount of light elements

- non candidate light elements: **Si** (unfavorable redox conditions), **O** and **H** (p too low during core-mantle differentiation)

- candidate light elements (formation conditions, bulk composition assumptions, chemical element partitioning between liquid metal and silicates):
  S≲0.5wt% and **C≲5wt%**

  … Dasgupta 2009; Chi 2014; Steenstra 2016,2017; Righter 2017

  At 5GPa:
  $\rho_{Fe0.5wt\%S}$~7300kg/m³ and $T_{liquidus}$~1950K

  $\rho_{Fe5wt\%C}$~ 7100kg/m³ and $T_{liquidus}$~1600K

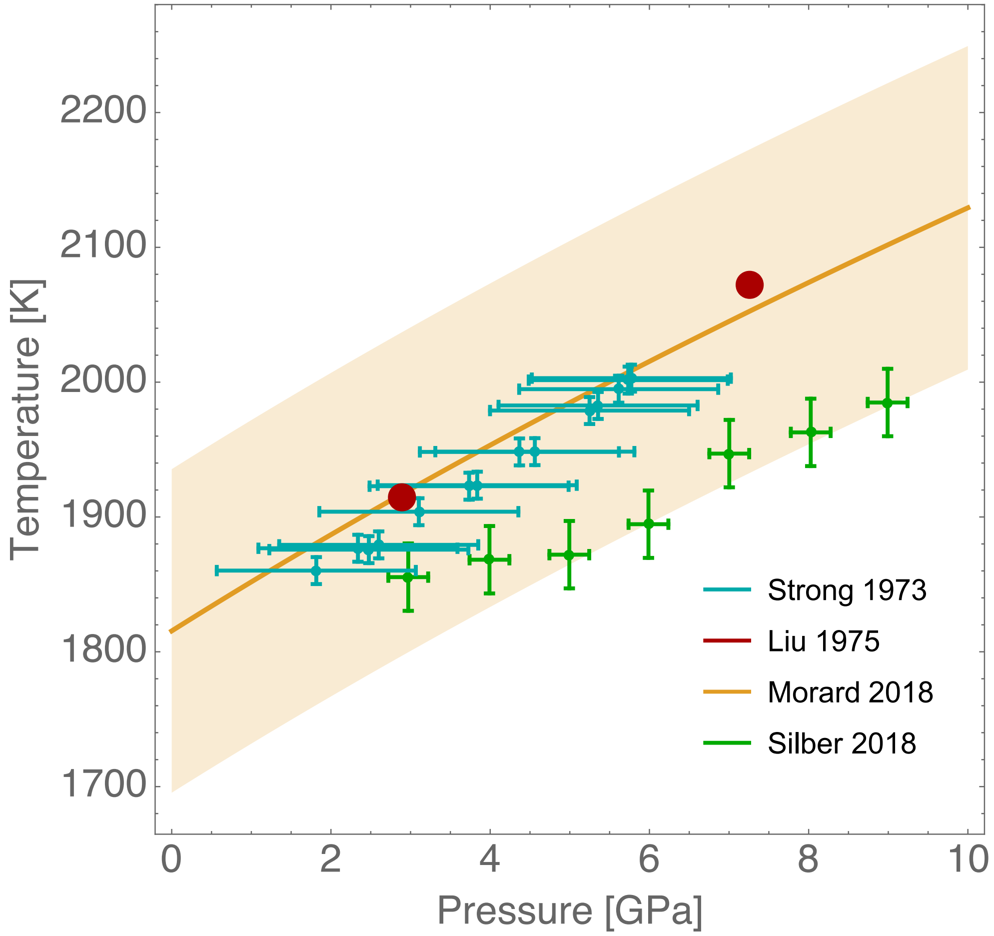
  → too dense to agree with core density inferences

  ⇒ need larger amounts of light elements

Core modeling

- iron-rich core can have a liquid and solid part
- radius of inner-core radius determined from liquidus temperature and core light element concentration
- need equations of state to compute relevant thermodynamic quantities for modeling interior structure and thermal evolution at relevant pressure and temperature conditions
  (e.g. density, thermal and chemical expansivity, heat capacity)
- equations of state and liquidus temperature of core alloys should be thermodynamically consistent

Fe liquidus



- liquidus deduced from high pressure data (p>10GPa, Morard et al 2018) is in good agreement with low pressure experimental data (Strong 1973, Liu 1975)

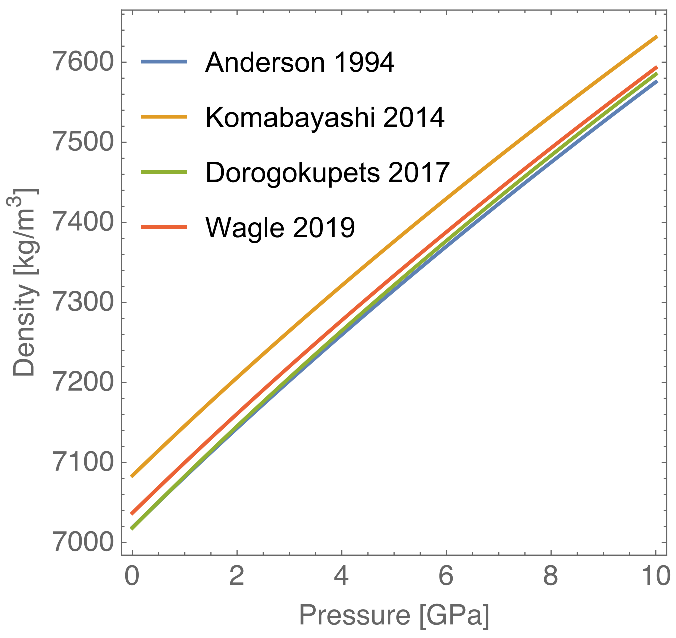
- uncertainty on melting temperature at 1bar ≲10K and at 5GPa ≳**150K**

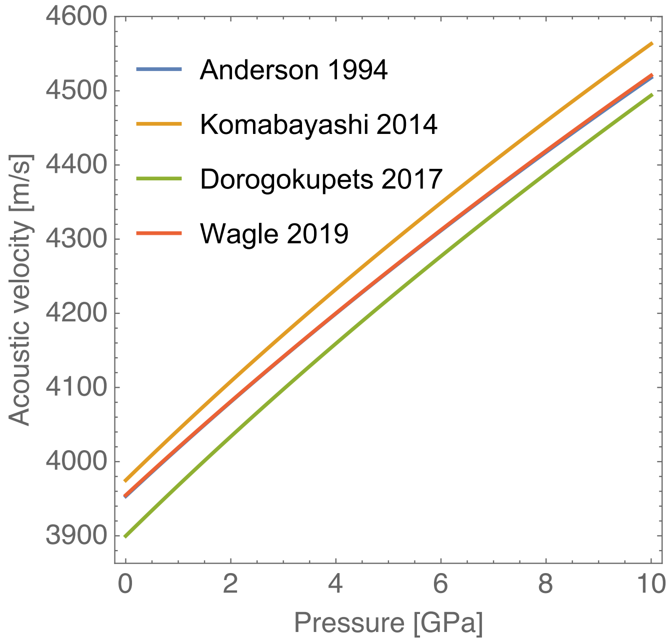
- temperature increase along Moon core adiabat ≲ **25K** !

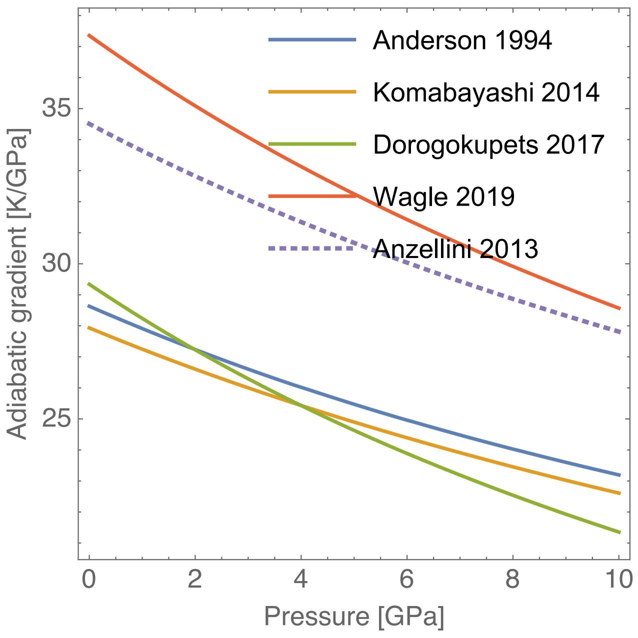
l-Fe equation of state

l-Fe eos are not derived from experimental data acquired at Moon core conditions:

- Anderson et al 1994 (1bar thermoelastic data and 1000GPa shock data)
- Komabayashi 2014 (eos of fcc and hcp Fe and Fe liquidus from Anzellini 2013)
- Dorogokupets et al. 2017 (1bar thermoelastic data, eos of fcc and hcp Fe and Fe liquidus from Anzellini 2013)
- Wagle and Steinle-Neumann 2019 (Ab-Initio)



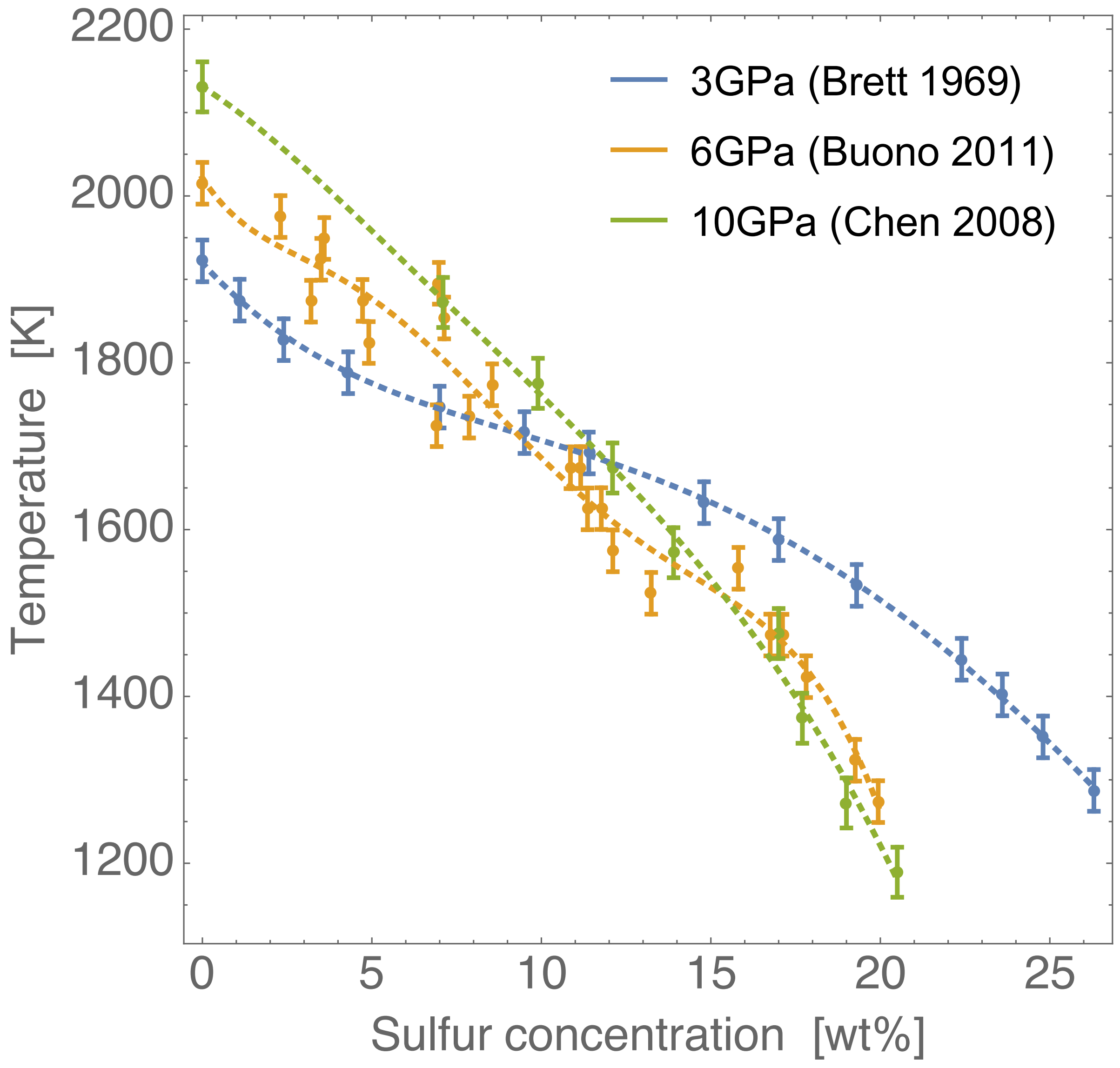




- along isentropes density differences are below 1% and acoustic velocity differences are below 2%
- but for thermal expansivity, heat capacity, and Grüneisen parameter the differences between the eos' can be quite larger
  ⇒ effect on core temperature
- all isentropes except that of Wagle et al. are less steep than the gradient along the Fe liquidus
  ⇒ bottom-up inner core growing for pure Fe and top-down for Wagle et al.
- all relevant thermodynamic quantities of l-Fe for structure and thermal evolution can be calculated from the eos'

Fe-S core model

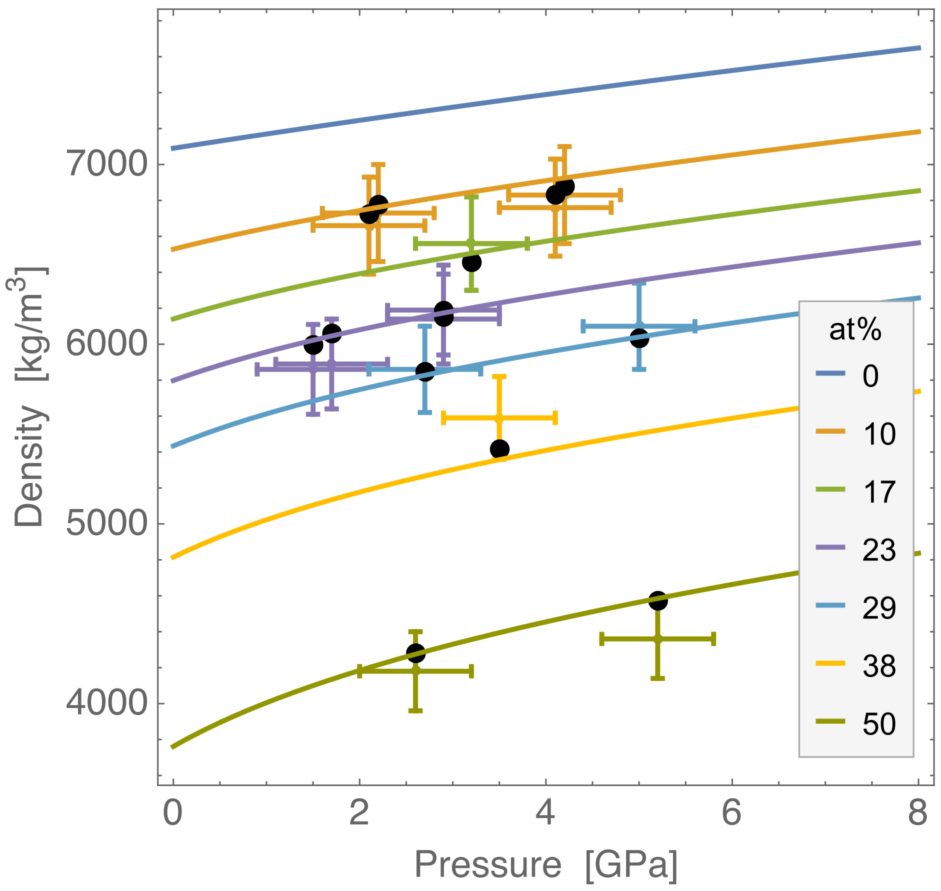
Iron-rich liquidus

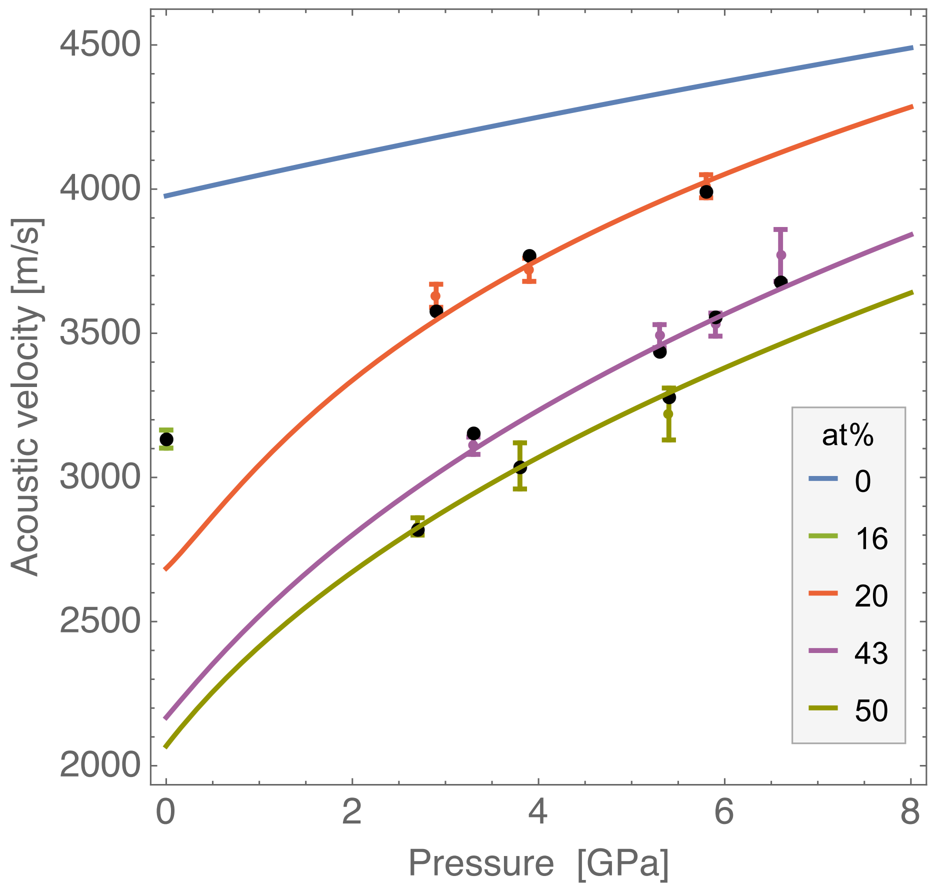


- highly non-ideal
- can be described with an asymmetric Margules model that has interaction parameters linear in p and T (Buono & Walker 2011)

$$
\begin{aligned}
G^l(X_{\mathrm{FeS}}, p, T) = & (1 - X_{\mathrm{FeS}})\, G^l_{\mathrm{Fe}}(p, T) + X_{\mathrm{FeS}}\, G^l_{\mathrm{FeS}}(p, T) + \\
& (1 - X_{\mathrm{FeS}})\, R\, T \ln(1 - X_{\mathrm{FeS}}) + X_{\mathrm{FeS}}\, R\, T \ln(X_{\mathrm{FeS}}) + \\
& X_{\mathrm{FeS}}(1 - X_{\mathrm{FeS}})\, [X_{\mathrm{FeS}}\, W_{\mathrm{Fe}}(p, T) + (1 - X_{\mathrm{FeS}})\, W_{\mathrm{FeS}}(p, T)]
\end{aligned}
$$

Elastic properties


Morard et al. 2018


Nishida et al. 2016

- densities of liquid Fe-S alloys at 5GPa in agreement with expected average Moon core density (3900-6750 kg/m^3)
- Buono & Walker model induces a concentration dependent but (p,T) independent excessive mixing volume that can explain the high pressure density data
- **but not** the acoustic velocity data

Thermodynamic model

- end-members l-Fe (Komabayashi 2014) and l-FeS

- asymmetric Margules model with pressure dependent excessive volume

$$G^l_{ex}(X_{\mathrm{FeS}}, p, T) = X_{\mathrm{FeS}}(1 - X_{\mathrm{FeS}})\,[X_{\mathrm{FeS}}\, W_{\mathrm{Fe}}(p, T) + (1 - X_{\mathrm{FeS}})\, W_{\mathrm{FeS}}(p, T)]$$

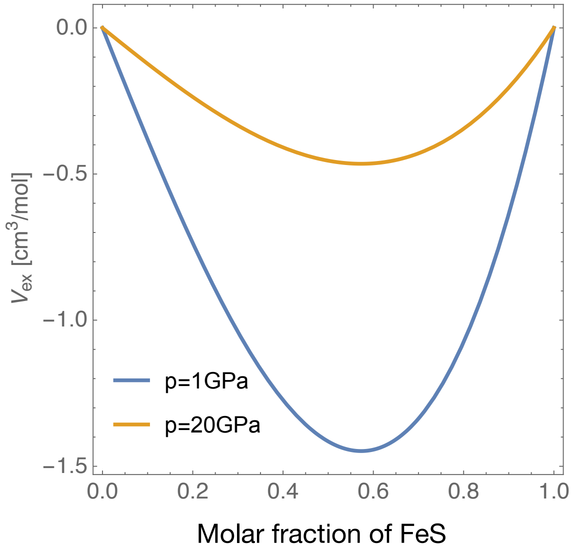
$$W_{\mathrm{Fe}}(p, T) = W_{\mathrm{Fe},H} - W_{\mathrm{Fe},S}T + W_{\mathrm{Fe},V}\int_0^p V_{ex}(p')\,dp'$$

$$W_{\mathrm{FeS}}(p, T) = W_{\mathrm{FeS},H} - W_{\mathrm{FeS},S}T + W_{\mathrm{FeS},V}\int_0^p V_{ex}(p')\,dp'$$

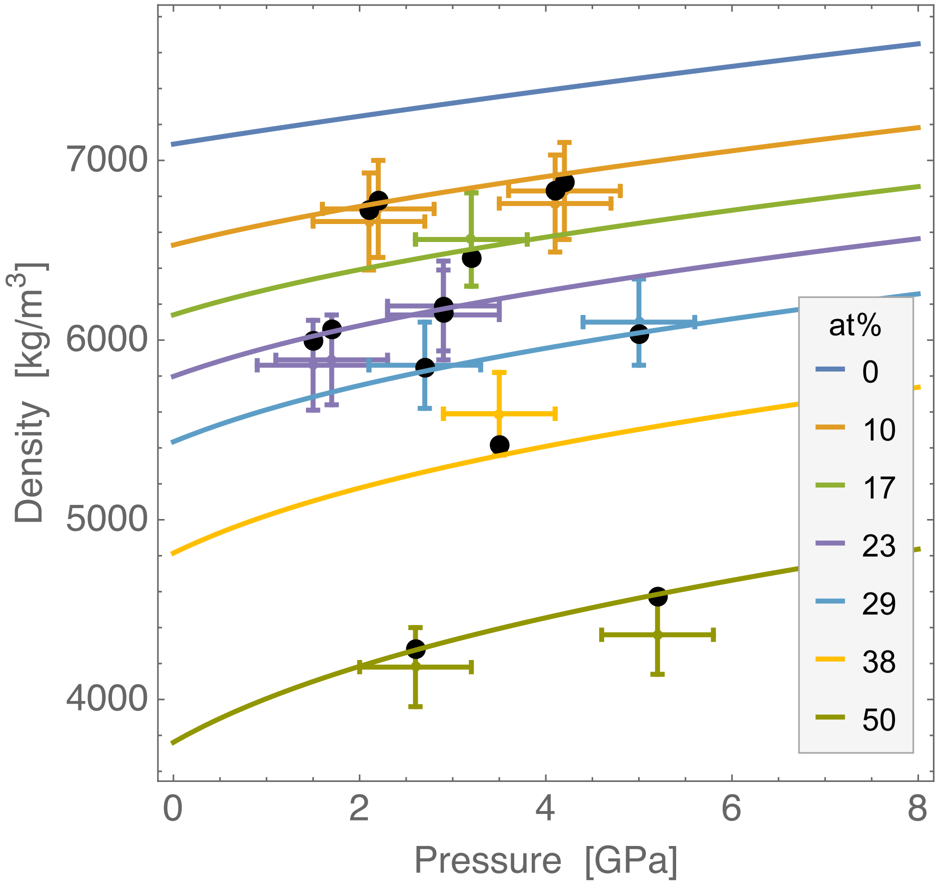
- EoS parameters for FeS (except ρ_{ref} and γ=1.3) (4) and interaction parameters (8) are estimated from liquidus, density, and acoustic velocity data

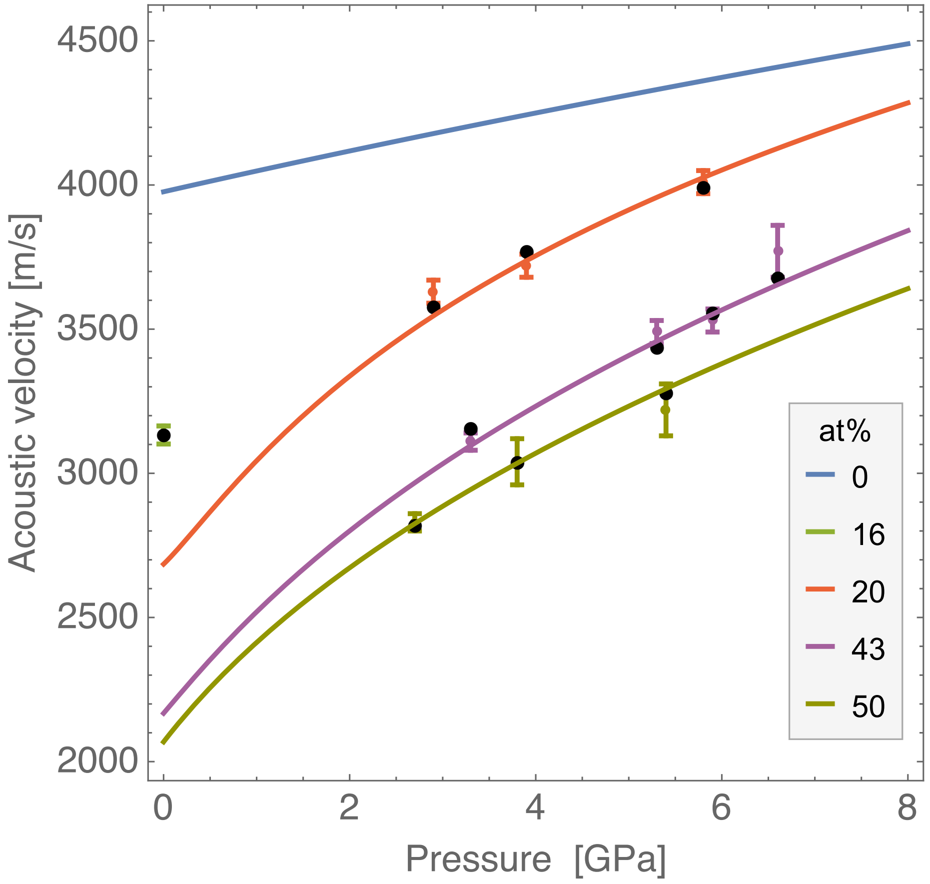
- ambient pressure density FeS from Kress 2007

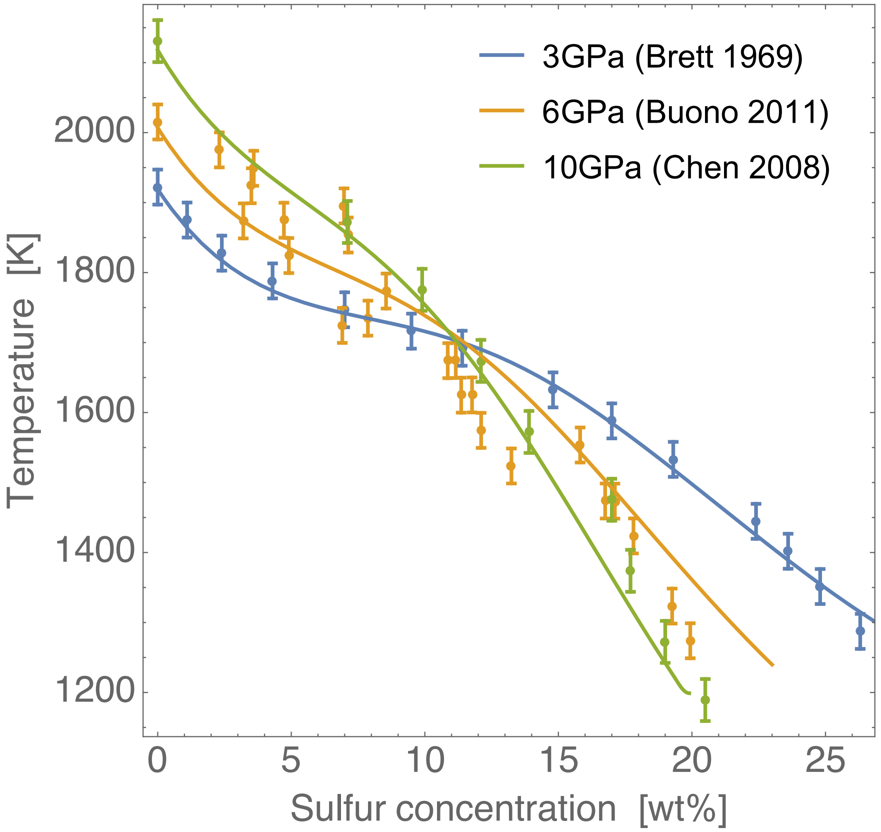
- use pseudospinodal eos
  (Baonza 1995) for V_{ex}
  →V_{ex} decreases with increasing pressure



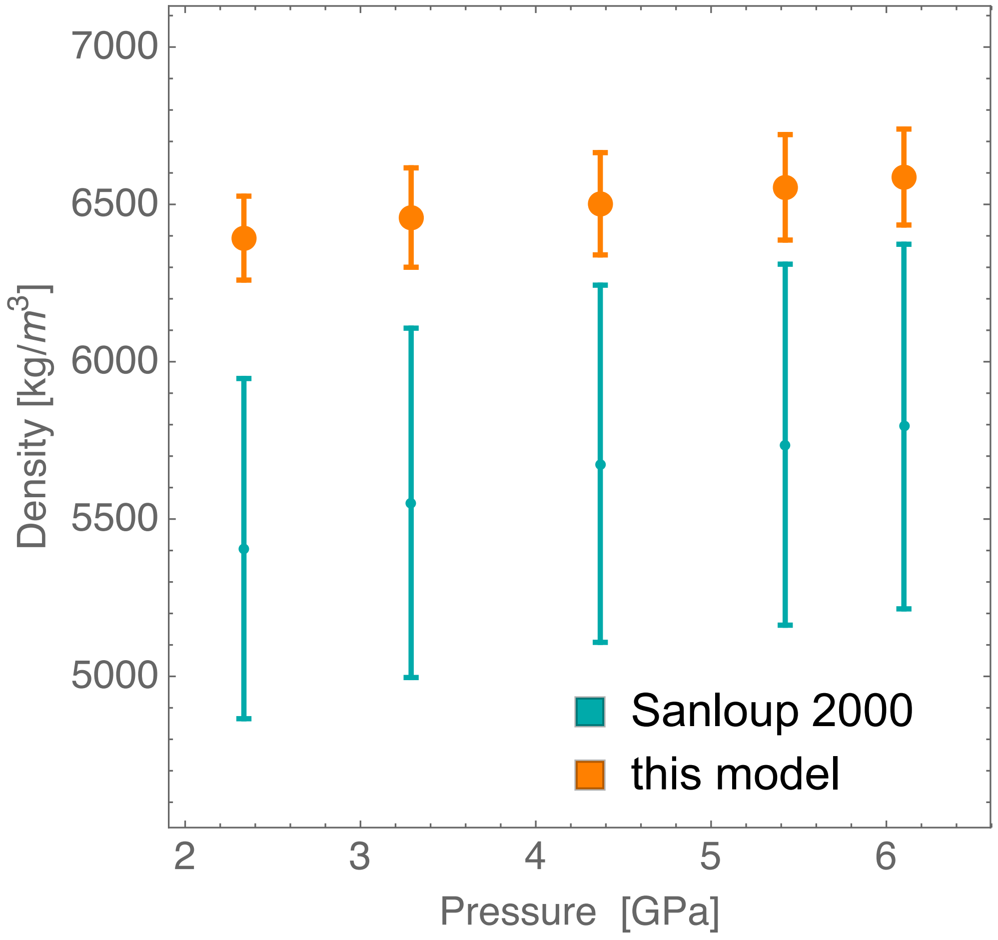
Data-Fit


Density [kg/m^3]
7000
6000
5000
4000
0
2
4
6
8
Pressure [GPa]
at%
0
10
17
23
29
38
50


Acoustic velocity [m/s]
4500
4000
3500
3000
2500
2000
0
2
4
6
8
Pressure [GPa]
at%
0
16
20
43
50


Temperature [K]
2000
1800
1600
1400
1200
0
5
10
15
20
25
Sulfur concentration [wt%]
3GPa (Brett 1969)
6GPa (Buono 2011)
10GPa (Chen 2008)

Comparison with liquid Fe-10wt%S data used in several Moon core models



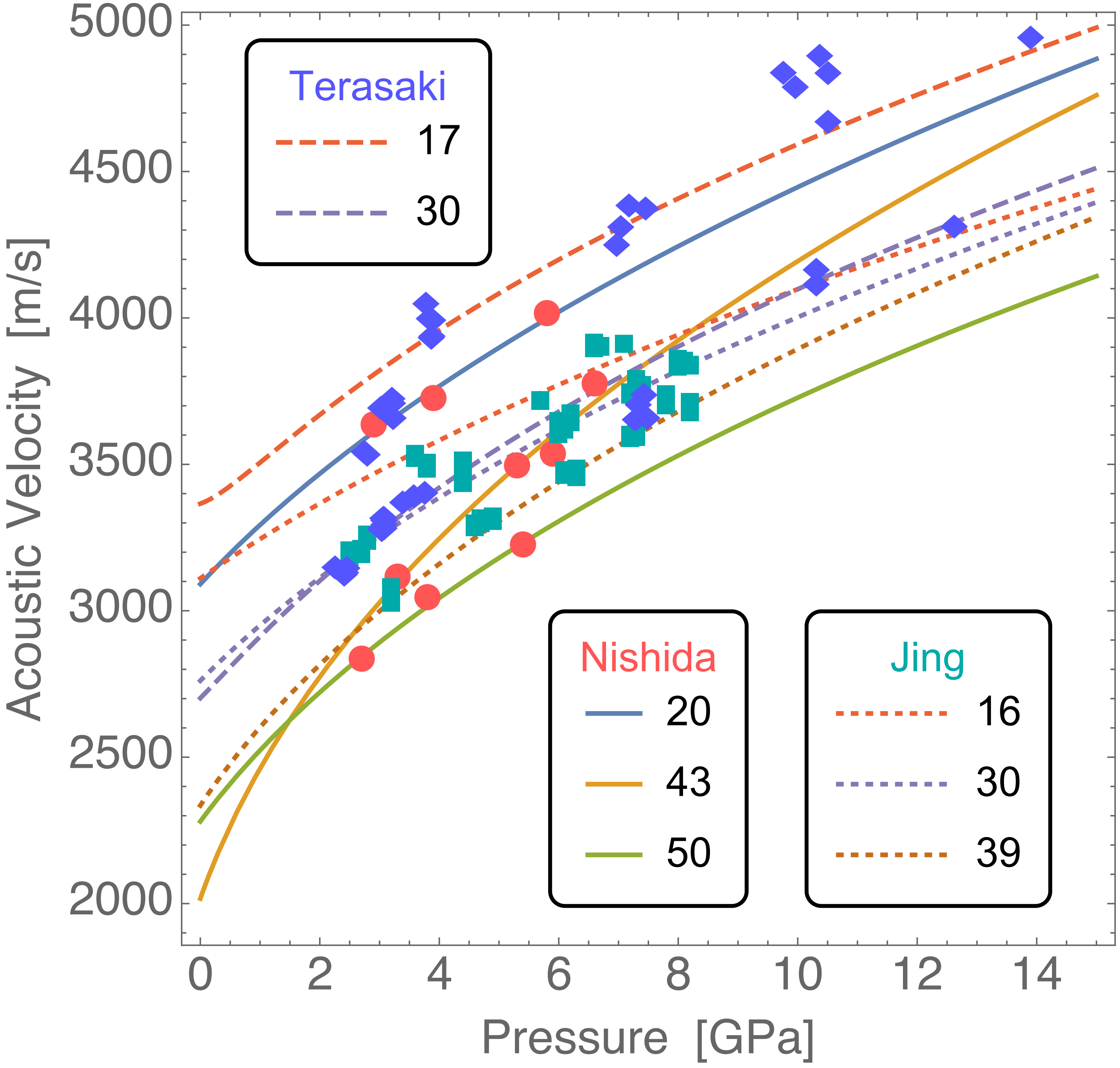
- uncertainty on elastic data induces errors on predicted densities of l-Fe-S alloys that are below 5% (taking into account correlations between eos parameters)

- predicted density of Fe-10wt%S is significantly larger than values reported by Sanloup et al. 2000 ⇒new elastic data and thermodynamic model requires more sulfur to explain average core density

Caveats

- estimated model parameters depend on l-Fe eos
- results depend on reference density of FeS (Kaiura 1979, Kress 2007)
- cannot fit Grüneisen parameter from the data
- cannot assess model predictions for liquidus for compositions above the eutectic because of lack of experimental data
- thermodynamic Fe-S model very much dependent on used elastic data set

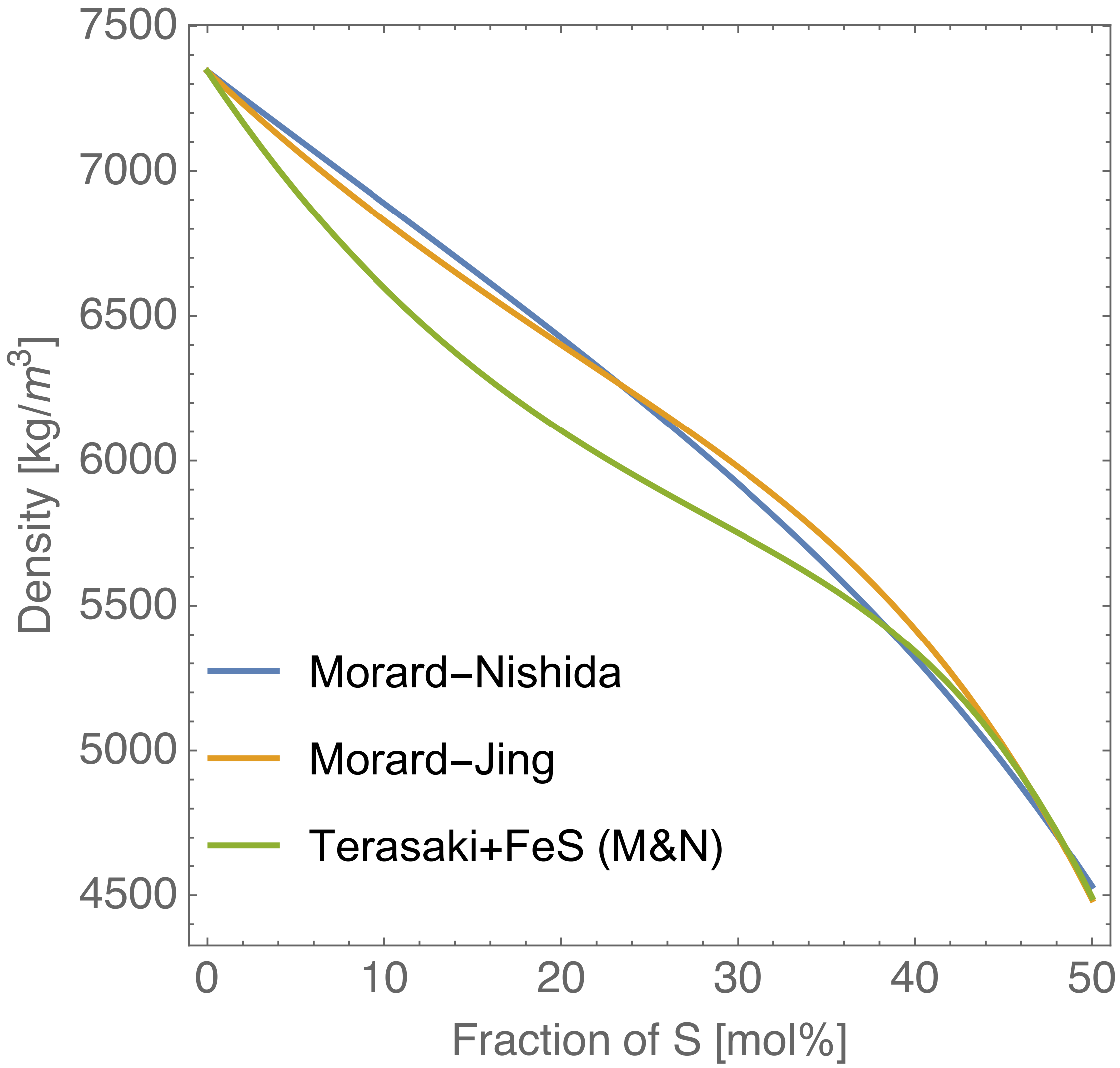
Acoustic velocity liquid Fe(Ni)-S

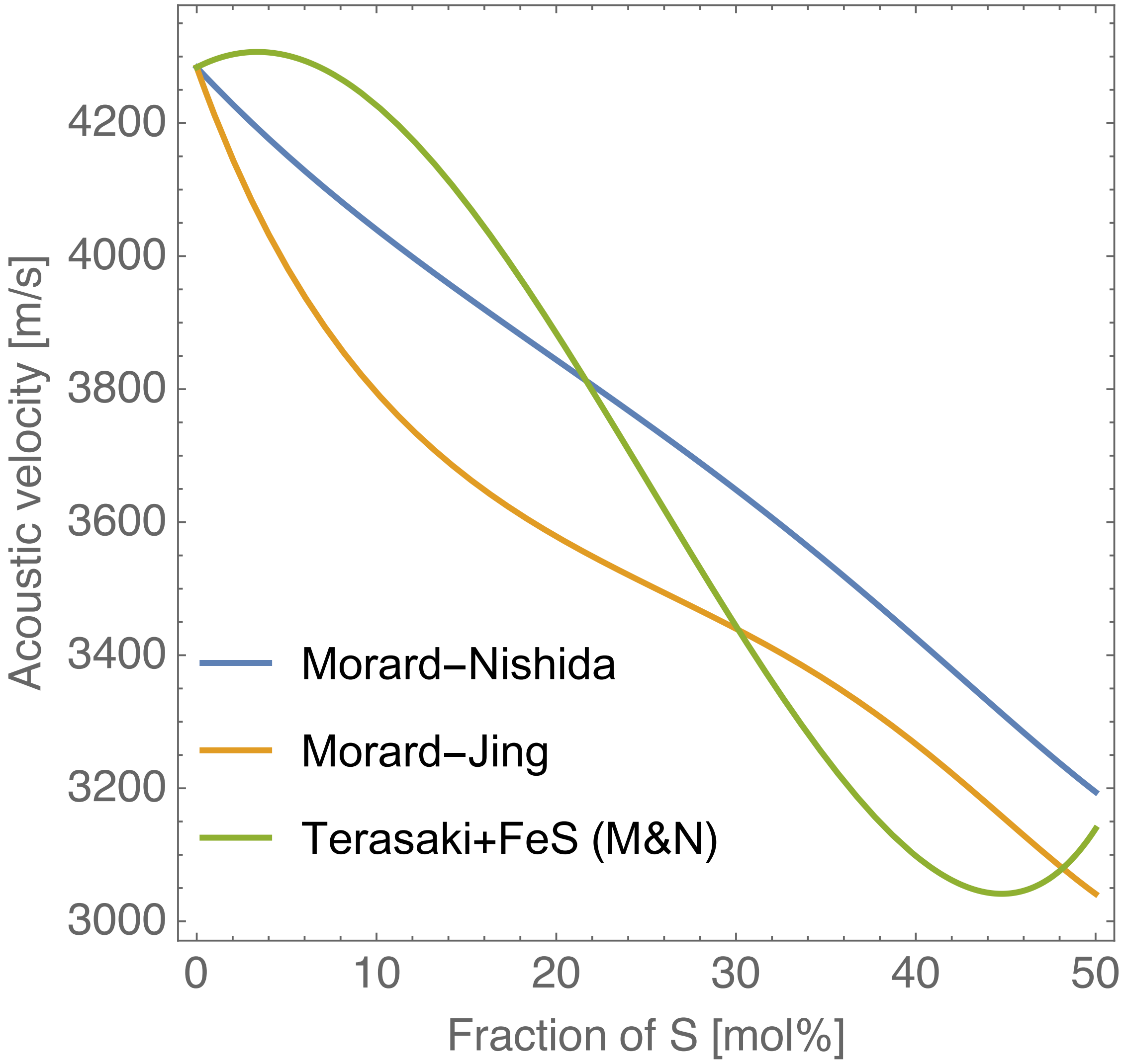


- Jing et al. 2014 Fe(16,30,39)at%S
- Nishida et al. 2016 Fe(20,43,50)at%S
- Terasaki et al. 201x Fe10at%Ni(17,30)at%S
- weak dependence on temperature (curves are on isotherms 1900K)

⇒ Inconsistency between different studies

Effect of elastic data on thermodynamic model (5GPa, 2000K)

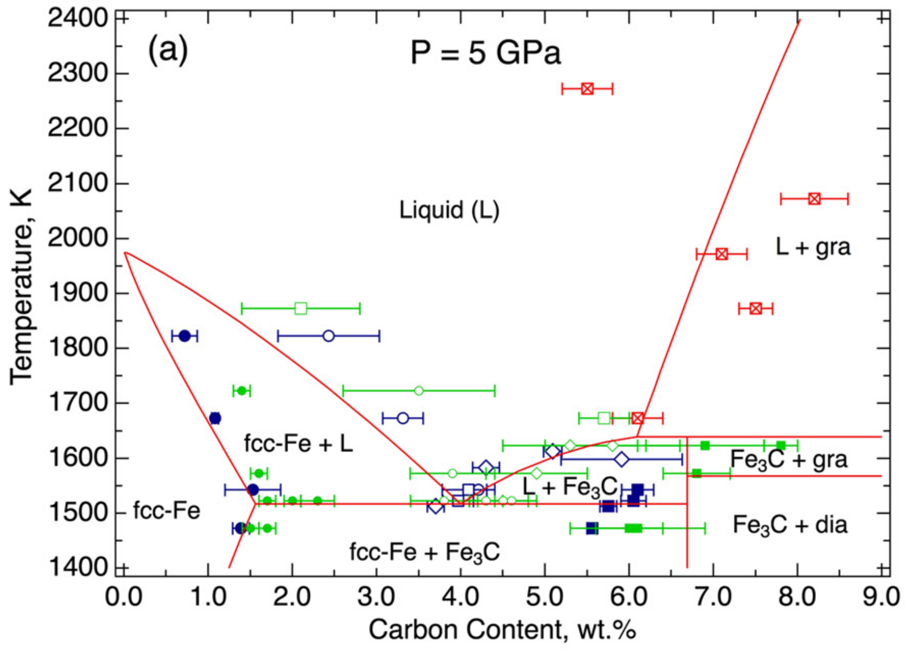




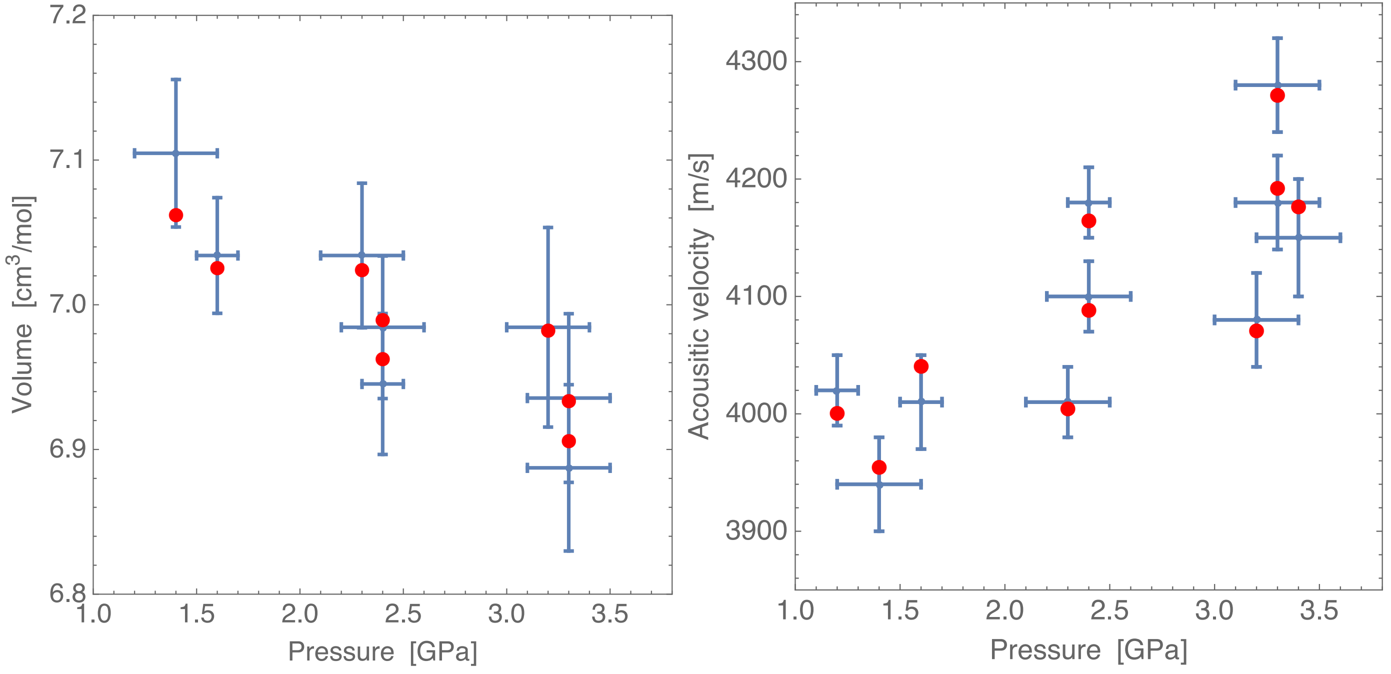
- density of liquid solution based on Morard 2018 density data depends weakly on acoustic velocity data
- but predicted acoustic velocities are quite different …

Preliminary Fe-C core model

Fei and Brosh 2014

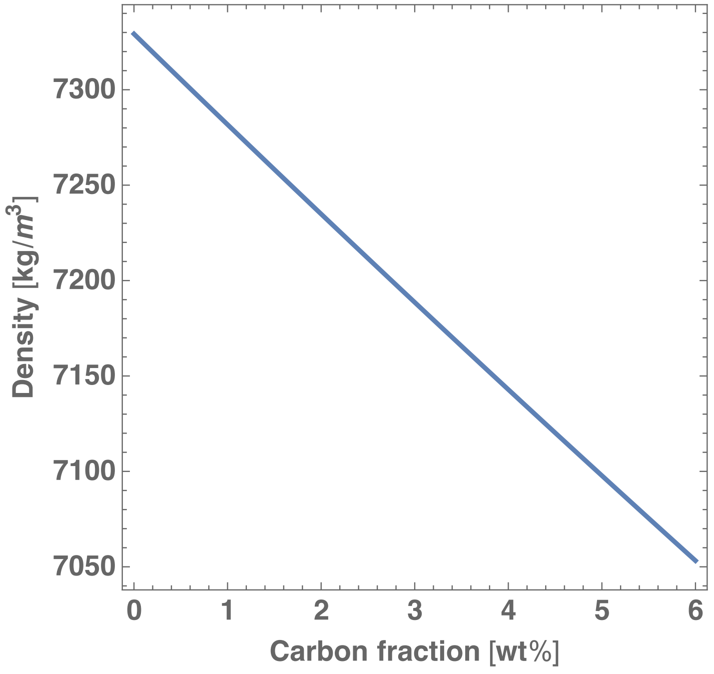


l-Fe3.5wt%C: Shimoyama et al. 2016



- at ~5GPa C saturation in l-Fe ≲7wt%C
- assume ideal mixture of l-Fe (Komabayashi 2014) and l-Fe3.5wt%C (Shimoyama 2016)

5 GPa, T=2000K



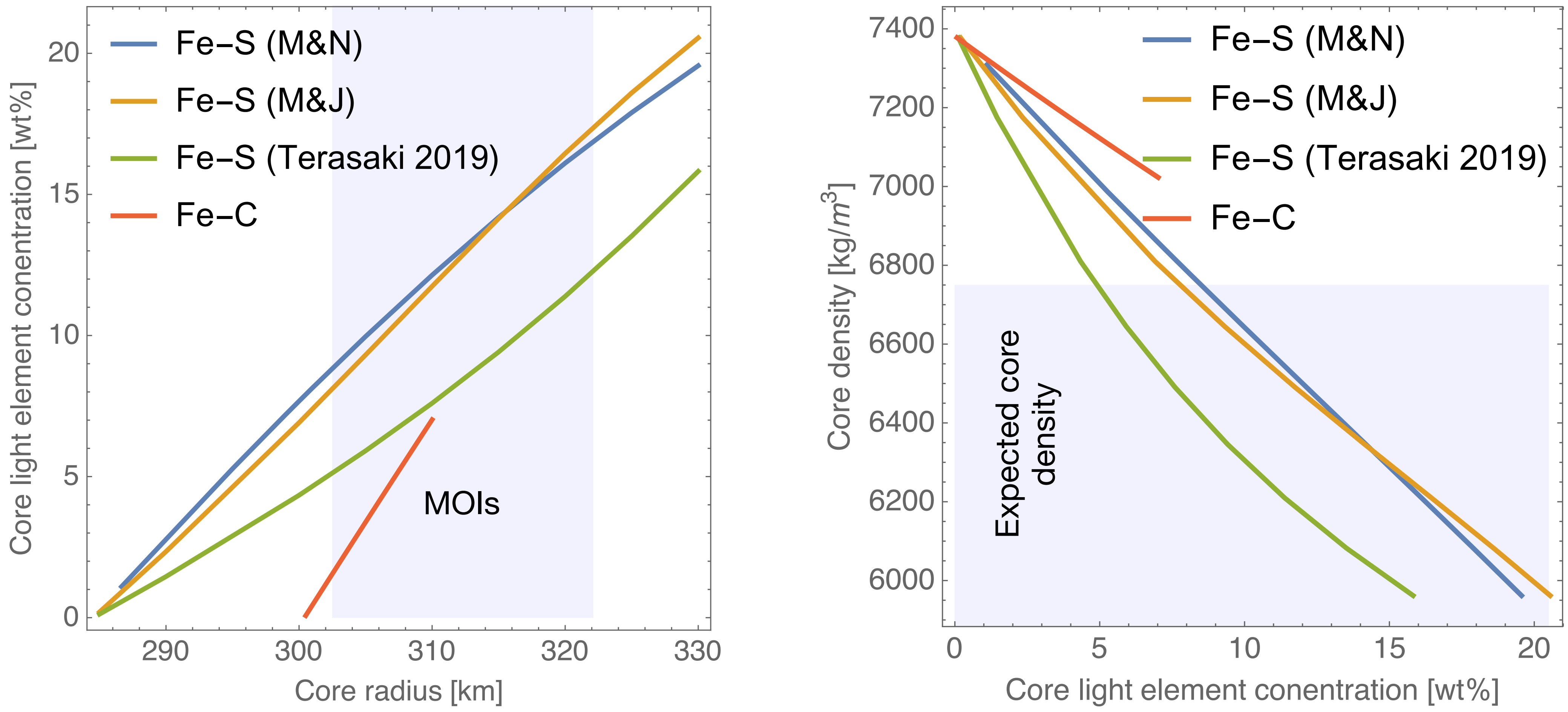
⇒ Density of liquid Fe-C significantly larger than **3900-6750 kg/m^3**

Moon models

- for illustration use the mantle density model of Weber et al. (2011)
- agree with the latest estimate of average shell moment of inertia (MOIs = 0.393112 ± 0.000012, Williams et al., 2014)
- core thermal evolution model based on Davies et al. 2015 and mantle evolution model based on Morschhauser et al. 2011

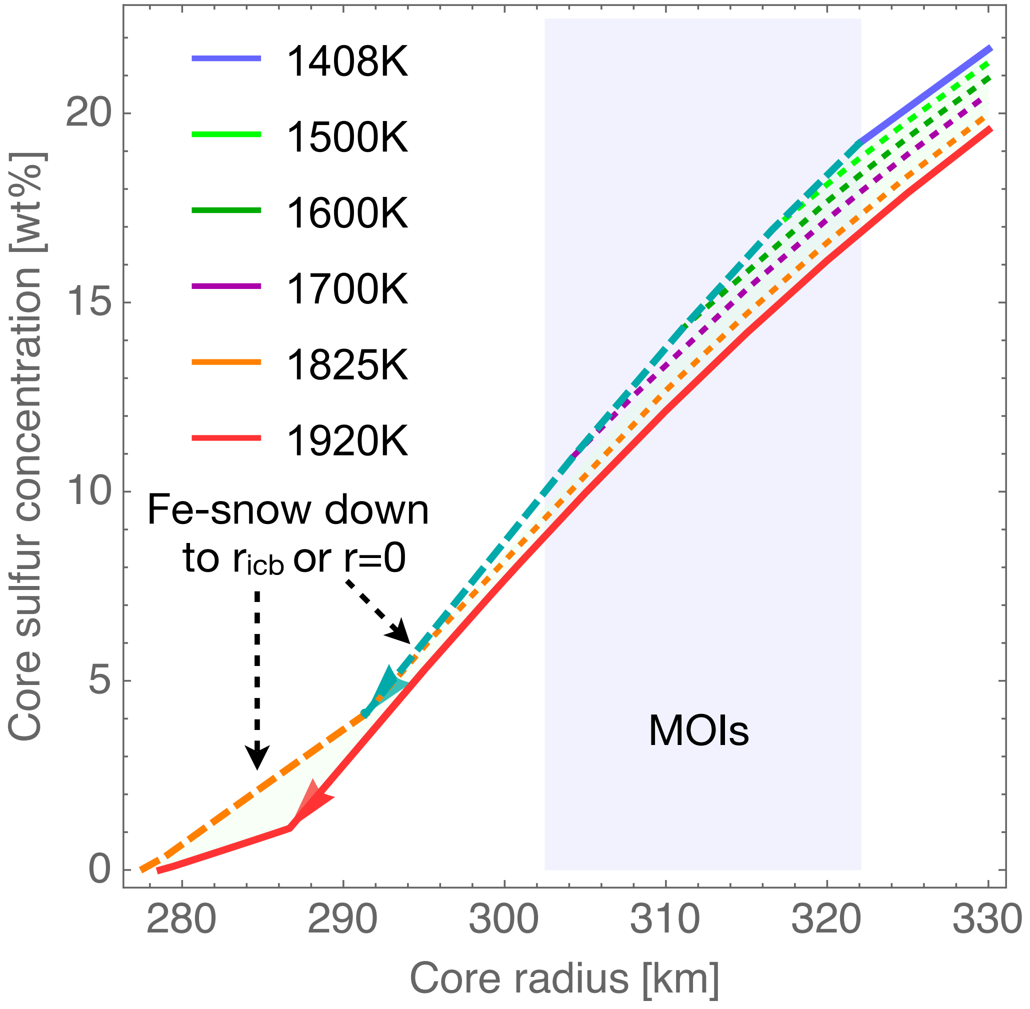
Structure functions:
Fe-S and Fe-C

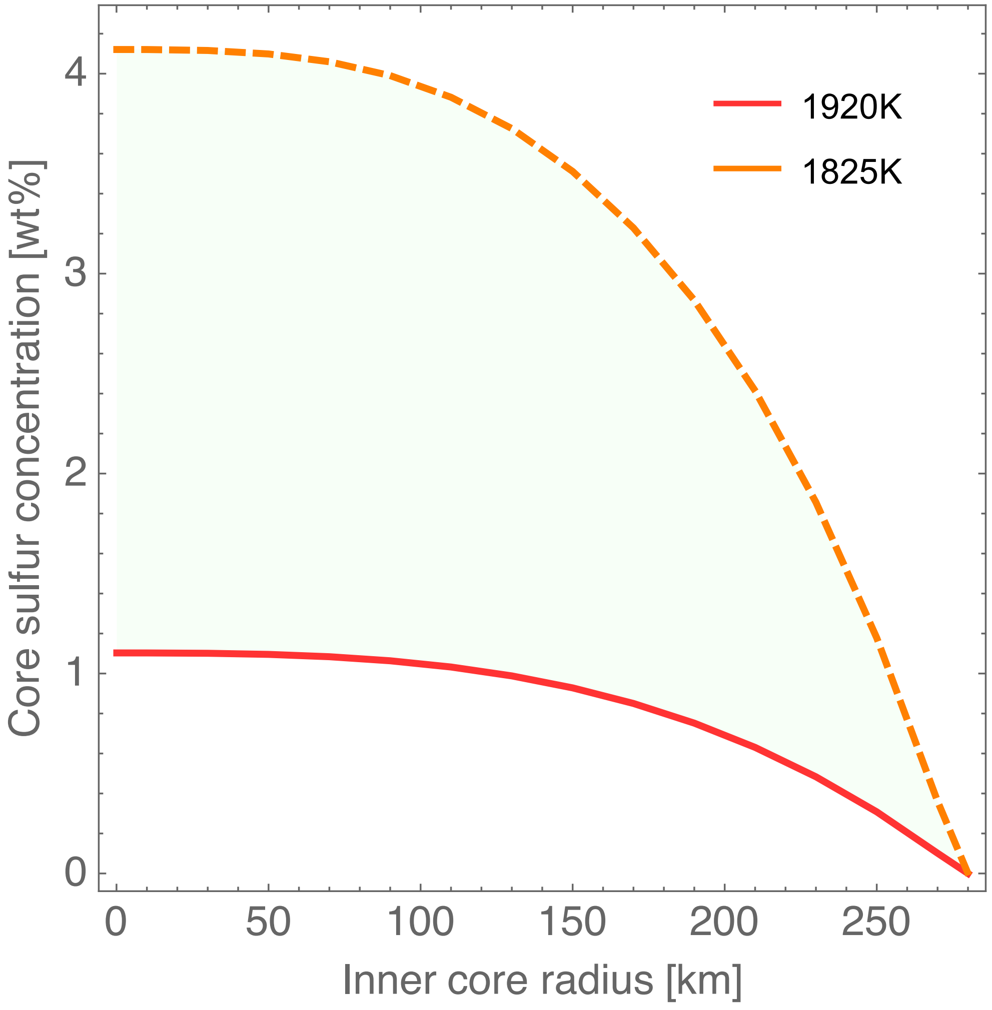
Core-mantle boundary Temperature: 1920K



- the required amount of S to match the expected core density of the Moon is significantly larger than what is deduced form core formation models
- the weight fraction of C in liquid Fe-C is below 7wt% and the density of such an alloy is significantly above what is expected for the core of the Moon

Structure functions Fe-S (Morard-Nishida)





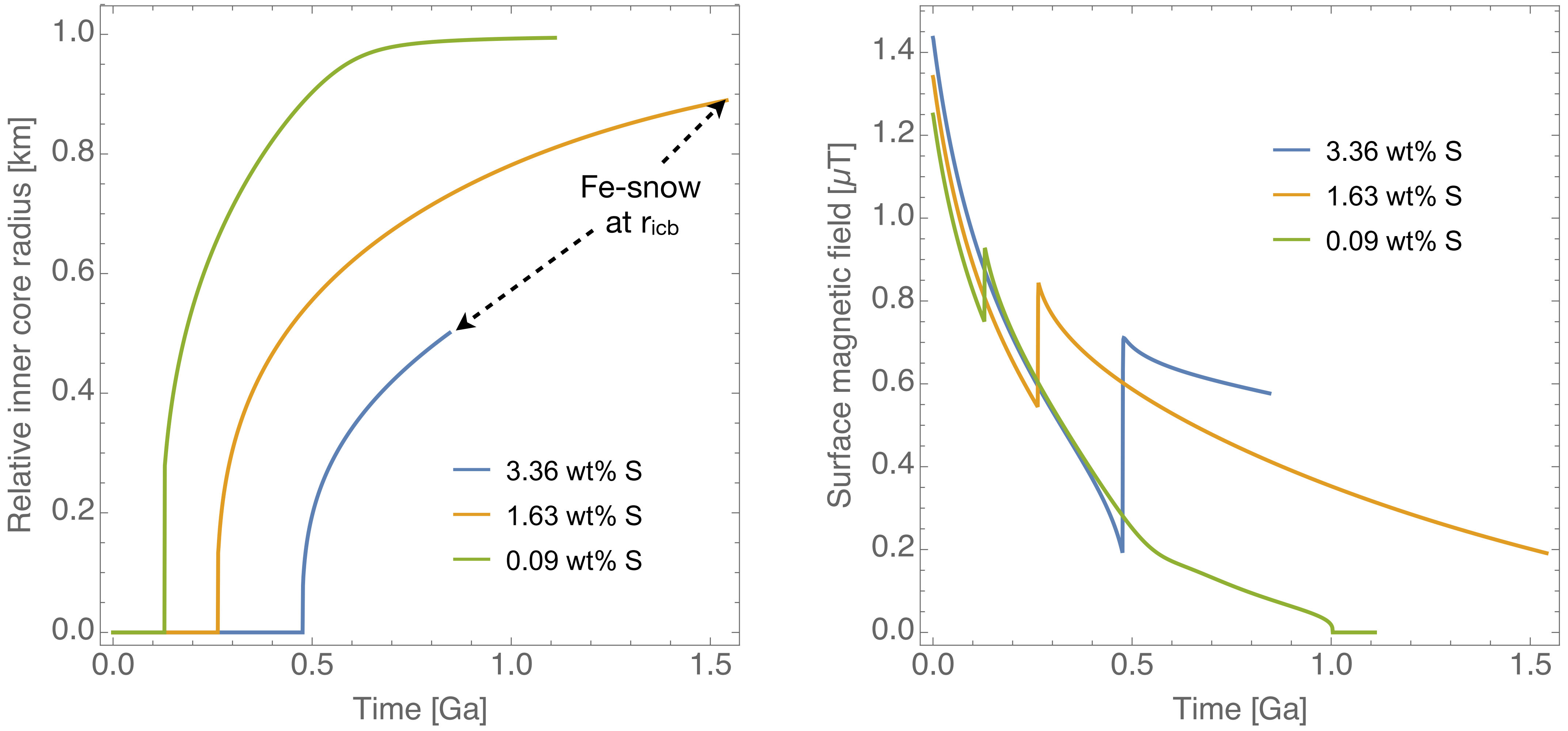
- models with the Weber et al. mantle cannot have an inner core (at 1σ)

- inner core possible if $r_{cmb} \lesssim 295$km and $x_S \lesssim 5$wt%

- bottom-up inner core growing requires $x_S \lesssim 4.2$wt%

- to avoid present-day lower mantle melting $T_{cmb} \lesssim 1920$K (Hirschmann et al. 2012)

Thermal evolution with bottom-up inner core formation



- all required thermodynamic quantities for core thermal evolution are computed from core model of this study (density, heat capacity, latent heat of crystallization, thermal- and chemical expansivity)

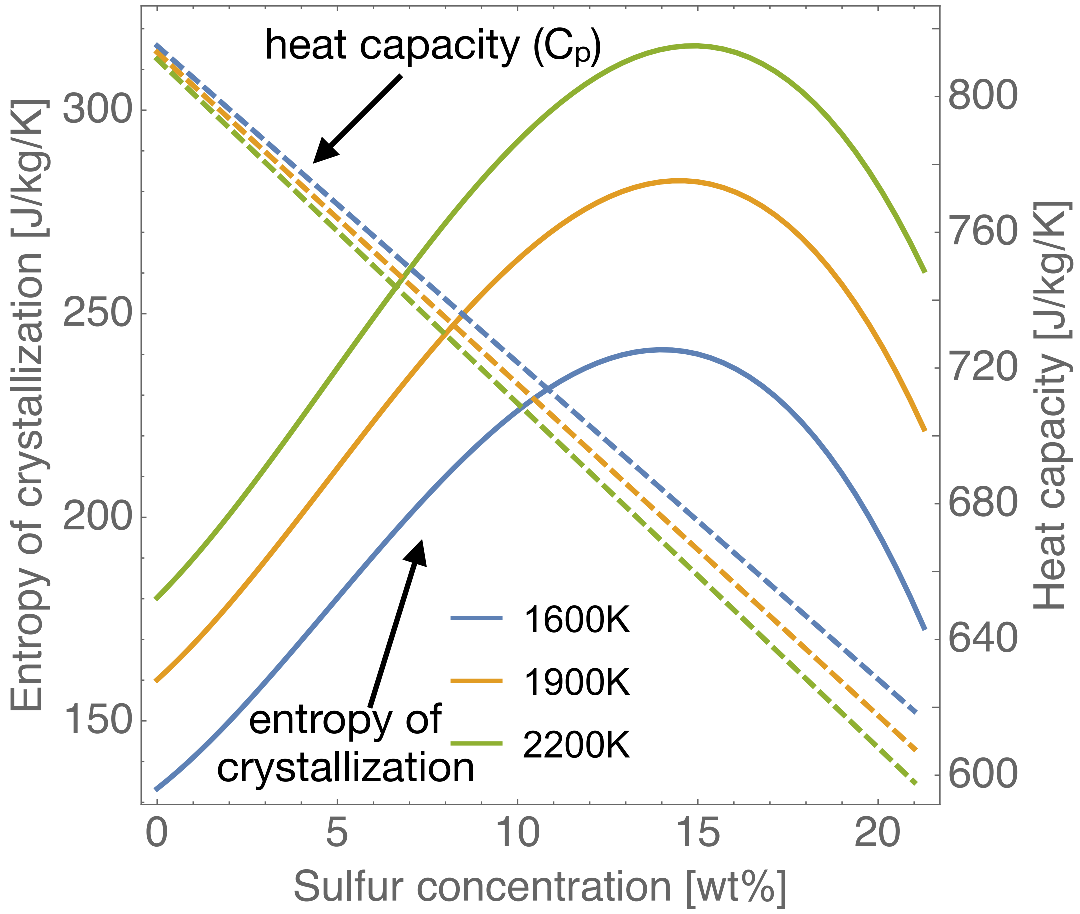
- main power and entropy source is latent heat

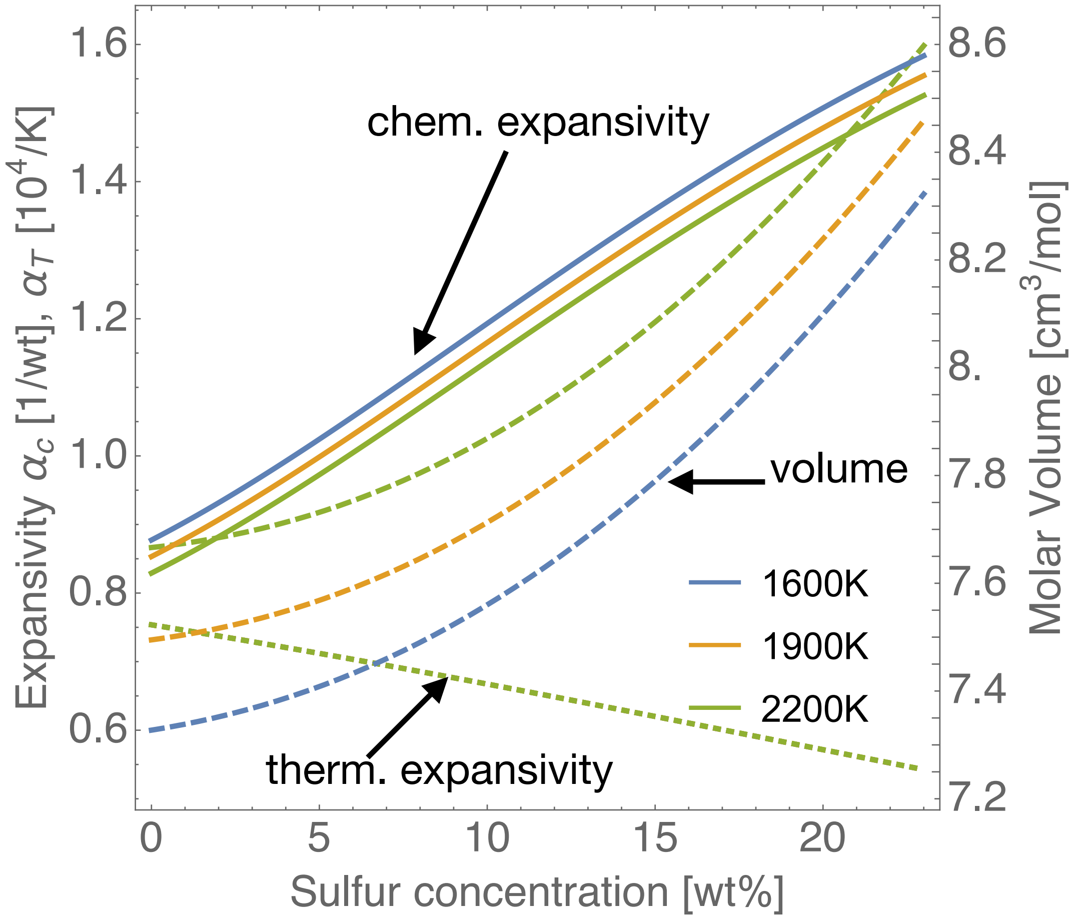
- timing of dynamo agrees with expected period of occurrence but predicted surface magnetic field is significantly below the 20-110μT that are expected to explain the lunar magnetic records (Tikoo et al 2017)

Conclusions

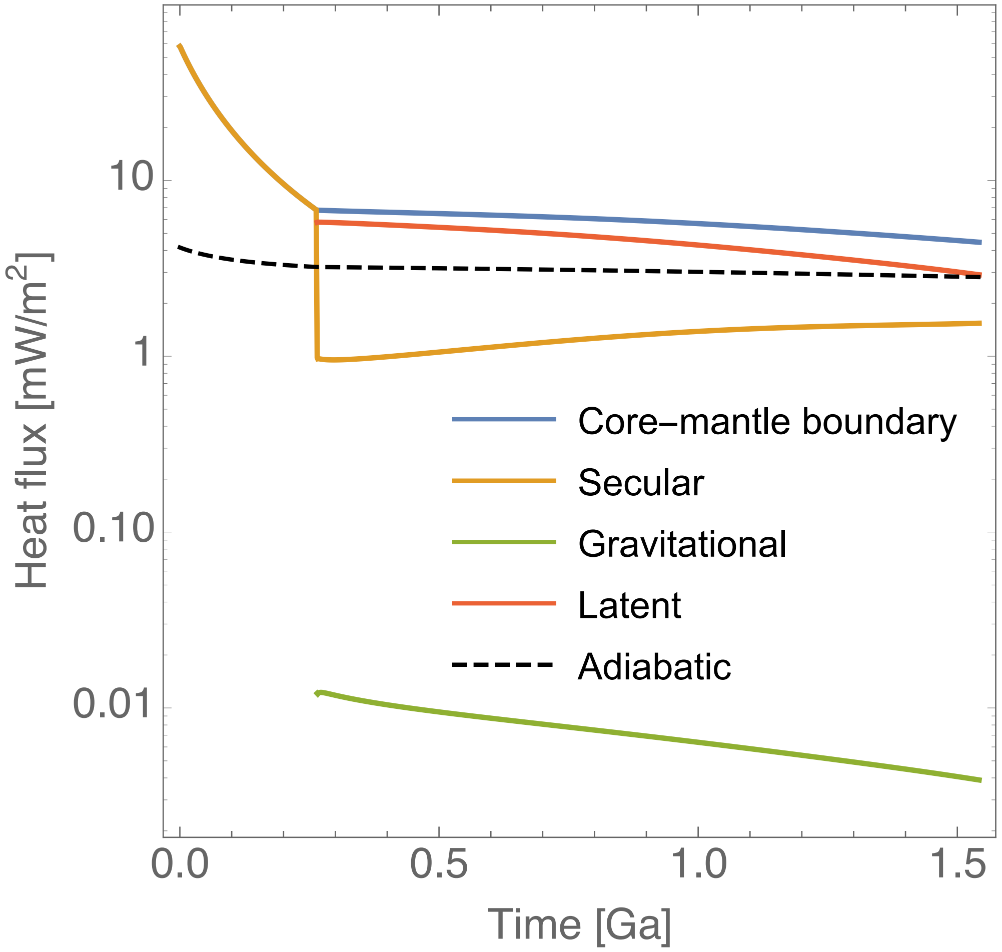
- melting data and new elastic data about Fe-S alloys can be described with a non-ideal mixing model that has a pressure dependent excess volume
- Fe-S models with an inner core and without a whole snowing liquid core cannot be much colder than ~1825K and those models have less than ~4.3wt% of sulfur
- models with an inner-core agree with the timing of occurrence of the lunar dynamo but not with the expected field strength
- but the amount of S required to match the expected core density is too large to allow for bottom-up inner core formation and significantly above what is expected from core formation models
- C cannot be the only light element in the core because even at saturation concentration such a Fe-C alloy is denser than the expected Moon core density

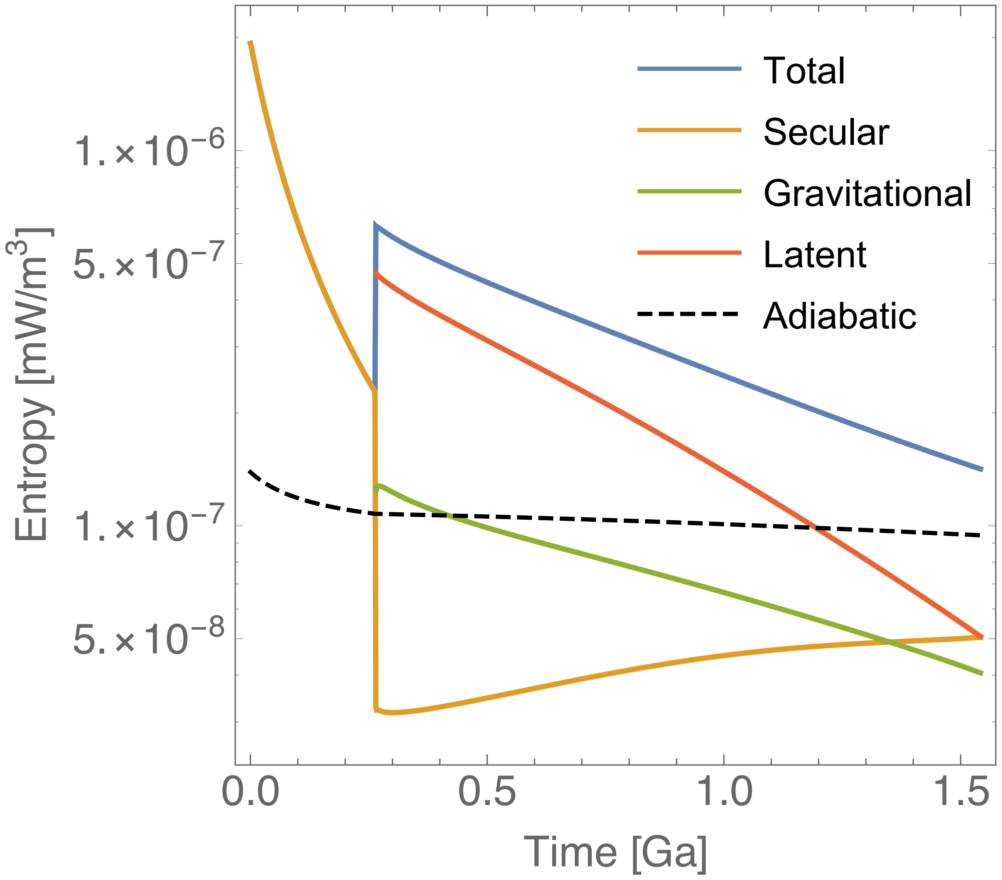
Thermodynamic quantities





Thermal evolution





Core composition

- Steenstra 2016
  depletion of siderophiles elements in the core can be explained if S>8wt%
  but S abundance in mantle implies S poor core
  but V and Cr abundances require either a S poor core with a differentiation temperature >3100K but core mass~2.5wt% (my models<1.3wt%) or S~8.5wt% with Tdiff~2200K
  difficult to explain anything with mCore<2.3wt%

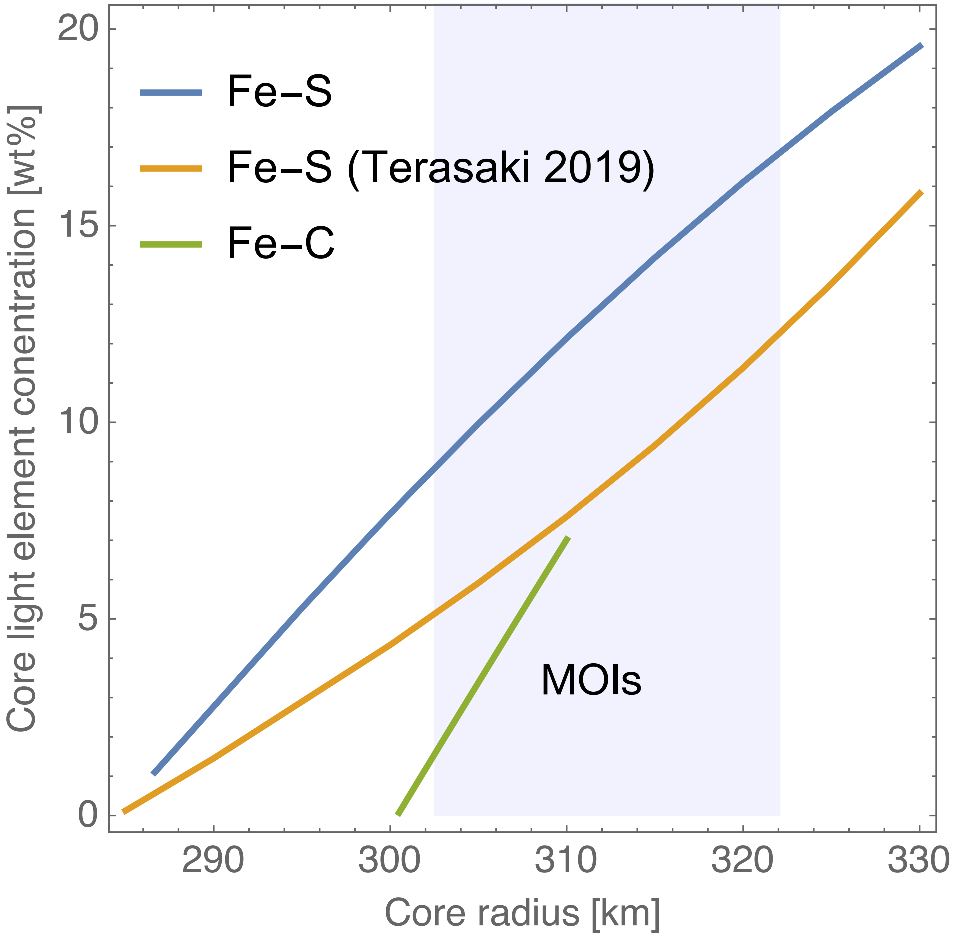
- Steenstra 2017
  to explain observed S,Se,Te in silicate Moon requires fully molten Moon at core-mantle equilibration

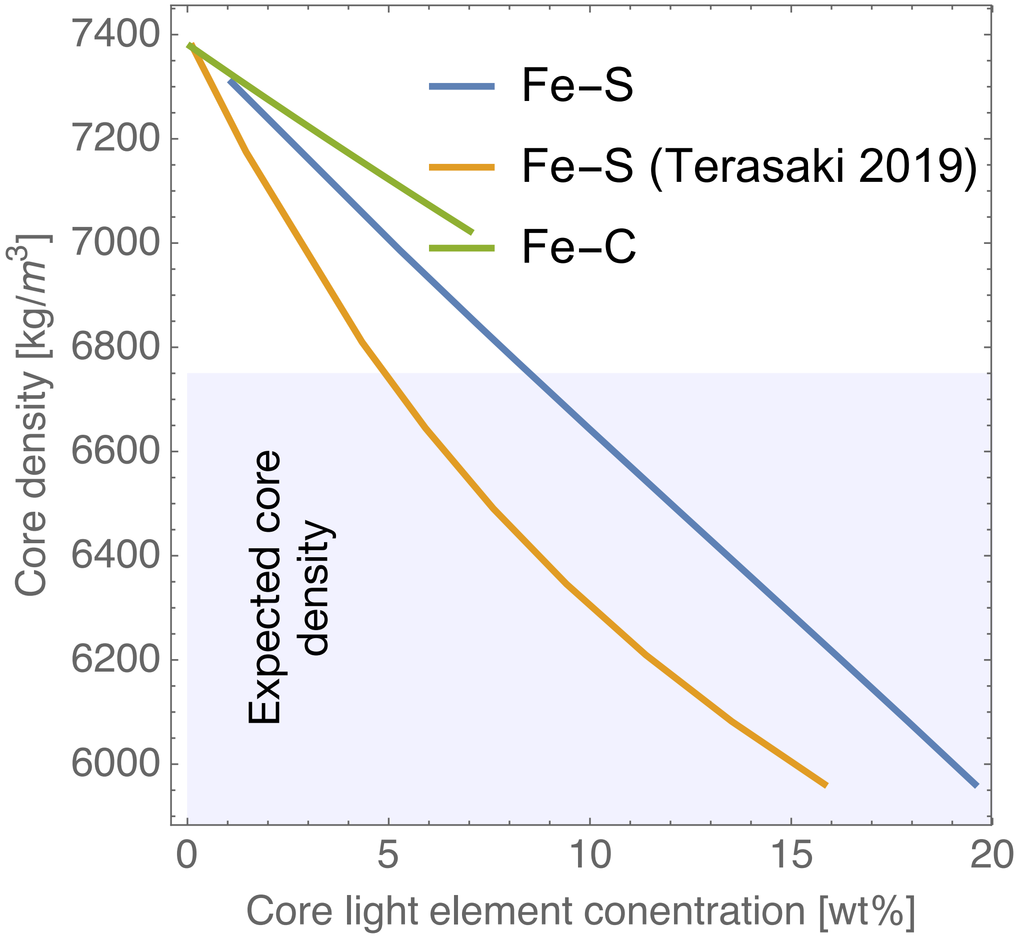
- Steenstra 2017
  metal-silicate partitioning of C,S,Ni and BSM (are they reliable?) abundances of S and C
  S<0.16wt%, main light element carbon up to ~4.8wt%

- Righter 2017

Structure functions: Fe-S and Fe-C

Core-mantle boundary Temperature: 1920K





- models based on elastic data of Terasaki et al 2019 require less sulfur at a given core radius to explain the density of the core

- C weight fraction in liquid Fe-C is below 7wt% and

- core densities of Fe-C models are significantly larger than the expected core density of the Moon